

Progress towards a source of cold, slow molecules for tests of fundamental physics

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Abstract

This thesis examines two beam sources of ytterbium fluoride (YbF), and assesses their viability for use in precision measurements of the electron electric dipole moment. The first source is a single-stage cryogenic buffer-gas source optimized for high extraction efficiency and low forward velocity. Velocity distributions of beams produced by this source have been measured, with corresponding mean speeds in the range 190 m s^{-1} to 210 m s^{-1} for flow rates between 10 and 40 SCCM. The characteristic YbF flux from this source has been measured as $(2.10 \pm 0.34) \times 10^9 \text{ sr}^{-1}\text{pulse}^{-1}$, and the flux of a similarly produced beam of ytterbium found to have a flux $(5.30 \pm 0.86) \times 10^9 \text{ sr}^{-1}\text{pulse}^{-1}$.

The second source is a two-stage cryogenic buffer-gas source, where the first stage is supposed to produce a high flux and the second stage is meant to slow the beam to low velocity. We find optimal behaviour running at lower pressures than the single-stage source, and have measured molecular beams with a peak velocity of 70 m s^{-1} . Although not fully optimised, the source shows clear evidence of deceleration in the second stage, and drastically outperforms even the best measured fluxes from the single-stage source in terms of molecules with velocities below 100 m s^{-1} . Typical fluxes from this source at its current state of development are $(6.8 \pm 0.7) \times 10^7 \text{ sr}^{-1}\text{pulse}^{-1}$.

In characterising the two-stage source, we have developed a new scheme to accurately measure the velocity distribution of molecular beams in the low signal-to-noise limit. We use the Doppler effect to address a small subset of velocities in a beam, bleaching population from a target level as we do so. Integrating over the total population loss of this level, we are able to reconstruct the true distribution with excellent fidelity, as we have demonstrated both theoretically and experimentally. We have applied this technique to beams of YbF produced in the two-stage source, and have found good agreement with results obtained using more traditional measurement schemes.

Declaration

I declare that the work presented here, unless otherwise stated, is my own. Where the work of others has been referenced, I have provided appropriate references and sources.

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To my family, absent and present.

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Chapter 1

Introduction

This thesis focuses on the design and implementation of two molecular sources for use in measurements of the permanent electron electric dipole moment (eEDM). We begin with an overview of the field of EDM measurement, before talking briefly about the current eEDM experiment being performed within our group. The Standard Model of particle physics (SM) and extensions beyond the Standard Model (BSM) predict exceptionally small eEDM values [1, 2, 3], so an attempted measurement of the eEDM requires exquisite sensitivity. As I will explain, this motivates the production of rotationally cold molecular sources with high fluxes and low beam velocities. I will conclude this section with a synopsis of the molecular beam and laser cooling techniques used in producing cold molecules, before outlining a scheme first suggested by Tarbutt *et al* [4] to perform an eEDM measurement using, as its source, a fountain of laser-cooled ytterbium fluoride (YbF) molecules.

1.1 From the electric dipole moment of the electron to molecular beams

Until the early 1950s, it was assumed that the properties of physics systems were invariant under the three discrete symmetries—parity (P), or the inversion of spatial co-ordinates; charge conjugation (C), the interchange of a particle with its antiparticle; and time reversal (T). These assumptions were first challenged by Purcell and Ramsey [5] who, with their student Smith, subsequently performed an explicit test of parity violation through an attempt to measure the EDM of the neutron [6]. Meanwhile, in 1956 it was proposed by Lee and Yang [7] that the weak interaction provides a mechanism for parity violation, with their assertions being validated by the work

of Wu *et al* [8]. In Wu's experiment, the correlation between the spin of ^{60}Co nuclei, $\mathbf{I}$, and the momentum $\mathbf{p}$ of electrons emitted through beta decay was measured, with parity violation being found as the electrons favoured the left-handed final state $\langle \mathbf{I} \cdot \mathbf{p} \rangle < 0$.

Following this discovery, Landau [9] suggested that the combined symmetry CP be preserved. The weak interaction acts on left-handed particles and right-handed antiparticles, so between P switching the handedness and C changing matter to antimatter the combined action of CP appears to be conserved. Later measurements on the K-meson [10], B-meson [11, 12], and D-meson [13] showed that even the CP symmetry is violated in nature.

A viable symmetry of nature is given by the combination of C, P, *and* T. First proposed by Schwinger [14] in relation to spin statistics, the symmetry CPT has since been rigorously proven to hold for local relativistic fields in a flat space-time [15, 16, 17]. From the axioms of its derivation, CPT violation would require us to abandon causality or Lorentz invariance [18]. As either of these results would lead to a paradigm shift in physics, tests of CPT invariance are ongoing; however, at present all results are consistent with the preservation of this symmetry [19, 20]. With CPT preserved, CP violation implies that T is also violated, with the degree of T violation equal in size and opposite in character to the CP violation.

Now, suppose we have an electron with axial angular momentum $\mathbf{S}$ and a permanent electric dipole moment $\mathbf{d}_e$. From the Wigner-Eckart theorem [21] these two first-rank spherical tensor operators must be co-axial, and hence $\mathbf{d}_e = d_e \mathbf{S}$. The action of time-reversal switches the sense of rotation of the angular momentum but leaves the dipole moment untouched. Similarly, acting on such a particle with the parity operator reverses the dipole moment but the angular momentum is unchanged. Diagrammatic examples of both are shown in figure (1.1). An electron with a permanent dipole moment does not respect the symmetries P or T which, via CPT invariance, means that CP must also be violated. We see then that a measurement of the eEDM is equivalent to a measurement of CP violation.

A large number of models have been suggested since 1964 to explain CP violation. One mechanism, which specifies the mixing between quark mass and weak-interaction eigenstates, is captured by the Cabibbo–Kobayashi–Maskawa (CKM) matrix [22] of the standard model. Within this formalism, the CP-violating eEDM components arise from the interaction between the electron and virtual quarks. Furthermore,

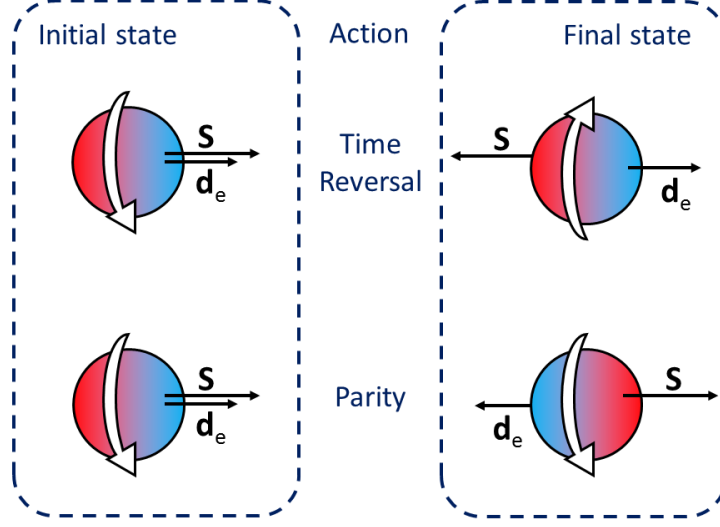


Figure 1.1: Action of time reversal and space inversion on a particle with angular momentum and a permanent electric dipole moment. Time reversal acts to “wind the clock backwards” and hence change the direction of rotation, whilst keeping the permanent dipole moment unchanged. Meanwhile, the action of space inversion reverses the charge asymmetry and hence the dipole moment, whilst having no action on the rotation.

it has been shown that the perturbation expansion of the interaction cancels up to three-loop order [23]. This effect leads to the standard model prediction [24, 25] for the eEDM of

$$|d_e|^{\text{SM}} \approx 10^{-38} e \cdot \text{cm}. \quad (1.1)$$

Compare this to the current sensitivity, set by measurements on the ThO molecule by the ACME Collaboration [26]

$$|d_e|^{\text{ThO}} < 8.7 \times 10^{-29} e \cdot \text{cm}, \quad (1.2)$$

with a quoted 90% confidence. Despite this incredible sensitivity, the current experimental limit and the standard model eEDM prediction differ by nine orders of magnitude. As a reference for this scale, two decades of careful and pioneering work has managed to improve the sensitivity by ≈ 2 orders of magnitude [27], so a direct measurement the SM eEDM of equation (1.1) is clearly out of reach for the foreseeable future. A plot of the progression of the eEDM limit is shown in figure (1.2).

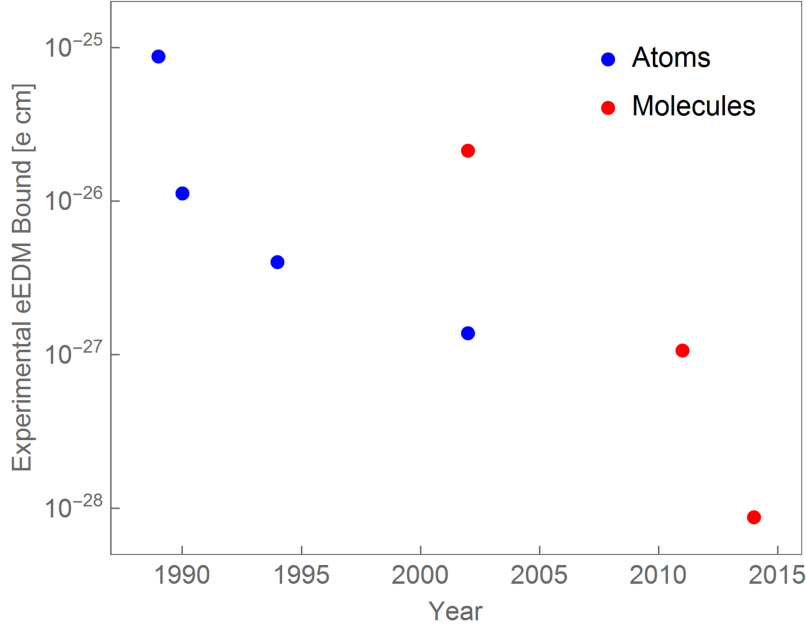


Figure 1.2: Progression in the upper bounds of the electron EDM as a function of time. Early experiments carried out on Cs and Tl atoms achieved sensitivities at which BSM models could start being addressed [3], before the shift to the diatomic molecules YbF and ThO gave an extra boost thanks to their large internal fields. Data is taken from [26, 44, 44] for the molecules, and from [27, 45, 46, 47] for atoms.

The standard model is not without its faults. By definition, it does not account for dark matter or dark energy, despite strong evidence obtained from the rotational speeds of stars in galaxies [28] and from the rate of expansion of the observable universe [29, 30]. It has also been shown that baryogenesis—the net production of matter over antimatter—requires levels of CP violation not accounted for by the standard model [31, 32]. To attempt to explain these additional behaviours a range of extensions to and departures from the standard model have been developed. However, as these models typically introduce new components into the “particle zoo” of high-energy physics, additional CP-violating processes and phases tend to arise. Consequently, the values of the eEDM predicted by these theories tends to be orders of magnitude larger than $|d_e|^{\text{SM}}$ —sufficiently so, in fact, that measurements of the precision of (1.2) and other current-generation experiments already form an excellent test of their validity [3]. An experiment that aims to measure the eEDM through increasing its sensitivity has two possible outcomes—either the null result is obtained

and the constraints on BSM theories are increased, or an eEDM is measured and physics beyond the standard model is found. In either case, such an experiment provides excellent insight into the laws and processes that govern the universe.

So how does one go about attempting to measure an eEDM? The Hamiltonian for the interaction between an eEDM and an applied electric field is

$$H_e = -\mathbf{d}_e \cdot \mathbf{E}, \quad (1.3)$$

and the corresponding energy $E_e = \langle H_e \rangle$ is the quantity we wish to determine. Performing this type of measurement on a bare electron is impractical, as the electric field will rapidly accelerate the charged particle from experiment. This concern is mitigated by performing the measurement on an electrically neutral system, such as an atom or molecule, but now an additional complication arises. If the electrons and nucleus are treated as non-relativistic point particles whose total Hamiltonian is governed by the Coulomb force, the effect of the eEDM will be shielded by the re-arrangement of charges within the system.

This result, known as Schiff’s theorem [33], was noted by Schiff himself to be strongly dependent on its initial assumptions. We can lift these, setting the nuclear volume to be finite and allowing the motion of the electrons to be relativistic, and in both cases $\langle H_e \rangle \neq 0$. It is shown in [34] that lifting the volume constraint gives a finite energy shift by virtue of allowing a mismatch between the spatial distributions of the charge and the EDM. Meanwhile, the motion of relativistic electrons forces us to apply the Dirac equation to our system. At low energies the solutions to the Dirac equation can be separated into a “large” and a “small” component, with the amplitude of the small spinor dropping to zero at zero velocity. The fully-relativistic Hamiltonian introduces an additional EDM energy term that is diagonal in the small spinor. This interaction can not be shielded as was the case in the non-relativistic theory, and again a non-zero energy arises from the effect. An in-depth explanation of this effect is given in both [34] and [35].

So far we have come to three conclusions—that measuring an electron EDM is a good idea, that the measurement must proceed using a neutral species rather than a bare electron, and that Schiff’s theorem will make life difficult unless the electron to be measured is relativistic and the species nucleus is large. In practice the relativistic criterion dominates in eEDM measurements, so we will not consider the role of the nucleus further. But which species should we perform our measurement on? Within the full relativistic calculation in [35], it is shown that applying an electric field to

an atom leads to the development of an internal electric field. The energy of the interaction between this field and an electron connects only the small components of the Dirac spinor, so is large only for fast-moving electrons. Using some reasonable arguments (that the effect is most pronounced when the electron is close to the nucleus), it can be shown that this effect boosts the energy of the eEDM perturbation by a factor

$$R \approx 10Z^3\alpha^2, \quad (1.4)$$

where Z is the proton number and α the fine structure constant. In practice, this means that elements more massive than magnesium have $R > 1$ and a measurement using an atom becomes *more* sensitive than a measurement involving a bare electron! This effect, first noted by Sandars [36], meant that many of the successful early eEDM measurements were performed on heavy atoms such as caesium [37], mercury [38], and thallium [27].

The situation becomes even more favourable in heavy polar molecules, where the “applied” field is provided by the strong internal fields of the molecule itself. The direction of this field is along the internuclear axis, with the unit vector in this direction denoted $\hat{\lambda}$. Explicitly invoking the Wigner-Eckart theorem for the electron EDM operator, the Hamiltonian for this interaction is

$$H_{\text{mol}} = -|d_e|E_{\text{eff}} \frac{\mathbf{S} \cdot \boldsymbol{\lambda}}{|\mathbf{S}|}. \quad (1.5)$$

The role of the applied field is to align the molecule, with the degree of alignment being proportional to the magnitude of the field. The effective electric field E_{eff} arising from the polarity of the molecule can be absolutely vast, with calculated values typically of the order of 10 GV cm^{-1} for eEDM-sensitive molecules [39, 40, 41]. With molecular alignment occurring on the 10 kV cm^{-1} scale [42], even modest laboratory electric fields can give rise to quite spectacular enhancement in the sensitivity to an electron EDM. For this reason, the search for an eEDM has progressed from atoms to molecules in recent years, with YbF [43] and ThO [26] being successful choices.

Historically, attempts to measure exceedingly small quantities have been performed with interferometers due to their great sensitivity, and an eEDM measurement is no exception. In this case the interferometer takes the form of a molecule, with the phase shift being between its internal states. From the Schrödinger equation, the time evolution of an energy eigenstate $|E\rangle$ with eigenvalue E is given by

$$|E(T)\rangle = |E(0)\rangle \exp\left(-\frac{iE}{\hbar}T\right). \quad (1.6)$$

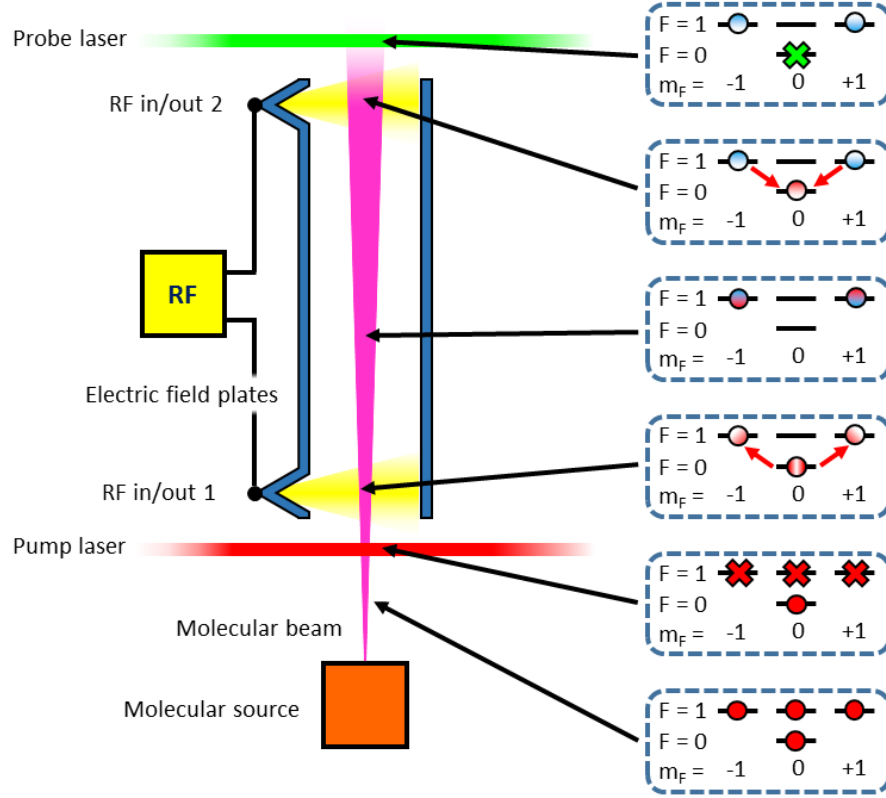


Figure 1.3: Schematic of the eEDM measurement experiment. Phases are shown diagrammatically through colour, and population removed by the pump and probe lasers are denoted by crosses. Molecules progress through the experiment from bottom to top.

The amount of phase acquired is therefore seen to be proportional to both the energy E , and the time for which the system evolves in the Hamiltonian, T . As the eEDM is predicted to be minuscule, so too is the energy shift arising from its contribution to the total Hamiltonian. We therefore need to allow a significant time T for the eEDM phase to accumulate if we are to make a successful measurement.

I will now describe the essence of how an experiment to measure the eEDM using YbF molecules is performed. An in-depth description is unnecessary for the present discussion; as such, I refer the interested reader to the theses of Devlin [48] and Smallman [49] for a more complete picture, with necessarily more brief presentations

being found in [44] and [43]. A pictorial representation of the eEDM experiment described here is shown in figure (1.3).

A beam of YbF molecules is produced with some characteristic forward velocity v_f . After pumping molecular population into the absolute ground state with a pump laser¹, the molecules enter a region of high electric field generated by applying a potential difference across a pair of large, flat plates. This field polarizes the internuclear axis along the field direction as described by equation (1.5).

Within the YbF ro-vibrational ground state manifold, angular momentum coupling between the electron and fluorine nuclear spins gives two eigenstates of the total angular momentum with quantum number $F = 1$ and $F = 0$, and projections $m_{F=1} \in \{-1, 0, 1\}$ and $m_{F=0} \in \{0\}$. An RF π -pulse sent down a transmission line transfers molecules from the absolute ground state $|F = 0, m_F = 0\rangle$ to the equal superposition

$$|\psi(0)\rangle = \frac{|F = 1, m_F = 1\rangle - |F = 1, m_F = -1\rangle}{\sqrt{2}} \quad (1.7)$$

Note that, as $\mathbf{F} = \mathbf{S} + \mathbf{I}$, in the extremal state $|F = 1\rangle$ the spin and total angular momenta are parallel. Furthermore, writing $|\psi(0)\rangle$ in terms of spherical tensors shows that this choice of superposition is orthogonal to the polarized internuclear axis. Allowing the total angular momentum to precess is therefore equivalent to allowing the spin to precess, and as we have previously discussed the spin and any electron EDM must be parallel.

A small magnetic field is then applied as gross control of the spin precession, and the molecule is allowed to fly freely between the electric field plates for a fixed time T . During the free-flight time, the states acquire a relative phase

$$\phi = \frac{T}{\hbar}(\mu_B B - d_e E_{\text{eff}}), \quad (1.8)$$

¹I gloss over the details here. I'll define N to be the rotational quantum number, and F the total angular momentum quantum number in the following. A pump laser is applied to the $|N = 0, F = 1\rangle$ state in the $X^2\Sigma^+$ ($v = 0$) manifold, coupling it to the spectrally distinct $A^2\Pi_{1/2}$ ($v = 0$) excited state. The energy splitting between $|N = 0, F = 1\rangle$ and $|N = 0, F = 0\rangle$ is large enough that the laser does not address the $|N = 0, F = 0\rangle$ state. The allowed decays from the excited state are to $|N = 0\rangle$ and $|N = 2\rangle$, but molecules returning to $|N = 0, F = 1\rangle$ are pumped away once more by the laser. This process repeats, with the net result of increasing the population in $|N = 0, F = 0\rangle$ and $|N = 2\rangle$ whilst completely depleting $|N = 0, F = 1\rangle$. Population that is transferred to $|N = 2\rangle$ is outside the pump linewidth and is lost to the experiment. More information about the angular momentum coupling in YbF can be found in appendix (A).

Due to this ϕ , the total wave function $|\psi(T)\rangle$ obtains some character of the state $[|F = 1, m_F = 1\rangle + |F = 1, m_F = -1\rangle]/\sqrt{2}$, which is not connected to $|F = 0, m_F = 0\rangle$ by the RF interaction. As such, applying a second RF π -pulse to the evolved state at time T gives a final population in the absolute ground state of

$$|\langle F = 0, m_F = 0 | \psi(T) \rangle|^2 \propto \cos^2 \phi, \quad (1.9)$$

which may be measured using the laser-induced fluorescence technique. Repeating the process using fresh molecules, this time with the electric field direction reversed, gives a relative phase

$$\phi' = \frac{T}{\hbar}(\mu_B B + d_e E_{\text{eff}}) \quad (1.10)$$

and the difference in relative phase between the two orientations is proportional to the eEDM. The magnetic field is chosen so that the amplitude of the phase shift $|\phi| \approx |\phi'| \approx \pi/4$ to maximise the phase contrast in the experiment.

The shot noise in a measurement of this type is given by [50]

$$\delta|d_e| \propto \frac{1}{T\sqrt{N}} = \frac{v_f}{L\sqrt{N}}, \quad (1.11)$$

where N is the total number of molecules that participate in the experiment and L is the maximum interaction length that molecules of characteristic velocity v_f can explore in time T . If our experiment is to be as precise as possible, we need to minimise equation (1.11). To do this, we can increase the free-flight time T to allow the eEDM interaction to drive a greater phase difference, and we can increase the number of molecules to reduce the uncertainty in the sample mean. Because of the beam divergence, the number of molecules that successfully traverse the experimental apparatus will scale as $N \propto 1/L^2$, where L is the length of the apparatus, and hence simply extending the experiment is not an option with these sources.

However, there is significant scope for improvement in the beam velocity. At present, the eEDM experiment produces YbF through the ablation of solid ytterbium in the presence of a 2% argon-SF₆ gas mixture. The gases are emitted from a pulsed valve, forming a supersonic molecular beam with mean forward velocity 590 m s⁻¹ and a velocity width² of ± 40 m s⁻¹ [48, 49]. The source divergence is set using a 2 mm

²In principle, as the time interval between the two RF pulses is fixed, the velocity width shouldn't factor into the discussion as long as the experiment is large enough that all molecules experience both π -pulses. In this case, all molecules will eventually be detected by the probe laser with probability

diameter skimmer placed 94 mm above the source; the molecular flux after the skimmer is $\approx 3 \times 10^9 \text{ sr}^{-1} \text{ pulse}^{-1}$ in the rovibrational ground state. Using the skimmer length scales to define the solid angle of the beam, we find that a typical shot contains $\approx 10^5$ – 10^6 YbF molecules. Adiabatic cooling in the beam produces molecules that are both rotationally and translationally cold, having temperatures of 1–5 K and 3–15 K respectively. In order to make a significant gain in the sensitivity, we would like to greatly reduce the forward velocity of the beam, whilst still maintaining the number of YbF molecules accessible to the experiment. I discuss our group’s solution to this problem, the development of a molecular fountain, in section (1.4).

We have discussed the role of electron EDM measurements in exploring beyond standard model physics, and seen how such an experiment might be performed. The experimental sensitivity requires an intense source of slow molecules, with great gains to be made in the limit of low beam velocity. I will now briefly introduce the molecular beam and laser cooling methods capable of producing cold and slow samples of molecules, before addressing the overarching goals of this study.

1.2 Molecular beams

When dealing with the molecules used in precision experiments, it is common to have to produce the test species *in situ*. The current YbF sources use the laser ablation of a solid ytterbium rod [48], whilst the cryogenic source used in the ThO eEDM measurement produces molecules through the ablation of a ceramic ThO₂ target [51]. Production methods used in older experiments include baking constituents in an oven [43]. In all cases the molecules are typically produced in a rotationally, vibrationally, and translationally hot state. If we used them immediately after production, we would expect the number of molecules in the ro-vibrational ground state to be exceptionally small³, and hence the $\sqrt{N}$ term in equation (1.11) will be suppressed. Similarly, if the molecules are translationally hot then they will have a significant forward velocity, suppressing the free evolution time T .

given by equation (1.9). In practice, the different velocity classes of molecules might experience field and RF intensity inhomogeneities differently, so using too broad of a velocity distribution would be unwise. For example, if the magnetic field is inhomogeneous in some small region, then this inhomogeneity would contribute a larger phase to ϕ for slow molecules than for fast molecules.

³In the case of the oven, the hot molecules are in thermal equilibrium with one another and hence the population in the lowest energy states is suppressed by Boltzmann-type factors. The distribution immediately following ablation is less clear, but a high multiplicity of levels will certainly be populated, driving population from the ground state as before.

A useful solution to this quandary is to mix the hot molecules with a cold, inert gas in a technique known as buffer gas cooling [52]. The typical buffer gas beam is produced by flowing a cryogenic noble gas through a confined volume, or cell, with a pressure in the cell of the order ≈ 1 Pa. Elastic collisions between the buffer gas and the hot species lead to rapid thermalisation of the rotational and translational energies to the buffer gas temperature [53]. As the noble gases are chemically inert even to fluorine chemistry [54], the buffer gas cooling method is extremely general, being applicable to molecules [55, 56], ions and their associated exotic states of matter [57], and even antimatter [58]! The cooled species may either be studied *in situ* with the buffer gas, or be allowed to escape from the cell in the form of a beam.

The choice of noble gas is quite interesting, with both helium and neon being commonly used [59]. When we talk of a collision cooling the internal molecular states, we are actually making a statement about how adiabatic a process the interaction is. It can be shown that the adiabaticity of a collision can be parametrised via the parameter [60]

$$\zeta = \sqrt{\frac{\pi\mu}{8k_{\text{B}}T}} \frac{R \Delta E}{h}, \quad (1.12)$$

where ΔE is the energy separation between the internal molecular states, μ is the reduced mass of the buffer gas–molecule system, R is the physical length scale parametrising the collision⁴ and T the temperature. In particular, if $\zeta \ll 1$ then the collision is likely to induce the non-adiabatic transfer of population between internal molecular states. It is instructive to consider the efficiency of 14K neon and 4K helium in performing cooling on a given transition. In this case,

$$\frac{\zeta(\text{He})}{\zeta(\text{Ne})} = \sqrt{\frac{\mu_{\text{He}} T_{\text{Ne}}}{\mu_{\text{Ne}} T_{\text{He}}}} \approx 0.87, \quad (1.13)$$

and we see that the helium buffer gas provides fractionally better cooling properties, although the effect is small. A more drastic effect is on the population of the lowest-lying rotational states, whose distribution in thermal equilibrium is given by the Boltzmann term

$$P(N, T) = \frac{1}{Z(T)} (2N + 1) \exp \left(-B \frac{N(N + 1)}{k_{\text{B}}T} \right). \quad (1.14)$$

⁴For example, the minimum of the 6-12 Leonard-Jones potential might be used as an approximation.

Here $B \approx 7 \times 10^9 \text{ Hz} \times h$ is the rotational constant of YbF [61], and $Z(T) = \sum_N P(N)$ is the partition function⁵. Comparing the population in $N = 0$ at $4K$ and $14K$, we find that

$$\frac{P(0, 4)}{P(0, 14)} = \frac{Z(14)}{Z(4)} \approx 3.43, \quad (1.15)$$

and the hotter neon buffer gas produces more than three times fewer molecules in the lowest rotational state. However, neon does have some benefits. Simulations have shown that a neon beam will produce a greater number of slow-moving molecules than a helium beam [62]. Additionally, at cryogenic temperatures neon will freeze to the available surfaces⁶, greatly improving the quality of the vacuum in the experiment.

If the molecules are emitted from the cell in the form of a beam, their characteristic forward velocity will in general be a function of the cell pressure (and, implicitly, temperature), and the size of the aperture between the cell and the outside environment. If the cell pressure is high enough that there are many collisions in the aperture, then the expansion of the buffer gas through the aperture gives rise to a supersonic jet [63]. Within the jet, all the thermal energy of the atoms or molecules is transferred into forward velocity via collisions, giving beams that are cold but fast. The technique has been significantly refined since its inception, with schemes that seed a hot species into an established supersonic beam giving lower temperatures [64] and techniques using rotating gas nozzles reducing the forward velocity [65]. The total experimental gas load can be reduced by using gas pulses [66], generated from piezoelectric [67] and solenoid valves [68].

On the other hand, if the cell pressure is so low that there are no collisions in the aperture then effusive beams of molecules can be formed. In this case, the cell aperture is small compared to the mean free path of the gas [69], and hence there is no collective motion through it. Instead, the aperture acts as a “sampling window” to the thermal distribution inside the cell, allowing molecules to leak into the outside environment rather than sweeping them from the cell. Molecules leave the cell with their thermal velocity, rather than being collectively forward-boosted as was the case in supersonic beams. For massive molecules being cooled by a buffer gas, this thermal

⁵Note that if $k_B T \gg B$ we may approximate the sum with an integral, obtaining $Z_\infty(T) = k_B T / B$.

⁶A cell designed to produce a neon beam will typically be constructed so as to have poor thermal coupling to a $\approx 4K$ cold stage, with the cell being heated to the required $14K$. All the non-cell surfaces, including radiation shields, then act as cryopumps to the neon.

velocity is significantly lower than the fully-boosted velocity arising from entrainment in a supersonic gas jet. However, as the probability of our species of interest leaving the cell is given by the odds of it reaching the aperture rather than the cell wall (where it will freeze and be lost), the extraction efficiency and beam brightness are typically rather low in this regime. Furthermore, as there is no cooling in the beam, the resulting velocity distribution is broad in comparison to that of the supersonic beam, meaning that some kind of velocity selection is often required if the beam is to be used in precision measurements. Early experiments simply used ovens to produce hot, effusive sources of atoms [70] and molecules [71], before improvements in vacuum technology caused a shift in the field towards supersonic beams. The field has enjoyed a renaissance lately, with buffer gas sources that are tuneable between the effusive and hydrodynamic regimes becoming the tool of choice for laser cooling experiments [72, 73]. A cryogenic source of YbF produced using the molecular beam techniques above will have a mean velocity $25 \text{ m s}^{-1} \leq v_f \leq 205 \text{ m s}^{-1}$ using a 4K helium buffer gas, or $45 \text{ m s}^{-1} \leq v_f \leq 170 \text{ m s}^{-1}$ for 14K neon⁷.

1.3 Laser deceleration and cooling

The premier technique for producing ultracold samples of certain types of atoms and molecules is that of laser slowing and cooling. First observed in the deflection of sodium beams by a resonant lamp [76], the field of laser deceleration really exploded in the 1970s with the advent of tuneable lasers [77]. Simultaneously, laser cooling was suggested as being possible for atomic vapours [81], before being demonstrated on trapped ions in 1978 [78]. The extension to cooling free-space atomic beams soon followed [82], with the development of Zeeman slower [83] and the frequency chip technique [84] allowing atoms to finally be decelerated to rest [85]. Now, finally, atoms could be trapped and cooled in all dimensions through the use of either optical molasses [86] or magneto-optical traps (MOTs) [87]. The complex level structure of molecules made them a more challenging prospect, but recent advances have led to the deceleration and cooling of SrF [73], CaF [88], and YO [89]. Even more excitingly, recent work has led to the formation of a magneto-optical trap of the diatomic molecule SrF by the group of David DeMille [74].

Let's take a step back and consider our present dilemma. From equation (1.11), a sensitive molecular source requires a long interaction time with the applied electric field. With the temperature of an atom in a MOT reaching the sub-mK regime as

⁷See, for example, pages 37 and 84 of [75].

a matter of course, the thermal velocity of a cloud of such atoms or molecules is bounded from above by $\approx 0.5 \text{ ms}^{-1}$. The maximum interaction time between the molecules and the electric field in this slow, ultra-cold regime is set by the shortest dimension of the electric field plates, which in our case is typically half their 12 mm separation [48]. We can now compare the characteristic time for thermal expansion within the plates, $6 \times 10^{-3} \text{ m} / 0.5 \text{ ms}^{-1} = 12 \text{ ms}$, to the current interaction time of $980 \mu\text{s}$, again from [48]. Through application of equation (1.11), we see that a source of molecules produced in this way would improve the current sensitivity by a factor of at least an order of magnitude.

So how does the laser cooling technique work? Let's consider a toy system of a two-level atom that is initially in its ground state. When the atom absorbs a photon from a resonant laser, it receives a change of momentum $\delta \mathbf{p} = \hbar \mathbf{k}$ in the direction of propagation of the light, defined by the $\mathbf{k}$ -vector $\mathbf{k}$. The excited state can decay through two processes. In the first, the excited state couples once more to the laser and emits a photon back into the laser mode. This process, known as stimulated emission, gives no net change in the atomic momentum. In the second, the excited state couples to the quantised vacuum field and emits a photon isotropically into a random orientation. Averaging over many such events, the momentum change from this spontaneous emission sums to zero and there is a net dissipation of energy and momentum from the atom [79].

At the start of this section, I carefully qualified my initial statement with the word "certain". The fact is that for many atoms, and the vast majority of molecules, laser cooling is exceptionally difficult if not impossible [90]. As the momentum of a typical atom or molecule is much larger than that of a photon, successful laser cooling requires many cycles of the process described above. For example, if we were to try to cool YbF using a laser with wavelength 552 nm, it would take ≈ 270 photons to remove 1 ms^{-1} of velocity from a single molecule. Now, in practice the actual internal structure is a far cry from the idealised two-level system considered above. If the excited state can couple to another state which is outside the linewidth of the cycling laser, no matter how weakly, then the huge number of cycles required to remove significant momentum from the atom or molecule will almost invariably lead population to be transferred into this dark state. If the probability of a decay into a dark state is q , then the number of cycles p before half the population is transferred into the dark state is

$$p = -\frac{\ln 2}{\ln(1 - q)}. \quad (1.16)$$

To set the scale, if $q = 10^{-3}$ then $p \approx 700$ and, using the values for YbF discussed above, deceleration of the beam beyond $\approx 3.7 \text{ m s}^{-1}$ is impossible⁸. This effect can be mitigated by adding an additional laser whose purpose is to repump population from the dark state back into the main cooling cycle.

As an example in an atomic species, the usual cooling cycle in ^{85}Rb is on the $5^2\text{S}_{1/2}(F=3) \rightarrow 5^2\text{P}_{3/2}(F=4)$ transition. However, because of the detunings required there is a small possibility for the laser to excite the $5^2\text{S}_{1/2}(F=3) \rightarrow 5^2\text{P}_{3/2}(F=3)$ line, which can spontaneously decay to the state $5^2\text{S}_{1/2}(F=2)$ [80]. As the splitting between the two hyperfine states within the electron ground state manifold is of the order 3 GHz, the state $5^2\text{S}_{1/2}(F=2)$ does not couple to the laser and hence cycling terminates. To mitigate this, a weak repump on the $5^2\text{S}_{1/2}(F=2) \rightarrow 5^2\text{P}_{3/2}(F=3)$ line is used, and the subsequent spontaneous decay back into $5^2\text{S}_{1/2}(F=3)$ returns the population back to the original cooling cycle.

The situation becomes drastically more complicated in molecules. As well as the orbital, electron spin, and nuclear spin angular momenta that are familiar from atomic physics, molecules have additional degrees of freedom relating to their rotation about their centre of mass, and the relative motion of their nuclei[91]. The selection rules that define whether a transition can cycle are determined from the conservation of total angular momentum in the photon-atom/molecule interaction⁹, so schemes can be found that close the transitions between the infinite manifolds of rotational states [92]. However, the relative motion of the nuclei plays no role in the angular momentum thanks to the Born–Oppenheimer separation, and so is not constrained in this way. For diatomic molecules the relative motion of its constituents gives rise to a vibrational energy, and the transitions between the various vibrational states are governed by what is in general the nonzero overlap of the vibrational wave functions. This is known as the Franck–Condon principle [93], and it sets strong constraints on the molecules which can be successfully laser cooled.

We can attempt to solve this using repump lasers as we saw for ^{85}Rb , but the complexity of the experiment grows rapidly. As the vibrational levels form another infinite manifold, the limit to the final velocity is really limited by the number of laser frequencies one has available to “plug” the leaks from the excited state. Be-

⁸This can be shown by noting that on average each cycle removes velocity $\mathbf{v}_0 = \hbar\mathbf{k}/m$ from a YbF molecule of mass m . The probability of a molecule becoming dark is $(1 - q)$, so the total change in beam velocity is $v_0 \sum_n (1 - q)^n = v_0/q$.

⁹See, for example, page 119 of [21].

cause the Franck–Condon matrix of YbF is not particularly diagonal [94], slowing by 10 m s^{-1} using this technique requires three re-pump lasers, in addition to the main cooling beam. Sidebands must be applied to each of these beams in order to effectively address the molecular hyperfine structure, and control of the polarization is also required to destabilise the magnetic projection dark states [95].

We see, therefore, that a laser-cooled source of YbF molecules is a desirable but difficult goal. The sensitivity gains from such a source have the potential to be enormous, but realisation requires both a sub- 10 m s^{-1} molecular beam and a large array of laser frequencies. A scheme for producing a source of this type was proposed by Tarbutt *et al* [4], which I summarise in the following section.

1.4 A molecular fountain of YbF

The suggested scheme is based on the loading of an optical molasses by a molecular beam of YbF molecules. Once within the molasses, the molecules would be cooled to $185\text{ }\mu\text{K}$, before being ejected in a controlled way into the eEDM experiment. An estimated 4.4×10^5 molecules would be produced by this source, maintaining the intensity of the current source. Due to the extremely low temperatures and maintained high flux, the sensitivity to the eEDM using this source is estimated to be $6 \times 10^{-31}\text{ e}\cdot\text{cm}$ within 8 hours of measurement, two orders of magnitude better than the current limit.

As the capture velocity for the molasses is $\approx 10\text{ m s}^{-1}$, we require an exceptionally slow molecular beam source to begin with. Thankfully, recent work in the group of John Doyle has led to the development of a new generation of buffer gas source [96]. Consisting of two gas cells separated by a small gap, these “two-stage” sources capture the best properties of both hydrodynamic and effusive beams. The first cell is operated in the hydrodynamic regime to provide efficient cooling and extraction, with molecules being swept directly into the second stage. The aperture from the second stage uses a fine copper mesh to reflect the buffer gas back into the beam, providing a small number of slowing collisions. Beams of CaH produced by this cell with peak forward velocities of 40 m s^{-1} and fluxes of 5×10^8 per pulse have been observed. Given that the mass of YbF is approximately four times greater than that of CaH, it is reasonable to assume that a fully-optimised two-stage source of YbF will have a velocity distribution peaked at 20 m s^{-1} .

This is still outside the capture velocity of the molasses, so the next stage is to

perform velocity selection on the beam. A curved permanent magnetic guide is suggested for this task. By tuning both the radius of curvature of the guide and the field strength of the permanent magnets, a limiting transmitted velocity can be defined. Velocities in excess of this do not make the bend and are lost. Additionally, helium atoms are not guided and are lost through vents in the guide geometry. This technique has previously been demonstrated by guiding beams of molecular oxygen [97], with an upper limit velocity of 70m s^{-1} . Our aim is somewhat lower, as we aim to remove all but the slowest 10m s^{-1} .

With the fast molecules and helium wind filtered away by the guide, we are now in a position to perform laser cooling on the YbF molecules. Since the publication of [4] the suggested pumping scheme has changed, with the current scheme shown in [94]. The main cooling transition is from the $X^2\Sigma^+(v=0, N=1)$ manifold to the $A^2\Pi_{1/2}$ excited state along the P(1) transition. Repump lasers address any population that reaches the first three excited vibrational states in $X^2\Sigma^+$. The logic behind connecting these repumps to different excited states is quite interesting. If one connects many states within the ground electronic manifold to a single excited state, in the high intensity limit population becomes distributed amongst all available levels in the cycle¹⁰. The actual distribution will depend on the relative oscillator strengths of the various transitions involved, but coupling an additional level in the ground state manifold to the system will reduce the total population in the remaining levels. Now, the maximum rate at which laser cooling can proceed is proportional to the excited state population, so the more vibrational, rotational, and hyperfine states from the ground state manifold that are coupled to the excited state, the slower the cooling rate. Breaking the repumping scheme up in this way, with the transitions only coupled to the main cycle by spontaneous emission, will avoid this issue as much as possible.

After 7 ms in the optical molasses the molecules are cold and ready for use. Removal from the cooling region and loading into the experiment can be performed by detuning one of the cooling lasers, giving the cold packet a small and tuneable acceleration from the cooling region. State selection is possible by intentionally forming dark states through blocking the light exciting a certain hyperfine state. From here the usual eEDM experiment described in section (1.1) can proceed, but now with the supersonic beam source replaced by one with ultra-low temperature and forward velocity.

¹⁰I demonstrate this effect in general terms in appendix (B.8).

1.5 Aims of this project

In order to realise a fountain source of YbF molecules, we must develop molecular beam sources that are amenable to laser cooling. To be more specific, we require beams with a significant slow fraction which can be loaded into a molasses, with or without some form of prior velocity filtering.

To this end, I present here the characterisation of two buffer gas sources of molecules. We have concluded the work of Bulleid [99], who used computational techniques to design cell geometries that provide optimal extraction efficiencies. We have also produced a two-stage molecular source in the style of Doyle [96], and we compare and contrast the two for viability in laser cooling experiments. Over the course of this exploration, we have also developed methods to accurately measure the velocity distributions produced from dim molecular sources, and have highlighted sources of bias in some established methods. We have also addressed the role of the ablation target in the production of molecular beams, considering the impact of thermal and mechanical changes in the system.

Chapter 2

Theory of buffer gas beams and cells

Before we proceed with our discussion and analysis of the single stage source, we first lay out the theoretical background of buffer gas sources of molecules. We will derive the relationship between various beam properties in both the effusive and hydrodynamic regimes, with particular attention paid to the number density in the cell and the velocity in the resulting molecular beam. By treating the thermalisation between hot atoms/molecules and a buffer gas as being the result of many elastic collisions, we will derive expressions for the typical scales required to efficiently cool a molecular beam. Finally, expressions for the time scales of diffusion and effusion in a cell are obtained, capturing the two limiting regimes in which molecular transport in the cell can occur.

2.1 Pressure regimes and the Knudsen number

The characteristic behaviour of a gas depends on its pressure. A high pressure gas is best treated as a continuous fluid where the Navier–Stokes equations can be used to determine its properties. On the other hand, in the low pressure limit we can consider each atom or molecule in the gas independently and apply kinetic theory. The two regimes are known as the hydrodynamic and effusive limits respectively.

To quantify the pressure at which these two regimes occur, we use the Knudsen number, Kn , defined via

$$\text{Kn} = \frac{\lambda}{L} = \frac{1}{\sqrt{2}n\sigma L}. \quad (2.1)$$

Here λ is the average length scale for intra-particle collisions known as the mean free path, n is the number density, and L is a characteristic length scale for the system we are considering. For example, L might be the length of a cell or the diameter of an aperture. The elastic cross-section for the gas is given by σ . We see that the Kn is inversely proportional to the expected number of collisions over a distance L for our gas. In the case where $\text{Kn} > 1$ the gas is in the effusive limit, whilst for $\text{Kn} < 10^{-2}$ the gas is fully hydrodynamic. Intermediate values of Kn correspond to a transitional regime, where neither theory provides a fully satisfactory description and we must consider elements of both the limiting cases. The pressures where these two limits lie depend on the equation of state of the gas in question; in the limit of an ideal gas, we see that $\text{Kn} \propto T/p$, where p is the pressure and T the temperature of the system.

Note that other dimensionless numbers can be used to characterise the behaviour of the gas. A popular alternative is the Reynolds number Re , given by

$$\text{Re} = \frac{\rho v L}{\mu}, \quad (2.2)$$

where ρ is the mass density of the fluid, v its velocity, and μ is the dynamic viscosity. The Knudsen and Reynolds numbers are connected through the Von Karman equation [100]

$$2\text{Ma} \approx \text{Kn} \times \text{Re}. \quad (2.3)$$

Here Ma is the Mach number, defined as the ratio between the flow velocity and the speed of sound in the fluid. In addition to the regimes defined previously, the Reynolds number is also typically used to parametrise the transition from laminar to turbulent flow. For flow through a smooth pipe, this transition occurs around $\text{Re} \geq 4000$ [101].

2.2 Low pressure flow and the effusive limit

We first turn our attention to the low-pressure limit, where gas particles may be treated individually rather than collectively. We are interested in two scenarios—the gas properties in our confined buffer gas cell, and its behaviour once outside the cell in the form of a beam.

As long as our gas is inert, we can relate the number density in the cell to the

flux from the cell¹. In the effusive limit, this can be calculated from the number of buffer gas particles inside the cell that reach the aperture in some time interval δt [75]. The number density n may be written in terms of the particle number N and the volume V via

$$n = \frac{dN}{dV}, \quad (2.4)$$

and the number density of particles with speeds in the interval δv arriving in the solid angle $\delta\omega$ is

$$n = \frac{\bar{n}}{4\pi} f(v) \delta v \delta\omega. \quad (2.5)$$

Here $\bar{n}$ is the total number density in the cell regardless of solid angle or velocity, and $f(v)$ is the probabilistic distribution of speeds therein. If the direction of motion of the particles relative to the normal of the plane of the aperture is defined by an angle θ , then the particles reaching the aperture in the interval δt will lie within a cylindrical region of volume

$$\delta V = v A \cos \theta \delta t, \quad (2.6)$$

where A is the aperture area. Combining equations (2.4), (2.5), and (2.6) and taking the infinitesimal limit, we obtain an expression for the number of particles reaching the aperture:

$$dN = A \frac{\bar{n}}{4\pi} v f(v) \cos \theta dv d\omega dt. \quad (2.7)$$

If the gas is thermal, the distribution of speeds will be Maxwellian,

$$f(v) dv = \frac{32}{\pi^2 \bar{v}^3} v^2 \exp\left(-\frac{4v^2}{\pi \bar{v}^2}\right) dv, \quad (2.8)$$

where the mean velocity $\bar{v}$ is given in terms of the temperature and particle mass m by

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}. \quad (2.9)$$

Inserting equation (2.8) into (2.7) and integrating over all speeds and directions, we find that the total flux through the aperture is given by

$$\frac{dN}{dt} = \frac{\bar{n} \bar{v} A}{4}. \quad (2.10)$$

Now, as the particle number is conserved, so too is the flux. In a typical experiment, we set the flux of buffer gas using a mass flow controller whose units are in standard

¹This statement is based on the conservation of particle number. If our gas is volatile it will stick to the walls of the cell and hence this condition is no longer valid.

cubic centimetres per minute (SCCM). The conversion factor between SCCM and the flux dN/dt in a perfect gas can be found by taking the time derivative of the equation of state,

$$\frac{dN}{dt} = \frac{p}{k_B T} \frac{dV}{dT}. \quad (2.11)$$

Now, 1 SCCM is equivalent to $10^{-6}/60$ cubic meters per second under the standard conditions $p = 10^5 \text{ Pa}$ and $T = 273 \text{ K}$. Inserting these values, we obtain

$$\frac{dN}{dt} [\text{atoms/s}] = 4.4 \times 10^{17} \frac{dV}{dt} [\text{SCCM}], \quad (2.12)$$

where quantities in the square brackets denote the units of the conversion. In the steady state, the flux into the cell must equal the flux out of the cell. Defining $\dot{N}_{\text{in}}$ as the flux from the mass flow controller, we obtain an expression for the maximum number density in the cell:

$$\bar{n}_{\text{max}} = 4 \frac{\dot{N}_{\text{in}}}{\mathcal{T} A \bar{v}}. \quad (2.13)$$

Here $\mathcal{T}$ is the transmittance of the aperture. In general, $\mathcal{T}$ will be less than unity due to collisions in the aperture region, an effect which reduces the effective size of the aperture and therefore increases the number density in the cell.

The beam properties follow from the in-cell derivation above. The probability of a molecule emerging through the aperture and into the beam is proportional to its velocity. Inputting this explicit dependence into equation (2.7) and normalising, we find that the beam velocity distribution $f_b(v)$ is given by [75]

$$f_b(v) dv = \frac{v}{\bar{v}} f(v) dv, \quad (2.14)$$

and the mean forward velocity is given by $\bar{v}_b = 3\pi/8 \times \bar{v}$. Another important beam property is the divergence. We calculate this by first noting that the number density resulting from an infinitesimal aperture area dA is

$$n(R, \theta) = \frac{\bar{n}}{4\pi R^2} \cos \theta dA, \quad (2.15)$$

where R is the distance from the aperture. The divergence follows from the full-width at half-maximum of the angular distribution of equation (2.15):

$$\Delta\theta = 2 \arccos \frac{1}{2} = \frac{2\pi}{3}. \quad (2.16)$$

We have therefore obtained expressions for the average number density in a buffer gas cell, and the velocity and divergence of the resulting beam, in the low cell pressure limit.

2.3 Temperature, pressure, and density in isentropic expansions

In this section, we will examine the isentropic expansion of a high-pressure fluid from a reservoir into the vacuum. Beginning with the first law of thermodynamics, we will obtain expressions linking the pressure, number density, and temperature in this limit. By invoking the conservation of energy, we will find an expression for the velocity of a molecular beam in terms of the pressure drop across the aperture. Finally, we will use the continuity equation to obtain an analytic expression for the minimum number density in the cell. The gas will be assumed to be calorically ideal, with constant heat capacities and an equation of state given by the ideal gas law.

The first law of thermodynamics links the change in specific internal energy de of a system to the specific work done, dW , and the specific heat dq applied to it. If the pressure is constant, then the heat applied per unit mass is

$$dq = de + Pd\left(\frac{1}{\rho}\right), \quad (2.17)$$

where the expression for the work follows from the usual form $dW = \mathbf{F} \cdot d\mathbf{x}$, expressed in terms of the pressure P and dividing through by the mass. We may also write down the total heat content of the gas, or enthalpy h , per unit mass:

$$\begin{aligned} h &= e + \frac{P}{\rho} \\ \implies dh &= de + \frac{dP}{\rho} + P d\left(\frac{1}{\rho}\right). \end{aligned} \quad (2.18)$$

Substituting equation (2.18) into (2.17) to eliminate the internal energy term we obtain an expression linking the changes in heat, enthalpy, and pressure:

$$dq = dh - \frac{dP}{\rho}. \quad (2.19)$$

We now define expressions for the specific heats corresponding to constant-volume and constant-pressure heating,

$$\begin{aligned} c_V &= \left(\frac{de}{dT}\right)_V \\ c_P &= \left(\frac{dh}{dT}\right)_P, \end{aligned} \quad (2.20)$$

where the use of ordinary rather than partial derivatives follows from the stipulation that our gas is ideal, following as it does the ideal gas law

$$P = \frac{R}{M} \rho T, \quad (2.21)$$

where R is the molar gas constant and M the molar mass for our gas. Our choice of the ideal gas law in terms of R rather than k_B is slightly arbitrary—the following discussion proceeds equally well in either case—but as we are dealing with a gas continuum it is slightly more pleasing to consider the gas as a collective rather than as individual particles. We will frequently see expressions in terms of the dimensionless ratio κ , where

$$\kappa = \frac{c_P}{c_V}. \quad (2.22)$$

Invoking this ratio allows us to obtain useful algebraic expressions for the heat capacities. Substituting equation (2.21) into (2.18), taking the temperature derivative, and substituting using equations (2.20) we obtain

$$\begin{aligned} c_V &= \frac{1}{\kappa - 1} \frac{R}{M} \\ c_P &= \frac{\kappa}{\kappa - 1} \frac{R}{M}. \end{aligned} \quad (2.23)$$

We now have enough information to obtain expressions linking the pressure, temperature, and mass density. Under isentropic expansion the heat exchanged is zero, so $dq = 0$. Applying this to equation (2.19) and transforming the enthalpy differential to a temperature differential, we obtain

$$\left(\frac{dh}{dT} \right)_P dT - \frac{dP}{\rho} = 0. \quad (2.24)$$

Using equations (2.23) and (2.21), we can simplify expression (2.24) into the easily integrable form

$$\begin{aligned} \left(\frac{\kappa}{\kappa - 1} \right) \frac{dT}{T} &= \frac{dP}{P} \\ \implies \frac{P}{P_0} &= \left(\frac{T}{T_0} \right)^{\kappa/(\kappa-1)}. \end{aligned} \quad (2.25)$$

Expressions for the temperature-density relation are found following the same procedure for equation (2.17), and for the pressure-density using equation (2.19):

$$\frac{\rho}{\rho_0} = \left(\frac{T}{T_0} \right)^{1/(\kappa-1)}, \quad (2.26)$$

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0} \right)^\kappa. \quad (2.27)$$

Together, equations (2.25), (2.26), and (2.27) fully describe the ideal gas parameters P, ρ, T in terms of the known reference values P_0, ρ_0, T_0 .

2.4 Velocity and Mach number in the high-pressure limit

For energy to be conserved in a flowing gas, the stored energy per unit mass—thermal, kinetic, and potential—must be conserved in time. For steady, one-dimensional, isentropic flow this corresponds to the requirement

$$v dv + dh = 0, \quad (2.28)$$

where v is the velocity of a gas infinitesimal in the fluid and the first term corresponds to the kinetic energy. Integrating equation (2.28) and using the assumption that the gas is calorically ideal,

$$h = c_p T, \quad (2.29)$$

we find an expression for the flow velocity in terms of the temperature:

$$\frac{v^2 - v_0^2}{2} = \frac{\kappa}{\kappa - 1} \frac{R}{M} (T_0 - T). \quad (2.30)$$

Let's take the known reference values for the velocity v_0 and temperature T_0 to correspond to values in the cell. In general, $v_0 < v$; taking this simplification, the velocity obtained under isentropic expansion is

$$v(T) = \sqrt{2 \frac{\kappa}{\kappa - 1} \frac{RT_0}{M} \left(1 - \frac{T}{T_0} \right)}. \quad (2.31)$$

The maximum possible velocity of the gas undergoing the expansion is obtained when the thermal energy has been fully converted into kinetic energy. Setting $T \rightarrow 0$ in equation (2.31), the maximum forward velocity is

$$v_{max} = \sqrt{2 \frac{\kappa}{\kappa - 1} \frac{RT_0}{M}} = c_0 \sqrt{\frac{2}{\kappa - 1}}, \quad (2.32)$$

where we have introduced the speed of sound

$$c_\alpha = \sqrt{\frac{\kappa R T_\alpha}{M}}. \quad (2.33)$$

For a monatomic ideal gas such as helium, $\kappa = 5/3$ and hence,

$$v_{max} = \sqrt{3}c_0. \quad (2.34)$$

We have therefore found an expression for the maximum possible velocity from a source operating in the hydrodynamic regime in terms of the known temperature in stagnant gas of the cell and the molar mass of the buffer gas used.

2.5 Cell number density in the high-pressure limit

Our next task is to obtain an expression for the number density of the gas in the cell in this regime. We will do this by using the continuity equation to relate the density and speed of sound in the aperture with their values in the cell. Under hydrodynamic conditions there will be a macroscopic flow through the buffer gas cell with some velocity. Hence the number density under these conditions defines a lower bound, in an analogous manner to the upper bound of equation (2.13). At the aperture the beam becomes supersonic and hence $\text{Ma} = 1$. This fact will allow us to write the number density in the cell by using the flow through the aperture as a reference.

The continuity equation for one-dimensional flow may be written in the form

$$d(\rho v \mathcal{T} A) = d(nv \mathcal{T} A) = 0 \implies nv \mathcal{T} A = \frac{dN}{dt}, \quad (2.35)$$

where dN/dt is the constant flux through the system and A is the cross sectional area. We require expressions for the number density and the velocity in terms of the Mach number. We label the number density and temperature at the aperture as n_a and T_a respectively. Rearranging equation (2.31) we obtain

$$v^2 = c_a^2 \frac{2}{\kappa - 1} \left(\frac{T_0}{T_a} - 1 \right), \quad (2.36)$$

where c_a is the speed of sound at the aperture, defined in terms of T_a . We can rewrite equation (2.36) in terms of the temperatures:

$$T_a = T_0 \left[\left(\frac{\kappa - 1}{2} \right) \text{Ma}^2 + 1 \right]^{-1}. \quad (2.37)$$

Invoking the condition $\text{Ma} = 1$ at the aperture, we substitute expression (2.37) into (2.33) to obtain

$$c_a = v_a = \sqrt{2 \frac{\kappa}{\kappa + 1} \frac{RT_0}{M}}. \quad (2.38)$$

For the number density, we note that

$$\left(\frac{n}{n_0}\right) = \left(\frac{\rho}{\rho_0}\right) = \left(\frac{T}{T_0}\right)^{1/(\kappa-1)}, \quad (2.39)$$

where in the last step we have invoked equation (2.26). Thus, inserting equation (2.39) into equation (2.37),

$$n_a = n_0 \left[\left(\frac{\kappa - 1}{2} \right) \text{Ma}^2 + 1 \right]^{-1/(\kappa-1)}. \quad (2.40)$$

We now have expressions that connect the number density inside the cell and in the aperture. We also, through equations (2.38) and (2.33), can link the speeds of sound in these regions. In the aperture, equation (2.35) gives

$$n_a c_a \mathcal{T} A_a = \frac{dN}{dt}. \quad (2.41)$$

Substituting equations (2.40) and (2.38) into (2.41), taking the limit $\text{Ma} = 1$ in the aperture, and solving for the number density in the cell, we find that

$$\bar{n}_{\min} = \frac{\dot{N}}{\mathcal{T} A c_0} \left(\frac{2}{\kappa + 1} \right)^{\frac{\kappa+1}{2(1-\kappa)}} = \frac{16}{9} \frac{\dot{N}}{\mathcal{T} A c_0}, \quad (2.42)$$

where in the final step we have again evaluated the co-factor for an ideal helium buffer gas. If we now compare the bounds of equations (2.13) and (2.42), we find that

$$\frac{\bar{n}_{\max}}{\bar{n}_{\min}} = \frac{9}{4} \frac{c_0}{\bar{v}} = \frac{9}{4} \sqrt{\frac{5\pi}{24}} \approx 1.82, \quad (2.43)$$

and the two approaches give agreement to within a factor of two. Therefore, even if we are in the intermediate regime and neither the kinetic nor fluid dynamic approaches are appropriate, our densities must still be tightly bounded and the two models will provide strong benchmarks against which to compare.

As an aside, note that the lower limit for the number density was derived for the hydrodynamic regime, and that the upper limit was derived for the effusive regime.

This does not mean that we will have lower pressure in the cell if our beam is supersonic! Rather, each theory is appropriate for a distinct, separate set of Knudsen numbers. Increasing the flow rate from the effusive to hydrodynamic regime will lead to the number density in the cell increasing as normal; however, the collective motion of the fluid in the hydrodynamic regime enhances extraction from the cell relative to the low-pressure case. Thus applying the kinetic theory in the hydrodynamic limit will lead to an overestimation of the number density in the cell.

Finally, we will write down an expression for the divergence angle from a fully supersonic source. The density distribution in this case is [102]

$$n(R, \theta) \approx n(R, 0) \cos^2 \left(\frac{\pi\theta}{2\phi} \right), \quad (2.44)$$

where ϕ is a structural term obeying $\phi \approx 1.4$ for monotonic gases. Then the divergence is again found from the full-width at half-maximum:

$$\Delta\theta = \phi < \frac{2\pi}{3}, \quad (2.45)$$

and we see that the supersonic beam has a narrower divergence than the effusive case. Note that, unlike for the densities, the effusive and hydrodynamic divergences do not bound the divergence for the intermediary regime. The effusive limit samples the thermal distribution inside the cell, and hence the effusive beam has no forward boosting that could narrow the divergence. Conversely, the pressure in the supersonic beam is typically high, leading to a strong pressure gradient across the beam that again increases the divergence. An intermediary beam can avoid both these cases, receiving just enough forward boosting to form a bright, narrow beam.

2.6 Elastic thermalisation inside a buffer gas cell

We now turn our attention to the thermalisation of an initially hot gas, such as is formed by the production of molecules via ablation or RF discharge, with a cold background gas. We will assume that the hot molecules are heavily diluted with respect to the cold buffer gas, such that the background temperature is constant over the thermalisation process. We will set the initial temperature of the hot gas species to be T_i , the background gas temperature as T_b , and the temperature of the hot species after N elastic collisions to be T_N .

To attack this problem, we first consider the effect of a single collision. We will model the background gas and the hot species as point particles with masses m and M respectively. The pre-collision velocities are v_i and V_i , and the velocities after the collision v_f and V_f . The calculation is greatly simplified by performing a Galilean transform into a frame co-moving with the centre of mass of the system. This centre-of-mass frame has velocity

$$\mathbf{V}_C = \frac{M\mathbf{V}_i + m\mathbf{v}_i}{M + m}. \quad (2.46)$$

We will denote quantities in this frame of reference with a tilde—for example, the initial velocity of the hot species becomes $\tilde{V}_i = V_i - V_C$. In this frame, we can write the total momentum vector $\mathbf{p}$ and energy E of the system as

$$\mathbf{p} = M\tilde{\mathbf{V}}_i + m\tilde{\mathbf{v}}_i = M\tilde{\mathbf{V}}_f + m\tilde{\mathbf{v}}_f = \mathbf{0} \quad (2.47)$$

$$E = \frac{M}{2}\tilde{V}_i^2 + \frac{m}{2}\tilde{v}_i^2 = \frac{M}{2}\tilde{V}_f^2 + \frac{m}{2}\tilde{v}_f^2. \quad (2.48)$$

We can re-arrange the initial and final velocities in equation (2.47) to obtain the conditions

$$\tilde{V}_i^2 = \frac{m^2}{M^2}\tilde{v}_i^2 \quad (2.49)$$

$$\tilde{V}_f^2 = \frac{m^2}{M^2}\tilde{v}_f^2, \quad (2.50)$$

which we may substitute into equation (2.48) to obtain the condition

$$\tilde{V}_i^2 = \tilde{V}_f^2, \quad (2.51)$$

and we see that, in the centre of mass frame, the collision must only change the direction of the particle and not its energy.

The temperature of a gas is only defined for an ensemble of particles, so in the following we will be evaluating ensemble averages of our terms with respect to their relevant distributions. We will assume that the buffer gas is thermal and stagnant, such that a Maxwell–Boltzmann type velocity distribution is appropriate. Note that in this case the ensemble average $\langle \tilde{\mathbf{v}}_{i,f} \rangle = 0$ in general.

We begin by transforming our initial velocity from the centre of mass frame to the lab frame,

$$\langle \tilde{V}_i^2 \rangle = \langle (\mathbf{V}_i - \mathbf{V}_C)^2 \rangle = \langle V_i^2 \rangle + \langle V_C^2 \rangle - 2\langle \mathbf{V}_i \cdot \mathbf{V}_C \rangle. \quad (2.52)$$

Applying equation (2.46) to the cross-term,

$$\langle \mathbf{V}_i \cdot \mathbf{V}_C \rangle = \frac{M}{M+m} \langle V_i^2 \rangle + \frac{m}{M+m} \langle \mathbf{V}_i \cdot \mathbf{v}_i \rangle \quad (2.53)$$

$$\implies \langle \tilde{V}_i^2 \rangle = \left(1 - \frac{2M}{M+m}\right) \langle V_i^2 \rangle + \langle V_C^2 \rangle, \quad (2.54)$$

where in the final step we have used the fact that the two gases have different distributions, at least one of whose means must be zero, to eliminate the term in $\langle \mathbf{V}_i \cdot \mathbf{v}_i \rangle$. We can perform a similar trick to obtain

$$\langle V_f^2 \rangle = \langle \tilde{V}_f^2 \rangle + \langle V_C^2 \rangle + 2\langle \tilde{\mathbf{V}}_f \cdot \mathbf{V}_C \rangle. \quad (2.55)$$

Invoking equation (2.51) and explicitly expanding $\langle V_C^2 \rangle$ while treating the cross terms as in equation (2.54), we find that

$$\langle V_f^2 \rangle = \frac{M^2 + m^2}{(M+m)^2} \langle V_i^2 \rangle + \frac{2m^2}{(M+m)^2} \langle v_i^2 \rangle \quad (2.56)$$

$$\implies \langle V_f^2 - V_i^2 \rangle = -\frac{2m}{(M+m)^2} [M \langle V_i^2 \rangle - m \langle v_i^2 \rangle]. \quad (2.57)$$

We now substitute equation (2.9) for the ensemble-averaged velocities in (2.57), remembering to keep track of the mass terms, and obtain the change in the temperature of the hot gas after one collision:

$$T_f - T_i = -\frac{2mM}{(M+m)^2} (T_i - T_b). \quad (2.58)$$

If $M \gg m$, the change in temperature will be slow and we can approximate the difference equation (2.58) by the continuous differential equation

$$\frac{dT}{dN} = -\frac{2mM}{(M+m)^2} (T - T_b) = -\chi (T - T_b), \quad (2.59)$$

which has the general solution

$$T(N) = T_b + (T(0) - T_b) e^{-N\chi}. \quad (2.60)$$

We see that the action of elastic collisions between the buffer gas and the hot species is enough to asymptotically reduce the temperature of our molecules towards the background level over the characteristic scale $1/\chi$. A more useful metric is the

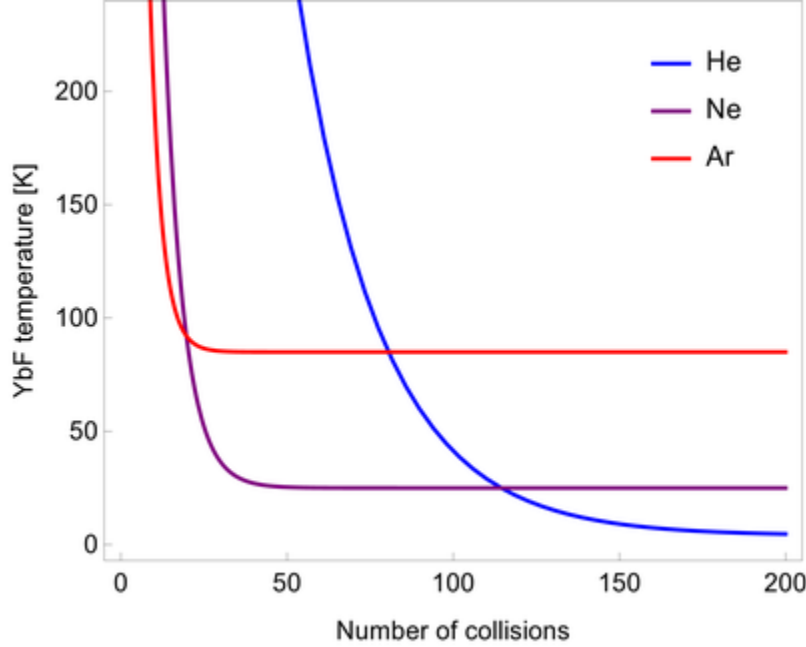


Figure 2.1: Thermalisation of 2000K ytterbium fluoride with 3 different buffer gases—4K He, 25K Ne, and 85K Ar. Using a more massive buffer gas drastically decreases the number of collisions required for thermalisation, but the baseline temperature is limited by the higher freezing points of the heavier noble gases.

number of collisions required to reduce the temperature to some known fraction of the buffer gas temperature. Rearranging equation (2.60), we find that

$$N = \frac{1}{\chi} \ln \left(\frac{T(0) - T_b}{\delta T} \right) \approx \frac{1}{\chi} \ln \left(\frac{T(0)}{\delta T} \right), \quad (2.61)$$

where $T = T_b + \delta T$ and the approximation on the right becomes exact in the limit $T(0) \gg T_b$ as usually happens in ablation processes. Applying equation (2.61), we find that it takes $N \approx 230$ collisions to cool ^{174}YbF from an initial temperature² of 2000K to 5% of the nominal helium buffer gas temperature of 4K. Using different

²The actual initial temperature in the plume is hard to pin down. It will certainly be bounded from below by the boiling point of Yb which, depending on the pressure in the cell, will be of the order 500–1000K [108]. One would also expect that the temperature of measured atoms and molecules be bounded from above by the first ionisation energy of Yb, 70,000K, as if it were much higher we might expect the entire cell to act like one giant Langmuir probe [109]. Similarly, the product dissociation energy of YbF is $\approx 40,000\text{K}$, which sets an upper bound on the temperature at which the chemical bonds between ytterbium and fluorine can occur [110]. We take the characteristic

choices of buffer gas can reduce the number of required collisions, as seen in figure (2.1), but the molecular temperature is adversely affected due to the higher freezing points of the more massive noble gases.

The maximum distance that a YbF molecule will travel is found by assuming that each collision changes only the magnitude and not the direction of its velocity vector. Then, using equations (2.1) and (2.61) we find that

$$l_{\max} = N\lambda = \frac{N}{\sqrt{2}\bar{n}\sigma}, \quad (2.62)$$

and the time taken to travel this distance is found using equation (2.9):

$$t_{\max} = \lambda \int_0^N \sqrt{\frac{\pi M}{8k_B T(N')}} dN'. \quad (2.63)$$

Using the known form for $T(N)$, we can solve the integral analytically³

$$\int_0^N \frac{dN'}{\sqrt{T(N')}} = \frac{2}{\chi\sqrt{T_b}} \left(\operatorname{arctanh} \sqrt{\frac{T_b + (T_0 - T_b)e^{-N\chi}}{T_b}} - \operatorname{arctanh} \sqrt{\frac{T_0}{T_b}} \right), \quad (2.64)$$

which, for our special case of $T_b = 4\text{K}$, $T_0 = 2000\text{K}$, $N = 230$ gives $t_{\max} \approx 5.13 [\text{s/m}] \times \lambda$, with the units of $t_{\max}$ being in seconds as usual. We can evaluate the mean free path in the two regimes discussed in sections (2.2) and (2.3) to obtain limiting values

$$1.2 \times 10^4 \left(\frac{\mathcal{T}A}{\mathcal{F}} \sqrt{T} \right) \leq l_{\max} \leq 2.2 \times 10^4 \left(\frac{\mathcal{T}A}{\mathcal{F}} \sqrt{T} \right), \quad (2.65)$$

where $\mathcal{F}$ is the flow rate measured in SCCM and the temperature and aperture area are measured in SI units. A typical thin aperture used experimentally has diameter of the order 4 mm, and $\mathcal{T} \approx 1$. Substituting the characteristic experimental parameters $T = T_b = 4\text{K}$ and $\dot{N}_{\text{in}} = 20\text{SCCM}$, we find that

$$1.5\text{cm} \leq l_{\max} \leq 2.7\text{cm}, \quad (2.66)$$

temperature of 2000K as this is a familiar and typical temperature barrier for chemical interactions; taking the upper limit of 70,000K as an initial temperature gives $N \approx 321$, as the logarithm gives us only weak dependence on the plume temperature.

³For example, the substitution $u(N) = e^{-N\chi}$ gets the system into a more amenable form immediately.

with the characteristic thermalisation time

$$0.18\text{ms} \leq t_{\text{max}} \leq 0.32\text{ms}. \quad (2.67)$$

Equation (2.66) sets quite stringent requirements on the minimum possible size of a buffer gas cell. If the distance between the target and the aperture is too short, the molecules will not be fully thermal by the time they leave the cell. However, naively making a cell which has a very large internal volume is not always the best move either. In the effusive limit the extraction efficiency of the source is A/Σ , where Σ is the internal surface area of the cell. Conversely, in the hydrodynamic limit the extraction efficiency tends to 1 as molecules are swept from the cell by the collective motion of the buffer gas. When parametrising the source we typically wish to tune our flow regime by increasing or decreasing the flux of buffer gas molecules through the cell. We see, therefore, that if we want to maximise the yield from the cell in the effusive regime we must choose internal dimensions that are close to the limiting thermalisation distance of equation (2.62).

Finally, we consider the time scales for diffusion and advection in a cell, as these will determine the total time a YbF molecule is retained before being ejected by the beam. Under the Chapman–Enskog approximation [111], the diffusion constant D for the co-mingling of two gases is

$$D = \frac{3}{16} \sqrt{\frac{2\pi k_B T}{\mu}} \frac{1}{\bar{n}\bar{\sigma}_D}, \quad (2.68)$$

where $\bar{\sigma}_D \approx 10^{-18} \text{m}^2$ is the thermally averaged diffusion cross section and μ is the reduced mass of the two gases. The time constant for the lowest order diffusion mode [112] through a cubic cell of length L is then

$$\tau_D = \frac{L^2}{3\pi^2 D}. \quad (2.69)$$

Conversely, if our molecular species is being swept out of the cell advectively then the time scale is just the ratio of the number of buffer gas atoms in the cell to the rate at which they leave the cell:

$$\tau_{ad} = \frac{\bar{n}L^3}{\dot{N}_{in}}. \quad (2.70)$$

The two processes here are in direct competition—a fully effusive cell will be diffusion-limited, while a hydrodynamic cell will have dynamics fully governed by the advection

of gas through it. Evaluation of these constants for a given cell geometry and flow parameter set can give crucial information about the actual thermalisation properties of our molecules.

We now have enough information to begin assessing and characterising molecular sources. We have introduced the two limiting regimes for laminar gas flow, and for each case determined expressions for the cell density, beam velocity, and beam divergence. We have shown how molecules in a stagnant gas volume will thermalise via elastic collisions with a buffer gas, and provided characteristic length and time scales for this process. Finally, we have spoken briefly about the two methods by which molecules can leave the cell and form a beam, and expressed the competition between the processes as two characteristic time constants for each behaviour. In the following section we will apply this analysis to a specially designed source, whose internal geometry is constructed in such a way as to produce a bright, subsonic beam of molecules.

Chapter 3

Characterising a single-stage beam source of YbF

Previous work undertaken in the group by Bulleid, Skoff *et al* [72, 99] have shown that computational modelling of gas flow through a buffer gas cell can provide predictions that are in good agreement with experimental measurements. The full Navier–Stokes equation was solved using the computational fluid dynamics program Star-CCM+. The finite-element method was used to split a three-dimensional representation of the cell into a mesh, with each element bounded by the mesh having constant properties. At every iteration, the action of adjacent elements was calculated, and updated estimates for each element saved. In the steady state, the model has converged once the properties of each element are constant.

Once the helium flow has been determined computationally, the molecular evolution can be calculated by solving the transport equation

$$\frac{\partial n_m}{\partial t} = \nabla \cdot (D \nabla n_m) - \nabla \cdot (\mathbf{v} n_m), \quad (3.1)$$

where n_m is a scalar field describing the molecular number density, $\mathbf{v}$ is the vector field describing the helium velocity, and D is the diffusion coefficient which, in general, may not be constant. Note that equation (3.1) contains both an advective and a diffusive term in competition, consistent with the discussion surrounding equations (2.69) and (2.70), but no source term. The absence of a source lies in our molecular production method; if we were able to produce YbF via capillary loading rather than ablation, a source term would have to be included as well as an initial condition.

Following the success of this method in describing the thermalisation and beam

properties of a molecular source, the same computational modelling scheme was applied to aid in the design of a new cell, the Hybrid Source. The goal of this design was to improve the molecular flux from the cell through careful control of the internal volume. Regions that did not directly contribute to the thermalisation such as internal corners were removed, and the gas inlet was placed at an angle to channel the helium flow over the ytterbium target efficiently. This created a high density region of helium near to the target, effectively reducing the thermalisation distance and increasing the extraction efficiency by creating molecules in a region of high flow.

The final design is shown in cross-section in figure (3.1), and consists of a 10 mm bore “chimney” drilled 20 mm into a solid copper block, with an angled base milled into the bottom of this cylinder. There was no well-defined aperture, and instead the entire top of the chimney was covered in 30% transmissive copper mesh to provide a wide aperture area, while still maintaining ideal effusive conditions between the channels of the mesh. The behaviour of this cell was modelled by Bulleid for a helium flow rate of 60 SCCM. The YbF was introduced to the cell as a spherical plume of diameter 5 mm, offset 2.5 mm from the centre of the target, and the extraction efficiency was found to be 63%. The mean velocity of the molecular beam was predicted to be 120 m s^{-1} , with an estimated divergence of 10° and a molecular flux of 2×10^{13} molecules per steradian per pulse.

In this section, we present the experimental realisation of the hybrid source. We have measured the temperature, forward velocity, and divergence of a molecular beam produced from this apparatus, and hence determined the characteristic molecular flux of the source. Based on this parametrisation, the hybrid source has been used elsewhere in the group as an integral part of the experiment to laser-slow calcium fluoride.

3.1 Experimental set-up

The apparatus, shown in cross-section in figure (3.3), is designed according to the principles outlined in chapter (2). It consists of a cryogenic buffer gas cell, a $\sim 4 \text{ K}$ heat-sunk helium line, a $\sim 260 \text{ K}$ sulphur hexafluoride (SF_6) line¹, a Nd:YAG ablation laser, and a set of spectroscopic apparatus that is used for the detection of

¹This line is not shown in the cross-section as it lies out of the plane of the cut. The SF_6 line enters the cell in the same plane as the Yb rod and the YAG window, and is directed directly onto the Yb target.

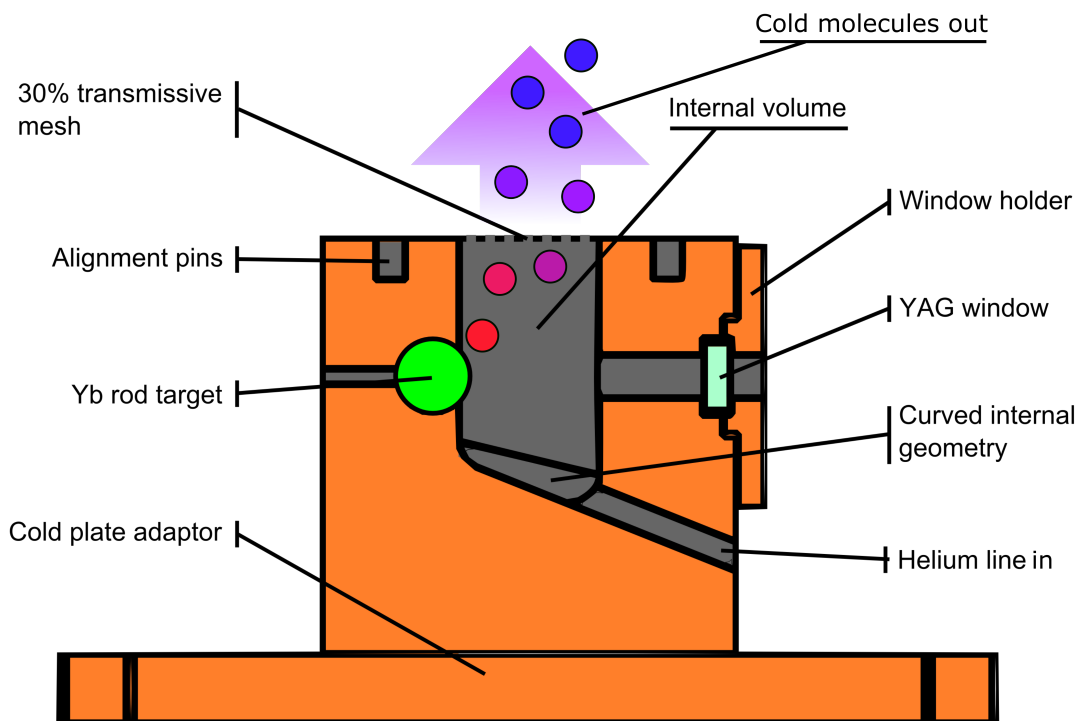


Figure 3.1: Rendering of a through-axis cross section of the hybrid source. The internal volume of the cell is shown in grey, and the external copper block is in orange. Helium enters from the bottom right and is swept over the Yb target (green) by the angling of the bottom of the cell. Alignment pins hold the mesh firmly against the top of the cell, and the small YAG window is gas-sealed using indium wire. Not shown in this cross-section is the orientation of the SF_6 line which lies in the plane defined by the Yb rod and the Nd:YAG window, and which points directly at the Yb target.

molecules and the measurement of beam parameters.

The hybrid source is a buffer gas cell made from a solid copper block. A hole of diameter 12 mm and depth 20 mm forms the internal volume where hot Yb reacts with SF_6 to form YbF, before being cooled sympathetically via elastic collisions with the 4 K helium. The cell is mounted on a large copper adaptor plate, which is itself mounted onto the cold head of an SRDK-415 Sumitomo Heavy Industries cryocooler module.

The cryocooler consists of two cold stages of temperatures $30\text{ K} \leq T_1 \leq 60\text{ K}$ and $3\text{ K} \leq T_2 \leq 8\text{ K}$, with vastly more cooling power available on the higher-temperature stage. This arrangement gives us a baseline temperature in the region of 4.5 K, with the exact value depending on our use of radiation shielding and our choice of apparatus.

Helium enters the experiment initially at room temperature, before being sequentially cooled to 30 K and then 4 K before the cell. To achieve this, the helium gas lines are wrapped around copper blocks, to which they are affixed by solder. These blocks, also known as bobbins, are then attached using brass screws to the two stages of the cryocooler. This maximises the thermal contact between the gas lines and the cooler. The cold helium flows into the bottom of the cell via a 3 mm diameter capillary, where its flow is shaped by the internal structure of the source.

We produce YbF radicals via the laser ablation of an ytterbium target in a fluorine-rich environment. The target consists of a solid Yb cylinder of diameter 8 mm that sits inside a through-hole drilled perpendicular but off-axis to the direction of helium flow. If necessary, we can rotate the rod during an experiment via a rotational feedthrough and a screw thread, exposing fresh target to the Spectron Nd:YAG laser used for ablation. For the experiments performed in this section, the YAG provided $\approx 100\text{ mJ}$ of energy per pulse, with a pulse width of 7 ns focussed to a $1 \pm 0.5\text{ mm}$ spot size. 260 K SF_6 is flowed continuously into the experiment via a thermally-insulated capillary tube. During ablation, the SF_6 provides a rich source of the fluorine required to produce YbF. Thermal insulation is provided by a 2 mm-thickness PEI insert to prevent the SF_6 from freezing in the capillary before reaching the cell.

To maintain the low temperatures required in a typical experiment, the system is kept to pressures under 10^{-5} mbar using a Kurt J Lesker vacuum chamber sealed with KF O-rings. An aluminium radiation shield anchored to the T_1 stage minimises the blackbody radiation power from the room-temperature vacuum to the T_2 stage. An additional, smaller shield is fixed to the T_2 stage. Made of copper and coated in activated carbon, the purpose of this second shield is to act as a cryosorb to the helium at temperatures below 10 K, reducing the background pressure close to the source.

The top surface of the cell is covered with a 30% transmissive mesh rather than an aperture. This follows the work of Doyle et al, who showed that the use of meshes

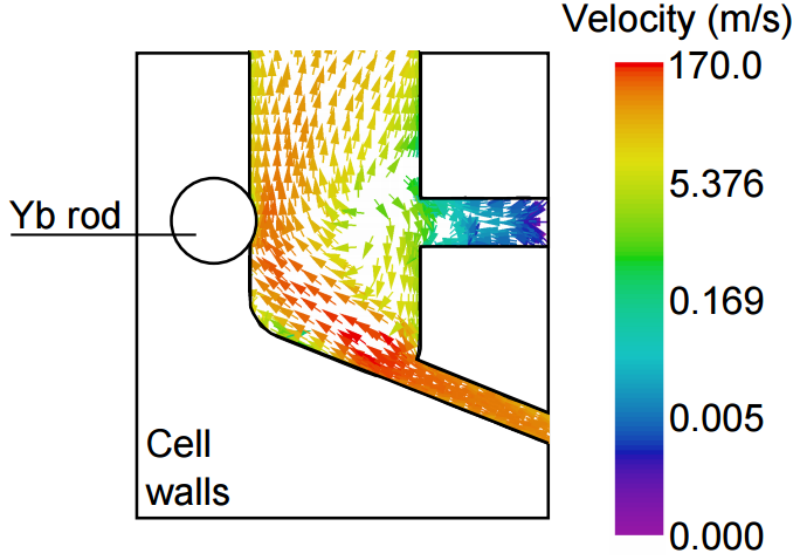


Figure 3.2: Flow of helium at 60 SCCM through the hybrid source. The magnitude of the velocity vector field is shown on a logarithmic scale, with the arrows giving the mean flow direction per unit element.

with channel size less than the collisional mean free path can produce bright, slow molecular beams. The mesh is made of copper, and is affixed mechanically using four brass screws to the top of the cell. A small amount of epoxy is also added to keep the mesh flush against the surface and prevent helium leaks.

There are two detection regions located 50 mm and 172 mm from the mesh. We probe on the $X^2\Sigma^+(v=0) \rightarrow A^2\Pi_{1/2}(v=0)$ band, with the exact choice of line depending on the type of measurement made. By scanning a Coherent 899 ring dye laser near the P-branch bandhead at 542.808 THz we obtain LIF spectra for the various P- and Q-branch rotational lines. The high density of lines here makes this region ideal for measuring rotational temperatures and daily alignment and troubleshooting tasks. We may also move away from the bandhead for tasks that require isolated lines, typically to the Q(3)–Q(6) lines² around 542.815 THz. We also have the capability to tune the laser to be resonant with Yb atoms. The ytterbium flux is typically an order of magnitude higher than that for YbF, a fact which is particularly useful when we attempt to make measurements that would otherwise have

²For a definition of exactly what constitutes a Q-line, see appendix (A).

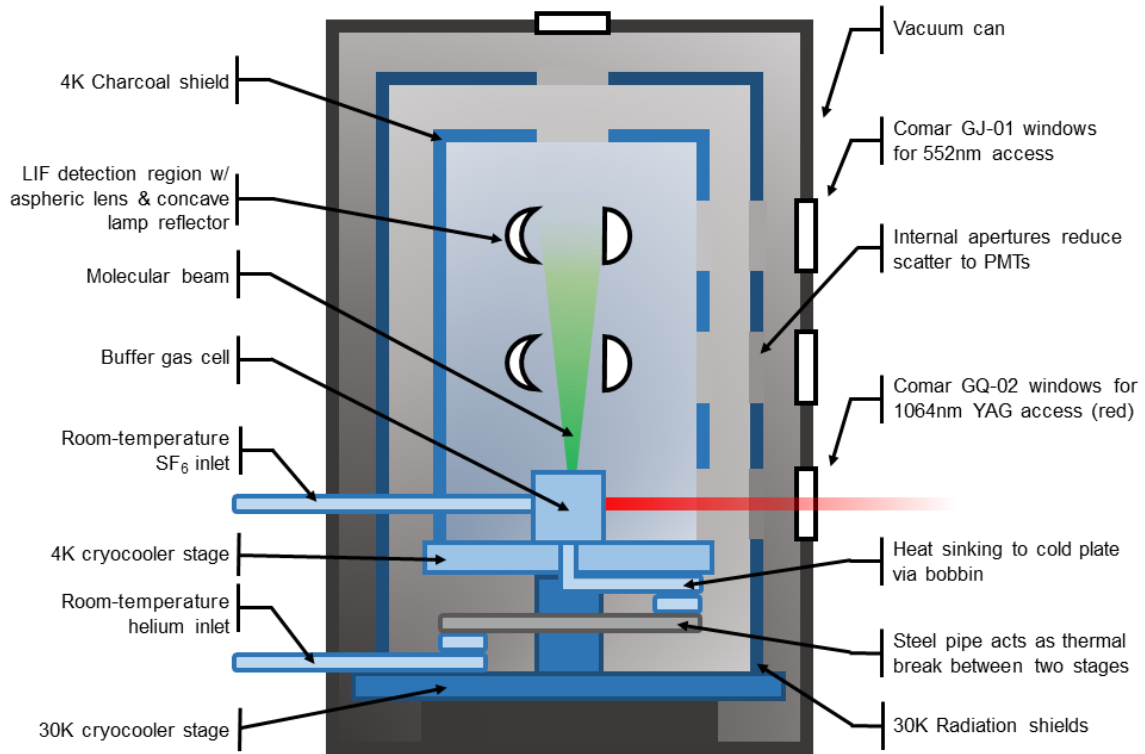


Figure 3.3: Sketch of the in-vacuum components of the experiment. Both gas lines enter at room temperature, with the helium line being thermalised to the two cold stages via two “bobbins”—solid copper blocks around which the gas lines are soldered. The LIF optics are held in an aluminium frame that is also heat-sunk to the 4 K stage.

poor signal-to-noise (e.g. absorption spectroscopy). We can also make use of the fact that Yb has no nuclear spin and hence no hyperfine structure, a fact which greatly simplifies measurements which require the fitting of Doppler-broadened profiles to spectral lines.

Scattered photons from the LIF process are collimated by an aspheric lens–concave reflector pair, before being focussed down outside the vacuum chamber by a second aspheric lens onto the surface of a photomultiplier tube (PMT). An iris and an infra-red filter directly before the PMT are used to spatially and spectrally filter out

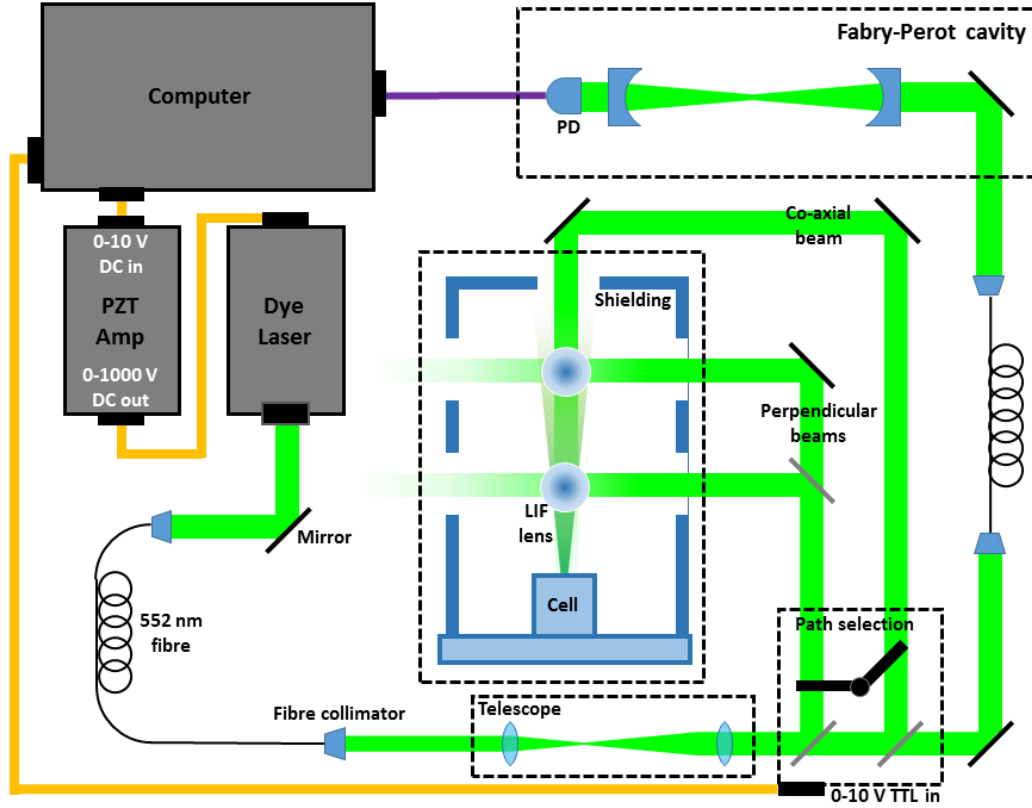


Figure 3.4: Sketch of the laser system used in measurements of the hybrid source. The software ScanMaster is used to generate patterns and record data. Here the laser piezo-electric transducer (PZT) is driven by an amplified 0–10 V input, while the perpendicular/co-axial beams are switched by triggering shutter(s) using a TTL signal. The frequency response of the laser is recorded via the peaks of a passive Fabry–Perot cavity. The vacuum can in this sketch is rotated by 90° axially compared with the details shown in figure (3.3). Computer outputs are shown in orange and inputs in indigo (or purple, for those who dislike alliteration).

infra-red light from our ablation laser. We use two types of PMT—a Hamamatsu R760 with 7% quantum efficiency at the first detector, and a Hamamatsu R2228 with quantum efficiency 8% at the second detector. The two PMTs are manually calibrated by using an LED to correlate the photon-counting and current-collecting modes of the equipment.

3.2 Measuring beam parameters using LIF

There are a range of different beam parameters that we wish to measure in order to characterise molecular beams produced by a particular source configuration. In order to determine the flux of ground state molecules per steradian per pulse, we must determine the velocity, translational temperature, and rotational temperature. The velocity distribution and beam divergence follows from these measurements, as does information about the confinement properties of the molecules in the cell, so understanding how we go about measuring the velocity and temperatures in question is important. In this section I'll outline the schemes used in each case.

The experimental apparatus has access for up to three probe laser beams at once. The first two are perpendicular to the direction of propagation of the molecular beam, and the third is parallel (and nominally co-axial) to it. The orientation of these beams with respect to the molecular beam, as well as the various other control systems and laser components, are shown in figure (3.4). All three beams typically intersect the centre of symmetry of the molecular beam, where the molecular density and hence LIF signal are maximised, but there is a small amount of flexibility in the pointing direction of the beams. Molecules addressed by the perpendicular lasers experience no Doppler shift of the laser frequency, while those addressed by the parallel beam observe a blue detuning of

$$\delta f = \frac{v}{c} f_0, \quad (3.2)$$

where v is the molecular velocity and f_0 the frequency of the laser. The fact that molecules experience a blue rather than red detuning is because, in our experiments, they travel antiparallel to the propagation direction of the laser.

Let's begin by discussing how we go about performing a typical LIF measurement of the rotational temperature of molecules in a molecular beam. Recall from our earlier discussions in section (1.2) that the rotational temperature parametrises the population of the various rotational energy states of molecules when they are in thermal equilibrium. Thus, a measurement of the population of a range of rotational levels allows us to determine the rotational temperature.

As we wish to measure the population in the rotational states regardless of the molecular forward velocity, we use the perpendicular lasers as our probe. The laser frequency is held at some initial, fixed value. If the laser is close to a resonance with a rotational transition in the molecule we observe an increase in the number

of spontaneously-emitted photons, which are emitted out of the laser mode and into a solid angle of 4π . Using photon collection optics, a proportion of these photons are collected and focussed onto a photomultiplier tube operating in constant current mode; this current is converted into a voltage, which is then recorded in 1–4 μs intervals depending on the time resolution required in a measurement³. The laser frequency is then stepped and the process repeated, with the relative frequency between steps recorded by monitoring the transmission of the laser through a 0.5 m Fabry–Perot cavity. The frequency stepping continues until a map of the number of scattered photons is constructed as a function of laser frequency. This map is a rotational spectrum for our given frequency range.

Now, if the probe laser intensity is high enough that the transition is saturated, all the population is driven from the ground rotational level and a corresponding number of photons are emitted, collected, and observed. In this limit, there is a direct correspondence between the measured intensity of a line in the rotational spectrum, and the proportion of molecules within that given rotational state⁴. As long as we have picked a spectral range which is well-understood, we should in principle know which transitions correspond to a given rotational state in the ground state manifold, and hence can map out the state populations as a function of rotational quantum number. The rotational temperature follows after a simple fit to the known distribution function.

Note that, for each value in our frequency scan range, we have a corresponding time-of-flight distribution recorded by the PMT. This arises for two reasons—firstly, the flow dynamics within the source mean that not all molecules leave at the same time; and second, the molecules emerge from the source with some finite-width distribution of velocities, leading to temporal spreading over the free-flight time to the detection region. We do not have to use the full time-of-flight distribution in order to determine the spectrum, but rather we can integrate over smaller time ranges in order to capture the behaviour of molecules with certain arrival times at the detector. This process is valid because integration and summation commute, so integrating

³The conversion between recorded voltage and number of photons is determined through calibration—the PMT is run in photon counting mode, then switched to voltage mode, for a range of light intensities and a calibration curve is developed.

⁴To keep the discussion simple, I’ve glossed over the role of optical cycling in this discussion. A molecule excited from a state within the ground state manifold, $|g\rangle$, to an excited state $|e\rangle$ has a finite probability to spontaneously decay back into $|g\rangle$, where it can again couple to the laser field, increasing the line intensity. This probability can be computed from the state projection factors, examples of which are given in appendix B of [48].

over the full time range is equivalent to breaking the time range into intervals, integrating over each interval separately, and then summing the resulting integrals. This fact allows us to determine the mean value of a given parameter within a given time interval, and hence to map out its (interval-averaged) time evolution.

The measurement of the translational temperatures and the molecular velocities are not much more complicated, but require us to use the parallel laser beam. Measurements of the velocity proceed by obtaining two spectra simultaneously—one with the parallel laser, and one with the perpendicular—and determining the relative Doppler shift between spectral features in the two spectra according to equation (3.2). In this case, the logic behind using the parallel laser is fairly transparent. Slightly less obvious is why we must use the parallel laser for measurements of the translational temperature. Just as the rotational temperature parametrised the width of the rotational state distribution in a beam of molecules, the translational temperature parametrises the instantaneous width of the beam velocity distribution. Transforming this distribution into frequency space with the help of equation (3.2), we see that the temperature is a function of the *width* of the measured spectroscopic lines. I discuss this broadening process more completely in section (3.3).

A typical LIF experiment is optimised to effectively collect photons emitted within a small volume, known as the detection volume. The extent of this volume is usually far less than the width of the molecular beam, so only a small volume of the beam is sampled by the probe. Now let’s decompose the molecular velocity, $\mathbf{v}$, into components that lie parallel and perpendicular to the molecular beam axis, $\mathbf{v}_{\parallel}$ and $\mathbf{v}_{\perp}$. We would expect the $\mathbf{v}_{\perp}$ component to become strongly correlated with the perpendicular position co-ordinate over a length scale $L \approx d \mathbf{v}_{\parallel} / \mathbf{v}_{\perp}$, where d is the aperture diameter of the source producing the beam. Molecules with greater $\mathbf{v}_{\perp}$ reach greater distances from the molecular beam axis than those with smaller perpendicular velocities. Because of this, any spatially local sampling of the molecules beyond the limit L will give only a subset of the total velocities within the beam, meaning that the measured widths of our spectroscopic lines (and, hence, the translational temperatures) underestimate their true values.

This is avoided if we use a parallel laser beam. Consider molecules with only parallel velocities $\mathbf{v}_{\parallel}$ moving on the molecular beam axis. Their position along the axis will again become correlated with $\mathbf{v}_{\parallel}$, but unlike in the $\mathbf{v}_{\perp}$ case now all molecules are guaranteed to pass through the detection region. Thus, as long as the probe is always on, we will eventually scatter photons from all parallel velocity classes, and the mea-

sured line width and translational temperature will be reflective of their actual values.

We have therefore discussed, in general terms, the measurement procedure of the rotational temperature, translational temperature, and velocity of molecules within a molecular beam. We must now apply these principles in order to parametrise our molecular source, a discussion of which is presented in the remainder of this chapter.

3.3 Translational temperature

We have determined the translational temperature of both Yb and YbF beams by measuring the Doppler broadening of the $^{174}\text{YbF } Q(0)$ and $\text{Yb } ^1S_0 \rightarrow ^3P_1$ transitions. We use the parallel probe laser, aligned to be co-axial with the molecular beam, for this measurement. The detection region of each PMT is a volume of $\approx 3\text{mm}^3$ on the molecular beam symmetry axis, which we mapped out by observing the scattering of laser light from a fine wire.

In the frame of reference of a particle moving with forward velocity $v \ll c$, the co-axial laser is observed with frequency $f = f_0(1 - v/c)$. Thus molecules with faster forward velocities will become resonant with the laser at lower frequencies than those with slower velocities. There are two processes which contribute to the spectral linewidth measured in this experiment. The natural broadening of the line is a consequence of the lifetime of the excited state τ_{es} and has Lorentzian character $\mathcal{L}$, whilst the thermal, or Doppler, broadening arises from the probability distribution for the velocities in the beam and is assumed to have Gaussian character $\mathcal{G}$. The cumulative contribution of these two effects is expressed by the Voigt profile :

$$\mathcal{V}(f) = \mathcal{L} * \mathcal{G}. \quad (3.3)$$

Far from the line centre the Gaussian character is suppressed by the exponential decay and the character of the Voigt profile is almost completely Lorentzian. The natural linewidth of the $\text{YbF } X^2\Sigma^+(v=0) \rightarrow A^2\Pi_{1/2}(v=0)$ transition (defined by $2\pi/\tau_{\text{es}}$) is 6MHz, whilst the thermal full-width at half-maximum at 4K is 56MHz. An approximation of the width of the Voigt profile in terms of the full widths and half maximum of its constituents is given by [113]

$$\phi_{\mathcal{V}} \approx 0.535\phi_{\mathcal{L}} + \sqrt{0.217\phi_{\mathcal{L}}^2 + \phi_{\mathcal{G}}^2}, \quad (3.4)$$

where $\phi_{\mathcal{G}}$ is the full width at half maximum of distribution $\mathcal{G}$. Applying this to our case, we find that the Voigt profile is almost completely Gaussian in character,

and that using a Gaussian fit is associated with a $\approx 12\%$ systematic underestimation of the temperature. This was particularly useful when we were determining the temperature of YbF, as we found that computationally fitting the Voigt fit was unreliable or failed completely for many spectra with poor signal-to-noise ratios and complex hyperfine structure⁵.

The Gaussian form of the Doppler broadening is given by

$$\mathcal{G}(f) df = \sqrt{\frac{Mc^2}{2\pi k_B T f_0^2}} \exp\left(-\frac{Mc^2(f-f_0)^2}{2k_B T f_0^2}\right) df, \quad (3.5)$$

where f_0 is the central frequency of the transition and M is the mass of the particle species whose temperature T we are trying to measure. By performing a fit to the lineshape of the form $\sim e^{-(x-x_0)^2/2\sigma^2}$, the fitted width σ is related to the temperature via

$$T = \frac{M}{k_B} \left(\frac{\sigma c}{f_0}\right)^2. \quad (3.6)$$

Using equation (3.6) we have determined the translational temperature of beams of ytterbium produced in the hybrid source as follows. As the natural linewidth of ytterbium is much less than the Doppler broadening, we fitted three Gaussians to the ^{172}Yb , ^{174}Yb , and ^{176}Yb isotopes using as our ansatz function

$$\mathcal{F}(f_1, f_2, f_3, A_1, A_2, A_3, \sigma, \mathcal{F}_0) = \mathcal{F}_0 + \sum_{j=1}^3 A_j \exp\left(-\frac{(f-f_j)^2}{2\sigma^2}\right), \quad (3.7)$$

where the line centres f_j , amplitudes A_j , width σ , and offset $\mathcal{F}_0$ are to be determined. All three isotopes were assumed to be in thermal equilibrium such that only one width σ was required. A plot of this fit function applied to an experimental Yb spectrum is shown in the leftmost pane of figure (3.5).

Following this fitting procedure, the Gaussian width is obtained as a function of time after ablation, and the temperature determined as in equation (3.6). A plot of this measured longitudinal temperature is shown in the rightmost pane of figure (3.5), determined from spectra obtained using the co-axial laser at a LIF detection region 172 mm from the cell aperture. Atoms which arrive at our detection point at

⁵Note that the natural linewidth of the $^{174}\text{Yb } ^1S_0 \rightarrow ^3P_1$ is of the order 100kHz, so a full Gaussian approximation is perfectly acceptable, having a maximum systematic error at 4K of $\approx 1\%$.

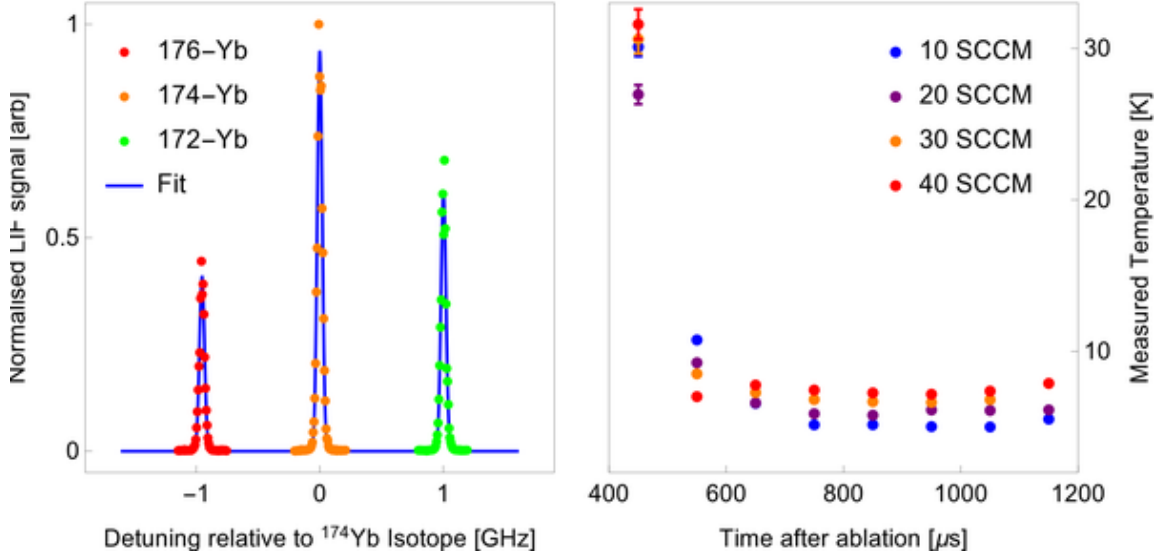


Figure 3.5: Gaussian fits to the three ytterbium isotopes (left), and the thermal behaviour measured 172 mm from the aperture (right) of ytterbium beams produced in the hybrid source. The fractional errors in the fit parameters (line centres, widths, amplitudes) to the isotopes were found to be $< 1\%$ in all cases.

early times are not fully thermalised. The degree of thermalisation is intrinsically linked to the time an atom or molecule spends in the cell. We will save a full discussion of this until after we present measurements of the beam velocity, but for now we state that this is consistent with an extended initial distribution of Yb essentially “filling” the cell volume. Ytterbium which is ejected directly towards the mesh will, in general, experience fewer collisions than ytterbium which is ejected away from it and must subsequently diffuse to the cell exit. Making this discussion quantitative requires knowledge of the retention time in the cell, which we may approximate from the forward velocity of the beam as I will show in section (3.7).

We have also measured the temperature at the near detection region 50 mm from the cell aperture; a plot of this measurement is shown in the rightmost pane of figure (3.7). However, there is a complication. Observe in figure (3.6) that the spectral lines measured using the co-axial laser become bifurcated. We have found that this effect is most pronounced between $\approx 550 \mu\text{s}$ and $\approx 1050 \mu\text{s}$. The fact that this behaviour is not mirrored in spectra obtained using a laser perpendicular to the direction of the

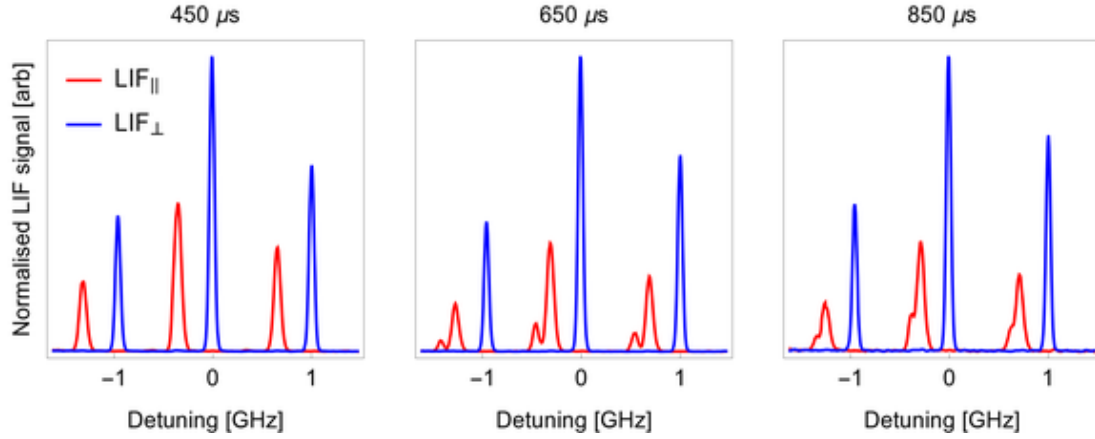


Figure 3.6: Evolution of the Yb spectrum recorded by performing LIF with a co-axial laser (red) and a perpendicular laser (blue). The atomic beam was produced using a helium flow rate of 20 SCCM, and was measured at a point 50 mm from the cell aperture. The spectrum obtained using the co-axial laser is Doppler-shifted relative to that measured by the perpendicular beam, and displays full Doppler broadening. At 650 μ s after ablation there is the emergence of a second family of peaks, corresponding to the arrival of faster molecules, which contribute greatly to the linewidth.

molecular beam implies that there has been a change in the forward velocity distribution of our molecules which arrive at the detector in this interval. Recall from figure (3.2) that the flow through the cell consists of two distinct regimes—a laminar, fast-moving region close to the Yb target, and an almost stagnant, recirculating region close to the YAG window. An atom or molecule entrained in the fast-flow region will be swept advectively from the cell, whilst a molecule trapped in the stagnant region must diffuse either to the mesh or to the laminar locale before it can leave. This suggests a mechanism for the late-arriving faster peak: that it consists of particles that thermalised within the recirculation region and then diffused into the laminar zone. The final contribution in this case would consist of slower molecules that have diffused through the mesh, and faster molecules that have diffused into the effusive region in the cell.

We can justify this suggestion by noting that the laminar and recirculating regions are roughly 5 mm in extent, so the average distance over which an atom or molecule must travel to pass from one region to the other is ≈ 2.5 mm. From equations (2.69)

and (2.70), the time scales for atomic diffusion and advection over this distance are $\approx 700\text{ }\mu\text{s}$ and $\approx 150\text{ }\mu\text{s}$ respectively. The average velocity of this second peak is $\approx 250\text{ m s}^{-1}$, so we would expect to see an atom or molecule that has diffused, been swept from the cell, then travelled 5cm to the detector after $\approx 1050\text{ }\mu\text{s}$, in reasonable agreement with our experimental results.

This discussion opens the door rather nicely for a point about determining the translational temperature using the Doppler broadening expression. Equation (3.6) is based on quite a bold assumption—that the velocity distribution is thermal, as is given in equation (3.5). However, the actual source of broadening in our experiment is the instantaneous velocity distribution of our beam, which very often will not be Gaussian in character. Supersonic beams are the exception, having a distribution which is typically taken to be an axially-shifted Gaussian with temperatures perpendicular and parallel to the beam direction not in equilibrium (the so-called ellipsoidal drifting velocity distribution). However, if the velocity distribution in the beam follows an effusive distribution then the procedure breaks down. We can perform the same process as in equation (3.5) with the distribution (2.14) to obtain the full-width at half-maximum

$$\sigma_{\text{eff}} \approx 1.03 \times \frac{f_0 \bar{v}}{c}, \quad (3.8)$$

which is narrower than the Doppler broadening term by

$$\frac{\sigma_{\text{eff}}}{\sigma_{\mathcal{G}}} \approx 1.03 \sqrt{\frac{1}{\pi \ln 2}} \approx 0.698. \quad (3.9)$$

In other words, application of equation (3.6) without consideration of the flow regime or the velocity distribution can lead to a significant systematic underestimation of the temperature by as much as $\sim 30\%$. Worse, the interesting flow dynamics typically occur in the transition region between the supersonic and effusive flow cases, where neither the kinetic nor gas dynamic approaches are appropriate. So using this method opens us up to a significant but unknown systematic error if we attempt to determine the translational temperature.

That said, is this error in measuring the translational temperature a problem? Measurements of this parameter are useful only because they parametrise the velocity distribution of our molecules. For spectroscopic purposes we care far more about the rotational temperature of our molecules—the relative populations in each rotational energy state. For scattering and deceleration experiments, the velocity distribution itself is required. Thus, as long as we have the velocity distribution of our beam and

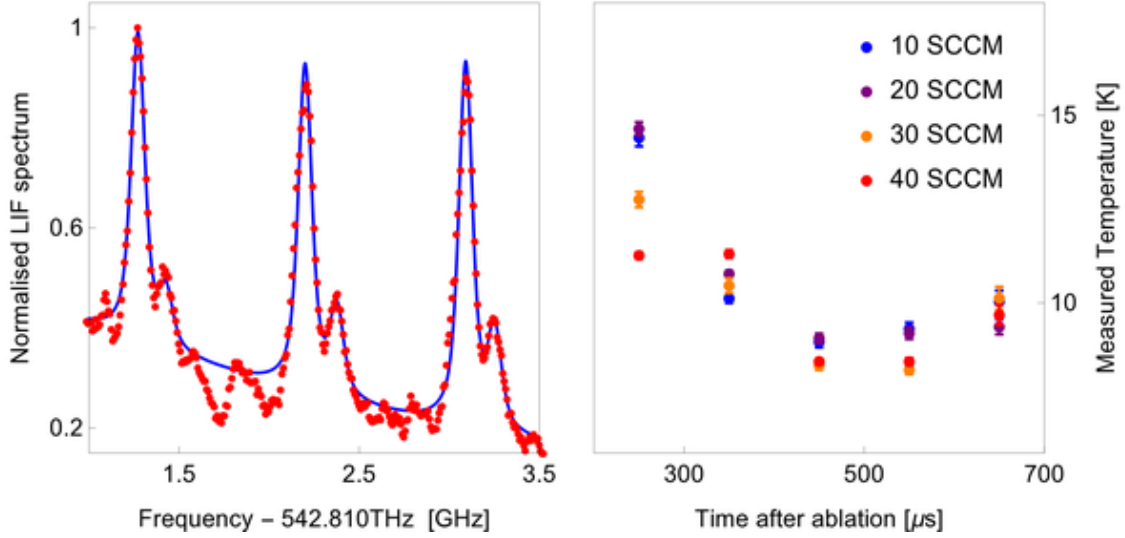


Figure 3.7: YbF spectrum obtained 450 μs after ablation at the bottom detection region and its corresponding 6-peak Voigt fit (left panel), and measured temperature using a Yb beam at the same position (right panel). The three main peaks in the YbF spectrum are, from left to right, the ^{174}YbF Q(0) line, the degenerate ^{176}YbF Q(1) and ^{172}YbF Q(0) lines, and the ^{174}YbF Q(1) line. The bifurcation of each of these peaks is a result of the fluorine nuclear spin giving rise to hyperfine structure. The background amplitude is not physical, and is a systematic resulting from the deterioration of the Yb ablation target with time.

the rotational temperature, we can still perform a complete parametrisation of our source. Whilst it is absolutely a problem if we apply a Gaussian fit with no regard for the flow regime, the translational temperature itself is often not the best measure for parametrising our beam. We therefore obtain the necessary velocity distributions in section (3.6), both on average and as a function of time.

Finally, we turn to measurements of the YbF temperature. Whilst fitting to the YbF line centres is simple, determining the widths in this experiment proved rather tricky. This is due to the significantly more complex rotational and hyperfine structure of the YbF molecule, specifically over the measured region near the P-branch bandhead where the rotational lines were most intense. The splitting between hyperfine components within a single rotational line was found to be of the order of the

Doppler broadening, meaning that the hyperfine components were only just resolved. However, we can check that the thermalisation is the same for both Yb and YbF by using our measured Yb temperature to fix the YbF linewidth. We have performed a fit of the full Voigt function, with the temperature fixed by the measured Yb temperature, over the ^{174}YbF Q(0), ^{176}YbF Q(1) / ^{172}YbF Q(0), and ^{174}YbF Q(1) lines of YbF. As we see in the left panel of figure (3.7), the fit properly captures the character of the 3 sharp, dominant peaks, without being broadened by the poorly-resolved hyperfine components. The temperature used for the particular fit shown in figure (3.7) was fixed at the measured value of (9.06 ± 0.13) K obtained from a Yb beam addressed at the same detection region at the same time after ablation.

3.4 Rotational temperature of YbF

The most common formalism for determining the rotational energy distribution is as follows. Once the molecules reach thermal equilibrium, the relative population of an internal state with energy E is assumed to be defined by the Boltzmann distribution

$$P(E) \propto e^{-E/k_B T}, \quad (3.10)$$

where T is the temperature associated with the energy in question. The relative populations of the rotational states of YbF can therefore give another measure of the temperature of the beam. The degeneracy of states within a given rotational manifold is $4 \times (2N + 1)$, where N is the rotational quantum number of the state and the factor of 4 arises from the coupling of the rotation to the electron and fluorine nuclear spins, giving 4 hyperfine states. Therefore, at a given temperature T the probability of measuring a molecule in the rotational state J is simply the number of states multiplied by their Boltzmann distributions

$$P(J) \propto \mathcal{D} e^{-E_{\text{rot}}/k_B T} \propto (2J + 1) e^{-BJ(J+1)/k_B T}, \quad (3.11)$$

where E_{rot} is the rotational energy, $\mathcal{D}$ is the state degeneracy, and B is the rotational constant of the molecule.

We have measured the rotational temperature of a beam of YbF molecules produced from the hybrid source at a flow rate of 20 SCCM. The spectrum was measured four times using the LIF technique at the bottom detection region, and the populations of the ^{174}YbF Q(1) through ^{174}YbF Q(4) levels determined by integrating over the relevant spectral lines. Using the known rotational constant $B = 7 \times 10^9 \text{ Hz} \cdot h$, fits of the form (3.11) were performed as a function of time. Plots of two fitted distributions are

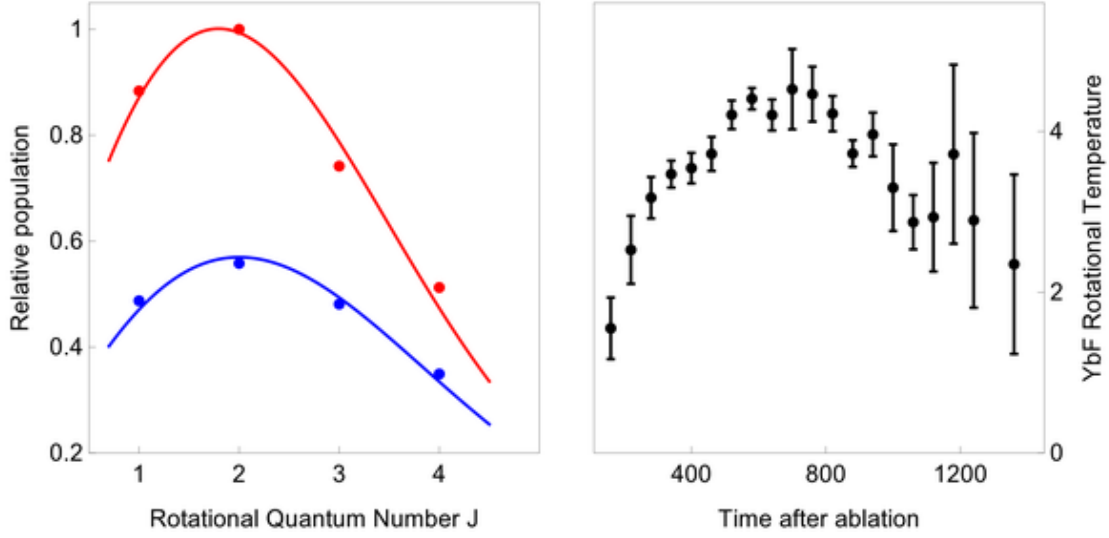


Figure 3.8: Fitted rotational level distributions (left), and derived rotational temperatures (right) for a 20 SCCM YbF beam from the hybrid source. The two curves in the left pane are obtained at times of 400 μ s and 640 μ s, with fits to equation (3.11) being performed. The errors in the rightmost pane come from uncertainties in the fit induced by an overall decay in signal at late times.

shown in the leftmost panel of figure (3.8), with the rotational temperature obtained from these fits in the right pane. We observe that molecules arriving before 400 μ s are rotationally much colder than the translational temperature or the cell temperature. This is likely to be a consequence of adiabatic cooling within the beam. After 400 μ s the beam is thermal with the helium, in rough agreement with the translational temperature results. Thus, despite the subtleties involved in measurements of translational temperature, we find by comparison to the rotational temperature of YbF that it still gives a good measure of the thermalisation properties within our beam.

3.5 Beam velocity

The velocity of the beam was determined using two spectra—one obtained using the coaxial laser, and one measured using a perpendicular probe beam. Experimentally we interleave measurements, switching between the two beams shot-to-shot using a

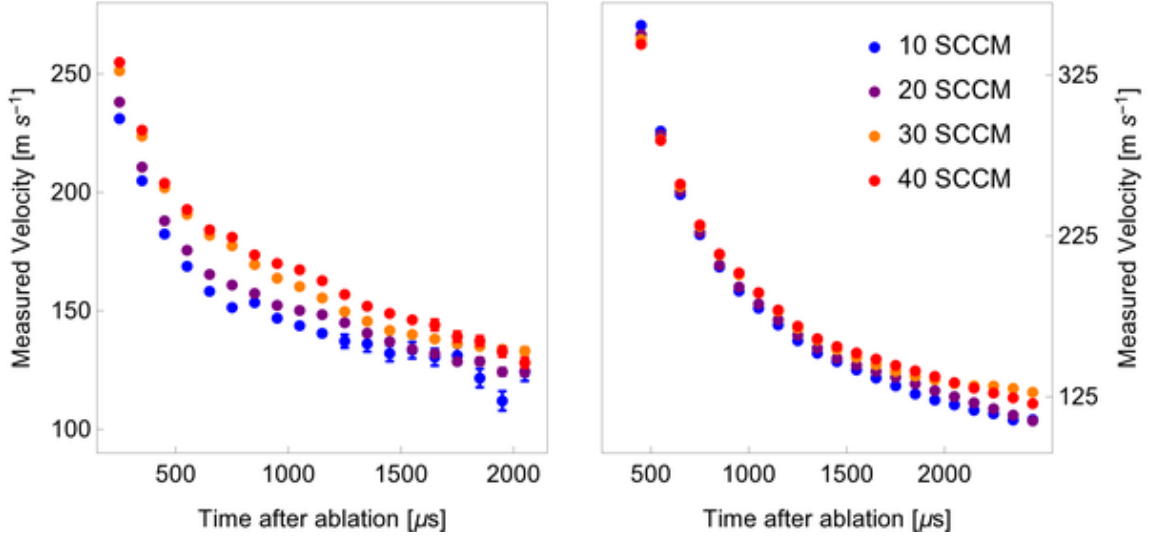


Figure 3.9: Measured forward velocities of ytterbium beams produced by the hybrid source for 4 different helium flow rates, measured at the lower (left) and higher detectors (right).

mechanical shutter in order to reduce systematic effects like laser drift and thermal changes in the buffer gas system.

Once the two sets of spectra have been obtained, the velocity is determined by examining the relative Doppler shift between co-axial and perpendicular measurements. We again perform fits of the form of equation (3.7) to determine the line centres, which we will define as $f_{\parallel}$ and $f_{\perp}$ for the co-axial and perpendicular measurements respectively. The instantaneous velocity is then given by

$$v_{\parallel}(t) = c \left(\frac{f_{\perp} - f_{\parallel}(t)}{f_{\perp}} \right) = c \frac{\Delta f(t)}{f_{\perp}}. \quad (3.12)$$

Measurements of $v_{\parallel}(t)$ for beams of Yb at our two detection regions are shown in figure (3.9). The measured forward velocity decreases as a function of time after ablation. This is likely to be caused by two processes. Molecules which leave the cell immediately after ablation are unlikely to have fully thermalised with the buffer gas, and hence will have a greater thermal velocity. Additionally, if a gas packet with some distribution of velocities leaves the source, the faster molecules will outrace

the slower molecules and arrive at the detector first. Measurements obtained at the lower, 5cm detector show clear stratification by helium flow rate—increasing the flow of buffer gas through the cell corresponds to more forward boosting of our beam. This same stratification occurs for measurements at the upper detector, albeit beginning at times 1000 μ s. This difference in behaviour is not a paradox. In the absence of collisions, we can project the measurements at the bottom detector to the top detector using the non-linear transformation

$$v_{\parallel}^t(t) = v_{\parallel}^b(t - \Delta z/v_{\parallel}^b), \quad (3.13)$$

where the superscript t (b) refers to measurements at the top (bottom) detection region, and Δz is the free-flight distance between b and t. The projected curve obtained by application of equation (3.13) is compared to the measured velocity at the top detection region in figure (3.10). We find good agreement between the two curves, suggesting that the results are consistent between detection regions. Note that this also suggests that there are no collisions between Yb and He atoms in the beam between the two detection regions—if there were, we would expect to measure faster velocities at t compared with projections from b. This result is consistent over all measured helium flows.

3.6 Velocity distribution of YbF

We now have all the information required to find the velocity distribution. Before we dive in we need to clear up one subtlety. To obtain the temporal profiles of the velocity and temperature, we have divided our time-of-flight spectrum into equal-width time intervals and evaluated the mean properties within them. This is important as it means that our velocity bins do not have equal width when we come to define the velocity distribution. More concretely, the width Δv will be related to our time binning width Δt via

$$\Delta v = \frac{dv}{dt} \Delta t. \quad (3.14)$$

Now, if we naively attempt to write our velocity distribution by connecting the velocity and time-of-flight amplitude within a given time-bin, we do so *in the interval* Δt . The velocity-time curves obtained in section (3.5) must be used to determine the scaling function dv/dt to compensate for the differing bin widths between the time and velocity domains.

We will make a distinction in this section between the instantaneous velocity distribution, obtained within some specific time interval, and the total velocity distribution,

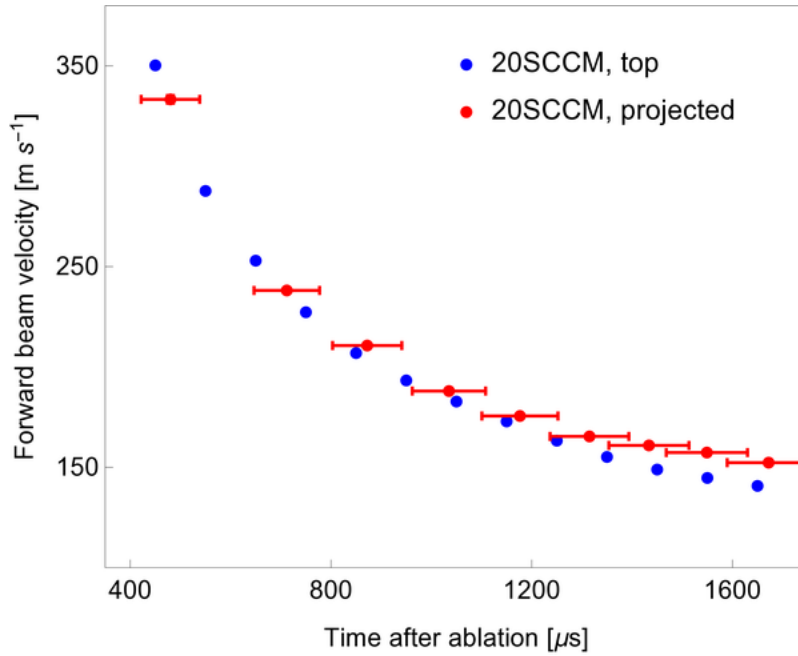


Figure 3.10: Measured forward velocity at the top detection region (blue), compared to data obtained at the bottom detection region that has been “projected” according to equation (3.13).

obtained by summing over all times. The instantaneous distribution tells us about the transient behaviour of the beam, whilst the total distribution gives us information about the total number of molecules produced over the lifetime of the beam within a given velocity interval.

With this in mind, let’s examine the form of the total velocity distributions in figure (3.11) obtained for the 10 SCCM and 40 SCCM flow rate cases. Both curves have similar means (194 m s^{-1} and 211 m s^{-1} respectively), but the low-velocity tail of the 10 SCCM distribution is pronounced with respect to the 40 SCCM case. This is to be expected from our observations in figure (3.9). The high-velocity wings of both distributions are very similar—this is likely due to the lack of thermalisation at early times in both cases. Note that, regardless of the tested flow rate, we do not produce an appreciable number of molecules with velocities below 100 m s^{-1} . This is in contrast with the predictions obtained by solving the Navier–Stokes equations, which predicted a mean forward velocity of 120 m s^{-1} at 60 SCCM.

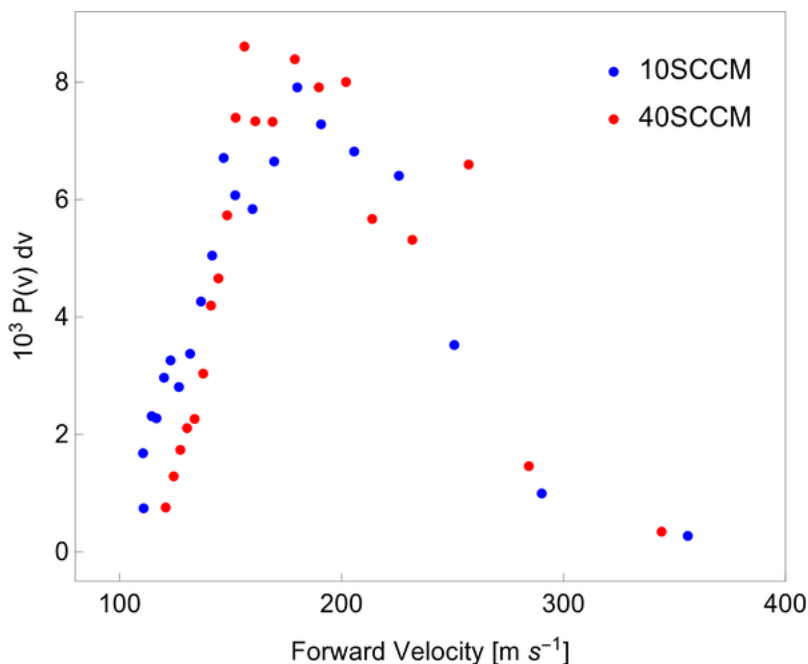


Figure 3.11: Measured total velocity distributions obtained for Yb with helium flow rates of 10 SCCM and 40 SCCM. The measurement relies on the data from section (3.5); specifically we have used data from the top detection region here.

Now let's think about the instantaneous velocity distribution at our detector. The lineshape measured experimentally is the convolution between the different broadening mechanisms present. Based on our discussions about the consistency of velocity measurements obtained at the two detection regions (see figure (3.10)), we have seen no evidence of collisions and hence can neglect pressure broadening. Our lineshape must therefore have two contributions—the natural component, and the component associated with the Doppler shift of each molecule or atom as it passes through the detection region. This gives us a method to determine the velocity distribution instant on instant: simply deconvolve our spectral lines with the natural lineshape, leaving only the component associated with the velocity distribution of the atoms and molecules.

This task is made substantially easier in our case as, for ytterbium, the natural linewidth is extremely small compared to the expected Doppler broadening. We can therefore approximate it as a Dirac delta function, at which point our velocity distribution is simply the measured lineshape. If this were not the case (for example,

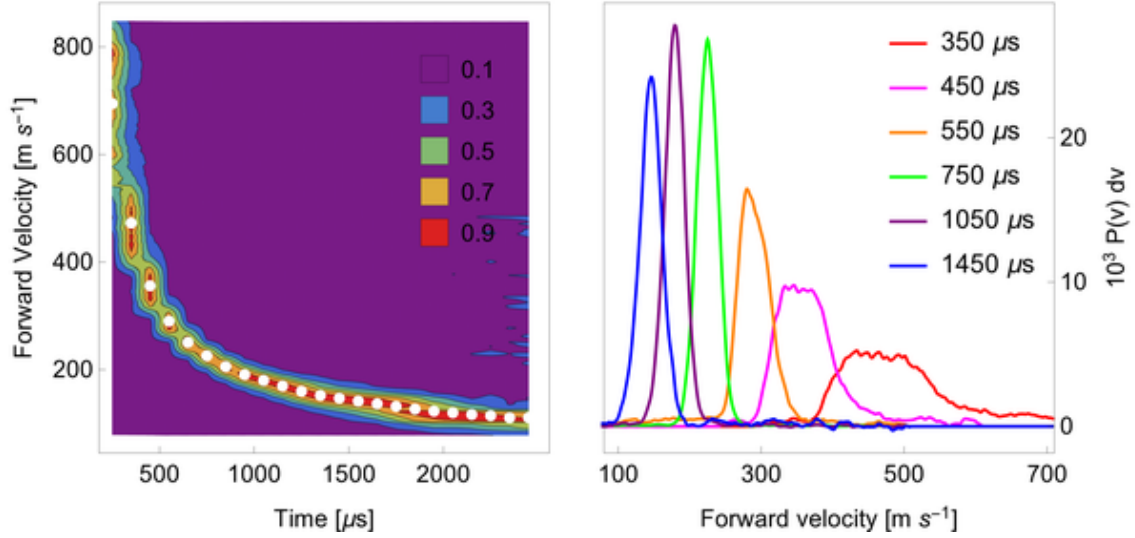


Figure 3.12: Instantaneous velocity distributions obtained from the spectral line-shape of the ^{174}Yb and ^{172}Yb $^1S_0 \rightarrow ^3P_1$ transitions (right pane), and the instantaneous distributions overlaid with the mean velocity (left panel). The mean velocity values are indicated by the white dots in the contour plot. Both data sets were obtained for 10 SCCM flow at the top-most detector.

for YbF), a good approximation would be to perform the deconvolution of a fully Doppler-broadened line, obtained using measurements with the co-axial laser, with the detection-volume limited narrower spectral lines obtained with the perpendicular beam. Some care must be taken if performing this mutual deconvolution, as if the detection region is large the process may lead to an artificially narrow instantaneous velocity distribution.

We have examined this behaviour, as seen in figure (3.12), for a beam of Yb at 10 SCCM helium flow rate. A contour plot of the evolution of the instantaneous velocity distribution as a function of time is shown on the left, and snapshots of the number of atoms with a given velocity are given in the rightmost panel. The colours in the contour plot represent the height of the distribution, normalised relative to the peak. Additionally, we have suppressed the zero so as not to complicate matters with the low-level random noise far from the peak, especially at late arrival times when the total signal is small. The mean velocities are shown by the white points.

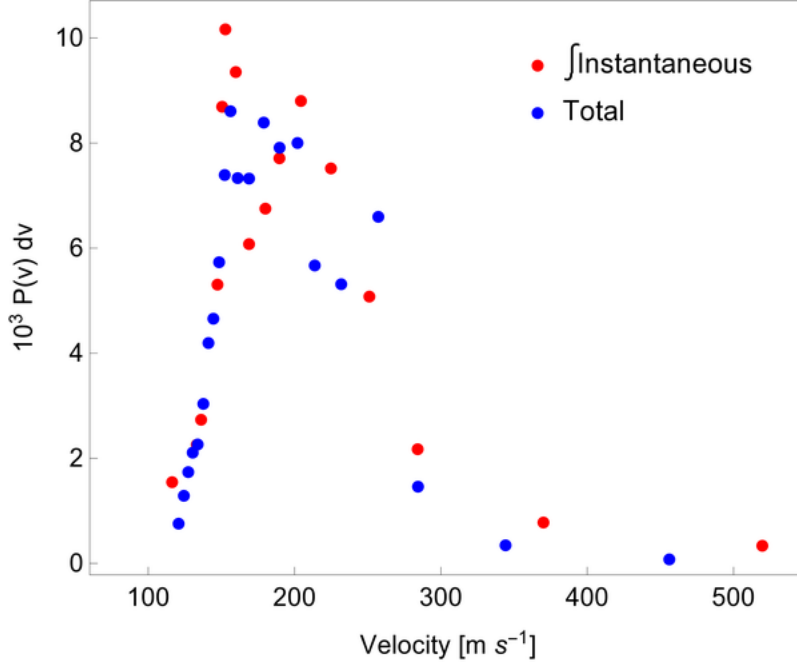


Figure 3.13: Comparison of the integrated instantaneous velocity distribution and the total velocity distribution obtained from the spectral lineshapes and Doppler shifts of the ^{174}Yb and ^{172}Yb $^1S_0 \rightarrow ^3P_1$ transitions.

We can draw a number of qualitative conclusions from the shapes of the instantaneous velocity distributions. In section (3.3) we discussed the implications of a non-Gaussian velocity distribution on the measured temperature; here we see immediately that this holds for velocity distributions reaching the detector before $450\text{ }\mu\text{s}$. The asymmetry of the distribution suggests that the beam is not fully supersonic here, in agreement with our observations in section (3.5). Somewhat unexpectedly, the velocity distribution at times later than $\approx 750\text{ }\mu\text{s}$ is well described by a Gaussian approximation, which we may not expect given that we have seen that the mean velocity tends to the effusive limit as $t \rightarrow \infty$.

The two interpretations of the velocity distribution are equivalent, as I shall now explain. The number of molecules $N(v, t) dv dt$ with a given instantaneous velocity distribution $P(v, t) dv dt$ is what we measure experimentally from the atomic lineshape. We can determine the mean velocity in the interval dt through $\bar{v}(t) = \int v P(v, t) dv$, and can associate this velocity with the total number of molecules in the interval,

$\bar{n}(t) = \int N(v, t) dv$. Correcting for the bin widths as in equation (3.14), we have found experimentally that the two distributions are equivalent, as is shown in figure (3.13).

3.7 Cell confinement

Having measured the forward velocity of our beam, we can infer the time atoms and molecules spend confined in the cell as follows. Assuming no collisions in the beam, the time taken for a particle to travel from the cell to the detector is $\tau_{\text{ff}} = x/v$, where x is the distance between cell and detector. The time particles spend thermalising in the cell, τ_c , is then

$$\tau_c = \tau - \tau_{\text{ff}}, \quad (3.15)$$

where τ is the arrival time at the detector.

We have obtained values for the confinement time in the cell; in figure (3.14) we examine the correlation between confinement and beam velocity (left pane), and translational temperature (right pane). We see that faster atoms and molecules are emitted from the cell at earlier times, and the slowest fraction of the beam spends the longest amount of time thermalising with the buffer gas. The time required to thermalise the beam is well bounded by the two theoretical limits set by equation (2.63), with 400 μs of total thermalisation time required for the molecules to reach the buffer gas temperature. At higher flows, atoms and molecules are trapped for longer in the cell once thermalisation is reached. This is not surprising as the diffusive timescale is proportional to the helium flow rate⁶, and supports our conclusion that the cell has two flow regions—a fast, hydrodynamic region where extraction is efficient, and a slower region whose properties are dominated by diffusion.

3.8 Beam divergence

The divergence angle of our molecular beam can be determined by measuring the transverse (as opposed to co-axial) velocity distribution $f_{\perp}(v_{\perp})$. If we can measure the full-width at half-maximum of $f_{\perp}$, $\Delta v_{\perp}$, the angular FWHM will be given by

$$\Delta\theta_{\perp} = 2 \arctan \left(\frac{\Delta v_{\perp}}{2v_{\parallel}} \right). \quad (3.16)$$

⁶The effusive timescale is unaffected as, in both regimes, $\bar{n} \propto \dot{N}_{\text{in}}$.

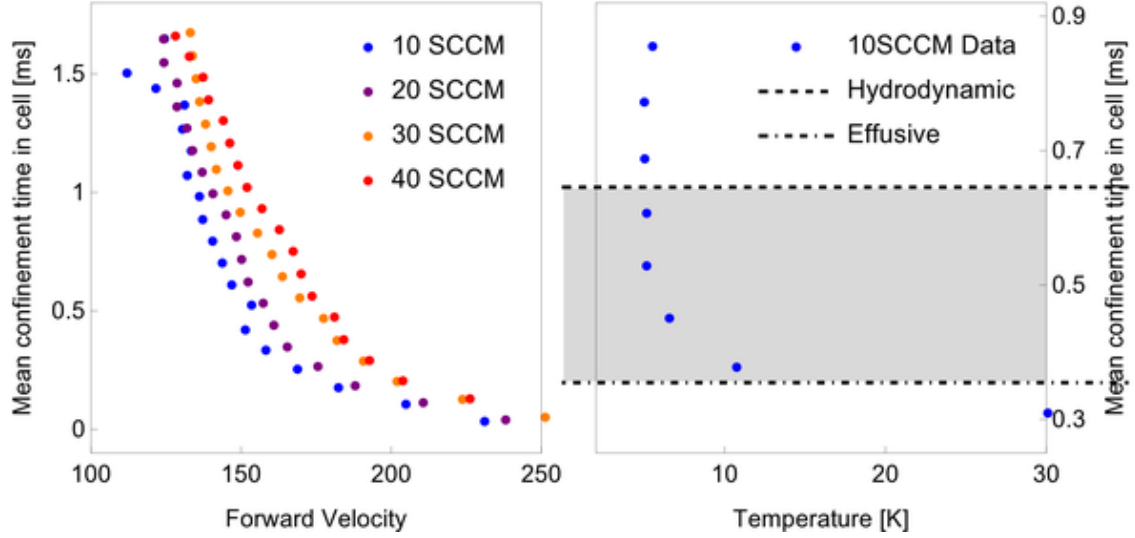


Figure 3.14: Forward velocity plotted against confinement time in the cell (left panel), and translational temperature against confinement time (right panel). The grey region is bounded by the hydrodynamic and effusive predictions for the thermalisation time, given by application of equation (2.63) in the two density limits.

In order to measure $f_{\perp}$, we cannot use the LIF technique used so far as, as we have discussed already, it relies on collecting fluorescence close to the focus of our collection optics and hence measures only a small transverse subsection of the phase space volume. Instead, we have collected an absorption spectrum of a beam of Yb. By measuring the total loss of beam intensity from a probe laser, we can sample the entire width of the distribution as required. We corrected for fluctuations in the laser intensity by monitoring an un-absorbed beam picked off from the main beam line using non-polarizing⁷ optics and focussed onto a fast photodiode.

We have performed this measurement for flow rates of 20 SCCM, and have obtained a mean divergence angle of $20^{\circ} \pm 5^{\circ}$. This value is based on a single measurement taken at $450 \mu\text{s}$ when the instantaneous flux was at its most intense, as even with our monitor of the instantaneous laser power the fractional change in intensity was of the order of 1%, with a signal-to-noise far less than unity. Note that the diver-

⁷Note that even for non-polarizing optics the transmitted and reflected intensities are still weak functions of polarization.

gence is significantly lower than both the effusive and supersonic limits, supporting our assertion that the beam arriving at early times is in the transitional rather than hydrodynamic regime. The dominant source of error in this measurement was the stability of the probe laser, which was subject to intensity fluctuations of up to 10% its total power. We couldn't completely remove this effect due to the polarization (and hence, splitting fraction to the comparator) also undergoing random noise during the measurement.

3.9 Molecular yield and ablation energy

We may also ask about the yield from the cell in terms of the ablation energy. A high-energy ablation laser will deposit a larger amount of energy into the target surface compared with the low-energy case, leading to a large amount of material confined close to the target surface at high pressure. It then expands through the buffer gas until the initial potential energy has been dissipated, ending as a static distribution due to molecule-gas collisions. Assuming that the final plume is spherical and the buffer gas is perfect, the final plume diameter ℓ_p is given from the work of Anisimov [114] via

$$\ell_p = G \left(\frac{x_0^2 \epsilon}{p} \right)^{1/5} E^{1/5} = a \times E^{1/5}, \quad (3.17)$$

where a is a constant of proportionality parametrising the buffer gas pressure p , initial ablation spot size x_0 , efficiency of energy transfer between laser and surface ϵ , and a hydrodynamic term $G \approx 0.45$ that arises from detailed gas-dynamic calculations.

To model of the yield as a function of YAG energy, we will assume that in the hydrodynamic regime all molecules from the plume which come to rest within the cell volume will eventually be swept into the beam. Conversely, molecules which are not brought to rest stick to the walls with probability 1. In this case the extraction efficiency is the volume of intersection between the internal geometry of the cell and the ablation plume; for our cylindrical cell of radius R intersecting a spherical plume of radius r , we obtain [115]

$$V_{\text{C}\cap\text{P}} = \frac{4\pi}{3} r^3 \theta(R - b) + \frac{4}{3} r^3 \arctan \left(\frac{2\sqrt{bR}}{b - R} \right) - \frac{8}{3} \sqrt{bR} \left(b^2 - R^2 + \frac{8}{3} bR \right). \quad (3.18)$$

Here b is the impact parameter, defined as the shortest distance between the centres of the cylinder and the sphere, and $\theta(R - b)$ is the Heaviside step function. In our

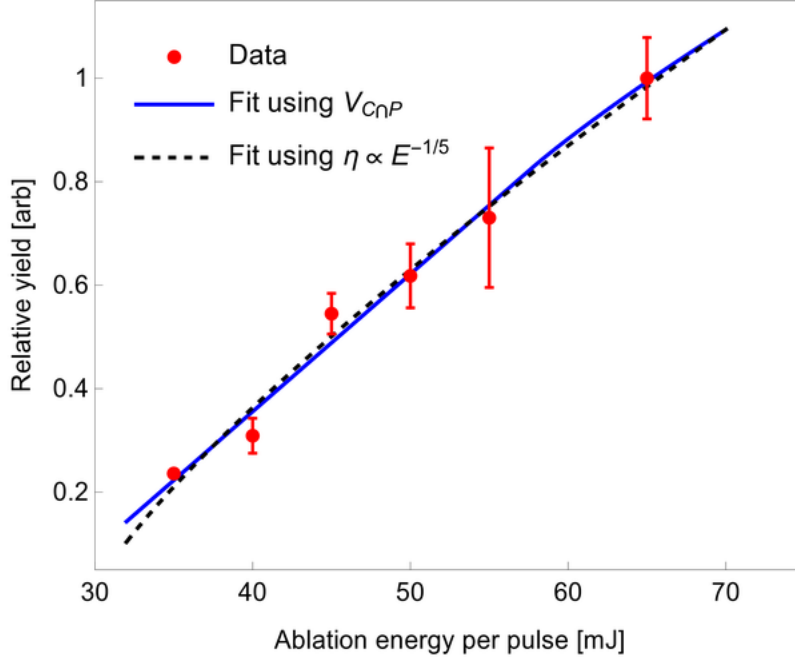


Figure 3.15: Measured variation in the molecular yield as a function of ablation energy, fitted to the volume of intersection model (solid curve) and the heuristic $\eta \propto E^{-1/5}$ model. The two descriptions provide a good fit to the data, as long as the work function of the target is not neglected.

case the plume must begin at the target, and hence $b = (\ell_p - 2R)/2$. The efficiency η of the ablation process can be estimated by evaluating the ratio of V_{CNP} with the plume volume in the absence of the cell, $4\pi r^3/3$. We may then substitute the energy equation (3.17) into the efficiency expression, and the total yield is assumed to be proportional to $E\eta$.

We have measured the total molecular yield on the ^{176}YbF Q(1) line as a function of YAG energy for a constant flow rate of 20SCCM and spot size of $1 \pm 0.5\text{mm}$; the results of this measurement are shown in figure (3.15). A fit of the form $A \times E \times \eta(a(E - E_0)^{1/5})$ was obtained, with the fit parameters being the total amplitude A , the offset which deals with the work function of the target E_0 , and the proportionality constant a . From the fit parameters, we find that η varies by at most 20% within the energy range and is extremely well described by the approximation $\eta \propto E^{-1/5}$. From the fitted value of a , we find that the coupling efficiency lies in the range $0.1 \leq \epsilon \leq 0.4$ depending on limiting flow regime used to calculate the

pressure. This value of ϵ is in agreement with previous measurements of the reflectivity $0.3 \leq 1 - \mathcal{R} \leq 0.4$, obtained by measuring the reflected YAG power from flat samples of polished and unpolished Yb using a fast photodiode. The work function was found to be 26.6 ± 1.3 mJ, below which the yield was immeasurably small.

3.10 Molecular flux

We now have a full characterization in terms of the velocity distribution, temperature, and divergence of our beam. This isn't the most useful characterization though as, due to the divergence term, the observed number of molecules will be a function of distance from the cell. The most useful metric is the number of molecules *per steradian divergence per shot per target quantum state within* some velocity interval Δv . We will define this metric as the total molecular flux Φ .

We have already parametrised the divergence, the velocity distributions, and the internal quantum state distribution⁸. Our remaining task is to correlate the photon count rate observed by our PMT detectors with the total number of molecules passing through the detection volume of our optics.

If light is emitted from a point source at the focus of our detection optics, the detection efficiency will be the solid angle subtended by these optics divided by 4π . However, our molecular beam is spatially extended so this simple approximation is not valid. To obtain a more realistic measure, we have simulated the optical properties of our detection system using a ray-tracing scheme.

A schematic of the detection optics is shown in figure (3.16). Rays are generated within a defined emission volume and are allowed to radiate with random orientation into the full 4π solid angle. In this way, they model the action of spontaneous emission from a molecule after interaction with the probe laser. If a ray intersects with the surface of any of the simulated optics it is appropriately reflected or refracted with 100% efficiency.

We found experimentally that an iris is necessary to reduce the flux of background light onto the PMT. Specifically, the ablation plume from the metal target acts as a bright, broadband source of photons which, if not dealt with, can saturate the PMT. The iris should, in theory, block all photons not collimated by the LIF optics

⁸The quantum state distribution is defined implicitly through the rotational temperature.

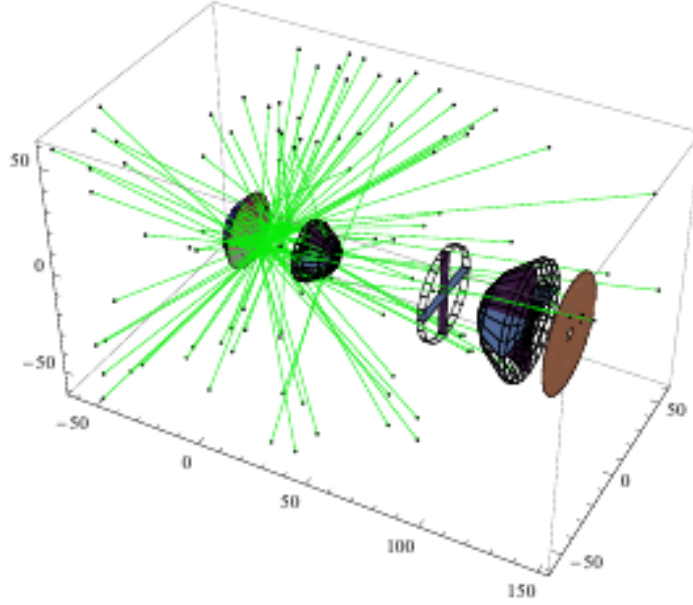


Figure 3.16: Schematic of the detection optics used for LIF experiments at the bottom detection region. All part numbers are from Comar. From left to right: 10-SR-33 concave lamp reflector, 16-AF-25 aspheric collimating lens, vacuum can window, 39-AF-50 focussing lens, 5 mm iris. The PMT tube is not shown, but is assumed to be 1 mm behind the iris. The green lines show samples of the simulated trajectories of fluorescence photons generated within the detection volume. The axes measure the various distances in millimetres.

from reaching the photosensitive face of the PMT; however, as the plume “flash” is bright and many of the vacuum components are shiny we still observe a small signal from reflected plume photons. Varying the iris diameter is enough to reduce this to a manageable level; however, we need to take this effect into account when we compute the efficiency of our optical set-up

A ray which passes fully through the system is detected 1 mm behind the iris; the angular response of the PMT is included by attenuating the contribution of each photon by its direction cosine relative to the normal of the detection plane. The geometric detection probability was taken to be the ratio of the number of collected photons, suitably attenuated, to the total number of simulated rays.

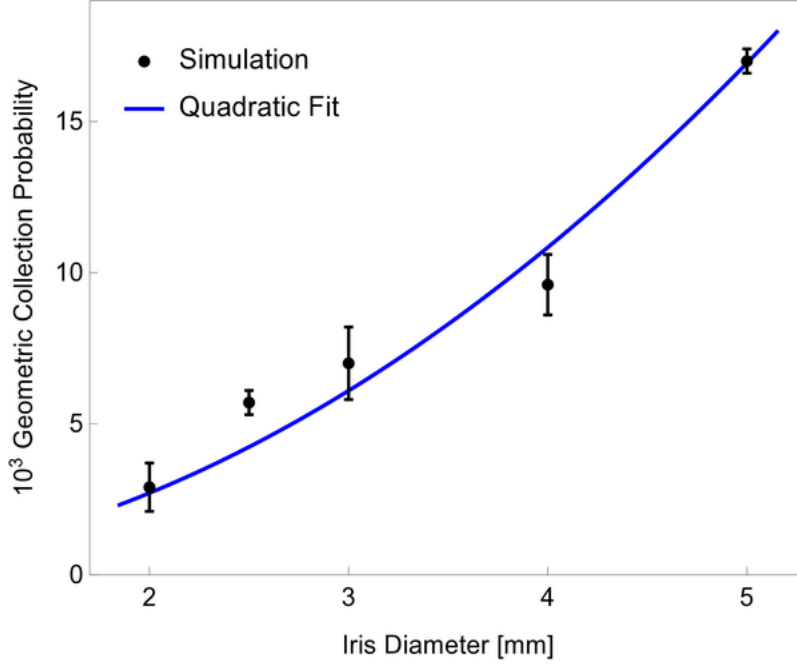


Figure 3.17: Simulated detection efficiency for the experimental collection optics, evaluated via ray tracing at the bottom detection region. The solid curve is the fit to the quadratic model. The error bars in the simulated data arise from the counting statistics of the rays.

We have evaluated this ratio for an emission volume $\Theta = 30 \times 1.5 \times 1.5 \text{ mm}^3$ in extent, with the extended dimension lying in the plane perpendicular to the optical axis. The size of this volume was calculated from the molecular beam divergence and the perpendicular laser diameter respectively. The detection efficiency was checked for iris diameters between 2 and 5 mm by simulating 2000 rays at a time; the quoted errors are the standard error between repeats. The simulation results are shown in figure (3.17). We find that, overall, we have poor detection efficiency over the beam width at the detector. This is due to the significant beam component outside the focus of the collection optics. The solid fit follows from a quadratic model, where opening the iris exposes the PMT face according to the square of the diameter.

We can now evaluate the molecular flux. If we measure a photon count rate $\dot{N}_0$

from our PMT, the actual photon rate from the molecular beam must be

$$\dot{N} = \frac{\dot{N}_0}{\mathcal{T}\eta\Pi}, \quad (3.19)$$

where the terms in the denominator are the various efficiencies and probabilities for a photon to make it to the detector: $\mathcal{T}$ is the product of the transmissions and reflectivities of the optical components, η is the quantum efficiency of the photomultiplier tube, and Π is the geometric collection probability discussed in figure (3.17).

We link the photon rate to the rate at which molecules cross the laser beam as follows. We may break the LIF process down into two steps. In the first, population is transferred from the ground state $|g\rangle$ to the excited state $|e\rangle$. In the second, spontaneous decay transfers population out of $|e\rangle$ to what will be in principle a number of states within the ground state manifold. The probability for a spontaneous decay event to return a YbF molecule to its original state is $\gamma_{g \rightarrow g}$, with the condition $0 \leq \gamma_{g \rightarrow g} \leq 1$. In the high-intensity limit⁹, we expect an average of

$$\mathcal{N} = \frac{1}{1 - \gamma_{g \rightarrow g}} \quad (3.20)$$

photons emitted per molecule before it becomes dark. Then the molecular rate is

$$\dot{N}_m = \frac{\dot{N}}{\mathcal{N}} = (1 - \gamma_{g \rightarrow g}) \frac{\dot{N}_0}{\mathcal{T}\eta\Pi}, \quad (3.21)$$

and the total number of molecules in the detection region may be found by evaluating the integral of equation (3.21). The divergence is taken into account by evaluating the solid angle of the beam Ω which, for a pyramidal geometry, takes the form

$$\Omega = 4 \arctan \left(\frac{w_b d_l}{2x \sqrt{4x^2 + w_b^2 + d_l^2}} \right), \quad (3.22)$$

where w_b is the width of the molecular beam, d_l is the laser diameter, and $x = w_b/(2 \tan[\Delta\theta_\perp/2])$ is the distance from the base of the pyramid, defined by w_b and

⁹The measurements presented here were obtained with a perpendicular beam power of 280 μ W and a 1/e beam diameter of 1.5mm. The magnitude of the transition dipole moment for both transitions is $0.454 \times 4.29 D$, from which we obtain a Rabi frequency $\Omega = 2.2 \times 10^7 \text{ rad s}^{-1}$. The time period for Rabi oscillations is then $\approx 300 \text{ ns}$, so that we expect to scatter at least 10 photons even for YbF molecules passing through the detection region at 500 m s^{-1} . Thus the high-intensity limit is a fine approximation.

d_1 , to its tip.

Once properly optimised, the mean number of photons observed from a measurement of the ^{174}YbF Q(0) transition from the hybrid source is $\int \dot{N}_0 dt \approx 6000$, with the integral bounded by $0 \leq \int \dot{N}_0 dt \leq 1.5 \times 10^4$ depending on the exact combination of parameters used. Within the lower $N = 0$ level of the Q(0) transition there are two hyperfine components separated by more than the laser linewidth; we assume that population is equally distributed amongst the magnetic sublevels therein, allowing us to treat the two levels separately. Evaluating all terms, we obtain a molecular flux of

$$\frac{N_m}{\Omega} = (2.1 \pm 0.34) \times 10^9 \text{ sr}^{-1} \text{ pulse}^{-1} \quad (3.23)$$

in the lowest ro-vibrational state of YbF. This is a benchmark value rather than the best case scenario, reflecting as it does the typical day-to-day intensities of the source. The absolute upper limit that we have observed is $\approx 6 \times 10^9 \text{ sr}^{-1} \text{ pulse}^{-1}$, obtained for a freshly-cleaned target with no surface imperfections.

We can play the same games to obtain the Yb flux. In this case the transition $^1\text{S}_0 \rightarrow ^3\text{P}_1$ is closed, and at experimental laser intensities, the slowest process will be spontaneous decay from the excited to ground state. For ^{174}Yb this process has a lifetime of $\tau_{\text{Yb}} = 875 \text{ ns}$. As I show in appendix (B.8), at high intensity the population becomes distributed amongst all available levels. The $^3\text{P}_1$ state has a multiplicity of 3 and the $^1\text{S}_0$ a multiplicity 1; however, using linearly polarized light we only connect one excited state to the ground state manifold so the maximum population in $^3\text{P}_1$ is $1/2$, the maximum possible scattering rate is $(3/4)(2\pi/\tau_{\text{Yb}})$, and the mean beam velocity $\bar{v} = 195 \pm 5 \text{ m s}^{-1}$ can be determined from the total velocity distributions shown in figure (3.11). This gives an average of 4.4 photons scattered by each Yb atom on the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition as it crosses the laser beam. We typically observe $\int \dot{N}_0 dt = 40000$ photons per shot in our experiment; combining all the terms, we find that our flux is $(5.3 \pm 0.86) \times 10^9 \text{ sr}^{-1} \text{ pulse}^{-1}$. From these crude arguments, we see that the ablation process is $\approx 28\%$ efficient in converting ytterbium to YbF.

3.11 Conclusion

We have exhaustively characterised the hybrid source, measuring the translational temperature, rotational temperature, forward velocity, divergence, total velocity distribution, instantaneous velocity distributions, and total flux of beams of Yb and YbF produced by the apparatus. While not living up to the full expectations predicted

by solving the Navier–Stokes equations, the source is reliable and produces a significant number of molecules with velocities $< 150 \text{ m s}^{-1}$ in the lowest ro-vibrational state. The shot-to-shot flux is comparable with that produced for buffer gas beams of other molecular species such as CaH [96] and outperforms that of the supersonic YbF source reported in [116], although in the latter case the higher experimental repetition rate of 10 Hz gives a greater flux per second. With proper care and maintenance, the source is stable over hundreds or thousands of shots.

The characteristics of the source are best understood through the competition of its diffusive and advective character. The high-flow region sweeps molecules efficiently from the cell, but the long-term character and slowest velocity molecules arise for very long confinement times within the cell. We have measured beams whose properties suggest that diffusion between the slow- and fast-moving helium regions occurs, leading to a splitting and broadening of spectral lines and a subsequent breakdown of the Doppler broadening approximations.

Within the beam, we have seen no evidence for collisional boosting between the two detection regions. The translational temperature is initially very hot, but the instantaneous velocity distribution at early times is hot-effusive in character. The rotational temperature is initially much colder than expected, before thermalising with the helium. The timescale for thermalisation within the cell has been inferred to be less than $650 \mu\text{s}$ for flow rates greater than 10 SCCM, in broad agreement with our observations of the translational and rotational temperature in the beam.

Chapter 4

Flux decay from an ablated metal target

In this section, we discuss some of the challenges involved when producing molecules via the laser ablation process. When performing a typical experiment, we will expose a fresh piece of a solid ytterbium target to a high-intensity Nd:YAG laser. A large number of sequential shots are then taken without moving either target or laser. We observe experimentally that the measured molecular flux decreases monotonically as a function of shot number, which will impact the signal-to-noise ratio of, and increase the shot noise of, any performed experiments.

An illustration of the flux-decay behaviour is shown in the two panels of figure (4.1), where the total yield from the hybrid source has been measured using the LIF method under two different ablation schemes. The first scheme, shown in the left panel of (4.1), was performed by Jongseok Lim and James Almond using an ablation energy per shot of $20.8 \text{ mJ pulse}^{-1}$. The ^{174}YbF Q(1) line was probed as a function of shot number at two different repetition rates, 2 Hz and 10 Hz. In the second scheme, shown in the right panel of (4.1), the intensity of the ^{174}YbF Q(2) line was measured at a repetition rate of 2 Hz over a significantly longer timescale. The ablation energy was 70 mJ pulse^{-1} , and in both cases the $1/e^2$ laser focus was $1 \pm 0.5 \text{ mm}$.

In the low-power case, we see that the yield from the cell at an ablation rate of 2 Hz is approximately constant, while it decays over a scale of ≈ 100 shots at 10 Hz. Moving to the high-power ablation case, we now observe a decrease in the 2 Hz repetition rate yield, albeit over a timescale of ≈ 500 shots.

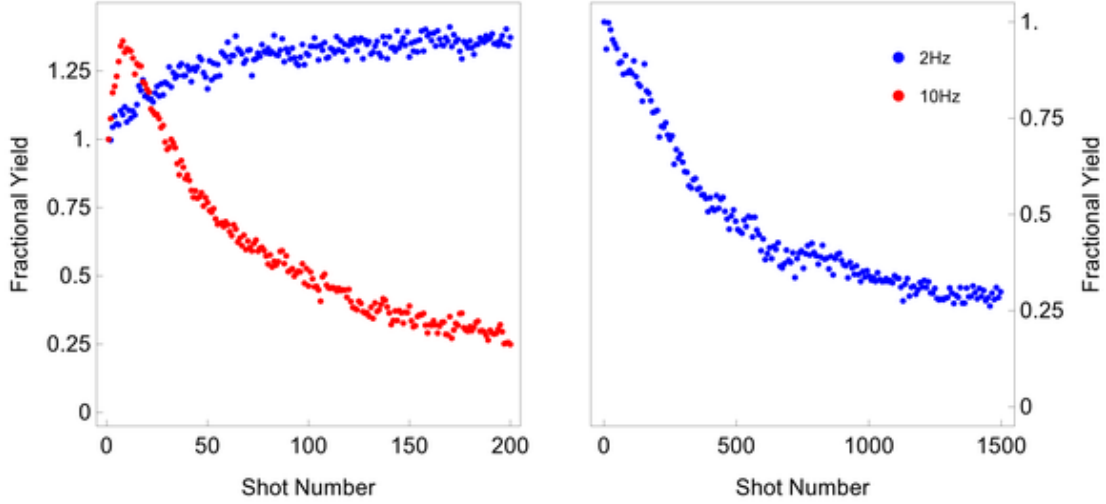


Figure 4.1: Change in measured molecular yield as a function of shot number at ablation energies of $20.8 \text{ mJ pulse}^{-1}$ (left) and 70 mJ pulse^{-1} (right).

We have examined two possible candidates for this behaviour. In the first, the majority of the ablation energy is transferred to the target in the form of heat, which dissipates slowly into the bulk of the material. In the second, the majority of the laser energy is transferred into removing material from the rod. Both cases lead to a predicted loss in the flux; the thermal case by changing the physical properties of the target, and the ablative case by changing its shape. We find that the thermal process is associated with a loss of signal on the timescale of ≈ 100 shots, while mechanical changes in the target surface reduce the yield over ≈ 500 shots under typical experimental conditions.

4.1 Thermal relaxation and the wetting problem

In the ideal ablation process, energy is efficiently transferred from the laser into breaking the internal structure of the target. A single infra-red photon from an Nd:YAG laser at 1064 nm has energy $\sim 1.2 \text{ eV}$, which is less than the binding energy of ytterbium in the solid of $\sim 1.83 \text{ eV}$ (see, for example, equation (4.20) below). Thus we might expect that there are Yb atoms in the target that have absorbed energy from the laser but have not been ablated from the surface. These atoms will

transfer heat to the bulk of the target. Understanding the flow of heat in this system can help us to signpost possible issues in the future—for example, if heat is not being efficiently dissipated, we might expect the formation of molten regions in the target which will tend to reduce the Yb yield.

We begin with a theoretical overview for the problem of heat conduction in a solid¹. In the following, we will derive an expression for the Green’s function of the heat equation, and use symmetry properties to apply this to the half- rather than full-volume in question. We will see that, under reasonable experimental conditions, heat is not well conducted away from the ablation region. Finally, we will examine how a theorised liquid layer would develop on the surface of the target, and discuss the implications if this is true.

A thermal distribution $h(x, t)$ within a material of thermal diffusivity κ and subject to a source term $\Psi(x, t)$ evolves following the heat equation

$$\frac{\partial h}{\partial t} - \kappa \nabla^2 h = \Psi(x, t). \quad (4.1)$$

It is useful to first determine the Green’s function for equation (4.1), $G(x, t)$, as our solution can then be expressed through the convolution $h(x, t) = G(x, t) * \Psi(x, t)$. The Green’s function is the solution of (4.1) with a point-source heat term; hence

$$\frac{\partial G}{\partial t} - \kappa \nabla^2 G = \delta(x)\delta(t). \quad (4.2)$$

Note that the heat source Ψ must be instantaneous in both position and time, so we require two Dirac delta functions on the right-hand side of equation (4.2). Physically, we might imagine constructing h by summing over a set of point source solutions G , appropriately weighted by a set of coefficients Ψ so as to match our system. Under free evolution, the solutions to the heat equation must be smooth and square-integrable. Taking the Fourier transform of (4.2) with respect to the position coordinate x , we obtain

$$\frac{\partial}{\partial t} \tilde{G}(k, t) + \kappa |k|^2 \tilde{G}(k, t) = \delta(t), \quad (4.3)$$

¹For more depth, I refer the reader to [117], particularly chapters 1, 2, 3, and 6.

where we have used the smoothness and square-integrability conditions $\partial G(\infty, t)/\partial x = G(\infty, t) = 0$ to evaluate the transformation of the spatial derivatives:

$$\begin{aligned}\int_{-\infty}^{\infty} e^{ikx} \frac{\partial^2 G}{\partial x^2} dx &= \left[e^{ikx} \frac{\partial G}{\partial x} \right]_{-\infty}^{\infty} - ik \int_{-\infty}^{\infty} e^{ikx} \frac{\partial G}{\partial x} dx \\ &= -ik \left[e^{ikx} G \right]_{-\infty}^{\infty} + (ik)^2 \int_{-\infty}^{\infty} e^{ikx} G dx \\ &= (ik)^2 \tilde{G}.\end{aligned}$$

The solution to equation (4.3) can be found using the ansatz solution $\tilde{G}(k, t) = \theta(t) \tilde{g}(k, t)$, where $\theta(t)$ is the unit step function. Direct substitution yields

$$\delta(0) \tilde{g}(k, t) + \theta(t) \frac{\partial}{\partial t} \tilde{g}(k, t) + \kappa |k|^2 \theta(t) \tilde{g}(k, t) = \delta(0), \quad (4.4)$$

from which we see immediately that the condition

$$\frac{\partial}{\partial t} \tilde{g}(k, t) + \kappa |k|^2 \tilde{g}(k, t) = 0, \quad (4.5)$$

along with the condition that $\tilde{g}(k, 0) = 1$, solves equation (4.4). Our ansatz is seen to be the product of a unit step with the homogeneous solution; the full solution in Fourier space is given by

$$\tilde{G}(k, t) = \theta(t) \exp(-\kappa |k|^2 t). \quad (4.6)$$

Applying the inverse transformation and returning to position space, we finally obtain the Green's function:

$$G(x, t) = \frac{\theta(t)}{(4\pi\kappa t)^{D/2}} \exp\left(-\frac{x^2}{4\kappa t}\right). \quad (4.7)$$

Here, D is the dimensionality of the system in question. For example, for the problem of heat conduction in 3D space, $D = 3$.

In the preceding discussion, we have implicitly assumed that the material in question fills the whole space such that both the temperature and temperature gradient vanish at infinity. It is very often the case, however, that we will have to deal with material discontinuities caused by the finite lengths and scales accessible experimentally. We can tackle problems of this kind using the “infinite slab” Green's function above. As an example, consider heat conduction in the half-plane $[0, +\infty)$ subject to the

Dirichlet boundary conditions $h(0, t) = h(\infty, t) = 0$. We know that the full-plane Green's function in equation (4.7) satisfies the second of these conditions. To satisfy the first, we define a new Green's function

$$G_p(x, t, \zeta) = G(x - \zeta, t) - G(x + \zeta, t) \quad (4.8)$$

defined on the full-plane but periodic in such a way as to demand the boundary condition be met. The variable ζ is to be integrated over in the convolution, which is now taken over the half-plane $[0, \infty)$. Similarly, an even combination of Green's functions will satisfy the Von Neumann type problem $\partial_x h(0, t) = 0$.

We now have an expression for the Green's function of the heat equation, from which the full solution can be obtained by evaluating the convolution with the source. Let us now turn our attention to the physical system in question—that of a solid Ytterbium rod irradiated impulsively at $t = 0$ by a laser with known mode shape.

Let's suppose that the heat profile of our rod at $t = 0$ is proportional to the local intensity of the ablation laser at the surface, and decays exponentially over some characteristic but small distance ϵ inside the bulk. We'll take the spatial mode of the ablating laser to be Gaussian with characteristic width w . Then the source term is:

$$\Psi(x, y, z, t) \propto \exp\left(-\frac{x^2 + y^2}{w^2}\right) \times \exp\left(-\frac{z}{\epsilon}\right) \times \delta(t) \quad (4.9)$$

The choice of a temporal point-source is appropriate for our system as the typical time scale for a single YAG pulse is < 10 ns; conversely, we will see that the expected time scale for thermal decay is of the order of hundreds of milliseconds, even in the presence of a heat-sinking region close to the ablation spot. The exponential decay with depth is chosen to simulate the small, but finite, optical path length in the bulk metal.

We now convolve the source term of equation (4.9) with the Green's function (4.7). This can be done analytically, as the convolution of two Gaussian functions has the known form

$$a \exp\left(-\frac{x^2}{b}\right) * a' \exp\left(-\frac{x^2}{b'}\right) = \pi^{1/2} a a' \sqrt{\frac{b b'}{b + b'}} \exp\left(-\frac{x^2}{b + b'}\right), \quad (4.10)$$

and the convolution between a Gaussian and a single-sided exponential decay is also known:

$$a \exp\left(-\frac{x^2}{b}\right) * \exp\left(-\frac{x}{b'}\right) \theta(x) = \frac{a \sqrt{b \pi}}{2} \exp\left(\frac{b - 4b'x}{4b'^2}\right) \operatorname{erfc}\left(\frac{b - 2b'x}{2\sqrt{b b'}}\right). \quad (4.11)$$

As we are ablating onto the surface of the rod and there is no heat-sinking, we will use the Von Neumann conditions above to demand that the heat gradient is zero at the rod-vacuum boundary when approached from below, $\lim_{z \rightarrow 0^-} \partial_z h(x, y, z, t) = 0$. Combining equations (4.7) and (4.9) with (4.10) and (4.11), and taking the symmetric Green's function combination to satisfy the Von Neumann condition, the heat profile is given by²

$$h(x, y, z, t) = \frac{\pi w^2}{w^2 + 4\kappa t} \frac{\theta(t)}{2} \exp\left(-\frac{x^2 + y^2}{w^2 + 4\kappa t}\right) \exp\left(\frac{\kappa t}{\epsilon^2}\right) \times \left[\exp\left(-\frac{z}{\epsilon}\right) \operatorname{erfc}\left(\frac{2\kappa t - \epsilon z}{2\epsilon\sqrt{\kappa t}}\right) + \exp\left(\frac{z}{\epsilon}\right) \operatorname{erfc}\left(\frac{2\kappa t + \epsilon z}{2\epsilon\sqrt{\kappa t}}\right) \right]. \quad (4.12)$$

In practice, we are really interested about the mean thermal behaviour in the region that is repeatedly ablated by a train of pulses. Due to the azimuthal symmetry in equation (4.12), we move into a cylindrical co-ordinate system with the radius defined on the $x - y$ plane, $r^2 = x^2 + y^2$. Thus, the mean temperature over the region that is repeatedly heated by the ablation laser is defined as

$$\bar{T}(t) \propto \frac{\pi}{2w^2\epsilon} \int_0^w r dr \int_0^\epsilon dz h(r, z, t). \quad (4.13)$$

Fixing the proportionality in equation (4.13) may appear troubling, but thankfully we are helped somewhat by the physics of the problem. Within this purely thermal model of the system, any material left on the surface must be just colder than the vaporisation temperature of ytterbium. If it were any hotter, we would expect it to undergo a transition to the gas phase and hence play no role in the thermal properties of the rod.

A plot of the time-dependent behaviour of the mean temperature $\bar{T}$ is shown in figure (4.2) for three different mode sizes. We note that the more tightly focussed our ablating laser beam is, the faster the thermal decay of the rod. This behaviour is expected, as we see from equation (4.13) that the decay rate is proportional to the curvature of the heat profile. We also note that a significant amount of heat is retained locally³ in the rod for up to half a second after ablation.

A natural question now is, does it matter? So what if we retain a little heat in the rod—we want to ablate it, rip it apart, make gas and plasma of it! Surely retaining heat in the rod can only help. This viewpoint would be true—if the only

²The algebra is quite tedious—we verified it with the help of Mathematica.

³Specifically, in the region $0 \leq r \leq w$ and $0 \leq z \leq \epsilon$.

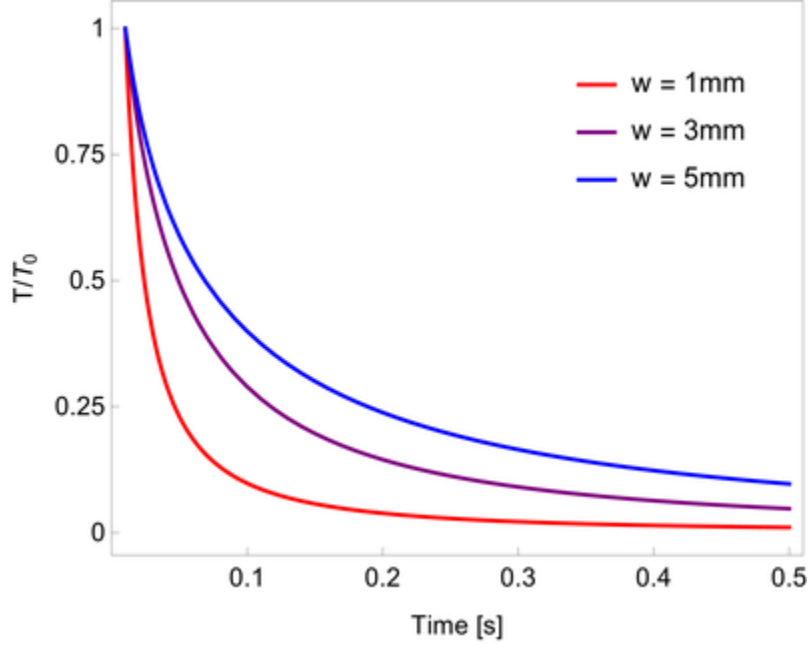


Figure 4.2: Thermal decay curves calculated using equation (4.13), normalised to the initial temperature $T_0 = \bar{T}(t = 0)$. The characteristic depth ϵ was taken to be 1 mm, and the thermal diffusivity was calculated as $3.46 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ [118]. The curves were obtained for three different characteristic intensity widths w of 1, 3, and 5 mm.

way in which material left the rod was via the direct sublimation of solid to gaseous ytterbium. In reality things are much more complicated. The ablation process proceeds via different pathways depending on the pulse width and energy. For example, a high-intensity laser can drive thermal shocks into the material bulk, leading to ablation via the process of spallation. More crucially, any ytterbium left in liquid form on the surface of our rod will heavily suppress the production of ytterbium from the surface [119]. The suppression occurs because particles that would usually be ablated are trapped by the fluid at the solid-liquid boundary.

Under atmospheric pressure, Yb evaporates at $T_{\text{l} \rightarrow \text{g}} = 1469 \text{ K}$ and melts at $T_{\text{s} \rightarrow \text{l}} = 1097 \text{ K}$. We have no information about the local pressure in the plume following ablation, but it is reasonable to assume that in general the cell pressure will be low enough that the ytterbium will boil at temperatures $T < T_{\text{l} \rightarrow \text{g}}$. Liquid Yb may therefore form on the surface of the rod, where it will slowly boil and be lost.

Let us try to make this discussion a little more concrete, without dipping into the grisly machinery of ablation too much. We do not know at exactly what temperature any liquid Yb will boil away, but it is a fair assumption that $T_{s \rightarrow l}$ is independent of cell pressure. We simulate a train of ablation pulses by modifying the source function of equation (4.9) as follows,

$$\Psi(x, y, z, t) \propto \exp\left(-\frac{x^2 + y^2}{w^2}\right) \times \exp\left(-\frac{z}{\epsilon}\right) \times \sum_j \delta(t - t_j), \quad (4.14)$$

with pulses of heat deposited into the material at regular intervals δt . From the properties of the Dirac delta function, the heat profile h_{train} is then simply

$$h_{\text{train}}(r, z, t) = \sum_j h(r, z, t - t_j). \quad (4.15)$$

We assume that $h_{\text{train}}(0, 0, 0) = T_{l \rightarrow g}$, which is unknown but assumed to be larger than $T_{s \rightarrow l}$. We now examine the total temperature profile of the system at each ablation time-step t_j . Regions obeying $h_{\text{train}}(r, z, t_j) > h_{\text{train}}(0, 0, 0)$ are assumed to be lost via ablation, while regions in the material obeying $\alpha h_{\text{train}}(0, 0, 0) < h_{\text{train}}(r, z, t_j) \leq h_{\text{train}}(0, 0, 0)$ are assumed to be in the liquid phase. Here $\alpha = T_{s \rightarrow l}/T_{l \rightarrow g}$ is the unknown ratio of the melting point to the boiling point whose value is bounded by $1097/1469 \leq \alpha \leq 1$.

We now construct the theoretical liquid volume V_{liq} for different values of α , and see if it is non-zero. The bounding surfaces $T_{s \rightarrow l}$ and $T_{l \rightarrow g}$ are constructed numerically by fixing the radius r and solving for the depth z . The volume enclosed by each isotherm is evaluated through the discrete integral in cylindrical co-ordinates

$$V = 2\pi \sum_j r_j z(r_j)(r_{j-1} - r_j), \quad (4.16)$$

with the amount of liquid defined as the difference in the volumes enclosed between both isotherms and the rod surface. We assume that the total shape of the rod doesn't change significantly in the process, so that the optical power at each point on the surface is constant shot-to-shot⁴.

The results of this simulation are shown in figure (4.3). The leftmost plot shows

⁴We examine the process of surface deformation in more detail in the next section.

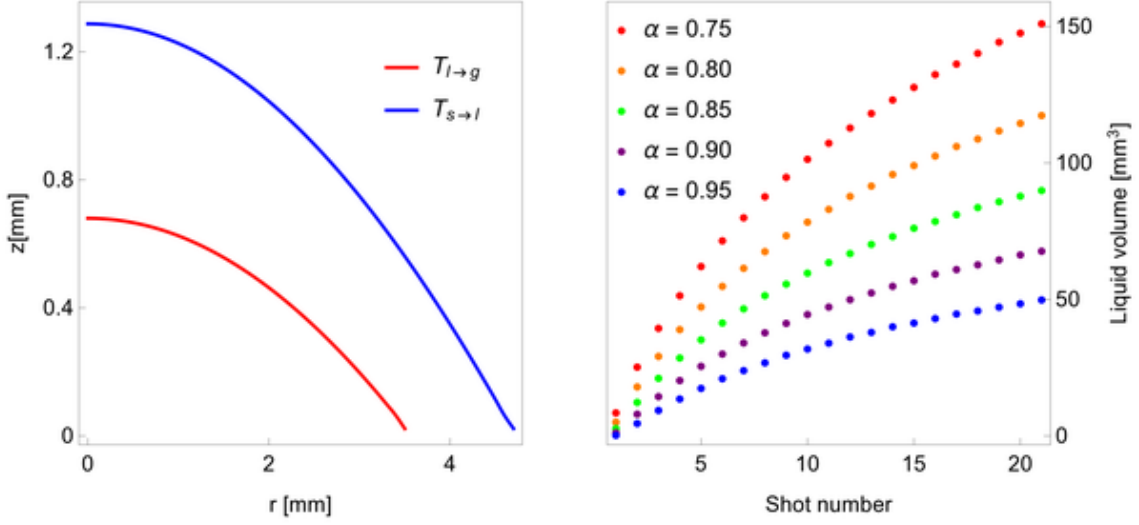


Figure 4.3: Example isotherms in a solid, semi-infinite Yb rod satisfying $T_{l \rightarrow g} = h_{\text{train}}(0, 0, 0)$ and $T_{s \rightarrow l} = 0.75h_{\text{train}}(0, 0, 0)$ after 10 shots at 10 Hz (left), and the predicted liquid volume remaining on the surface as a function of shot number for different values of α (right). In both cases, $w = 5 \times 10^{-3}$ m and $\kappa = 3.46 \times 10^{-5}$ m² s⁻¹.

two isotherms for a system irradiated by a train of 10 pulses with temperature ratio $\alpha = 0.75 \sim 1097/1469$. The rightmost plot shows the liquid volume calculated using this method as a function of the shot number. In both cases, the irradiating laser had characteristic width $w = 5 \times 10^{-3}$ m and the repetition rate was 10Hz. We see that, even if $\alpha \sim 1$, a significant volume of fluid ($> 2w^2\epsilon$) is expected to wet the surface of the rod after 20 shots with the laser, with the situation becoming significantly worse for higher boiling points.

Before moving on, we should address the limitations of the model presented above. We have drastically simplified the ablation process into something purely thermal, ignoring the fast dynamics and high intensity behaviours implicit in the process. The model has some capacity to handle these dynamics by assuming that processes like thermal shock and phonon scattering set the scale ϵ before the more familiar slow thermal decay begins. However, a real ablation process involves some rich physics that we have ignored completely. For example, we expect some of the liquid Yb to be expelled, material clusters to form, energy to be lost through black-body radiation, plasma shielding in the plume, and much more. We are also unable to say qualita-

tively how the wetting process would reduce the flux, other than to state that it is unfavourable! We conclude that, with the simplistic nature of the model in mind, the wetting process outlined above is at least a feasible explanation for the rapid decay in signal observed experimentally. We should also expect a significant heat load on the Yb rod, and take steps in future designs to effectively heat-sink our targets.

4.2 Target deformation

In the preceding section, we developed a simple model based on heat conduction to try to explain the reduction of signal for high ablation shot rates. We found that lasers with a broad mode profile would lead to heat being retained on the surface of the target, and suggested reasons why this could lead to a reduction in observed molecular flux. A key part of this model was the assumption that the local shape of the target surface was unchanged as a function of time, keeping the shot-to-shot heating constant.

In this section, we present a model that may explain the reduction in molecular flux by considering how local deformation of the target affects the intensity of light striking the surface. Using energy-conservation arguments, we estimate the total number of Yb atoms leaving each point in the surface per shot, and iteratively transform the structure of the rod to account for this. The number of molecules lost from the surface is then assumed to be proportional to the number detected in the beam downstream.

We begin by examining how the instantaneous intensity experienced by the target varies as a function of the surface shape. Let's consider the case of the semi-infinite rod introduced in section (4.1). We lift the requirement that the surface of the rod lies at $z = 0$, and instead allow it to vary according to the function $S(x, y)$. Let's again suppose that the mode centre of our ablation laser lies at $(0, 0, 0)$ in the Cartesian volume, and for the sake of simplicity let's begin by discussing only the plane along which $y = 0$. We will eventually make use of the mode symmetry of the laser to evaluate the system in cylindrical co-ordinates, but this complication is unnecessary for our understanding at this stage.

We set up the problem as shown in figure (4.4). The surface function $S(x)$ is illuminated by laser light with local intensity vector $\mathbf{J} = -J\hat{\mathbf{z}}$, where $\mathbf{z}$ is a unit vector in the z direction. A surface element between x and $x + \delta x$ is considered. The unit vector perpendicular to $S(x)$ is $\mathbf{n}(x)$, and we choose δx to be small enough that

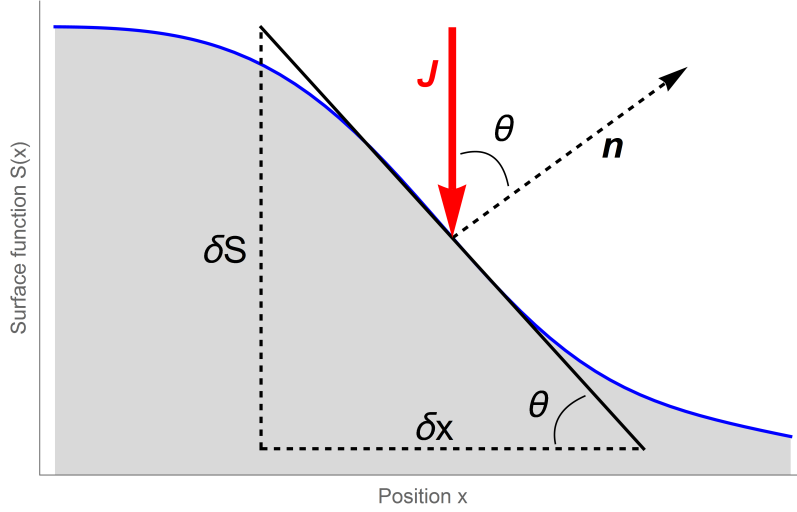


Figure 4.4: Set-up of the system. A solid ytterbium rod (grey) is ablated by a laser with intensity vector $\mathbf{J}$, propagating in the negative z direction (red). The rod surface is described by the function $S(x)$, and is allowed to vary under repeated ablation.

$\partial_x S(x) = \partial_x S(x + \delta x)$ —in other words, S is locally flat on the region δx . The laser intensity within δx is then $J_{\text{eff}} = \mathbf{J} \cdot \mathbf{n} = |\mathbf{J}| \cos \theta$. From the geometry of the problem, we also see that $\tan \theta = \delta S / \delta x$. Thus,

$$J_{\text{eff}} = |\mathbf{J}| \cos \arctan \left(\frac{\partial S}{\partial x} \right) = \frac{|\mathbf{J}(x)|}{\sqrt{1 + (\partial S / \partial x)^2}}, \quad (4.17)$$

where in the last line we have exploited the identity

$$\cos x = \frac{1}{\sec x} = \frac{1}{\sqrt{1 + \tan^2 x}}. \quad (4.18)$$

We see from equation (4.17) that if $S(x_0)$ is locally steep, then the laser intensity at x_0 is correspondingly reduced. In the absence of local heating and thermal dissipation in the target or plume, the yield following ablation should be proportional to the laser intensity. Therefore, we would expect less material to be ablated from this point. We will see later that the ablation process is, at least at some level, self limiting—if our laser starts to bore a hole into the target, $\partial_x S(x)$ will increase at the edges of the hole and hence reduce the overall yield. Additionally, as the bottom of the hole is at the intensity maximum, its gradient can only increase as a function of shot number.

In reality, S is a function of two variables—position, and the number of shots on the same piece of material, N . For the N th shot, the surface will have been ablated $N - 1$ times previously. If $\mathbf{J}(x) \neq \mathbf{J}(x, N)$, then it follows that

$$J_{\text{eff}}(x, N) = \frac{|\mathbf{J}(x)|}{\sqrt{1 + \left(\frac{\partial}{\partial x} S(x, N - 1)\right)^2}}. \quad (4.19)$$

Thus, in order to determine the variation in the yield as a function of shot number, we solve iteratively for $J_{\text{eff}}(x, N)$. Our remaining task is to estimate how much material is removed in each ablation pulse.

We define the amount of energy required to remove one Yb atom from the bulk of a solid material as the binding energy, E_{Yb} . We determine this energy from the thermodynamic properties of the system, namely

$$E_{\text{Yb}} \approx \frac{1}{A_v} C_p \Delta T + Q_{\text{fus}} + Q_{\text{vap}}, \quad (4.20)$$

where C_p is the specific heat capacity of Yb, ΔT is the difference between our initial temperature and the boiling point of Yb, Q_{fus} is the latent heat of fusion per mole of Yb, Q_{vap} is the latent heat of vaporization, and A_v is Avogadro's constant. Inputting known values, we obtain $E_{\text{Yb}} \approx 1.83$ eV. Suppose now that in the ablation process energy is transferred from the laser into the vaporisation pathway with efficiency η . Then the number of atoms removed from the target is

$$N_{\text{mol}} = \eta \frac{E_{\text{las}}}{E_{\text{Yb}}}, \quad (4.21)$$

where E_{las} is the total energy of a single ablation pulse. The removed volume of a single ytterbium atom, V_{Yb} , is calculated by assuming a hard-sphere structure with diameter equal to twice the covalent radius of Yb.

Given these numbers and our typical experimental parameters, do we expect this process to be an issue? Let's take $\eta = 0.5$, $w = 10^{-3}$ m, and $J_{\text{eff}} = |\mathbf{J}| = 100$ mJ/pulse. Then the total number of atoms emitted is $N_{\text{at}} \approx 2 \times 10^{17}$. If they are emitted mainly over a region of area πw^2 , then the average depth of material removed is $d \approx 1.5$ μm . We expect this issue to become a problem when the surface gradient becomes significant, or $d \sim w$. With this choice of parameters, this occurs after ≈ 650 shots. In contrast to the local heating problem then, we expect this process to

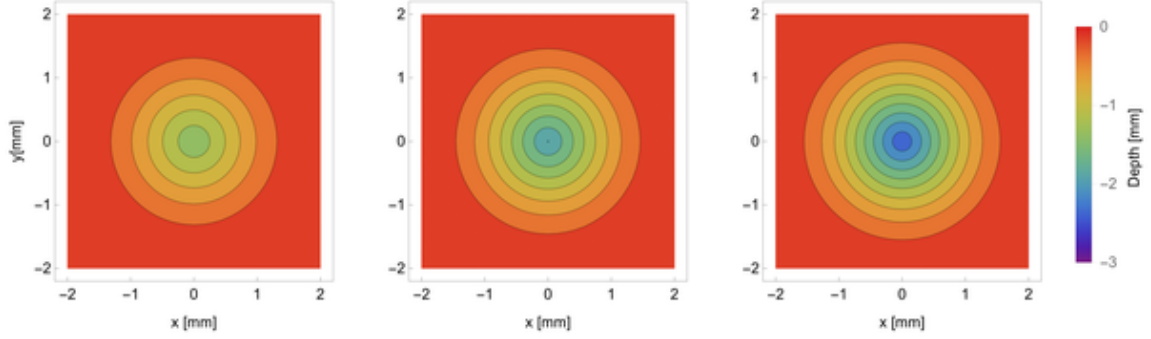


Figure 4.5: Distortion of an initially flat target after 1000 (left), 1500, and 2000 (right) shots. We have taken the coupling efficiency $\eta = 0.5$, the total laser energy to be $E_{las} = 100$ mW, and the laser spatial mode is given by equation (4.22) with $w = 10^{-3}$ mm.

lead to an irreversible loss of signal over hundreds of ablations, rather than a rapid but reversible loss of signal over tens of shots.

We now have enough information to try and predict the loss of flux due to mechanical changes to the surface of the target. Our approach is based on the use of equation (4.19) as follows. We define our rod to fill the same Cartesian half-volume as before, and take as our initial condition a flat metal surface: $S(0, x) = 0$. We split the space into discrete, concentric rings with width δr and area $2\pi r \delta r$, and define our laser intensity as

$$|\mathbf{J}(r)| = \frac{E_{las}}{\pi w^2} \exp\left(-\frac{r^2}{w^2}\right), \quad (4.22)$$

which follows from the requirement in circular co-ordinates that $\int_0^\infty 2\pi r |\mathbf{J}(r)| dr = E_{las}$. If δr is sufficiently small, then the total energy transferred to a ring element lying between r and $r + \delta r$ is

$$E_{ring} = \int_r^{r+\delta r} 2\pi r J_{eff}(r, N) dr \approx 2\pi r \delta r J_{eff}(r, N), \quad (4.23)$$

and the number of atoms emitted from the ring follows from equation (4.21):

$$N_{at}(r, N) = \frac{2\pi \eta r \delta r J_{eff}(r, N)}{E_{Yb}}. \quad (4.24)$$

The change in the surface function within this ring is then

$$\Delta S(r, N) = -\frac{N_{\text{mol}} V_{\text{Yb}}}{2\pi r \delta r} = -\frac{\eta J_{\text{eff}}(r, N) V_{\text{Yb}}}{E_{\text{Yb}}}, \quad (4.25)$$

and we can close the iterative loop by updating the surface function as follows:

$$\begin{aligned} \frac{\partial}{\partial r} S(r, N) &\approx \frac{S(r + \delta r, N) - S(r, N)}{\delta r} \\ &= \frac{S(r + \delta r, N - 1) - S(r, N - 1)}{\delta r} + \Delta S(r, N). \end{aligned} \quad (4.26)$$

We have solved this system iteratively for the case of $\eta = 0.5$, $E_{\text{las}} = 100$ mW, and $w = 10^{-3}$ m. The surface functions $S(r, 1000)$, $S(r, 1500)$, and $S(r, 2000)$ are shown in figure (4.5), and demonstrate the increasing depth and width of the “pitting” induced by the repeated ablation process. Despite the Gaussian nature of the mode shape the deformation is closer to conical in form, with a sharp minimum at the centre of the pit. This is because the process removes more material from regions with a small surface gradient than regions that are steep. Now, using equation (4.26) with an initially flat surface we see that $S(r, 1) \propto J_{\text{eff}}(r, 1)$ and the surface matches the laser mode. This shape is then distorted by repeated ablation, which will tend to reduce the curvature in the surface.

The total yield, $\int_0^\infty 2\pi r N_{\text{at}}(r, N) dr$, is shown in figure (4.6) as a function of the shot number for various combinations of E_{las} and w . We note two general trends. The first is that turning up the laser power isn’t necessarily a good idea if we wish to optimise the amount of signal in the long run. Compare, for example, the curves $E_{\text{las}} = 100$ mW, $w = 0.5$ mm and $E_{\text{las}} = 50$ mW, $w = 1$ mm. While the initial yield from the high-intensity laser is better by a factor of 2, it decays rapidly on the hundred-shot time scale, before crossing the low-intensity curve after 410 shots. This is because the high-intensity laser damages the target surface far more rapidly than the low-intensity laser, leading to a reduced intensity per unit area at the surface.

Secondly, we point out that a small change to the mode width of the ablating laser is sufficient to drastically reduce this problem. Consider now the curves $E_{\text{las}} = 100$ mW, $w = 0.5$ mm and $E_{\text{las}} = 100$ mW, $w = 2$ mm. The beam with the larger spatial mode exhibits almost no change in yield with respect to shot number, losing only 3% in flux over 2000 shots. In comparison, the ablation beam with the narrow spatial mode loses 76% of its yield in the same period. In general, narrower ablation distributions have a faster decay due to this process.

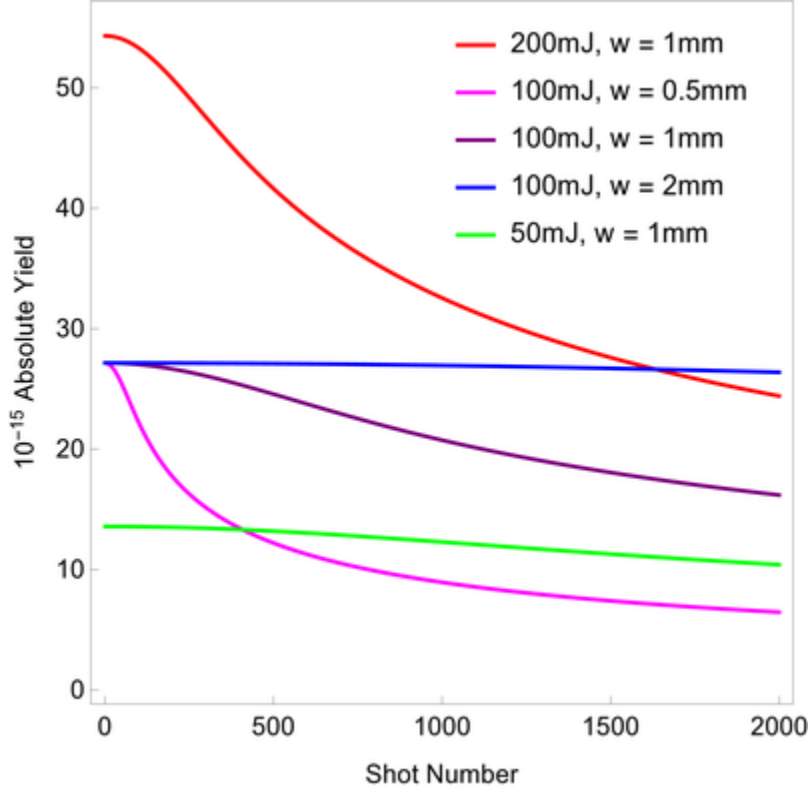


Figure 4.6: Predicted ablation yield as a function of shot number for a range of different mode widths and powers. We again took as our initial condition $S(r, 0) = 0$, and used $\eta = 0.5$. The decay has a particularly strong dependence on mode size; comparison of the magenta to the blue curves shows that changing w by a factor of 4 is enough to completely remove this effect.

The mode shape is also crucial to the severity of this effect. In theory, a top-hat type mode should give constant yield regardless of power, as the only regions where the intensity gradient is non-zero have zero width. Unfortunately, this system is unstable—any small deviations in the mode shape will lead to a mismatch between mode and surface which rapidly spreads. It is nevertheless important to see if a change to a non-Gaussian mode will improve the signal stability. To this end, we have simulated the yield for two new mode shapes—a fourth-order super-Gaussian

$$|\mathbf{J}_{SG}(r)| = \frac{2}{w^2\pi^{3/2}} \exp\left(-\frac{x^4}{w^4}\right), \quad (4.27)$$

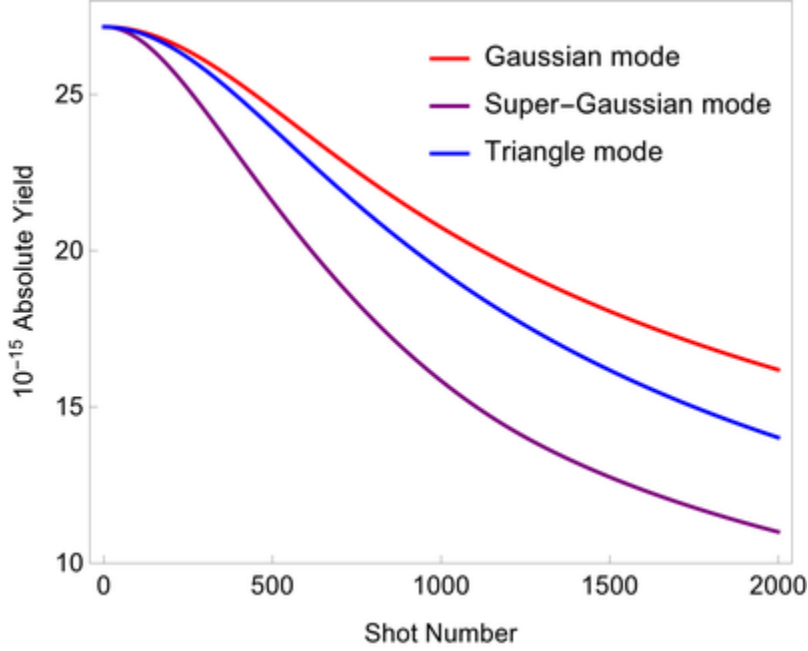


Figure 4.7: Predicted ablation yield as a function of shot number for three different mode shapes—the Gaussian defined in equation (4.22), the super-Gaussian of equation (4.27), and the triangular mode from equation (4.28). In all cases $\eta = 0.5$, $w = 1$ mm, and $E_{\text{Las}} = 100$ mW.

which has a flatter peak than the Gaussian, and a triangular mode

$$|\mathbf{J}_{Tr}(r)| = \frac{3(e-1)^2}{\pi e^2 w^2} \left(\frac{1-e}{ew} r + 1 \right) \quad (4.28)$$

defined on $0 \leq r < ew/(e-1)$. Both modes are normalised in the same way as $|\mathbf{J}(r)|$ and all have the same $1/e$ radius of w by construction. Yields for these mode shapes as a function of shot number are shown in figure(4.7). We see that the wide, flat peak of the super-Gaussian increases the decay rate of the yield compared to the other modes. The triangle mode itself is rather interesting, as it already has its local curvature minimised. An ablation shot therefore removes the same amount of material from all points in the hole, leading to the formation of a perfect, stable cone structure. Despite this, the flux from triangular-mode ablation still decays faster than that obtained using a Gaussian mode.

Finally, we can ask what happens if our initial surface isn't smooth but instead has

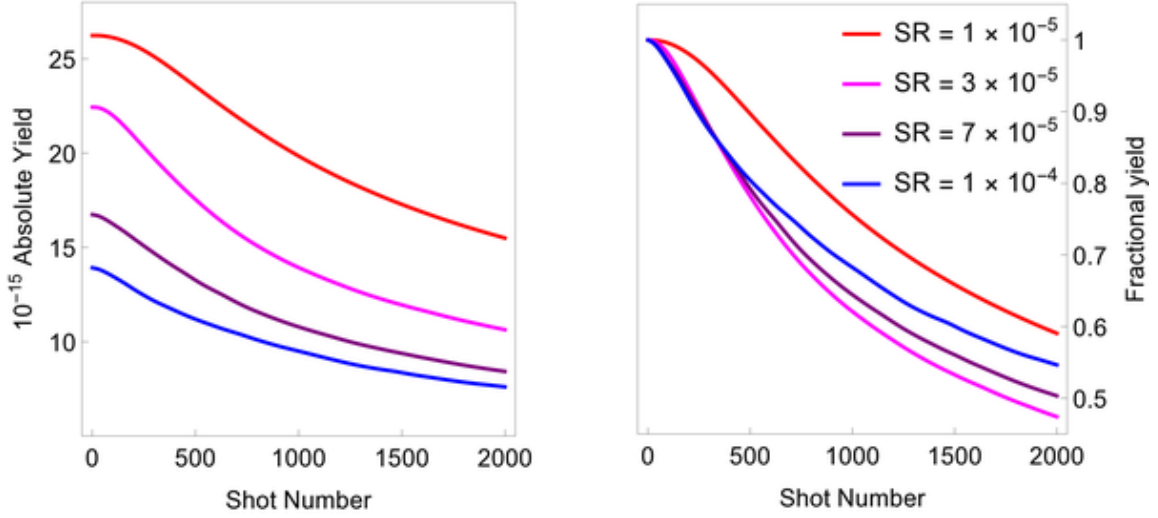


Figure 4.8: Absolute and normalised yield obtained according to the initial condition (4.29), $\eta = 0.5$, Gaussian laser mode width $w = 1$ mm, and $E_{\text{las}} = 100$ mW. Each curve is the mean of 80 simulations, with the surface function re-drawn from the normal distribution before each.

some local roughness. We simulate this effect by seeding our initial surface with normally-distributed noise such that, for each ring element r_0 , the instantaneous surface is given by a random variable S_0 drawn from the distribution $f_{S_0}(x)$:

$$S(r_0, 0) = S_0 \sim f_{S_0}(x) = \frac{1}{\sqrt{2\pi}(SR)} \exp\left(-\frac{x^2}{2(SR)^2}\right). \quad (4.29)$$

Here SR is the characteristic surface roughness, and varies between 10 and 100 microns in this simulation. The absolute and normalised yield for targets with different SR values are shown in figure (4.8). We see immediately that an initially rough target impacts on both the overall yield and on the per-shot decay rate. This should not be a surprise—the roughness acts to increase $\partial S/\partial r$ locally, reducing the yield, and to drive the system away from the Gaussian case, which we saw in figure (4.7) will increase the decay rate.

If we know the characteristic r and $S(r, 0)$ scales, and if $SR \ll w$, we can use equation (4.19) to write down the variation in the initial yield exactly. In our case,

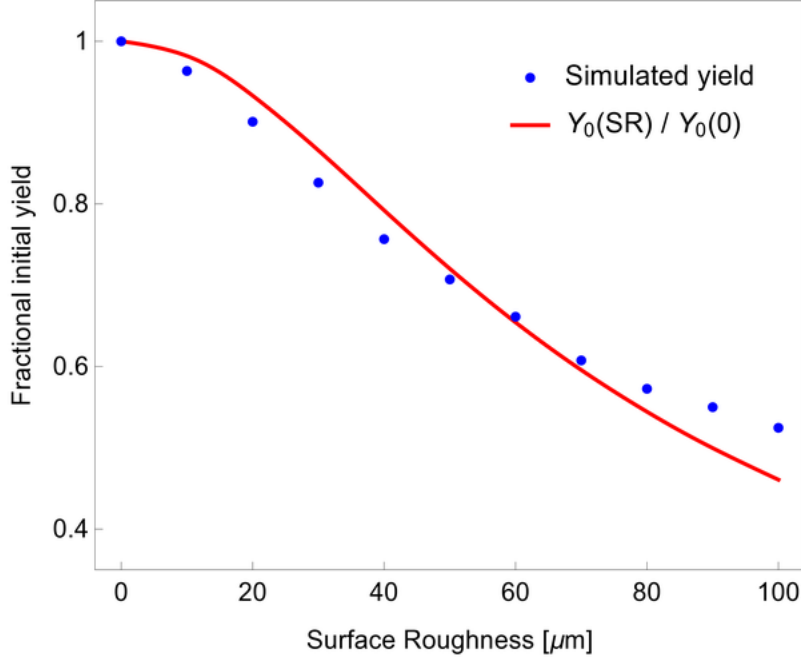


Figure 4.9: Comparison of the simulated first-shot yield with the prediction of equation (4.32), using the same parameter set as figure (4.8). We see good agreement up to $SR = 50$ microns, after which the model starts to underestimate the yield with respect to the data. All values are normalised according to the $SR = 0$ case.

this amounts to determining the average variation of $\alpha = |S(r + \delta r, 0) - S(r_0, 0)|$ for adjacent ring elements. This can be determined by noting that the probability of obtaining a certain value of α is just the joint probability of obtaining two independent random variables from equation (4.29) with difference α , integrated over all possible permutations:

$$P(\alpha) = 2 \times \frac{1}{2\pi\sigma^2} \int_0^\infty \exp\left(-\frac{x^2 + (x + \xi)^2}{2SR^2}\right) dx, \quad (4.30)$$

where the factor of two arises as we care about the magnitude of the gradient, not just its sign. The average variation $\bar{\alpha}$ is then

$$\bar{\alpha} = \int_0^\infty \alpha P(\alpha) d\alpha = \frac{2 + \sqrt{2}}{2\sqrt{\pi}} SR, \quad (4.31)$$

and thus the variation in initial yield is given by substitution into equation (4.19):

$$Y_0(SR) = Y_0(0) \left[1 + \left(\frac{2 + \sqrt{2}(SR)}{2\sqrt{\pi} \delta r} \right)^2 \right]^{-1/2}. \quad (4.32)$$

We have compared this curve against the simulated first-shot yields in figure (4.9), taking in both cases $\delta r = 50$ microns. We find good agreement between the simulated data and the theoretical line, although this agreement seems to become less good as δS increases above $2\delta r$. This may be because the theoretical line deals with the average variation, whilst in our simulations we have influence from localised larger gradient values. We see from both the model and the simulated data, however, that a surface with $\delta S/\delta r > 1$ is undesirable, as it reduces our initial yield by more than 25%.

We conclude this section with a short review of our obtained results. We have shown that the act of ablation can lead to significant changes in the surface structure of the target, with a corresponding reduction in the yield. To reduce this effect, a broad, low-intensity ablation laser is preferable, with the action of doubling total laser power being roughly equivalent to halving the beam diameter on overall signal stability. Of the laser modes we tested, we found that the Gaussian case is preferable, although this was by no means an exhaustive search. Finally, we should try to make sure that our target is smooth, and that the depth scale of any amplitude modulation on its surface be less than double the length scale over which it occurs.

4.3 Conclusion

We have examined both the thermal and mechanical behaviour of a solid ytterbium rod under ablation. We found evidence that repeated ablation causes significant heating near the surface of the rod, and suggested a wetting process which could explain the rapid but reversible loss of yield from the target. We then considered how repeated ablation changes the surface structure of the target, and demonstrated how this process leads to a slower but permanent loss of signal.

To examine the viability of the structural deformation model, we have compared it with the data in the right-hand panel of figure (4.1). Because the exact properties

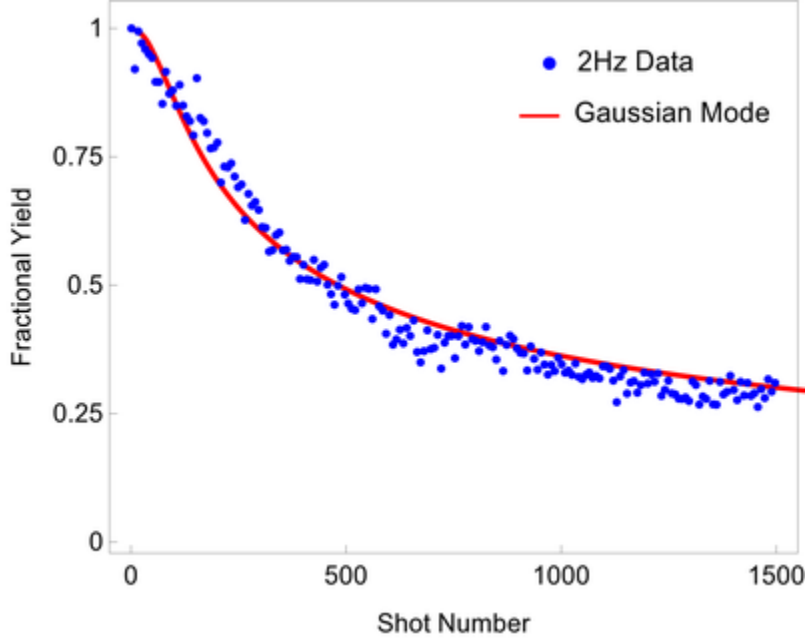


Figure 4.10: Measured yield decay, compared with a fit using an ablation laser with a Gaussian mode with the width the only free parameter. The fitted spot size of $(610 \pm 10) \mu\text{m}$ agrees within error with our measured beam diameter.

of the surface and the laser were unknown, we have taken the laser mode to be Gaussian and performed a single-variable fit by allowing the laser spot size to float within the uncertainty range of the measured ablation mode diameter, $(1000 \pm 500) \mu\text{m}$. A plot of this result is shown in figure (4.10). From the fit, we obtain a fitted spot size of $(610 \pm 10) \mu\text{m}$; taking as a measure of agreement the calculated residual sum of squares of 0.22, we find that the average deviation of experimental points from the fit is ≈ 0.03 , or 3% of the measured maximum. We conclude that, as the model provides a good fit to the data with only one free parameter, it provides a viable explanation for the observed trend.

It is much harder to quantify the thermal model, as the exact mechanism of the proposed thermal changes within the target are unclear. For example, in the low-intensity case shown in the left-hand panel of figure (4.1), the yield initially increases for both repetition rates. This is not something that the thermal model, at present, is able to describe. The model does predict that heat is trapped close to the point of ablation at higher repetition rates, and I have suggested a possible reason why

this might lead to a corresponding reduction in the molecular flux with the wetting model. However, the evidence supporting the validity of this model is much more slender - the best that we have been able to say is that the thermal process is significant at 10 Hz and not at 2 Hz, and that heat builds up over tens of shots, which is in rough agreement with the time constant for signal decay in the 10 Hz case.

If the thermal processes are indeed a problem, they can be minimised by running at a low repetition rate, or using a narrow laser mode. Conversely, the mechanical processes require a broad laser mode in order to be minimised, with the additional stipulation that the mode of our laser be Gaussian and the target surface smooth. Thus, if we optimise for yield stability, we require a narrow, Gaussian laser mode with a repetition rate significantly below 10 Hz. We should also take special care of our target, removing ablation damage where possible and addressing fresh pieces of target where necessary. These strategies were used extensively when testing the two-stage cell, a discussion of which follows in section (5).

Chapter 5

Designing and testing a two-stage source of YbF

5.1 Introduction to the two-stage source

In their pioneering work “A Cold and Slow Molecular Beam”, Lu *et al* [96] demonstrated that a carefully designed buffer gas source could exhibit favourable properties of both the hydrodynamic and effusive regimes. A buffer gas source has two figures of merit which exist in something of a competition—flux and beam velocity. Thermalisation of a heavy molecule requires a large number of elastic collisions between the hot species and the buffer gas; however, if the pressure is raised too much then boosting occurs through the cell aperture and the forward velocity of the beam is increased.

The classical approach to this problem is to run in the effusive regime. Unfortunately, the flux of effusive beams is typically rather poor due to their low extraction efficiency. We can estimate the efficiency of these sources by comparing the aperture area to the internal area of the cell. At the point where a beam just becomes effusive $\text{Kn} = 1$ and hence the aperture width $L = \lambda$. From equation (2.62) we know that the internal dimensions of an effective source are defined via the maximum elastic thermalisation distance. Thus the extraction efficiency η is of the order

$$\eta \sim \frac{L^2}{l_{\text{max}}^2} = \frac{1}{N^2}, \quad (5.1)$$

where N is the number of collisions required for elastic thermalisation, a process which occurs on the length scale l_{max} . which for our typical conditions gives $\eta \approx$

$2 \times 10^{-3} \%$. In comparison, a fully hydrodynamic beam has theoretical extraction efficiency $\eta = 100\%$. A useful figure of merit is the relative sensitivity of an EDM experiment using an effusive or hydrodynamic source. The sensitivity S scales linearly with time in the apparatus and with the square root of the number of molecules measured; taking the limiting mean supersonic and effusive velocities we obtain

$$\frac{S_{\text{Eff}}}{S_{\text{SS}}} = \sqrt{\frac{5\pi}{8N^2} \frac{M}{m}} = 0.04. \quad (5.2)$$

Here M is the YbF mass and m is the helium mass. We see that, despite the forward velocity of an effusive source being $\approx 10\times$ lower than the supersonic limit, the extraction efficiency of effusive sources of YbF are poor enough that they are not a good choice for precision measurements.

The two-stage source first outlined by Lu *et al* [96] rather neatly circumvents this problem by separating the thermalisation and beam-forming regions. Molecules are produced in a cell operating in the hydrodynamic regime where the extraction efficiency is good, before being fed into a second, slowing cell. This slowing cell utilises a mesh aperture to reflect helium atoms back into the molecular beam, reducing the net forward velocity. The pressure in the second stage was found to be crucial, as one must carefully balance the number of slowing collisions within the second stage with the reboosting collisions outside the aperture. To fine-tune this pressure, a small gap was left between the two cells and vents were fitted close to the mesh aperture. Using this scheme effusive-type velocity distributions of CaH were measured, with an extraction efficiency of 0.5%. This is already enough to increase S in equation (5.2) to ≈ 1 , but also opens the door on many laser cooling schemes that otherwise could not be applied to YbF.

In this section, we report on the current state of a two-stage beam of YbF molecules. We have not been able to replicate the work of Doyle’s group, but have obtained velocity distributions whose low-energy tail would be very amenable to laser cooling. This chapter will deal chronologically with the efforts to design the cell and explore its available parameter space, before suggesting improvements that might be made to future iterations of the experiment.

5.2 Designing a two-stage source of YbF

We did not know *a priori* what the correct design parameters for YbF would be, or even which parameters tuned strongly the low-velocity behaviour of the two-stage

source. Because of this, the main design aim for this source was adaptability. The system was made according to as simple a design as possible so that different components could be switched out, modified, or extended should they not fulfil their purpose.

The available parameter space for the cell was known to be large—in contrast to the hybrid source, we would also have control over the inter-cell separation, the diameters of two apertures, the porosity of the meshes, and the length of the slowing cell, none of which could be changed while the experiment was cold and instead required a two-day turnaround. To try and reduce this, the cell was designed such that it could be converted into a jack arrangement to give control over the inter-cell separation while cold. Although this capability was never used, the potential is nevertheless there in the designs for enthusiastic future experimenters.

The design process centred on using the analytic expressions derived in section (2.6) to estimate the thermalisation scales in the first buffer gas stage. We kept some of the key elements of the hybrid source, using again a solid metal target mounted on a rotary feed-through, in conjunction with a warm SF_6 line, to produce our YbF molecules. We moved away from the internal geometry of the hybrid source and instead settled on a simple, axially-symmetric design based on concentric cylinders and apertures. The flow behaviour from the hybrid source has been seen to be complex, with different flow regimes competing within the same volume. This complexity would have been difficult to account for when the second stage was added.

In terms of beam velocity, the best published results from the CaH two-stage beam were obtained for helium flows in the range 1–10 SCCM. This requirement lead us toward increasing the internal volume of our first stage cell relative to the hybrid source in order to preserve the thermalisation condition of equation (2.65). The internal volume of our first stage is cylindrical, with total bore length 30 mm and diameter 15 mm. If the distance from the target to the aperture plate is ℓ and the aperture area is A , then the minimal distance between the target and the cell exit $L_{\min}$ is

$$L_{\min} = \sqrt{\ell^2 + (\ell - \sqrt{A/\pi})^2}. \quad (5.3)$$

Applying the upper bound condition of equation (2.65), the minimum flow rate required for full thermalisation is

$$\dot{N}_{\text{in}} = 2.2 \times 10^4 \frac{A\sqrt{T}}{\sqrt{\ell^2 + (\ell - \sqrt{A/\pi})^2}} \quad (5.4)$$

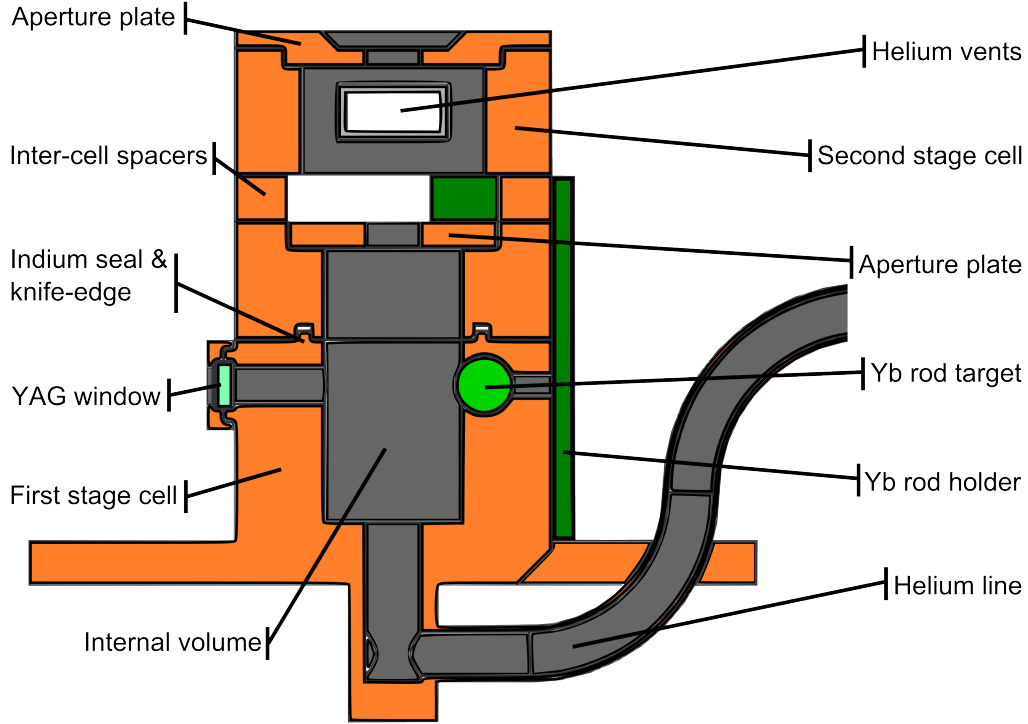


Figure 5.1: Rendering of a through-axis cross-section of the two-stage cell. The internal volume of the cell is shown in grey, while the copper walls are depicted in orange. The internal volume of the cell is now axially symmetric, in contrast to the hybrid source, but we have maintained the YbF production scheme. The SF_6 line is co-planar with the Nd:YAG window and target but is not shown in this illustration.

which, for our first stage cell using a 4 mm diameter aperture gives $\dot{N}_{\text{in}} \approx 2.6$ SCCM. This choice of cell parameters, while not fully spanning the flow rate range of Doyle, was considered to be a good baseline—we would be able to address a wide range of helium flows without increasing the internal volume too much. Lower flow rates were accessed by mechanically fixing a copper extender to the cell, which consisted of a 20 mm long solid copper block with a 15 mm through-hole bored into it.

The design for the second stage was motivated by considering the number of collisions required to remove a certain amount of forward momentum from a YbF molecule. Consider the case of a 1D collision between a buffer gas atom, mass m , and a molec-

ular species with mass M . Applying the conservation of energy and momentum, we may write down the velocity after $N + 1$ collisions as

$$v_{N+1} = \frac{1}{m + M} (2m\bar{v} + (M - m)v_N), \quad (5.5)$$

where $\bar{v}$ is the velocity of the buffer gas. From equation (5.5) we can obtain the difference equation

$$\frac{v_{N+1} - v_N}{(N + 1) - N} = \frac{2m}{m + M}(\bar{v} - v_N) \implies \frac{dv}{dN} = \frac{2m}{m + M}(\bar{v} - v), \quad (5.6)$$

and the correspondence between the difference and differential equations becomes exact in the limit $M \gg m$. In a two-stage cell, we are interested in collisions between an incident beam of molecules and a counter-propagating beam of buffer gas atoms. Furthermore, if the first stage is operated in the hydrodynamic regime then $v(0) = -\bar{v}$. Solving the differential equation in (5.6) subject to this initial condition gives

$$v(N) = \bar{v} \left(1 - 2 \exp \left[-\frac{2mN}{m + M} \right] \right), \quad (5.7)$$

and we see that the momentum of a given molecule is reversed over $\sim (m + M)/2m$ collisions. We define the slowing number, N_s as the number of collisions required for the direction of motion of a molecule to first change sign, which is obtained for

$$N_s = \frac{m + M}{2m} \ln 2. \quad (5.8)$$

We can evaluate the slowing number for both CaH and YbF to obtain $N_s \approx 4$ and $N_s \approx 17$ respectively, suggesting that we should scale the length of the second stage in our design to be $\approx 4\times$ that of Doyle's design.

The limiting scales set by equation (5.8) assume everything acts in a one-dimensional¹, ballistic manner. Conversely, if the second stage acts as a more conventional buffer gas source then we might think of the slowing process as being thermal in nature, proceeding on a scale proportional to the square of the molecular mass. The square-root ratio of YbF to CaH masses is ≈ 2 , which suggests that our second stage should be twice the length of Doyle's design.

¹Extending to 3 dimensions amounts to considering the mean scattering angle; we find that each collision removes on average half the amount of momentum of the 1D model. However, the ratio of slowing numbers remains unchanged. The full 3D calculation is addressed in section (6.8).

Ultimately, we decided to start our experimentation at the shortest length limit, as predicted thermally. This choice was made for pragmatic reasons, as we would still expect to see some degree of slowing even with a shorter than optimal second stage, and in practice it is far easier to add length to a design (using inserts or extenders, for example) than it is to remove it (which requires a large amount of work on a milling machine or wire eroder).

The thermal anchoring between the two cells is ensured by using either tight-fitting copper legs, or longer brass rods and additional copper strips joining the two stages. The temperature of both stages is monitored using Lakeview thermistors, although in practice we have found that the temperature of the two stages agrees to within 0.1 K regardless of the set-up we’ve used. Helium enters the first stage cell through a 6 mm ID pipe drilled into the bottom of the cell and then soldered to 1/4” copper tube, which is in turn heat-sunk to the 4 K stage using a series of bobbins.

The new design also allowed us to act on our findings from the hybrid source. We moved away from using high-energy YAG pulses to produce our molecules, preferring instead to use lower energies focussed more tightly on the target to mitigate thermal effects. We also began, as a matter of course, to polish the metal target rod until smooth every time we broke vacuum in an attempt to reduce surface roughness effects. A common issue with the hybrid source was the failure of the SF₆ line insulation, which led to the line freezing. Early designs were concerned with holding the line tightly in place, the result of which was a large surface area for heat conduction between the line and the insulating PEEK insert. To prevent this problem with the two-stage cell we made use of the recent advances in 3D printing to make insulating jackets that held the line on two sets of three sharp-tipped points, minimising the contact area while still holding the line steady. The line itself was also frequently polished using 1200 grit emery cloth to reduce its emissivity, and hence the radiative load into the 4 K cell.

We did not have access to the Coherent 899 ring laser over the course of this experiment, moving instead to an amplified 1104 nm diode laser frequency-doubled using a periodically-poled lithium niobate crystal. The more limited frequency range of this set-up prevented us from using the ytterbium-based characterisation techniques shown in our work on the hybrid source. We are still able to obtain measurements of the velocity, temperature, and velocity distribution; however, a measurement of the beam divergence has thus-far eluded us, and we have characterised the rotational

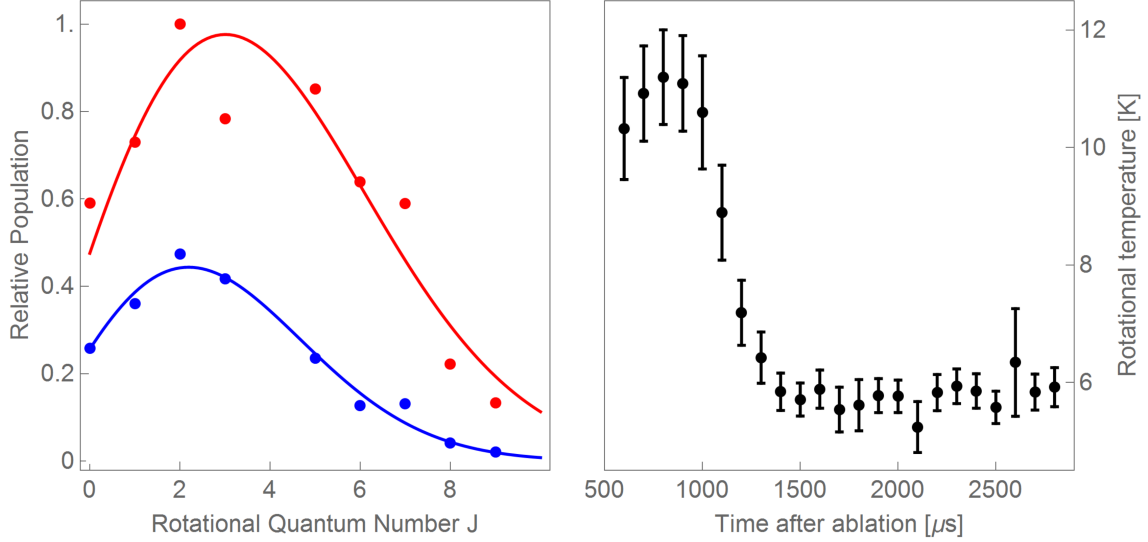


Figure 5.2: Fitted rotational level distributions (left) and calculated rotational temperatures (right) for a 20 SCCM YbF beam from the two-stage source. The two curves in the left pane were obtained for the ^{174}YbF isotope at times of 1000 μs (red) and 2000 μs (blue). The thermalisation curve in the right pane was obtained after averaging across all three isotopes, with the associated errors being propagated fitting errors.

temperature but not the translational temperature.

5.3 Initial data and the comparison of the hybrid and two-stage sources

A useful first test of the apparatus was to evaluate the similarities between the hybrid and two-stage sources. We set the inter-cell separation to 5 mm and used the same 30% transmissive mesh as the hybrid source. A 20 SCCM helium flow rate was used to evaluate the rotational temperature and beam velocity of the system within a detection region 142 mm from the cell exit.

The rotational temperature was evaluated following the formalism of section (3.4). The populations of the ^{172}YbF , ^{174}YbF , and ^{176}YbF Q(0) to Q(9) lines were mea-

sured using the LIF technique, and fits of the form $(2J + 1) \exp[-BJ(J + 1)/k_B T]$ taken to determine the temperature. Samples of these fits are shown in the leftmost panel of figure (5.2), with the isotope-averaged temperature in the right pane. The errors were calculated by propagating the fit errors for the three isotopes through the mean. We now compare these results to the hybrid source case, shown in figure (3.8), which were obtained at a detector 50 mm from the cell exit. The rotational temperature of YbF from the hybrid source had reached thermal equilibrium after $\approx 400 \mu\text{s}$, at which point the measured velocity at the detector was $\approx 200 \text{ m s}^{-1}$. Molecules with this velocity would arrive at the 142 mm detection region $460 \mu\text{s}$ after passing through the 50 mm region, so if the hybrid- and two-stage sources were comparable we would expect to see thermal behaviour $\approx 860 \mu\text{s}$ after ablation. In contrast, the measured beam from the two-stage source is thermal after $\approx 1400 \mu\text{s}$. This implies two possible consequences—either the confinement time in the cell has increased, or the flow dynamics of the source make it fundamentally worse for thermalisation. We will address this shortly, after examining the velocity profiles for the source under these conditions.

The Doppler method of section (3.6) was used to measure the forward velocity of the beam, shown in the left panel of figure (5.3). We have determined the hydrodynamic and effusive limits using the measured temperature profile determined in figure (5.2) and find that the beam begins almost fully supersonic in character, before asymptoting towards the effusive limit as $t \rightarrow \infty$. Recall in figure (3.12) that our velocity distributions were hot, but not supersonic in form with a long high-velocity tail appearing hot-effusive in character. We do not see this in figure (5.3), with the mean velocities proceeding monotonically towards the effusive limit, although it is possible that our data simply do not extend into a region where this hot-effusive behaviour is apparent.

The velocity distribution for the beam was obtained in a slightly different way to the formalism of section (3.6). Rather than explicitly evaluating the gradient, a resampling technique was used to force equal bin-widths in the velocity domain. The velocity and arrival time were correlated using a fit of the form $v(t) \propto 1/(t - t_0)$, from which the unequal time-width bins Δt_u corresponding to equal velocity-width bins could be determined. The mean time-of-flight was then integrated over each Δt_u to obtain the corresponding amplitude for each velocity. The fit is shown by the orange curve in the left panel of figure (5.3), and the resulting distribution is compared with that of the hybrid source in the right panel.

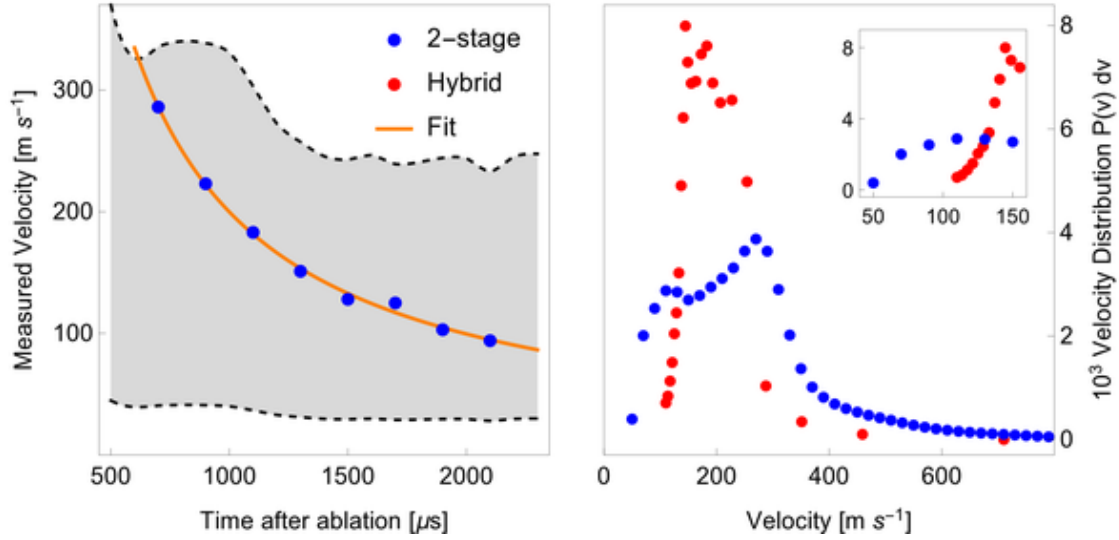


Figure 5.3: Measured velocity and corresponding velocity distribution from the two-stage source running at 20 SCCM helium flow. In the left panel we have the velocity as a function of time, shown relative to the bounding supersonic and effusive limits, and a calibration fit of the form $v(t) \propto 1/(t - t_0)$, where t_0 is a constant to be determined. In the right panel, we compare the velocity distributions of the two-stage and hybrid sources, with the inset zooming in on the low-velocity tails.

The two-stage velocity distribution is significantly broader than the distribution measured 172 mm from the aperture in the hybrid source. Perhaps more excitingly, for the first time we observe a significant amount ($\approx 10\%$) of population with velocities below 100 m s^{-1} , as is shown in the inset of figure (5.3). The means of the two distributions are the same to within 10 m s^{-1} , having values of 248 m s^{-1} and 240 m s^{-1} for the two-stage and hybrid sources respectively. Thus we conclude that, within the flow rates used to characterise the hybrid source, the action of the second stage is to broaden the velocity distribution relative to the hybrid case without acting strongly on the mean.

The unusual shape of the distribution can be qualitatively explained by inserting the measured time-dependent rotational temperature into an ansatz. In figure (5.4) we compare the measured distribution to effusive and 200 m s^{-1} boosted Gaussian distributions with the velocity-dependent temperatures of figure (5.2). Whilst

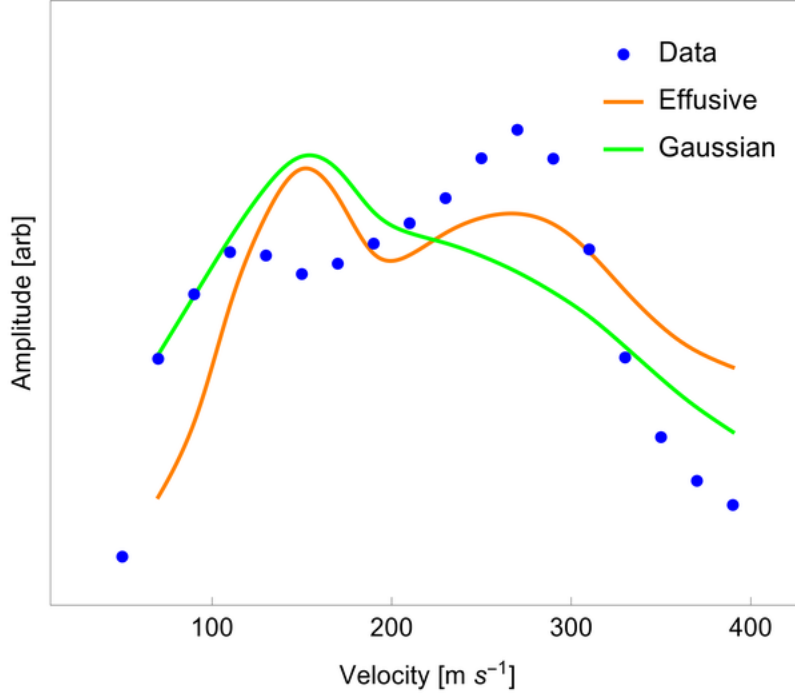


Figure 5.4: Two-stage cell velocity distribution, with effusive and boosted-Gaussian predictions. Neither model is a particularly good fit to the data, but the double-peak structure arises naturally if we assume a velocity-dependent temperature.

both models fail to properly capture the low-velocity region of the distribution, the double-peak structure arises naturally, as does the broadening due to the increased temperature in the high-velocity region. The amplitude of the effusive and Gaussian curves is physically meaningless, as in general we cannot analytically normalise them and we do not have enough data to do so numerically. Instead the areas under the three trends within the plot region have been set equal in order to make qualitative comparisons of the width and structure more intuitive.

Finally, we turn our attention to the thermalisation of YbF molecules in the two-stage source given the confinement time in the cell, determined in the same manner as for the hybrid source in section (3.7). We plot this in figure (5.5), compared with the rotational and translational temperatures measured in the hybrid source. For both sources we see that thermalisation occurs after $\approx 400 \mu\text{s}$, demonstrating that the thermalisation “lag” between the hybrid and two-stage cells is simply down to their different beam characteristics. The different flow character within the two cells

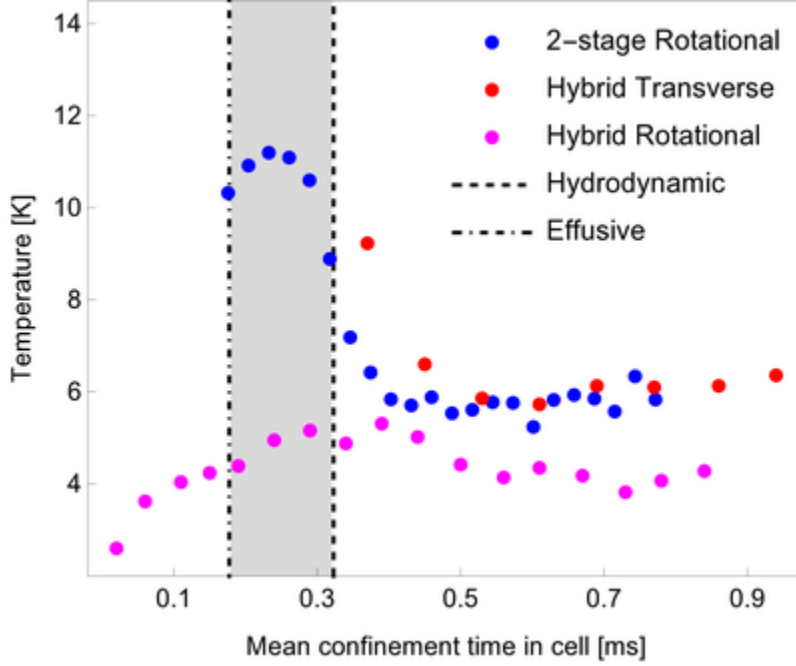


Figure 5.5: Temperature as a function of mean confinement time in the cell, showing the thermalization of the rotational temperature in the two-stage source, and both the translational and rotational temperatures in the hybrid source. The three temperatures all reach their respective asymptotes after $(400 \pm 50) \mu\text{s}$ of cell confinement, showing that both configurations perform equally well at thermalising YbF molecules.

does not adversely affect the thermalisation properties.

We have compared the forward velocity, velocity distribution, rotational temperature, and thermalisation characteristics of a two-stage cell operating in the hydrodynamic regime with the hybrid source and have found them to be qualitatively similar. The two-stage cell has a significant low-velocity tail relative to the hybrid source, and a much broader total distribution. We have explained this by noting that the molecules are not thermal, and that inserting the functional form for their temperature into ansatz distributions captures some of the characteristics of the measured distribution. The thermalisation of molecules within the two-stage cell occurs on the same time scale as for the hybrid source, but the rotational temperature reaches a higher asymptote due to the higher baseline temperature of the source.

We have observed molecules with velocities as low as 50 m s^{-1} . However, Doyle’s group have measured beams with mean velocities as low as 40 m s^{-1} , which implies that we are a long way from the optimum parameter space for the two-stage cell. The next section provides an account of our initial optimisation attempt, in which we examined the helium flow rate, inter-cell spacing, aperture diameters, and mesh pore size.

5.4 Transporting molecules using a permanent magnetic guide

In section (5.3) we evaluated the forward beam velocity and velocity distribution from a two-stage buffer gas source using the Doppler method. However, this technique is, in general, rather slow and inefficient. The co-axial beam will typically bleach the resonant molecules, with two detrimental effects. The first and most damaging is that, as the slowest molecules spend the longest being bleached, we have a systematic bias towards higher velocities. On a more benign level, once the population has been pumped away the fluorescence in the detection region is from the more slowly-cycling non-resonant molecules and hence the observed number of photons is typically rather small. This measure is therefore both inefficient *and* inaccurate.

Whilst the inefficiency is not an issue when the signal-to-noise ratio in the experiment is good, there is absolutely no guarantee that this condition holds everywhere in the experimental phase space. Once slow molecules have been detected, then a rigorous optimization procedure can take place and accurate measurements are appropriate; however, for now we simply wish to narrow our search of the available space as much as possible.

This may seem like a problem—we need to rapidly measure the velocities of molecules for a very large set of experimental parameters, but the method for measuring the velocity strongly limits the speed of this exploration. We need, therefore, an alternative scheme for measuring the velocity distribution of molecules from our cell that is quick and resilient to low signal-to-noise ratios that may occur experimentally.

If all the molecules in the beam left the cell at the same instant, this would not be a problem—we could simply measure the time-of-flight profile of our beam, which would arise purely from the velocity distribution of the molecules due to the correlation between arrival time and beam velocity. Unfortunately, in figure (5.5) we

have seen that the confinement time of molecules in the cell is significant, with a minimum value for thermalisation of $\approx 400 \mu\text{s}$, which is approximately the free-flight time for the slowest molecules from the hybrid source arriving at the bottom detector. We might simply try moving the detection region far from the source, where the free-flight time is much greater than the cell confinement time; doing so reduces the number of molecules crossing the detection region by $1/z^2$, where z is the distance between source and detector, and hence the signal-to-noise criterion fails.

A solution to this problem is to build a guide for molecules so that they can be transported far from the source without diverging. Since ground-state YbF molecules are magnetic, a convenient guide can be built using permanent magnets. The ideal permanent magnetic guide is constructed so as to provide a potential barrier for molecules in the weak-field-seeking manifold of states. Ignoring for a moment the loss mechanisms, the net effect is to guide half of the molecules produced within the $N = 1$ rotational state whose transverse kinetic energy is less than the magnetic potential. The fact that we only capture a small subset of the available transverse velocities is not a problem. The effective detection volume for our optics is $\approx 2 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$, and hence the maximum transverse velocity we observe in a detection region 5 cm from the source is $\approx 1/50$ times the forward velocity. Given that we are interested in molecules with forward velocities $\leq 100 \text{ m s}^{-1}$, then the maximum transverse velocity we expect to detect is $\approx 2 \text{ m s}^{-1}$. In comparison, the maximum guided transverse velocity for YbF in a 1-Tesla magnetic well will be $\approx \sqrt{2\mu_B/M_{\text{YbF}}} \approx 7.5 \text{ m s}^{-1}$, where μ_B is the Bohr magneton and we have assumed that the guiding occurs in the Paschen–Back regime. Thus we can, in principle, use a magnetic guide to transversely trap the molecular beam close to the cell, translate these molecules until the free flight time is much greater than the confinement time, then use the time-of-flight to determine the velocity distribution from the cell.

To this end, we have constructed a 225 mm long straight magnetic guide. Formed of 4 sections, each section has 8 permanent dipole magnets in an octupole arrangement, with both radial and longitudinal spacing between each magnet to allow helium to escape from the guide. Cuboid neodymium–iron–boron magnets with width 3.5 mm and depth 12.5 mm were arranged around a circular bore of diameter 10 mm, giving an average open area of 18.6%. As the magnets had a large remanence of 1.44 T, ARMCO Pure Iron shielding was used to quench the field away from the ends of the guide. The whole arrangement was held in position by an aluminium framework. The guide was mounted from a hole drilled into the radiation shields, allowing it to thermalise to $\approx 30 \text{ K}$ and hence reduce the possible thermal load onto the cell and

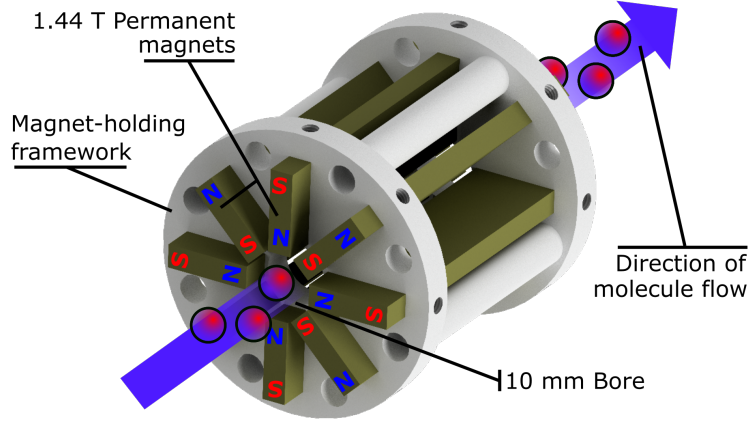


Figure 5.6: Schematic of one of the four sections of the magnetic guide. The 8 permanent magnets are held in place via an aluminium framework; the framework length is 45 mm, and the large circular plates have thickness 5 mm. The sections are separated by spacers, leaving a 1 mm spacing between the magnets in successive sections. The orientation of the magnet poles are shown on the front surface of the section, and the molecular flow through the bore is indicated by the blue arrow.

cold head. A sketch of one of the guide sections is shown in figure (5.6).

In order to evaluate the effectiveness of the guide, we have simulated its phase space acceptance and the Majorana spin-flip transition probability within the well. The field is modelled using the Halbach formalism for trapezoidal-section magnets [120]. A complex magnetic field $B^* = B_x + iB_y$ is defined, representing the two-dimensional multipole field in the $x - y$ plane. If the multipole order is $2 \times O$ and $O > 1$, we can write the field as

$$B^* = B_r \sum_{j=0}^{\infty} \frac{O + jM}{O + jM - 1} \times \left(\frac{z}{r_1}\right)^{O+jM} \left[1 - \left(\frac{r_1}{r_2}\right)^{O+jM-1}\right] \times \mathcal{K}(O + jM, \epsilon, M), \quad (5.9)$$

where M is the number of magnets, $z = x + iy$ is the complex distance from the centre of the array, B_r is the remanent field at the magnet surface, and r_1 (r_2) is the inner (outer) radius of the array. The geometric term $\mathcal{K}$ is defined via

$$\mathcal{K}(n, \epsilon, M) = \cos\left(\epsilon \frac{\pi}{M}\right) \sin\left(n\epsilon \frac{\pi}{M}\right) \frac{M}{n\pi}, \quad (5.10)$$

where $\epsilon \leq 1$ is the effective angular size of each magnet: $\epsilon = 1$ equates to the case where the magnets are all touching, while $\epsilon = 0$ models the magnets as having zero size. In practice the sum in equation (5.9) can be truncated to first order, with the resulting errors being small and localised close to the magnet surface. Furthermore, the guiding is proportional to the magnitude of the field, with the real scalar $B = |B^*|$ giving the amplitude required.

Once we have a magnetic field strength, the transverse phase space acceptance follows from the conservation of total energy for a molecule in the guide. At a given position within the field r , a weak-field-seeking particle will need to have a certain minimum amount of kinetic energy to reach the magnets and escape from the guide. Setting this kinetic energy equal to the magnetic energy, we obtain

$$v_{\max}(r) = \left(\frac{2 g_F m_F \mu_B}{M_{YbF}} [B(r_1) - B(r)] \right)^{1/2}, \quad (5.11)$$

where g_F is the g-factor of the state-manifold F , and m_F labels the magnetic projections of that manifold. In the Paschen–Back regime $g_F \approx g_s \approx 2$ and $|m_F| = |m_s| = 1/2$, and hence $g_F m_F \approx 1$ and the bounding velocity reduces to a particularly simple form. The calculated phase space acceptance is bounded by the red curve of figure (5.7), and agrees broadly with our earlier order-of-magnitude calculation for the maximum trapped velocity.

Majorana transitions occur when molecules in weak-field seeking states cross areas of low magnetic field where their motion induces a spin-flip to high-field seeking states. In this region, not only does the field amplitude change but so too does the direction of the magnetic field vector. To capture this effect, it is useful to transform into an instantaneous frame that co-rotates with the magnetic field. The un-rotated Hamiltonian for the Zeeman effect is

$$H_Z = g_S \mu_B B_z S_z = g_S \mu_B T_0^1(B) T_0^1(S), \quad (5.12)$$

where S is the electron spin operator, and in the final step we have introduced the spherical tensor operators $T_j^i(Q)$ [21, 91]. If we wish to rotate equation (5.12) by an angle β about the y -axis, the rotation operator $\hat{D}$ we must apply is

$$\hat{D} = \exp \left(-i \frac{S_y \beta}{\hbar} \right), \quad (5.13)$$

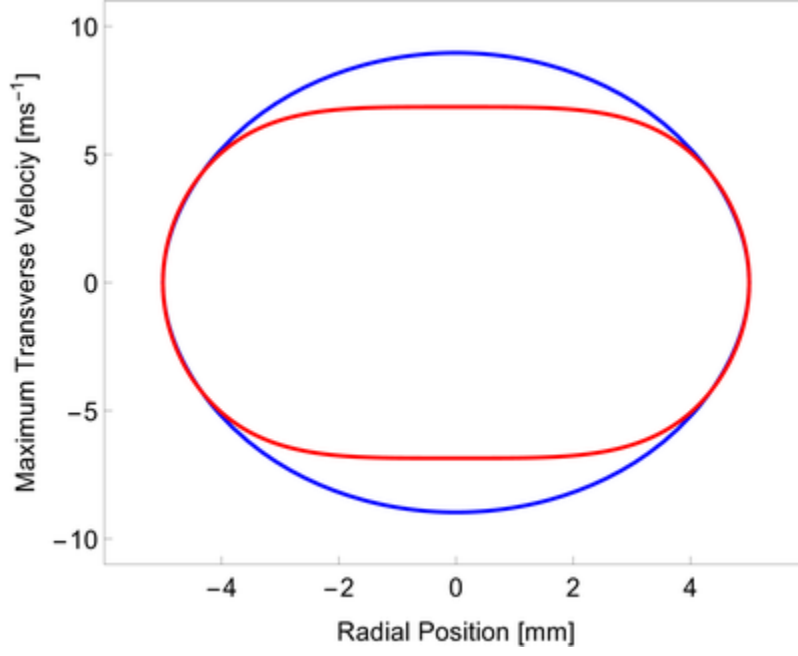


Figure 5.7: Theoretical transverse phase space acceptance of our octupole magnetic guide given $\epsilon = (1 - 0.186)$ (red), compared with the equivalent quadrupole (blue), both calculated in the Paschen–Back regime using the Halbach formalism of equation (5.9).

which is most easily proved in the infinitesimal case where β is small:

$$H'_Z = \hat{D}^{-1} H_Z \hat{D} \quad (5.14)$$

$$\approx g_S \mu_B B_z \left(1 + i \frac{S_y \beta}{\hbar}\right) S_z \left(1 - i \frac{S_y \beta}{\hbar}\right) \quad (5.15)$$

$$\approx B_z S_z + i \frac{B_z \beta}{\hbar} [S_y, S_z] \quad (5.16)$$

$$= B_z (S_z - \beta S_y). \quad (5.17)$$

Comparison with the action of the infinitesimal rotation matrix shows that the transformation $S_z \rightarrow S_z - \beta S_y$ corresponds to a rotation in the plane $y - z$ as required. Moving into this co-rotating frame, the Schrödinger equation is

$$i\hbar \frac{\partial}{\partial t} (\hat{D}^{-1} |\psi'\rangle) = \hat{D}^{-1} H_Z \hat{D} (\hat{D}^{-1} |\psi'\rangle), \quad (5.18)$$

where $|\psi\rangle = \hat{D}^{-1} |\psi'\rangle$ is the unrotated state vector. Using the known properties of the unitary operator $\hat{D}$, it follows that

$$i\hbar \frac{\partial}{\partial t} |\psi'\rangle = \left(H'_Z + S_y \frac{d\beta}{dt} \right) |\psi'\rangle, \quad (5.19)$$

where both H'_Z and $\omega = d\beta/dt$ are functions of time. Following Wall et al [121], we now expand $|\psi'\rangle$ into the instantaneous eigenfunctions of H'_Z , such that $H'_Z |m\rangle = E_m |m\rangle$ and $\langle m|\psi\rangle = c_m$. Then, as $\langle m'|\psi\rangle = \delta_{m',m}$ we can write equation (5.19) in terms of the expansion coefficients

$$i\hbar \frac{\partial}{\partial t} c_{m'} = \sum_m \left(\langle m'| H'_Z + \omega S_y - i\hbar \frac{\partial}{\partial t} |m\rangle \right) c_m. \quad (5.20)$$

Now, we can express the expectation of the time derivative in equation (5.20) by noting that the set of $|m\rangle$ diagonalises H'_Z :

$$H'_Z = \sum_{m''} E_{m''} |m''\rangle \langle m''|. \quad (5.21)$$

Taking the derivative of both sides and simplifying, we find that

$$\frac{\partial H'_Z}{\partial t} = \sum_{m''} |m''\rangle \langle m''| \frac{\partial E_{m''}}{\partial t} + E_{m''} \left(|m''\rangle \frac{\partial}{\partial t} \langle m''| + \langle m''| \frac{\partial}{\partial t} |m''\rangle \right) \quad (5.22)$$

$$\implies \langle m'| \frac{\partial H'_Z}{\partial t} |m\rangle = \delta_{m,m''} \delta_{m',m''} \frac{\partial E_{m''}}{\partial t} + (E_m - E_{m'}) \langle m''| \frac{\partial}{\partial t} |m''\rangle, \quad (5.23)$$

where the final step follows from $\langle m''|m\rangle = 0 \implies \partial \langle m''|m\rangle / \partial t = 0$ and applying the chain rule. For the case $m \neq m'$ we find that

$$\langle m'| \frac{\partial}{\partial t} |m\rangle = \frac{1}{E_m - E_{m'}} \langle m'| \frac{\partial H'_Z}{\partial t} |m\rangle \quad (5.24)$$

and, by combining equations (5.20), (5.21) and (5.24), we can write our transformed Schrödinger equation in the form

$$i\hbar \frac{\partial c_{m'}}{\partial t} = E_{m'} c_{m'} + \sum_m \left(\langle m'| \omega S_y - \frac{i\hbar}{E_m - E_{m'}} \frac{\partial H'_Z}{\partial t} |m\rangle \right) c_m. \quad (5.25)$$

Finally, we use a similar trick to the Optical Bloch Equations and write

$$c_m = a_m \exp \left(-\frac{iE_m t}{\hbar} \right) \quad (5.26)$$

to transform away the self-interaction term and hence obtain the workable expression

$$i\hbar \frac{\partial a_{m'}}{\partial t} = \sum_m \left(\langle m' | \omega S_y - \frac{i}{\omega_{m,m'}} \frac{\partial H'_Z}{\partial t} | m \rangle \right) a_m \exp(-i\omega_{m,m'}t), \quad (5.27)$$

where $\hbar\omega_{m,m'} = E_m - E_{m'}$. We now note a few key features of equation (5.27). The eigenfunctions $|m\rangle$ are linear combinations of the usual molecular hyperfine states. For YbF, we can describe states within the $X^2\Sigma^+(v=0)$ manifold using a Hund's case (b)² coupling scheme. The rotational level N couples to the spin of the radical electron S forming an intermediate quantum number J . J then couples to the fluorine nuclear spin I forming total angular momentum F , whose projections m_F have their degeneracy lifted by the action of the magnetic field. A far more complete discussion is given in appendix (A). We label the wavefunctions by their quantum numbers in the usual way, giving $|\psi\rangle = |(N, S)J, (J, I)F, M_F\rangle$. The Hamiltonian H'_Z mixes states with the same m_F but different F , whilst S_y couples states with different values of m_F . As the rate of change of β is only large near the guide centre, we express the matrix elements of S_y in terms of the zero-field molecular eigenfunctions, obtaining

$$\begin{aligned} \langle \psi' | S_y | \psi \rangle &= \frac{i}{2} \sqrt{\frac{3}{2}} \sum_{p=\pm 1} \begin{pmatrix} F' & 1 & F \\ -m'_F & p & m_F \end{pmatrix} \begin{Bmatrix} J & F & 1/2 \\ F' & J' & 1 \end{Bmatrix} \begin{Bmatrix} 1/2 & J & N \\ J' & 1/2 & 1 \end{Bmatrix} \\ &\quad \times (-1)^{F+F'+2J'+N+1-m'_F} \sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)}, \end{aligned} \quad (5.28)$$

where the various symmetries and transition rules are expressed through the 3-J and 6-J symbols. In particular the selection rule $\Delta m_F = \pm 1$, relating to changes in the total angular momentum projection, is particularly characteristic of this interaction. The degree of mixing is proportional to the total magnetic field strength, the rate of field rotation, and the rate of change of field amplitude. As we can adiabatically connect the high and low field eigenstates, in the following we will label the states by their zero-field quanta $|F, m_F\rangle$.

We can apply equation (5.27) to our molecular states to see how their population changes as a set of molecules follows a given trajectory. The exact choice of trajectory is, to some extent, unimportant, as the factors which lead to non-adiabatic transitions between the states are how close a molecule comes to the centre of the trap, and how fast it is moving there. We have examined the worst-case scenario by defining a set of molecular trajectories that lie on straight chords to the circular

²See pages 226–228 and 936 of [91] for a more complete discussion.

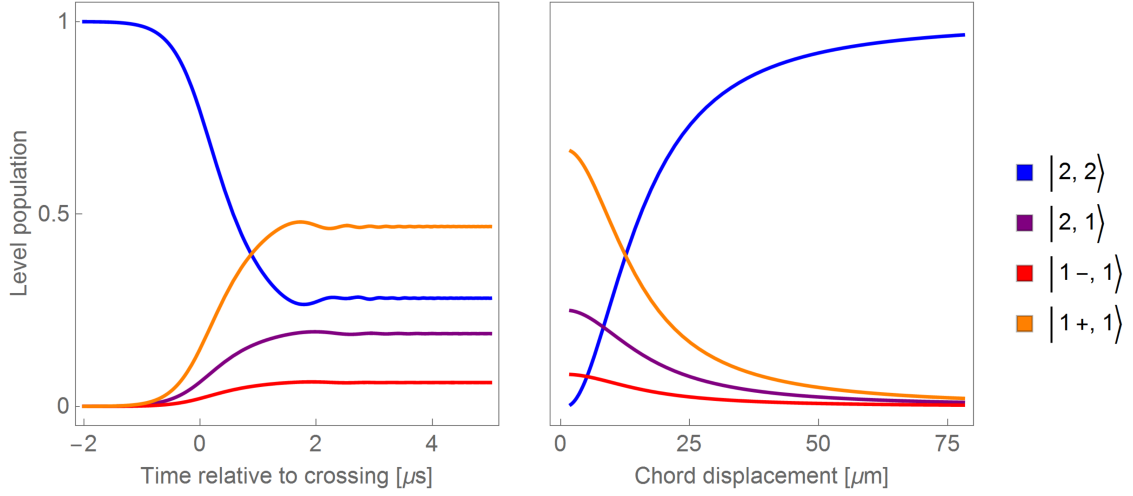


Figure 5.8: State transfer within $N = 1$ from $|F = 2, m_F = 2\rangle$ into the three allowed decay modes: $|F = 2, m_F = 1\rangle$, $|F = 1+, m_F = 1\rangle$, and $|F = 1-, m_F = 1\rangle$. The left panel shows the temporal behaviour for a chord trajectory that passes $10\text{ }\mu\text{m}$ from the guide centre, and the right panel shows the final population in each state as a function of closest approach to the middle of the guide.

magnetic geometry. The magnetic potential and field angle are projected onto the chord, along which the molecule undertakes one-dimensional motion. The maximal velocity at the centre is taken by beginning the molecular trajectory at the edge of the guide with zero velocity, before being accelerated by the magnetic potential. Were the velocity set to be non-zero at this point the molecule would escape from the guide and hence would not have been trapped in the first place.

A single pass along each chord is taken, and the loss in population from the weak-field states is obtained at the end of the pass. Whilst the result of applying equation (5.27) is, in general, a superposition of states, a single molecule will collapse to one of the instantaneous eigenstates through interaction with the environment. This decoherence will take, at most, the timescale of a single transit across the guide. We therefore interpret the populations following one chord transit as a probability distribution for the final states—if we monitored many molecules with the same chord trajectory and binned them according to their final, measured state, their distribution would be exactly the final state distribution predicted by equation (5.27).

We must also consider the energy change of each state as a function of the magnetic field. This has been calculated elsewhere within the group by Michael Tarbutt, who determined the matrix elements and eigenfunctions for the full molecule + Zeeman Hamiltonian within a given rotational state. Once a numerical form has been obtained, the chain rule can be applied to the energy derivative in (5.27) to obtain

$$\frac{\partial E(B)}{\partial t} = \frac{dE}{dB} \frac{dB}{dx} \frac{dx}{dt}. \quad (5.29)$$

Application of the form of the Zeeman energy, equation (5.9), and the solved equations of motion of the trajectory along the chord finally allow us to numerically solve equation (5.27). A simple example is shown in the left panel of figure (5.8), where the population was initially confined in the $|F = 2, m_F = 2\rangle$ level of the $N = 1$ rotational manifold, before following a chord trajectory with closest approach to the centre of $10\,\mu\text{m}$. As the projection quantum number of the initial state $m_F = 2$ is extremal, it is not coupled to any states via H'_Z and hence the three transitions here are induced by the changing *direction* of the magnetic field, rather than the amplitude. The right panel of figure (5.8) shows the final population of each of the 4 coupled states after a single pass across the centre of the guide, as a function of closest approach. We see that this effect only becomes problematic when molecules pass within $45\,\mu\text{m}$ of the centre, beyond which the probability of remaining in $|F = 2, m_F = 2\rangle$ drops below 90% and hence the population is efficiently and rapidly transferred from $|F = 2, m_F = 2\rangle$ to the other states.

We have verified this effect for the full weak-field-seeking manifold of states within $N = 1$, consisting of the $m_F = 0, 1, 2$ states of $F = 2$ and all projections of $F = 1+$, by considering a simulation where population is initially equally distributed between all 6 levels. The molecules again propagate along the chord trajectories, and the total loss of population from the 6 levels was measured. The results are shown in figure (5.9), having summed over all the strong-field and weak-field-seeking states. Despite the many additional state couplings, we find that the boundary of the “zone of death” is now $\approx 41\,\mu\text{m}$ from the centre, in good agreement with the simpler simulation shown in figure (5.8). As the chord trajectories completely fill the phase-space of the guide, the fractional loss per guide transit will be approximately given by the ratio of the area in which Majorana transitions are significant to the internal area of the guide. Applying our results for the full weak-field manifold, we obtain as a worst-case estimate for the Majorana losses of 6.7×10^{-5} per transit, or approximately 67 spin-flip transitions per million molecules per oscillation within the guide.

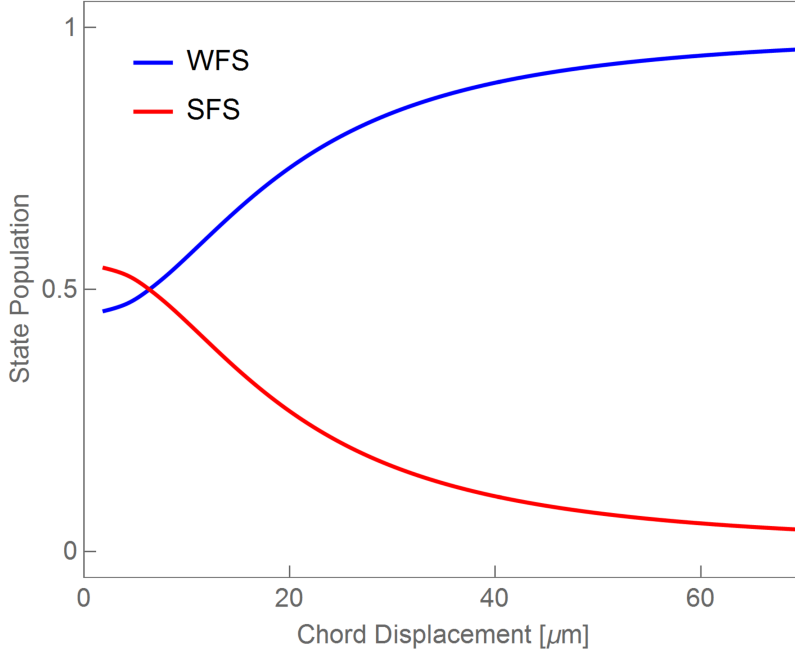


Figure 5.9: Total state transfer from the weak-field-seeking (WFS) states to the strong-field-seeking states (SFS) within the $N = 1$ rotational manifold of YbF.

The bounding velocity for our octupole is 6.85 m s^{-1} . An ultra-slow YbF molecule with forward velocity 10 m s^{-1} and transverse velocity 6.85 m s^{-1} will therefore undergo ≈ 17 oscillations within the guide; using the calculated Majorana loss rate, the probability of that molecule reaching the end of the guide is 99.88%. We conclude that this octupole guide should be unaffected by Majorana losses for any reasonable experimental forward velocities³. Combined with the wide phase-space acceptance, we find that a permanent octupole guide provides an efficient way to correlate arrival time and velocity for our molecular beams.

³We can solve for the number of guide crossings necessary for the Majorana losses to reach 50%, then use the bounding octupole velocity to obtain a maximum forward velocity of $v_f \approx 0.017 \text{ m s}^{-1}$ under these circumstances.

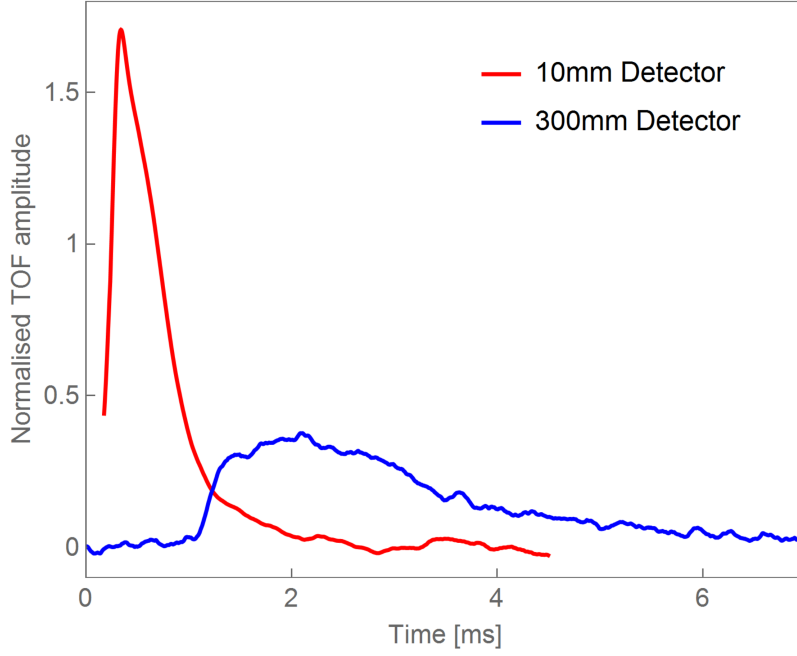


Figure 5.10: Time-of-flight distributions before the magnetic guide 10 mm from the second-stage aperture, and after the guide 300 mm from the aperture. The helium flow rate in both cases is 4 SCCM, and the two distributions have been normalised so as to have unit area.

5.5 Free-flight and confinement times for a guided beam of YbF

In our discussion in section (5.4), we have suggested that a suitably-long free-flight distance between source and detector is sufficient to correlate the molecular arrival time and the instantaneous beam velocity. If t is the time since ablation, and t_c the time a molecule spends in the cell, then the molecular velocity v_m is

$$v_m = \frac{x}{t - t_c}, \quad (5.30)$$

where x is the distance between cell and detector. In the limit of a distant detector, $t \gg t_c$ and we can accurately express the molecular velocity using, for example, the measured time-of-flight profile.

To test this situation experimentally, we have simultaneously measured the source

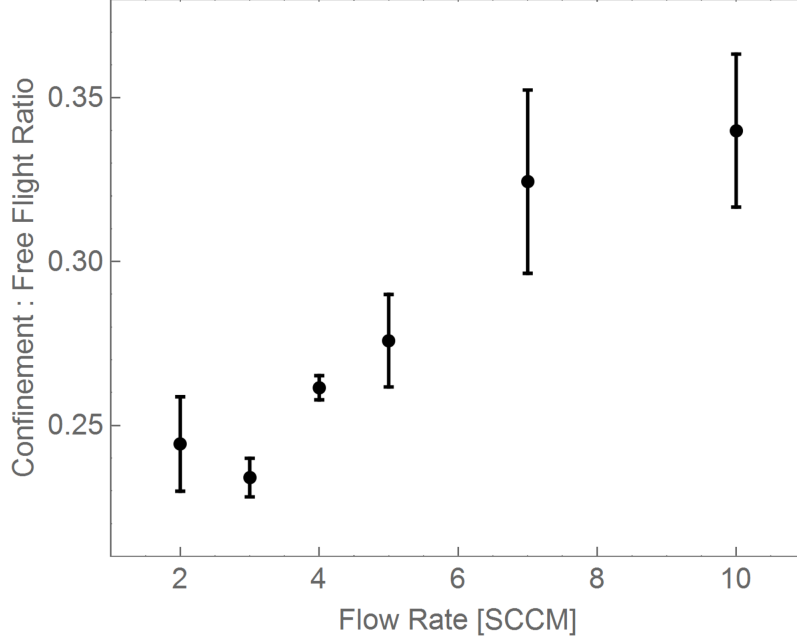


Figure 5.11: Evaluation of $t_c/(t - t_c)$, having determined t_{ff} through equating the integral areas over intervals of the form (t_j, ∞) . The error here is the standard error following fixing A over 18 equally spaced intervals, $5\% \leq A \leq 90\%$.

function and downstream time-of-flight distribution from our two-stage cell. The cell was set-up in the first-stage extended configuration, and the time-of-flight profile 10 mm and 300 mm from the second stage aperture was recorded using the LIF method. We probed on the $X^2\Sigma^+(v=1) \rightarrow A^2\Pi_{1/2}(v=0)$ transition at the lowest detection point, and the $X^2\Sigma^+(v=0) \rightarrow A^2\Pi_{1/2}(v=0)$ transition at the upper region; this was to ensure that the action of probing before the guide did not change the measured distribution in the top region through, for example, hyperfine pumping into strong-field-seeking states. At the lowest detection region, $t_c \approx t$ and the recorded TOF distribution is a good representation of the source function, a fact that we use to evaluate the ratio $t_c/(t - t_c)$ at the distant detector. Plots of the two time-of-flight distributions are shown in figure (5.10), obtained for a helium flow rate of 4 SCCM and normalised so as to have unit area.

In order to compare regions between the two profiles, let us perform a rescaling such that the total square-integrable area under each TOF curve is unity. We now integrate the source function on the interval (t_0, ∞) and obtain some area A . As we

have seen in, for example, figure (3.9), the mean molecular velocity takes the form of a monotonically-decreasing function of time, so on average we do not expect to see molecules overtake one another in the beam. Via the monotonicity property and population conservation, if we then integrate the TOF at the distant detector over some interval (t_1, ∞) and obtain the same area A , we must have the same molecules present in both integral regions, and hence may connect t_0 and t_1 via $t_1 = t_0 + t_{\text{ff}}$, where the free flight time is $t_{\text{ff}} = t - t_c$.

We have performed this analysis on our simultaneously measured time-of-flight profiles, with the results shown in figure (5.11). At higher flow rates molecules tend to spend longer within the cell, and as the beam approaches the hydrodynamic limit the mean forward velocity also increases. A combination of these effects increases the ratio t_c/t_{ff} and hence t is a less good approximation to t_{ff} in this limit. Flows below 4 SCCM have $t_c/t_{\text{ff}} \leq 0.25$, although over all tested flows the ratio always lies below 0.35.

In optimising the source, we need to know the number of slow molecules present in the beam. As we saw in figure (5.3), the key difference between the hybrid and two-stage source is the number of molecules with forward velocities below $v = 90 \text{ m s}^{-1}$. Applying equation (5.30) in conjunction with the worst-case measured ratios $t_c/(t - t_c)$ from figure (5.11), we find that this corresponds to molecules arriving at the upper detector at times $t \geq 5 \text{ ms}$. We therefore take as our figure of merit the total number of molecules N_5 detected at the upper detector in the time interval $(5 \text{ ms}, \infty)$, and aim to optimise this through exploration of the available parameter space.

5.6 Characterising cell configurations using distant TOF profiles

We are now ready to characterise a range of cell configurations using the N_5 figure of merit. We have tested three basic cell configurations. In the first the cell parameters are as specified in section (5.2), with the total first-stage length of 30 mm and a second-stage length of 14 mm. In the second the first stage was extended by 20 mm to aid with the thermalisation properties at low flow rates. In the final, the first-stage extender was removed and a 20 mm second-stage extender was added. The first-stage extender was constructed from a solid block of copper, whilst the second-stage extender was made by soldering a thin net of copper sheet and heat sinking it from the vents. In all three cases a 3 mm diameter first stage aperture was used.

Preliminary data from the first stage showed strong variation in the beam properties with ablation laser position for larger apertures where the in-cell pressure was lower, and we didn't want the flow dynamics to be dominated by the ablation process.

Within each cell configuration, we varied both the inter-cell spacing and the helium flow rate. The flow controls the pressure in both cells, whilst the spacing determines the pressure differential between the cells. Collisions within and outside the second stage are crucial to the operation of the source. We require a large number of helium–YbF collisions within the second stage in order to remove the majority of the YbF forward momentum, and yet must have a low enough pressure that we have very few re-boosting collisions after the second-stage aperture. Balancing these two factors is the most challenging aspect of this source. A simple estimation of the lower-limit inter-cell separation can be made by first noting that moving the two cells apart by a distance L exposes a surface area $2\pi R_c L$ to the vacuum, where R_c is the second stage cell radius. If the second stage is sufficiently large, we can model it as an effusive buffer gas cell. We can then apply equation (2.13), assuming that the aperture area consists of the inter-cell separation area, the vents, and the second stage aperture, to obtain the number density in the second stage. Now, the transition to effusive flow occurs when $\text{Kn} = 1$, for which the mean free path must equal the mesh pore diameter Π . Solving for L , we obtain

$$L = \frac{1}{2\Pi R_c} \left(\sqrt{\frac{4\pi m}{k_B T}} \sigma \Pi \dot{N}_{\text{in}} - (2A_v + A_a) \mathcal{T} \right), \quad (5.31)$$

where A_a is the second stage aperture area and A_v is the vent area. Applying the known design and experimental parameters, we find that for flow rates in the region $2 \leq \dot{N}_{\text{in}} \leq 10$ SCCM, the minimum length required for effusive flow should be $0.1 \leq L \leq 1.8$ mm. With this in mind, we examine inter-cell separations of the order of 1 mm to try and obtain the lowest possible forward velocities.

In figure (5.12) we compare the results of the first and second configurations over a range of helium flows and for two inter-cell spacings. For the first configuration we find little dependence of N_5 on either the flow rate or the inter-cell separation. On the other hand, adding the first stage extension leads to a strong increase in the behaviour of N_5 as a function of cell separation. Focussing on the 2 mm-separation data in this second configuration, we observe that the number of slow molecules initially increases as a function of flow rate, suggesting that the helium density in the second stage was too low for significant slowing of the beam at 2 SCCM flows. Above 5 SCCM the trend levels off, implying that we have reached an optimum pressure in

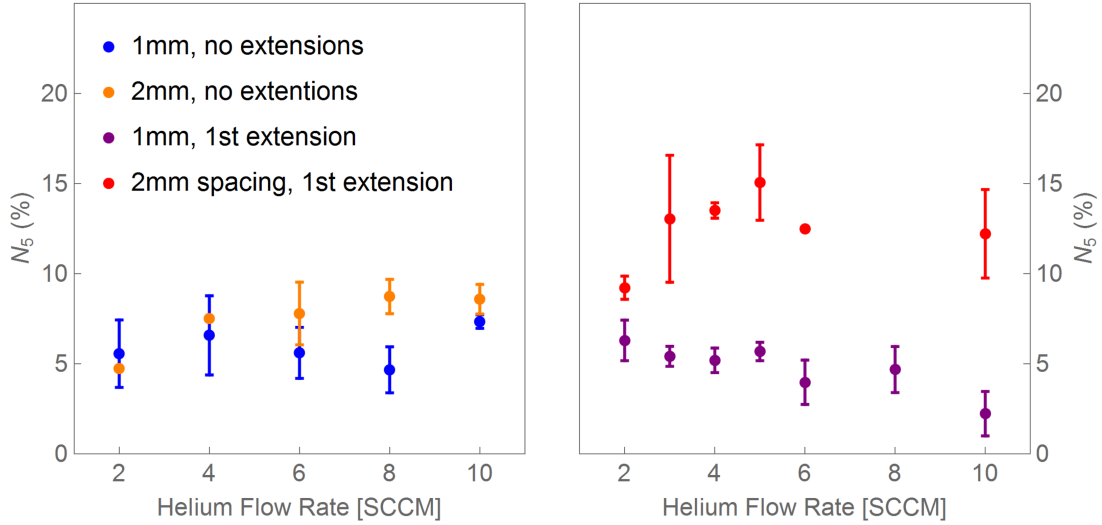


Figure 5.12: Measured N_5 parameters for two cell configurations, as a function of inter-cell separation and helium flow rate. The blue and orange data points show the slow fraction for the two-stage cell in its baseline configuration, while the purple and red points were obtained with a 20 mm extender fixed to the first stage. The errors are the standard error in the mean of the data at each flow.

the second stage. If the inter-cell separation is too low we expect a higher pressure in the second stage and hence $\text{Kn} < 1$, implying a faster forward velocity and a smaller N_5 measurement. Hence we should not be surprised that the 1 mm separation data gives the lowest values of N_5 in the “first extension” data.

We have also examined the effect of extending the second stage whilst leaving the first stage unchanged. A plot of these data is shown in figure (5.13). The action of extending the second stage is to provide a way of increasing the number of collisions in the second stage without increasing the total helium pressure therein. The effusive condition of equation (5.31) does not necessarily mean that molecules will be slowed, as a typical YbF molecule will require ≈ 20 collisions with helium in the second cell to be significantly reduced. In practice, the action of extending the second stage should compress the profile of N_5 to lower flow rates, as we will obtain a greater amount of slowing in the second stage for a given pressure. In figure (5.13) we observe a sharp peak in the 1 mm separation data for a helium flow rate of 3 SCCM. The behaviour for the 3 mm separation data is less clear due to the larger standard

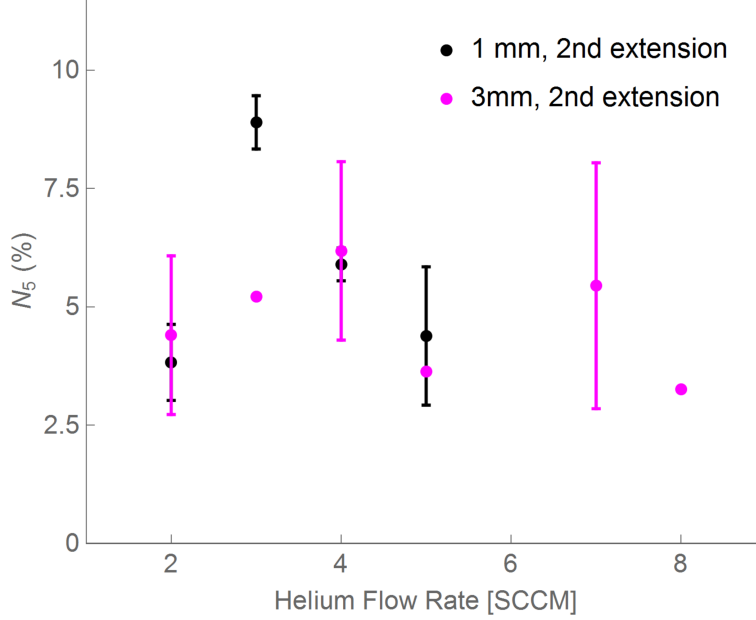


Figure 5.13: Measured N_5 parameters for the third cell configuration, with an extended second stage.

error in the set, but it does not appear to exhibit the same properties, possibly as a result of the lower second-stage pressure for this configuration.

We draw two conclusions from the total data presented in this section. The first is that, in the case of the extended first stage, increasing the inter-cell separation from 1 mm to 2 mm increases our figure of merit N_5 . As the only change between the two cases should be to decrease the pressure in the second stage, this suggests that the balance of pressures between the two cells, and hence amount of slowing in the second stage, is sensitive to the inter-cell separation. Quite why this effect should be strongest for the extended first stage is unclear—perhaps we have better thermalisation scales at low flows, or a lower effect of ablation on the beam properties—but it seems clear that extending the first stage will be beneficial to our results.

Additionally, increasing the length of the second stage appears to change the shape of the measured N_5 profile. The increase at 3 SCCM for the 1 mm separation, 2nd extension data is intriguing, as it extends well beyond the standard error of the surrounding peaks. With this in mind, we began examining in more detail the effect of

extending the second stage of our two-stage source. However, first we must return to the role of the magnetic guide, whose role in this experiment transpires to be somewhat less than benign.

5.7 Helium collisions and intra-guide boosting

Throughout the measurements of all our data obtained using the magnetic guide thus far, we have observed a reduction of the measured flux with increasing helium flow rate. A plot of this is shown in figure (5.14), where the data points are the normalised flux measured at the detector after averaging over all tested cell configurations. This is in contrast to the work of Skoff *et al*, who have previously shown that increasing the flow rate leads to an approximately linear increase in the flux (See [122], figure 6.5 for an example). One possible explanation for this effect is the role of He–YbF collisions in the magnetic guide, which we examine in this section.

Given our previous work on Majorana-type transitions in the guide, it is natural to first check if collisions will lead to transitions between m_F levels and hence from weak- to strong-field-seeking states. However, Tschersbul *et al* [123] have simulated this effect, finding the cross-section to be of the order $\sigma \approx 0.04 \text{ \AA}^2$, or 4 orders of magnitude lower than the diffusive cross-section measured by Skoff. Thus, unless there are > 10000 collisions in the guide, we do not expect spin-flip transitions to play a role in this phenomenon.

However, collisions between He and YbF can transfer enough transverse momentum to the guided molecules to boost them from the guiding potential. To model this, we assume that the transverse velocity distributions of the helium and YbF in the guide are of Maxwell-Boltzmann form, with the YbF distribution truncated at the escape velocities from the guide. For a given YbF transverse velocity v_{YbF} , the helium velocity v_{He} can only lie within a certain bound to ensure that the YbF molecule is not lost:

$$v_{\text{He}} = \pm \left| \frac{(M + m)v_c - (M - m)v_{\text{YbF}}}{2m} \right|, \quad (5.32)$$

where v_c is the maximum trapped velocity, and equation (5.32) follows from equation (5.5). Integrating over this bound, then summing over all trapped YbF velocities, we obtain the probability for a YbF molecule to survive a single collision within the guide.

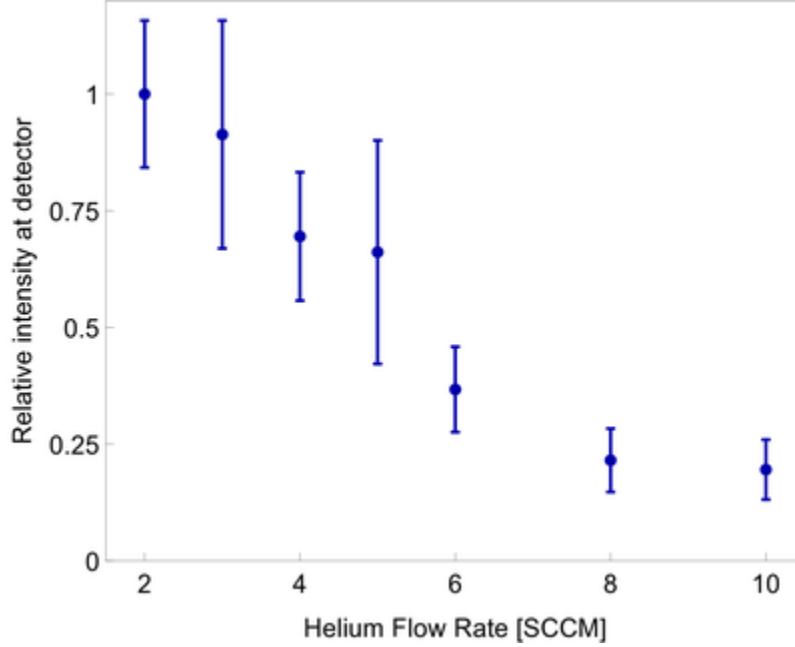


Figure 5.14: Observed decrease in yield as a function of helium flow rate, obtained from a comprehensive review of all collected data up to this point.

Next, we must determine the helium number density in the guide. The magnetic field does not guide the helium; rather it must leave through the open area or remain confined. The open area is 18.6%, which we will take as the loss probability if an atom reaches the side wall of the guide, $\mathcal{T}$. The number of times an atom reaches the side wall is approximately

$$N(z) = \frac{v_x z}{v_z x}, \quad (5.33)$$

where the direction z is along the guide and x is transverse within it. The transverse velocity v_x is taken to be the mean thermal velocity, whilst the forward velocity is taken from Huzler's four-fifths model for beams in the intermediate flow regime [59]:

$$v(\text{Re}) \approx 1.4 \bar{v}_{\text{He}} \sqrt{1 - 4\text{Re}^{-4/5}}, \quad (5.34)$$

where $\bar{v}_{\text{He}}$ is the helium thermal velocity. The helium number density in the guide after a distance z is then $\nu(z) = \nu(0) \mathcal{T}^{N(z)}$, with the number density of helium atoms at the guide entrance $\nu(0)$ following from the flux as usual. The distance between the guide and the cell also reduces the helium number density due to beam

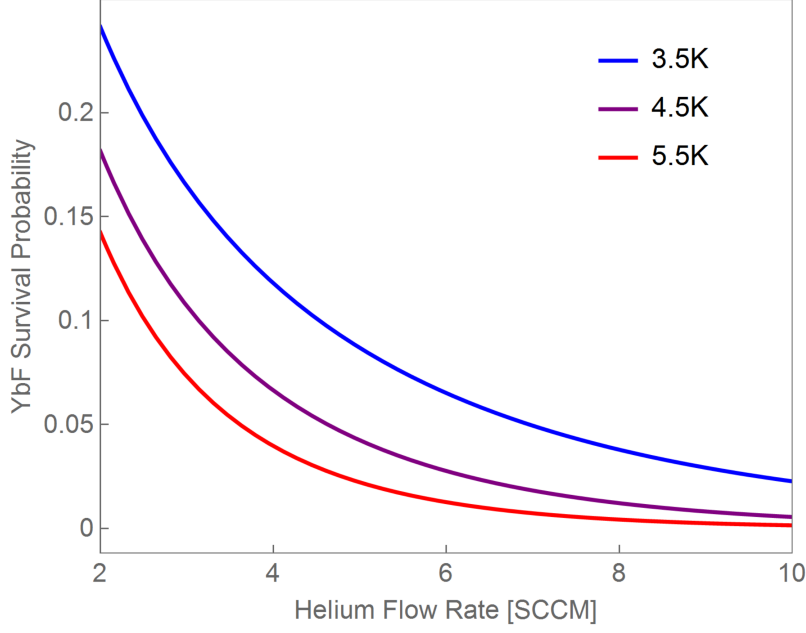


Figure 5.15: Simulated total survival probability after the guide, with losses assumed to arise from elastic collisions with the background helium gas.

divergence; in the absence of additional information, we assume the same measured value as section (3.8). Once $\nu(z)$ is known, the number of collisions in the guide can be evaluated and, as the survival probability after one collision has been determined, the fraction that survive a trip in the guide follows. A plot of the simulated total transmission probability P_s for our guide is shown in figure (5.15). As expected, P_s is a monotonically-decreasing function of the flow rate bounded on $0 \leq P_s \leq 1$, and increases as the helium temperature decreases. This thermal behaviour arises because if the helium is cold less momentum is transferred on average per collision.

We will now assume that the molecular flux from the source increases linearly as a function of helium flow rate $\dot{N}_{\text{in}}$, in a way that is consistent with the observations of Skoff et al. Then the expected yield measured at the end of the guide is $\propto \dot{N}_{\text{in}} P_s(\dot{N}_{\text{in}})$. In figure (5.16) we compare this predicted flux to measured experimental values. The temperature in the simulation is taken to be 4.6 K, determined from our experiment through direct measurement of the cold head temperature using thermistors, and the yield is normalised relative to the 2 SCCM yield in both cases. The experimental error bars arise from the standard error in the data set. Despite

having no free parameters⁴, the model offers excellent agreement to the data, predicting the strong intensity reduction as a function of flow. This model therefore suggests that elastic collisions in the guide are a problem that lead to a significant reduction in the measured molecular flux.

We should note that certain assumptions have been made in the theoretical description above. By limiting the discussion to 1-D collisions, we have implicitly assumed that the velocity components of the buffer gas atoms are both well-defined and separable. However, in appendix (D) I show that repeated elastic collisions between a point-like gas particle and a macroscopic wall will eventually completely mix the velocity components of the particle. This process occurs over $N_{cc} \approx 2^{a/z}$ collisions, where a/z is the characteristic microscopic roughness gradient and is of minimum order unity. This mixing process happens in the effusive regime, when the mean free path for inter-particle collisions exceeds the bore diameter of the guide. However, as the majority of the collisions will occur while the in-guide density is high, I do not expect this process to have a large impact on the resulting prediction.

The loss of molecules is problematic, but not necessarily fatal to an experiment—we simply have to work a bit harder collecting repeat data sets to overcome the worse signal-to-noise ratio. Unfortunately, the significant number of collisions will also lead to the forward-boosting of our YbF molecules. For flows in the range 2–10 SCCM we expect ≈ 10 –50 collisions; if a YbF molecule is initially at its forward effusive velocity at 4.6 K, then the collisions in the guide would result in re-boosting from 26 m s^{-1} to anywhere between $\approx 60 \text{ m s}^{-1}$ and $\approx 135 \text{ m s}^{-1}$. This is not ideal! Based on this, we concluded that the guide was likely doing more harm than good in our characterisation of the two-stage source—the comparatively small open area resulted in a high helium number density for far longer than in a regular, un-guided beam. With the guide as used here, we would not expect to see distributions of the type reported by Doyle et al, with our minimum observable velocity being the lower reboosted limit of 60 m s^{-1} . We therefore decided to remove the guide, and attempt to perform source characterisation via the measurement of the Doppler shift in YbF spectra.

⁴The constant of proportionality between flux and extraction efficiency is removed once we move to the relative intensity scale.

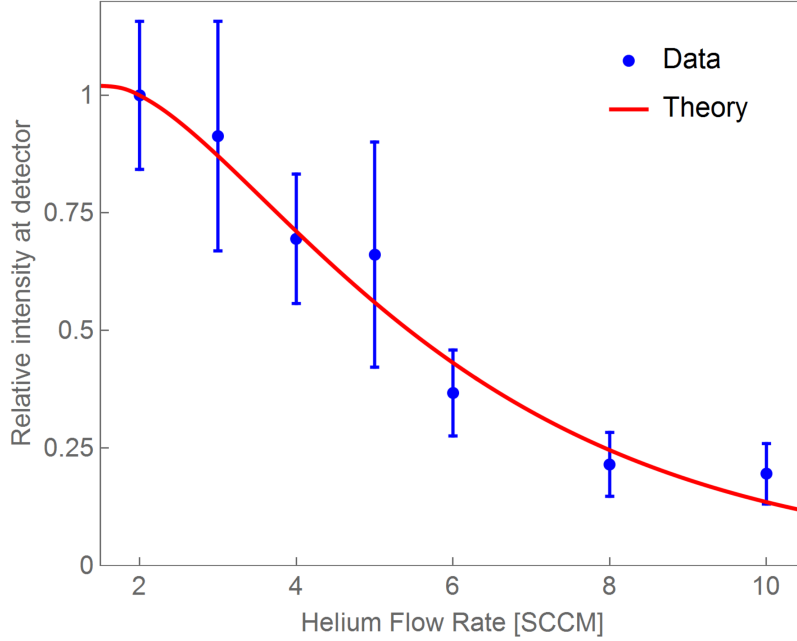


Figure 5.16: Simulated yield, compared with experimentally measured yield, through the magnetic guide as a function of helium flow rate at a temperature of 4.6K

5.8 Direct Doppler measurements and the optical bleaching problem

Having removed the guide, we installed a set of LIF collection optics 5.5 cm from the end of the second stage and performed direct measurements of the beam velocity within this new detection region. The third cell configuration, consisting of an extended second stage and the normal first stage, was used as it gave a strong dependence of the N_5 measure as a function of helium flow rate. The inter-cell separation was 1 mm, and the mesh on the side vents had a pore size of 700 μm . As before, spectra were obtained using lasers oriented in the co-axial and perpendicular directions, and the relative Doppler shift between spectral lines was taken. As the detection region was close to the top surface of the cell, we pumped on the $X^2\Sigma^+(v=0) \rightarrow A^2\Pi_{1/2}(v=0)$ transition and observed decay on the spectrally distinct $A^2\Pi_{1/2}(v=0) \rightarrow X^2\Sigma^+(v=1)$ band; this allowed us to remove our pump scatter using a narrow-band bandpass filter with transmission centred at 565 nm. Four sets of spectra were obtained, with the mean determined velocities used to generate a calibration fit of the form $v(t) \propto 1/(t - t_0)$ as before. Plots of the raw data,

along with the associated calibration fit, are shown in figure (5.17).

The velocity distribution was obtained by integrating over the mean time-of-flight profile for each flow rate, with the integration bins determined from the calibration curves. The obtained distributions, and their generating TOF functions, are shown in figure (5.18). As we are close to the source, it is not possible to define a measure of N_5 in the usual way; instead, we recall that by definition N_5 parametrises molecules with forward velocity less than 90 m s^{-1} . Performing this integral on the velocity distributions in figure (5.18), we obtain the approximate values of 9%, 10%, and 25% for the 2, 4, and 6 SCCM flow cases respectively, an improvement by a factor of at least 50% in all cases on the values reported in figure (5.13). This lends further credence to our assertion that the boosting effect of collisions in the guide were a significant problem in our earlier distribution-measuring method.

The standard practice when performing these measurements was to interleave data taken using the co-axial and perpendicular beams, with a mechanical shutter triggered via TTL logic used to switch the beams on and off. When the co-axial laser was used, it would be allowed to illuminate the detection region for the entire duration of the shot so as to capture the full profile of the arriving molecules. However, having taken a number of these measurements we realised that the co-axial probe laser may also act as a pump, depleting the levels whose populations we are trying

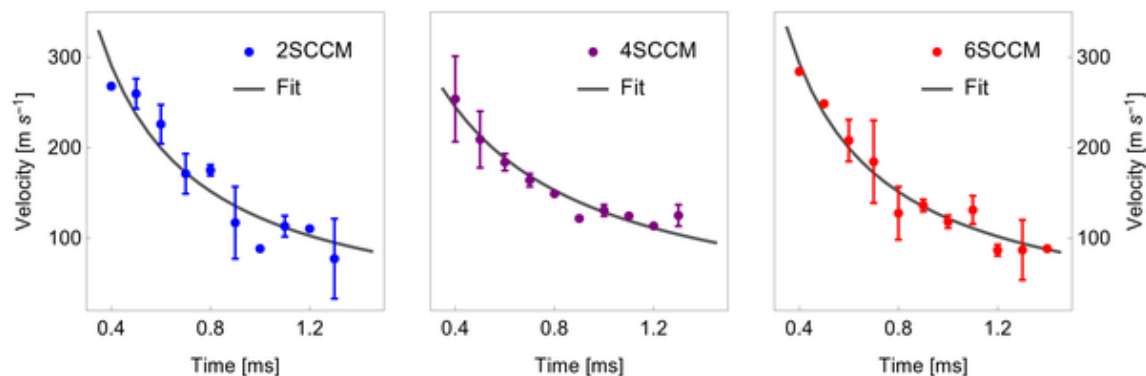


Figure 5.17: Mean velocity measurements at 2, 4, and 6 SCCM helium flow rates, determined from the Doppler shift of spectral features in the P-branch bandhead. The errors are the standard error in the mean of the 4 measured velocities obtained for each point.

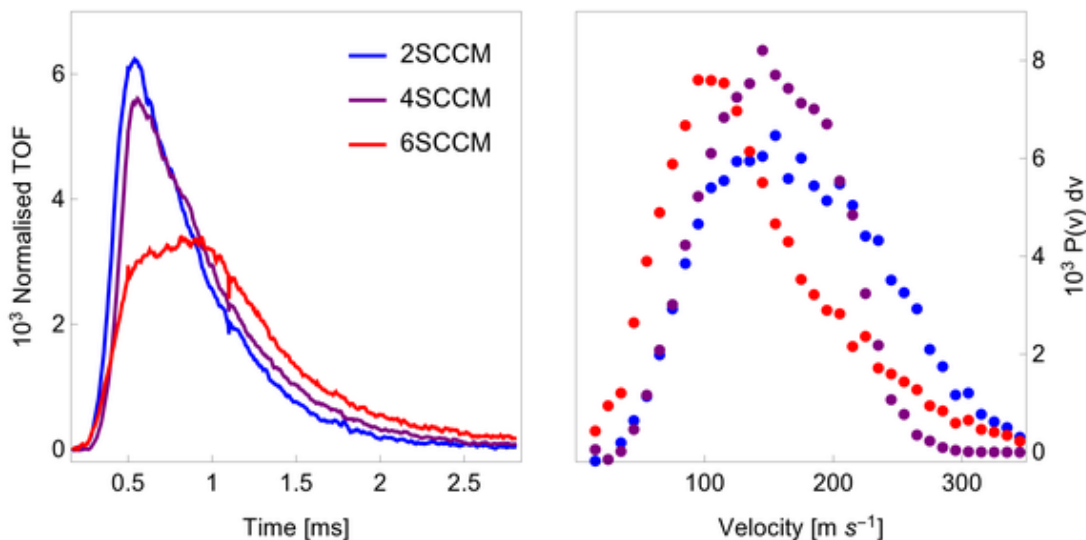


Figure 5.18: Time-of-flight and subsequent velocity distributions measured 5.5cm from the cell exit using the Doppler method.

to infer. Worse, this pumping effect is intrinsically linked to the forward velocity of the molecules, as slower molecules will spend longer in the pump and hence lose a greater amount of population to leak states than faster molecules.

To test if this was an issue, we constructed a fast optical shutter using an RF switch and an acousto-optic modulator (AOM) to decouple our probe laser from an optical fibre when a TTL signal was applied. The rise time of the optical switch was measured using a fast photo-diode to be $(37 \pm 2) \mu\text{s}$, in which time the laser intensity would rise from 10% to 90% of its maximum value. Using a helium flow rate of 4 SCCM and probe laser intensity of 2.3 mW cm^{-2} , we again scanned both the co-axial and perpendicular beams over the P-branch bandhead, and obtained shifted and un-shifted spectra from which the relative velocity was obtained. The start time of the co-axial beam was then stepped by $200 \mu\text{s}$, and this whole process repeated. In this way, molecules that would otherwise have been bleached well before reaching the detection region were still able to be detected at later times.

Let's first examine the behaviour of the mean time-of-flight distributions obtained by stepping the co-axial beam to later and later times, as is shown in figure (5.19). Each curve is the result of a different laser switch-on time, normalised to the area

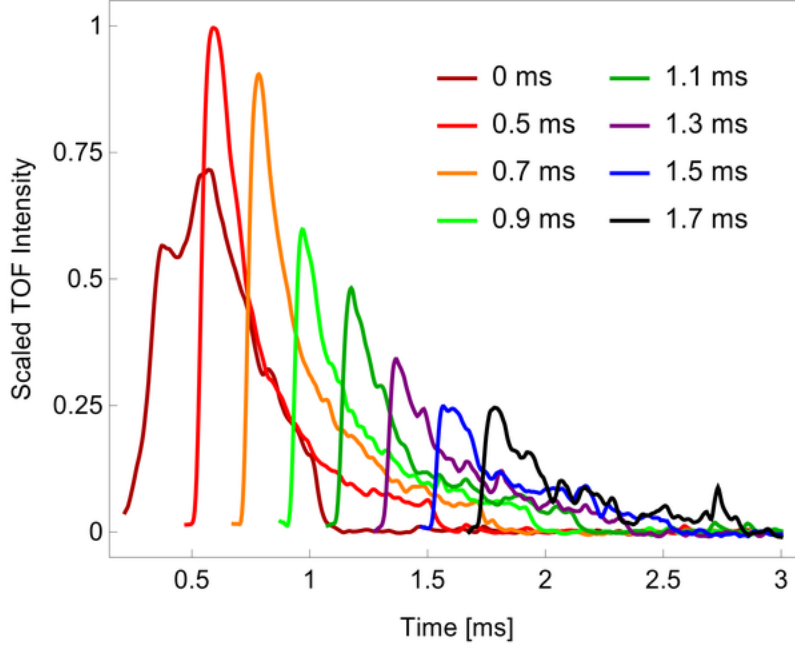


Figure 5.19: Time-of-flight distributions obtained using the co-axial laser, fast-shuttered with an AOM switch, at a detection point 5.5 cm from the cell aperture.

under its respective perpendicular-beam TOF profile so as to remove the effect of signal decay between shots. Each of the curves obtained between 0.5 and 1.7 ms have the same features—a strong initial increase to a sharp peak after $\approx 50 \mu\text{s}$ after the laser is first switched on, followed by a decay. Let's define the yield for a certain switch-on time τ after a time t as $Y_\tau(t)$. As all the molecules are coming from the same source under the same conditions, if bleaching were not occurring we would expect

$$Y_{\tau_1}(\tau_2) = Y_{\tau_2}(\tau_2) \quad (5.35)$$

within experimental error. The fact that $Y_{\tau_1}(\tau_2) < Y_{\tau_2}(\tau_2) \forall \tau_2 > \tau_1$ is compelling evidence that optical bleaching is occurring between the cell and the detection region, and is induced by the probe laser.

We can make this assertion more concrete by determining the velocity distribution for our AOM-switched data. We determine the beam velocity for time bins $\tau_j \leq t_j \leq \tau_j + 100 \mu\text{s}$ using the Doppler method, and extract a calibration curve as usual. The velocity-time curve and corresponding fit is shown in figure (5.20), from which we see immediately that the measured velocity is lower in a way which is

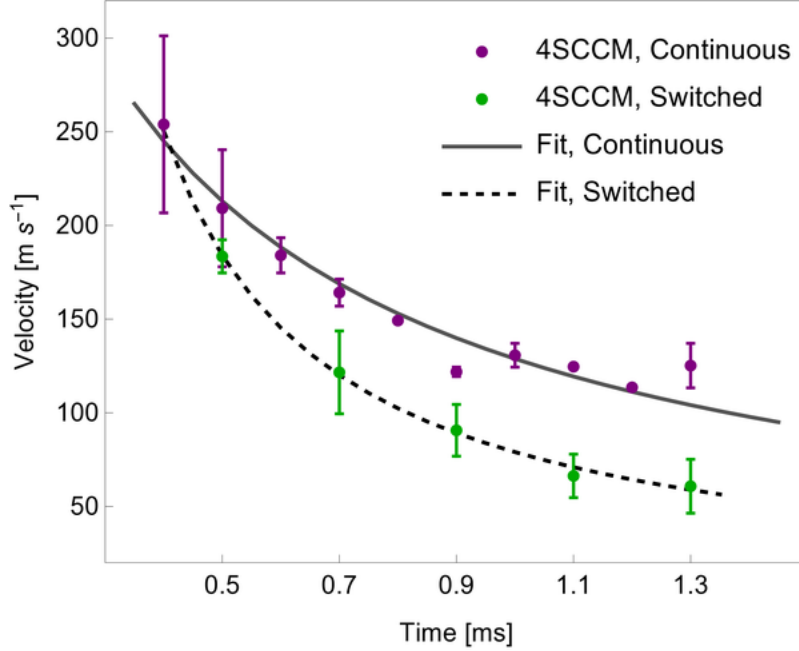


Figure 5.20: Velocity-time measurements obtained using the fast-switching method to reduce the effect of optical bleaching, compared to the un-switched case.

statistically significant. The velocity distribution was obtained using the re-binning method as usual, and is shown in the green curve of figure (5.21). We see immediately that the measured velocity distribution is significantly different to the un-switched case in the right panel of figure (5.18). The peak of the pulsed-laser distribution is at $(70 \pm 8) \text{ m s}^{-1}$, as opposed to $(155 \pm 8) \text{ m s}^{-1}$, and the corresponding means of the distributions are 128 m s^{-1} and 150 m s^{-1} respectively.

To try to explain this phenomenon, we approximate the real molecular levels as an ideal three-level Λ system and examine the fluorescence from a target state within the detection region both with and without pumping. As we are examining behaviour within the P-branch⁵, we assume that our laser is exciting the P(1) line—in this case, the only allowed decays are back to the $N = 1$ manifold, or to a higher vibrational state that is not coupled to the laser. We model the molecular behaviour using the 3-level optical Bloch equations, with the excited state coupled to one lower-energy state and spontaneous decay possible to both lower levels. Following the formalism set out in appendix (B.5), we set the Rabi rates $\Omega_{e,g_1} = \Omega$ and $\Omega_{e,g_2} = 0$ and use

⁵This notation is explained in more detail in appendix (A)

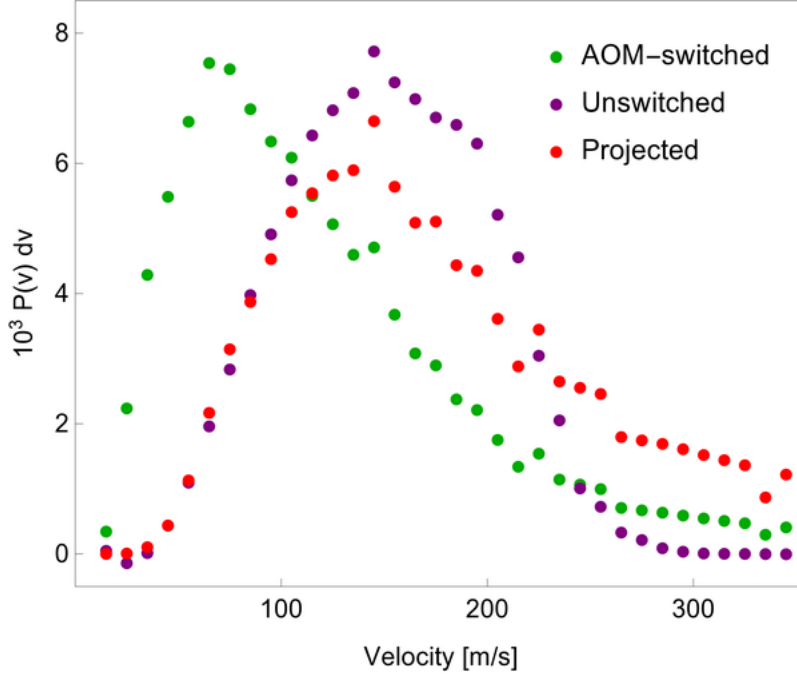


Figure 5.21: Velocity distribution obtained using the fast-switched laser, compared with that obtained using a constant co-axial probe.

the known branching ratio for the $A^2\Pi_{1/2}(v=0) \rightarrow X^2\Sigma^+(v=0)$ transition of 0.928 to determine interplay between the levels in the ground state manifold. For the P(1) transition there are 12 states in the $X^2\Sigma^+(v=0)N=1$ manifold coupled to 4 excited states in $A^2\Pi_{1/2}(v=0)J=1/2$ through the laser. In appendix (B.8), we show that the maximum excited state population is the inverse of the total number of states. Therefore, we expect to see no more than $4/12 = 1/3$ of the population within the excited state manifold at once. To compensate for this within our effective three-level simulation, we reduce the dipole matrix element between the excited state and ground state manifolds by a factor of 3, giving $\Omega_{e,g_1}/\Omega = 0.181$ from the known transition dipole matrix element of the P(1) transition. The total dipole moment and spontaneous decay rate are as before.

The optical Bloch equations set up as discussed above were solved numerically, and the number of photons N_p emitted by each velocity class v in the detector region

was calculated via

$$N_p(x_0, x_1, v) = \Gamma \int_{x_0/v}^{x_1/v} \rho_{e,e}(t) dt, \quad (5.36)$$

where $\Delta x = (x_1 - x_0)/2$ is the spatial extent of the region where photons are to be collected; for the case of the detection region, this is taken to be a 2 mm length symmetrically distributed about the $x_{\text{det}} = 5.5$ cm detection point. The systematic bias introduced by the unswitched relative to the switched case is then given by the ratio $N_p(x_{\text{det}} - \Delta x, x_{\text{det}} + \Delta x, v)/N_p(0, 2\Delta x, v)$, or the ratio of photons scattered in the region *given bleaching before reaching the detector* to those scattered in the region if no bleaching had occurred. A plot of this ratio is shown in the leftmost panel of figure (5.22).

We have evaluated this bias ratio, and applied it to our measured velocity distribution obtained using the fast-switching method; the results of this are shown in the red curve of figure 5.21. Whilst not fully capturing the character of the unswitched velocity distribution, we see that the effect leads to a systematic bias towards higher velocity classes. The high-velocity tail of the projected distribution drives the mean above that of the unswitched mean, but the peak velocities, determined by fitting Gaussians to the data, agree to within error (151 ± 1) m s⁻¹ and (154 ± 4) m s⁻¹ for the unswitched and projected distributions respectively).

At this point, it is useful to take a step back and examine the totality of the evidence. Using a continuous co-axial laser, we have measured the velocity distributions of three YbF beams. At a later date, we performed the same measurement using a pulsed co-axial laser. We observed the hallmarks of bleaching, an effect which could logically lead to a velocity-dependent bias, and developed a simple model to see if the results were consistent. Applying the model to the existing data, we obtained a good agreement to the low-velocity and peak-velocity character, but could not explain the resulting high-velocity tail. Whether this deviation lies in the elapsed time between measurements (three weeks of real time, in which the experiment was taken apart and the target cleaned) or in the model being overly simplified it is hard to say. To attempt to clarify this, we have re-binned our fast-switched data to only look at longer bleaching times. A plot of the resulting velocity distribution for bleaching times $\tau_j + 200 \mu\text{s} \leq t_j \leq \tau_j + 300 \mu\text{s}$ is shown in the right-most panel of figure (5.22), compared with the data obtained immediately after the switch. The mean of the resulting distribution is 141 m s⁻¹, making it clear both by inspection and by comparison of the means that the data obtained for longer bleaching times is shifted to a higher velocity. Thus we can say with certainty that, despite any day-to-day changes

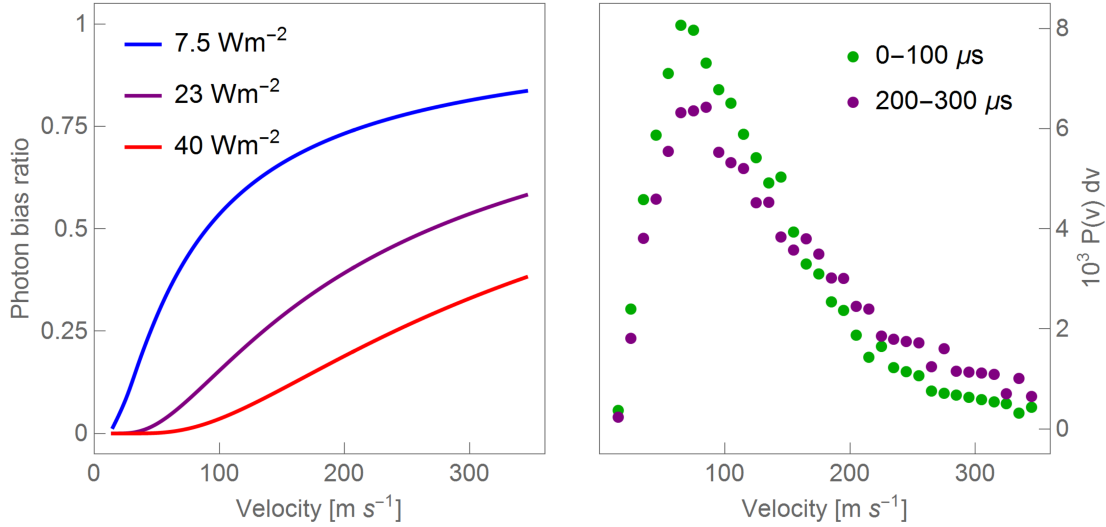


Figure 5.22: Photon bias ratio $N_p(x_{\text{det}} - \Delta x, x_{\text{det}} + \Delta x, v)/N_p(0, 2\Delta x, v)$ for three different laser powers (left panel) and variation of the velocity distribution with total bleaching time (right panel).

in the source function and despite the inadequacies of our simple model, bleaching is occurring and it produces a real systematic bias that is, at best, unhelpful to our future measurements.

5.9 Moving forward—extrapolation or innovation?

We have seen that the Doppler method, our old workhorse, can be subject to a velocity-dependent bias and have alleviated this effect by performing measurements using a time-switched laser. To obtain our velocity distributions using this method, we divide our measured time-of-flight spectra into equal-width time bins and, for each time bin, determine the mean velocity from the Doppler shift of the measured spectrum. A correlation curve of mean velocity versus time is obtained, from which the TOF distribution is re-binned and integrated to obtain the equal-velocity widths and hence the velocity distribution is obtained.

This is all well and good, but we must be careful about the interpretation of such data. The limiting factor in our velocity-time correlation curve is the signal-to-noise ratio of the spectrum which, for our equal time-bin integrals, is essentially propor-

tional to the mean TOF amplitude within the bin. However, the molecules that arrive at the peak of the TOF have a different velocity to those which arrive at the peak of the velocity distribution. To illustrate this, let's consider the peak velocity of an effusive beam. From the form of (2.14), the modal velocity v_{mp} can be found by evaluating the turning points of the distribution, yielding

$$v_{\text{mp}} = \sqrt{\frac{3\pi}{8}} \bar{v}. \quad (5.37)$$

The corresponding time-of-flight distribution for a collisionless beam is found by substituting $v = x/t$ and $dv = dv/dt dt$ for the free variable and integral element respectively; performing this evaluation and simplifying, we obtain

$$P(t)dt = \frac{32}{\pi^2 \bar{v}^4} \frac{x^4}{t^5} \exp\left(-\frac{4x^2}{\pi \bar{v}^2 t^2}\right), \quad (5.38)$$

from which the most probable time t_{mp} is found to be

$$t_{\text{mp}} = \sqrt{\frac{8}{5\pi}} \frac{x}{\bar{v}}, \quad (5.39)$$

which in turn corresponds to a most-probable x/t velocity of

$$v'_{\text{mp}} = \sqrt{\frac{5\pi}{8}} \bar{v}. \quad (5.40)$$

From the ratio $v'_{\text{mp}}/v_{\text{mp}} \approx 1.3$, we see that the peak of the time-of-flight distribution, and hence the peak sensitivity using this method, is shifted towards the higher velocity side of the underlying speed distribution. For the effusive distributions considered above with constant-amplitude noise, the signal-to-noise at $v = 0.5v_{\text{mp}}$ is only 7% of that at the peak of the TOF⁶, whilst the signal to noise at $v = 1.5v_{\text{mp}}$ is still 88% the peak value.

This isn't such a problem when the signal-to-noise ratio is good, but for our case where we are both critically interested in the low-velocity behaviour AND have a best-case signal-to-noise ratio of order 5–10 we are in trouble. It becomes increasingly difficult to assign meaningful Doppler-shifts to spectra once the signal-to-noise

⁶An easy way to see this is to note that, for small velocities, the effusive distribution scales as v^3 . Now $v'_{\text{mp}} \approx 2.6 \times (0.5v_{\text{mp}})$, so the sensitivity under constant noise at $v = 0.5v_{\text{mp}}$ will scale as $\approx 2.6^{-3} \approx 6\%$, which is in good agreement with the calculation using the full effusive distribution.

ratio drops below 1, simply because the centre of our spectral peaks become lost in the background noise of the experiment. To illustrate this, I have performed a simple simulation, shown in figure (5.23). 17 samples from a Gaussian curve⁷ with width $\sigma_i = 1$ and zero mean were intentionally obfuscated by random noise. The noise spectrum acts on the amplitude of the samples from the Gaussian, and was parametrised according to the normal distribution with width equal to a well-defined signal-to-noise (S:N) ratio. Each noisy set of samples was fitted to a Gaussian $G(x)$ using the `NonlinearModelFit` function of Mathematica, with the fitting curve having the form

$$G(x) = A \exp\left(\frac{(x - \bar{\nu})^2}{2\sigma^2}\right), \quad (5.41)$$

where A , $\bar{\nu}$, and σ were fitting parameters to be determined. From this the mean of $G(x)$, $\bar{\nu}$, was found. This process was repeated 2000 times, obtaining a set of 2000 values for $\bar{\nu}$. From this set, a histogram of the frequency of x_0 values, with bin width of 0.03, was constructed; this histogram was converted into a probability distribution by a simple rescaling.

This probability distribution $P(\bar{\nu}) d\bar{\nu}$ for the measured value of the mean $\bar{\nu}$ is shown in the left hand plot of figure (5.23) for signal-to-noise ratios of 2 and 10. We see from the width of $P(\bar{\nu}) d\bar{\nu}$ that the uncertainty in the mean for S:N = 2 is much greater than that for S:N = 10. We can make this more concrete by comparing the width of $P(\bar{\nu})$ with the width of our initial distribution; doing so, we obtain the right hand plot of figure (5.23). Reducing the signal-to-noise ratio leads to a corresponding increase in the uncertainty in the mean, with a measurement of the mean of a peak with S:N = 2 having an error bar of $\approx 0.3\sigma_i$. Thus, if the signal-to-noise is of the order 1 or less (as it must necessarily be far from the TOF peak, where we are currently interested), our uncertainty in any measurements of the frequency will be of the order of the Doppler-broadened width of the spectral lines. In other words, the uncertainty in the velocity will be approximately the entire width of the velocity distribution we wish to measure!

Another black mark against the Doppler method is its efficiency. Suppose we use

⁷Why 17 samples? A fully Doppler-broadened peak for the $A \rightarrow X$ transition in 6 K YbF has a width of ~ 290 MHz, so 17 samples gives a resolution of ~ 15 MHz or ~ 10 m s⁻¹, depending on if we are interested in frequency or velocity. This is much less than the typical hyperfine splitting for the lowest-lying rotational states within the X-state manifold of YbF, so would adequately map the spectrum of YbF at 6 K if the noise were low enough. On the other hand, if the signal-to-noise was poor we might focus on taking lots of repeats of a small number of points, so taking a larger number of samples is inappropriate.

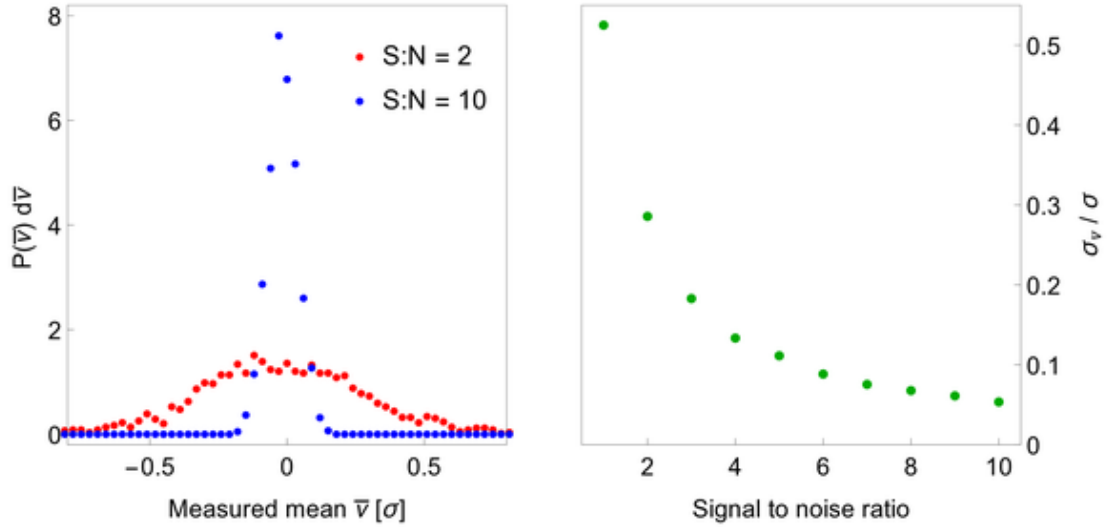


Figure 5.23: Distributions generated by determining the mean of noise-obscured Gaussian samples, for signal-to-noise (S:N) ratios of 2 and 10 (left), and the width of these distributions (right). Increasing the S:N increases the uncertainty in the measured centre of a noisy distribution, with a S:N of 2 having an error in the mean of $\approx 0.3\sigma_i$, where σ_i is the width of the initial, un-obfuscated distribution.

the current scheme to attempt a measurement of a velocity distribution with characteristic width σ . As we scan the laser from low to high frequency, we measure first the Doppler-shifted spectral features, then the un-shifted features. The total range over which we must scan is therefore the sum of the widths of the Doppler-shifted and un-shifted features, *plus* the distance between them, which is approximately the spectral width of the distribution we are trying to measure. This is shown diagrammatically in figure (5.24).

Let's compare the widths of spectral features obtained with a perpendicular and a parallel probe, such as we might use in a typical Doppler measurement of the velocity distribution. The molecular beam emitted from a buffer gas cell will have cylindrical symmetry. Due to beam divergence, only a small subset of the total radial velocity space is present within the detection volume of the perpendicular probe beam; hence, a measurement with this beam leads to the observation of spectrally narrow features. In contrast, the parallel beam can access all molecules in the axial

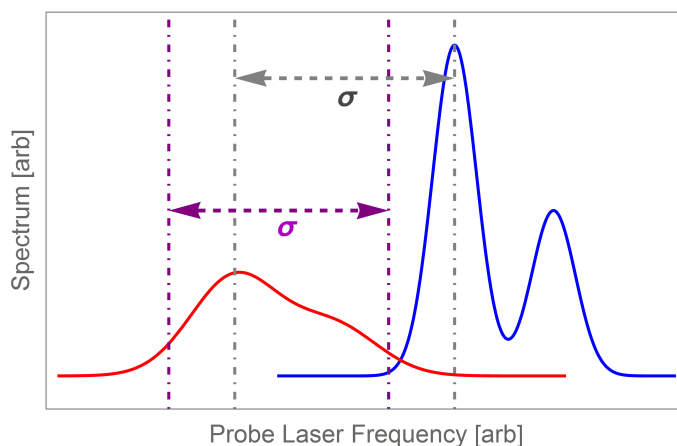


Figure 5.24: Illustration of the sampling inefficiency of a Doppler scheme measurement. The fully Doppler broadened spectrum (red) obtained by the parallel beam has some width σ . We determine the mean velocity by comparing the peak-to-peak separation between the parallel spectrum and the perpendicular spectrum (blue), the maximum extent of which must also be of order σ . This means we must scan our laser across a total frequency width $\sim 2\sigma$.

velocity space, and will therefore record a fully Doppler broadened spectrum. The total width we must scan our lasers over is therefore at least 2σ , and may in practice be more. We see that the Doppler scheme is *inefficient*, because to fully determine an object of width σ we must measure over a width of $> 2\sigma$. A method which could determine a distribution of width σ experimentally across a width σ would be at least twice as efficient. This fact becomes very relevant if we have poor signal-to-noise, and must take many repeat data sets to improve our measurement statistics.

Finally, we should talk about the role of extrapolation in the measurements performed thus far. In order to access information about the lowest-velocity molecules, we have relied on extrapolation of the velocity-time behaviour using our fitted calibration curves, which are defined over the parts of the spectrum with good signal-to-noise ratios. This opens a whole can of worms as, in order to perform the fits, we must first assume a form of the velocity-time relation and then hope that it does not change in the extrapolated region.

As is shown in, for example, figure (5.17), the fits have described the data well so far. Where this method has been used, I have been very careful to show the raw

data and the resulting calibration. Further, in the low-velocity tail of the distribution any deviation dv/dt should be small, so we are relatively insensitive to changes in this region. However, an element of doubt still remains. We could continue to perform the measurements as before, using an AOM switch to avoid the bleaching problem and assuming that the extrapolation scheme is valid. But it would be much more compelling if we had a method of measuring these low velocities unambiguously—to see them directly, free from inference and with some level of robustness to the various systematics we have observed thus far.

To this end, we have developed a new measurement scheme for determining the velocity distribution of molecules in the low signal-to-noise limit. In this scheme, presented in detail in chapter (6), we bleach molecules from a target transition, then measure the total loss of signal at a detector. For a given bleaching time, the number of lost molecules can be shown to be directly proportional to the amplitude of the velocity distribution within some velocity bin, with the bin width determined by the bleaching time and laser power. The method is immune to the bleaching biases discussed in section (5.8), and as it is a direct measurement on the velocity space does not suffer from the signal-to-noise and extrapolation issues presented here. We therefore decided to change our detection scheme once again, finally settling on the bleaching method which was used to obtain the remaining measurements of the source.

Chapter 6

Measuring velocity distributions from a two-stage source using optical bleaching

6.1 Motivation

In chapter (5), we laid out the principles behind our design of the two stage cell and made an initial attempt at parametrising it. A magnetic guide was constructed in order to increase the free-flight time of YbF in our molecular beam, in the hope that this would strongly correlate the arrival time at the detector and the molecular velocity. Unfortunately, we found that collisions between the helium buffer gas and YbF within the guide were likely to be boosting our beam velocity. After removing the guide, we attempted direct measurements of the velocity distribution using the usual Doppler technique. Using this method, we saw an increased number of slow molecules in comparison to the guided case, but found compelling evidence that optical bleaching from the parallel probe laser was introducing a systematic bias in our measurement.

Following these set-backs, we re-evaluated our techniques. In section (5.9) I laid out the evidence against continuing to take measurements using the Doppler method. I concluded that, despite the successes of this technique when used to measure intense molecular beams, it was unsuited to the current task of measuring the velocity distributions of slower, dimmer beams.

In this section, I suggest an alternative approach which has been successfully im-

plemented in our parametrisation experiments. The technique relies on intentionally bleaching molecules from a target molecular state using a parallel pump laser, then using the fact that the degree of bleaching decreases as the detuning of the pump laser from the molecular resonance is increased. This means that a carefully-tuned pump laser can selectively bleach molecules within certain, well-defined velocity classes. Measuring the total loss of intensity in the beam after bleaching gives us the number of molecules with a certain velocity class, while changing the frequency of the pump allows us to address new velocity classes on the fly.

I begin by simulating an experiment of this type, solving the optical Bloch equations using the formalism laid out in appendix (B). I show that a bleaching measurement performed on a physically realistic system can give a reasonable representation of the true velocity distribution, and develop error-correction techniques which improve the accuracy of the method. Using this method, I attempt a further characterisation of the two-stage cell, before verifying the method through comparison with a carefully-performed Doppler measurement of the velocity distribution of a molecular beam.

6.2 Introduction to the scheme

We propose a scheme that measures the degree of bleaching of the $|X \Sigma^+, v = 0, N = 0, J = 1/2, F = 1\rangle$ hyperfine state¹, via the $^{174}\text{Q}(0)$ transition. We use a counter-propagating laser beam red-detuned from resonance by $\delta_{\text{c-p}}$; in the frame of reference of a molecule with velocity v , the observed detuning is therefore $\delta_{\text{c-p}} - f_0 v/c$, where f_0 is the fundamental frequency of the $^{174}\text{Q}(0)$ transition, and c is the speed of light. Molecules are pumped from $|X \Sigma^+, v = 0, N = 0, J = 1/2, F = 1\rangle$ into² $|X \Sigma^+, v = 0, N = 0, J = 1/2, F = 0\rangle$, $|X \Sigma^+, v = 0, N = 2\rangle$ and $|X \Sigma^+, v \geq 1\rangle$ via spontaneous decay at a rate

$$\Gamma_{\text{eff}} = \Gamma_{\rho_{\text{e,e}}(t)}, \quad (6.1)$$

¹The ground state manifold of YbF is well described using the formalism of Hund’s case (b); see pages 224–231 of [91] or appendix (A) for more information. X labels the state as being the ground electronic state, $\Sigma = 0$ is the electronic angular momentum of the state, $v = 0$ the vibrational quantum number, $N = 0$ is the rotational angular momentum, $J = N + S$, and $F = J + I$ the total angular momentum quantum number. S is the electron spin angular momentum, and I the nuclear spin angular momentum.

²Kets where I have not fully specified the full set of quantum numbers should be considered to be labelling the set of states for which the specifications in the ket hold true. For example, $|\Sigma, v \geq 1\rangle$ labels all states with electronic angular momentum Σ and vibrational quanta $v \geq 1$.

defined analogously to equation (B.88). In appendix (B), specifically equations (B.89–B.90), I show that increasing the total detuning beyond some optimum value is enough to strongly reduce the excited state population. Thus, only molecules with velocities “close” to the resonance $\delta_{\text{c-p}} = f_0 v_{\text{res}}/c$ should be bleached. Therefore, measuring the remaining population via a second, perpendicular probe laser then comparing the total bleached signal to the unbleached signal should give a good measure of the number of molecules with velocities $v \sim v_{\text{res}}$.

Before proceeding with the measurement, we first wish to simulate the system. This will allow us to check that the measurement is robust, and gives a fair representation of the underlying physics. The goal of the simulation is to reconstruct an ansatz velocity profile given some reasonable assumptions, and to examine any systematic effects that occur as a result of the scheme. As such, we do not aim for absolute realism, and instead reduce the problem to a 4-level system whose parameters can be easily examined computationally. The toy system has three low-energy states forming a ground state manifold, consisting of our test state $|v = 0, N = 0, F = 1\rangle$, the lower hyperfine state $|v = 0, N = 0, F = 0\rangle$ which is separated from the test state by the hyperfine splitting 170 MHz, and a dark “leak” state representing both $|v = 0, N = 2\rangle$ and $|v \geq 1\rangle$ to which population is lost beyond the scan range and bandwidth of our probe laser. As the hyperfine splitting of the $|A^2\Pi_{1/2}, v = 0, \Omega = 1/2, J = 1/2\rangle$ state of ^{174}YbF is small, we model both the hyperfine components via a single composite excited state.

The simulation proceeds as follows. First, we calculate the change in the test state population for a bleaching time of $\tau = 50\text{ }\mu\text{s}$, given a range of detunings and laser powers. We determine the analytic time-of-flight (TOF) profiles measured at the detector from an ansatz velocity distribution, then calculate the TOFs when the pump laser is both on and off. As not all the molecules leave the cell instantaneously, we then convolve these TOFs with an “escape function” whose purpose is to model this finite escape time. Finally, we evaluate the difference in the time-integrals of the pumped and un-pumped molecules. Repeating this for many different initial detunings builds up a “measured” velocity distribution, which we compare with our initial ansatz.

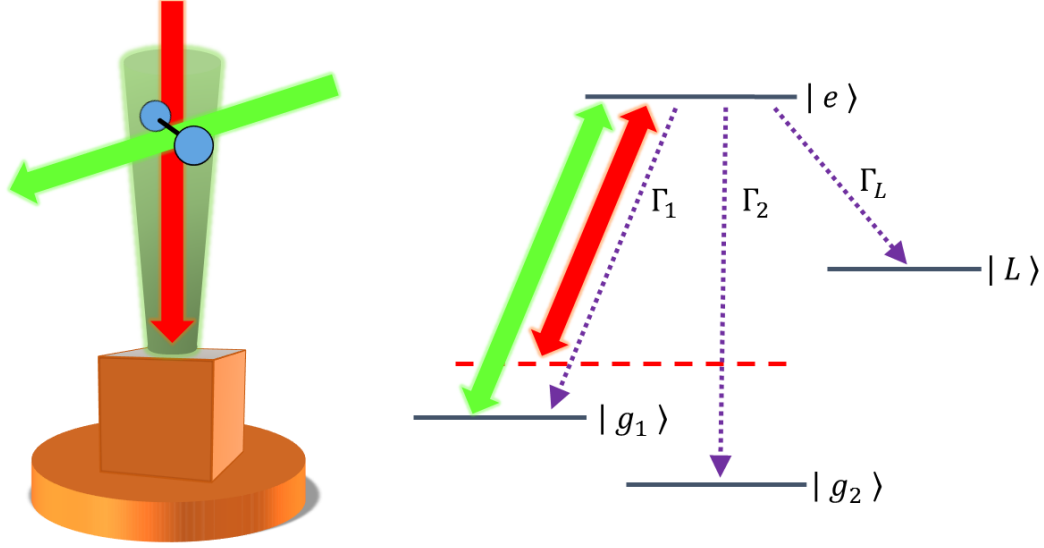


Figure 6.1: Diagrammatic representation of the toy 4-level scheme described in section (6.2). The state of interest is labelled $|g_1\rangle$, with the lower hyperfine level being $|g_2\rangle$ and the “leak state” $|g_L\rangle$. The molecule is pumped from $|g_1\rangle$ by the counter-propagating red-detuned beam (red arrow), before its population is read out by the resonant probe (green arrow). Decays proceed from the excited state into the three states in the ground state manifold at rates Γ_j .

6.3 Partial transition rates and the transition dipole operator

Recall from equation (B.31) the definition of the spontaneous transition rate between a pair of atomic or molecular levels:

$$\Gamma_{\text{spn},\alpha,\beta} \propto \omega_{\alpha,\beta} |\langle \alpha | \mathbf{d}_{\alpha,\beta} | \beta \rangle|^2, \quad (6.2)$$

where we have now made explicit the dependence on the transition dipole moment $\mathbf{d}_{\alpha,\beta}$ and the transition frequency $\omega_{\alpha,\beta}$. However, we often have a manifold of both excited states $\{\beta\}$ and ground states $\{\alpha\}$. In this case, the total spontaneous decay

rate is obtained via the sum

$$\Gamma_{\text{spn}} \propto \sum_{\alpha,\beta} \omega_{\alpha,\beta} |\langle \alpha | \mathbf{d}_{\alpha,\beta} | \beta \rangle|^2 \equiv a \sum_{\alpha,\beta} \omega_{\alpha,\beta} |\langle \alpha | \mathbf{d}_{\alpha,\beta} | \beta \rangle|^2. \quad (6.3)$$

In the special case that $\omega_{\alpha,\beta} \simeq \omega_{\alpha',\beta'} \forall \alpha, \alpha', \beta, \beta'$, we can pull out the transition frequency from the sum in (6.3) as a common factor $A = \omega_{\alpha,\beta} a$.

The parameter measured experimentally is usually the total spontaneous emission rate Γ_{spn} (see, for example, [107]). How, then, can we evaluate the transition rates in our simplified toy system? We must expand the total spontaneous rate as follows:

$$\Gamma_{\text{spn}} = \sum_j \Gamma_j. \quad (6.4)$$

Let us begin by writing one of the Γ_j as a sum over a subset of the levels in the excited and ground state manifolds

$$\Gamma_j = A \sum_{\xi,\chi} |\langle \xi | \mathbf{d}_{\xi,\chi} | \chi \rangle|^2, \quad (6.5)$$

where $\{\xi\} \subseteq \{\alpha\}$ and $\{\chi\} \subseteq \{\beta\}$. We now substitute equation (6.3) into (6.5) to eliminate the constant of proportionality A :

$$\Gamma_j = \Gamma_{\text{spn}} \frac{\sum_{\xi,\chi} |\langle \xi | \mathbf{d}_{\xi,\chi} | \chi \rangle|^2}{\sum_{\alpha,\beta} |\langle \alpha | \mathbf{d}_{\alpha,\beta} | \beta \rangle|^2}. \quad (6.6)$$

Each partial decay rate Γ_j requires different subsets $\{\chi_j\}$ and $\{\xi_j\}$, generated by partitioning $\{\alpha\}$ and $\{\beta\}$. If we define Ξ as the family of subsets $\{\xi_j\}$, then the expansion (6.4) is true as long as

$$\cup \Xi = \{\alpha\}, \quad (6.7)$$

and equivalently for the family of the subsets $\{\chi_j\}$, and $\{\beta\}$.

We may also wish to evaluate the total Rabi rate for the manifold of states, given an electric field of known intensity. This can be accomplished by writing

$$\Omega = \sum_j \Omega_j = -\frac{\mathbf{E}}{\hbar} \cdot \sum_{\alpha,\beta} \langle \alpha | \mathbf{d}_{\alpha,\beta} | \beta \rangle, \quad (6.8)$$

Simulation parameter	Value	Simulation parameter	Value
Hyperfine splitting [MHz]	170.26	$\Omega_{e,t}/\Omega$	-0.454
Total transition dipole moment [D]	4.39	$\Omega_{e,h}/\Omega$	0.454
Γ [GHz]	$2\pi/28$	$\rho_{t,t}(0)$	3/4
$r_{e,t}$	0.464	$\rho_{h,h}(0)$	1/4
$r_{e,h}$	0.155	τ_{int} [μs]	50

Table 6.1: Molecular parameters used to simulate the change in test state population $\rho_{t,t}(\infty)/\rho_{t,t}(0)$. $r_{e,h}$ is the branching ratio to the lower hyperfine state (labelled $|g_2\rangle$ in figure (6.1)).

where in the final step we have used the explicit form of equation (B.25) and assumed that the classical electric field addressing each of the states is equal (as is the case when we are “grouping” levels into a toy system). Again, the experimentally derived quantity normally used is the total transition dipole moment. It is convenient to write the partial Rabi rate in terms of the total rate (which is easily calculated from the total transition moment and the electric field):

$$\Omega_j = \Omega \frac{\sum_{\xi,\chi} \langle \xi | d_{\xi,\chi} | \chi \rangle}{\sum_{\alpha,\beta} \langle \alpha | d_{\alpha,\beta} | \beta \rangle}. \quad (6.9)$$

Both equations (6.6) and (6.9) rely on evaluating the matrix elements of the transition dipole operator. These have been evaluated for our state by Jack Devlin in [48].

6.4 Optical bleaching in the 4-level system

We begin the simulation by evaluating the time dynamics of the toy system shown in figure (6.1) using the optical Bloch equations. To rapidly and exactly map out the parameter space, we apply the analytic methods presented in appendix (B.6) to the governing equations for the four-level system. The interaction matrix has dimensions 10×10 rather than 16×16 , as the leak state is not coupled to the excited state by the laser and hence its coherences form a closed sub-set that do not influence the time dynamics of the rest of the system. The interaction time with the laser is set to $\tau_{\text{int}} = 50 \mu\text{s}$, and we examine the dependence of the system on the

pump laser detuning and pump intensity. The change in population in the test state, $\rho_{t,t}(\infty)/\rho_{t,t}(0)$, is given by

$$\frac{\rho_{t,t}(\infty)}{\rho_{t,t}(0)} = \frac{1}{\rho_{t,t}(0)} \left[\rho_{t,t}(\tau_{\text{int}}) + \frac{\Gamma_{e,t}}{\Gamma_{\text{spon}}} \rho_{e,e}(\tau_{\text{int}}) \right], \quad (6.10)$$

where the branching ratio $r_{e,t} = \Gamma_{e,t}/\Gamma_{\text{spon}}$ is the fraction of the population that decays from the excited state to the test state, and $\rho_{e,e}$ is the excited state population³. The probe is simulated by simply reading out $\rho_{t,t}(\infty)$, a simplification which becomes exact in the limit of a high-intensity probe. We also assume that population is initially equally distributed between the Zeeman sub-levels of the test and lower hyperfine states, such that $\rho_{t,t}(0) = 3/4$.

The final simulated population is shown in figure (6.2), and the simulation parameters are tabulated in table (6.1). We note a few general features of the phase space. The broad “dip” at zero detuning is expected, and is caused by population being pumped from the test state and into the lower hyperfine and leak states. Moving away from the resonance the pumping proceeds at a slower rate. In appendix (B.8) I show that the excited state population decreases as a function of detuning for a range of systems, so this property should not be a surprise. However, we also have a peak at a detuning of $\Delta_{\text{HFS}} = -170.26$ MHz. This feature is caused by population being transferred from the lower hyperfine state to the test state. Experimentally, this second feature would indicate molecules moving with velocity $v_{\text{fast}} = v_{\text{res}} + c \Delta_{\text{HFS}}/f_0 \simeq v_{\text{res}} + 94 \text{ m s}^{-1}$, instead of the v_{res} we are aiming to measure. As we shall see later we do indeed observe these molecules, and must correct for their presence in the analysis procedure.

6.5 Simulated TOF profiles, with and without bleaching

We now have enough information to simulate nominal time-of-flight profiles, and hence attempt to compute the velocity distribution using this method. First we choose a nominal laser power. To make a useful measurement, we want to maximise the amount of bleaching while minimising the power broadening of the transition. We see in figure (6.3) that increasing the power much beyond $\sim 30 \text{ W m}^{-2}$ is enough

³When the probe is switched off, any population still in the excited state will decay into the lower-energy states according the branching ratios for the transitions.

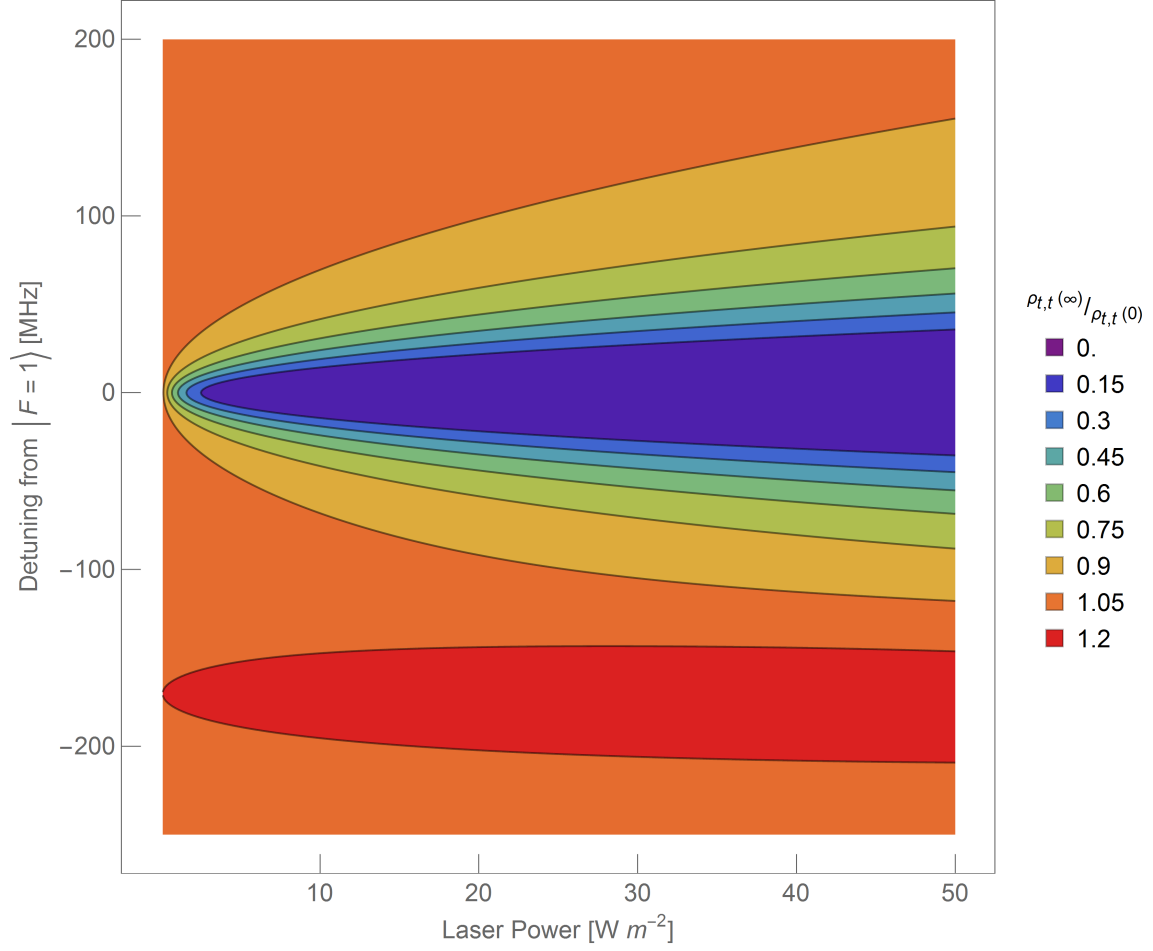


Figure 6.2: Simulated experimental read-out of population in the test state, $\rho_{t,t}(\infty)/\rho_{t,t}(0)$, assuming a high-intensity probe.

that the accumulation peak begins to wash in to the depletion dip. On the other hand, the mean bleached signal plotted in figure (6.3) suggests that in order to maximise the experimental signal, we should use as much laser power as possible. We settle on a compromise of 25 W m⁻², as this gives a significant total pumped fraction of $\sim 10\%$ without too much interference between the accumulation and bleaching processes. We denote our choice of bleaching profile as $B_{\Omega}(\delta)$.

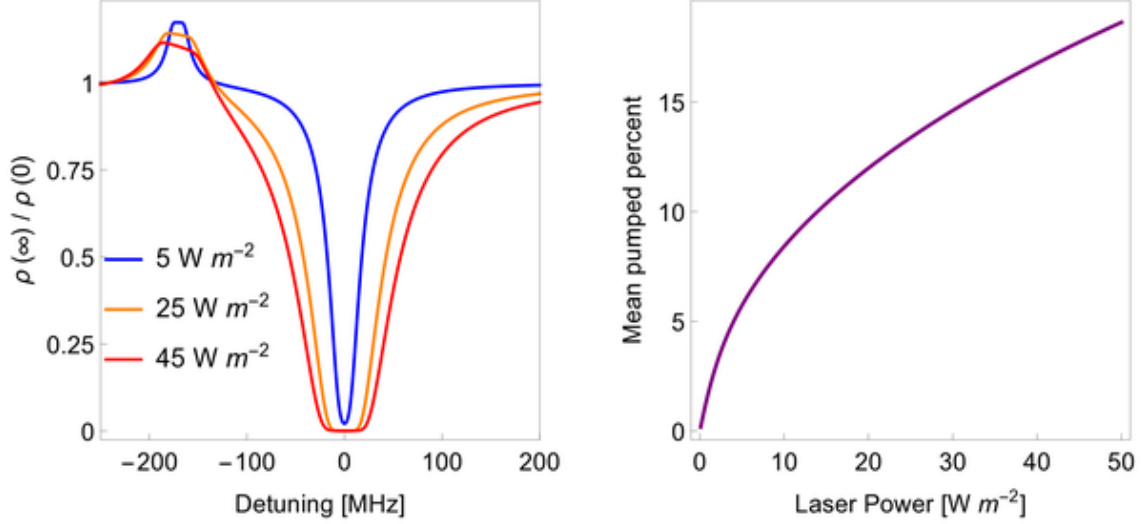


Figure 6.3: Population and mean population pumped from the test state as a function of the laser power. The mean pumped population is calculated by integrating over the detunings, then dividing by the integration range. The minimum and maximum detunings in the integral are the limits of the simulation, $\delta_{\min} = -470$ MHz and $\delta_{\max} = 300$ MHz.

We now begin to build up the form of the time-of-flight profile used in this experiment. We start by stating an ansatz for the form of an underlying velocity distribution, from which we can derive the arrival time of different velocity classes. We will assume that there are no collisions in the beam so that the acceleration of individual molecules is zero, and hence we can write the velocity in the familiar form $v = x/t$, where x is distance and t is the time. A suitable choice is the effusive velocity distribution:

$$P(v) dv = \frac{32v^3}{\pi^2 \bar{v}^4} e^{-4v^2/\pi \bar{v}^2} dv, \quad (6.11)$$

where m is the molecular mass, k_B is the Boltzmann constant, T is the molecular temperature (assumed to be isothermal across the beam), and

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}. \quad (6.12)$$

Substituting for the velocity, and remembering also to transform the increment $dv = dt dv/dt$, we obtain an expression for the time-of-flight of the molecules a distance x from the point of emission:

$$P(t) dt = \frac{32x^4}{\pi^2 \bar{v}^4 t^5} e^{-4x^2/\pi t^2 \bar{v}^2}. \quad (6.13)$$

As the bleaching profile is also a function of the velocity, it too can be recast into the time domain. In a 1D model, if all the molecules leave the cell on a time scale much shorter than the free-flight time to the detector, the bleached time-of-flight signal will be of the form $P'(t) dt = B_\Omega(t) P(t) dt$.

Of course, the real world isn't one dimensional. The molecular beam will have a characteristic divergence caused by the transverse velocities of its constituents⁴. Suppose we assign to a particle in the beam a transverse, thermal velocity distribution to go alongside its effusive forward distribution. Such a particle will only be observed in the detection volume of an experiment if its forward velocity, transverse velocity, and initial position all align in just the right way. Let's assume that the molecular source has a circular aperture of diameter d_{app} , and the detection volume a width d_{det} . A collisionless particle emitted from the source at position $-d_{\text{app}} \leq 2p \leq d_{\text{app}}$ must have a velocity in the range $(2p - d_{\text{det}})/2t \leq v_\perp \leq (2p + d_{\text{det}})/2t$, where t is the flight time of the molecule. Thus the probability of a molecule emitted at a point p reaching the detection volume is

$$D(p, t) = \int_{(2p-d_{\text{det}})/2t}^{(2p+d_{\text{det}})/2t} \frac{2}{\pi \bar{v}} e^{-4v^2/\pi \bar{v}^2} dv \quad (6.14)$$

$$= \frac{1}{2} \left[\text{erf} \sqrt{\frac{m}{2k_B T}} \frac{(2p + d_{\text{det}})}{2t} - \text{erf} \sqrt{\frac{m}{2k_B T}} \frac{(2p - d_{\text{det}})}{2t} \right]. \quad (6.15)$$

We now integrate $D(p, t)$ across the whole circular aperture to obtain the full divergence correction:

$$\Delta(t) = \int_0^{d_{\text{app}}/2} 2\pi p D(p, t) dp. \quad (6.16)$$

The integral in equation (6.16) can be evaluated analytically, and leads to a rather long expression that we do not state here. We merely note that, having now corrected for bleaching and beam divergence, the form of the simulated time-of-flight

⁴If we were not operating in the effusive regime, inter-molecular collisions would also contribute to this effect. This is the hydrodynamic equivalent of getting jostled as you try to escape from a rush-hour train.

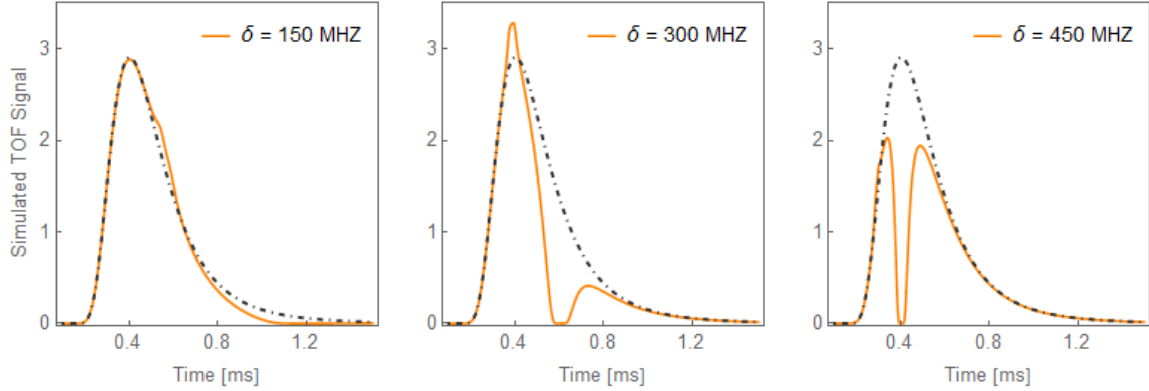


Figure 6.4: Simulated time-of-flight profiles, assuming the instantaneous yield function $Y(t) = \delta(0)$. In each case the bleached (solid line) profile is compared with the unbleached (dot-dashed line). Increasing the red-detuning of the pump addresses faster molecules, which arrive earlier at the detector.

profile is now given by $P''(t) dt = \Delta(t) B_{\Omega}(t) P(t) dt$.

Finally, we need to compensate for the finite time a molecule spends in the buffer gas cell after ablation. If the source is fully thermal, then it will tend to emit some molecular yield that is a function of time only, $Y(t)$. The exact form of the yield function will vary strongly depending on the geometry of the cell and the buffer gas flow regime used. We will use some sensible functional forms for $Y(t)$ based on diffusion arguments in the following work. The final form of the simulated time-of-flight function is then⁵ $\Pi(t) = Y(t) * (\Delta(t) B_{\Omega}(t) P(t) dt)$.

In figure (6.4) we plot the special case of a point-time molecular source—i.e. the yield function $Y(t)$ is well approximated by a Dirac delta function. This limiting case holds when molecules leave the source on time scales much shorter than the free-flight time. The laser is red-detuned by $\delta = 150, 300$, and 450 MHz from resonance with the test state in each case, with the mass and temperature in equation (6.13) being the helium mass and the cell temperature of 5 K respectively⁶. The detector is assumed to be 10 cm from the source, which has a 5 mm diameter aperture.

⁵The appearance of the convolution comes from the fact that each moment in time is acting as a molecular source. The more familiar direct analogy comes in diffusion problems, when we wish to model the effect of an extended source as a convolution over a set of distributed point sources.

⁶Anecdotally, this choice of parameters reproduces our measured time-of-flight profiles in the laboratory with reasonable fidelity.

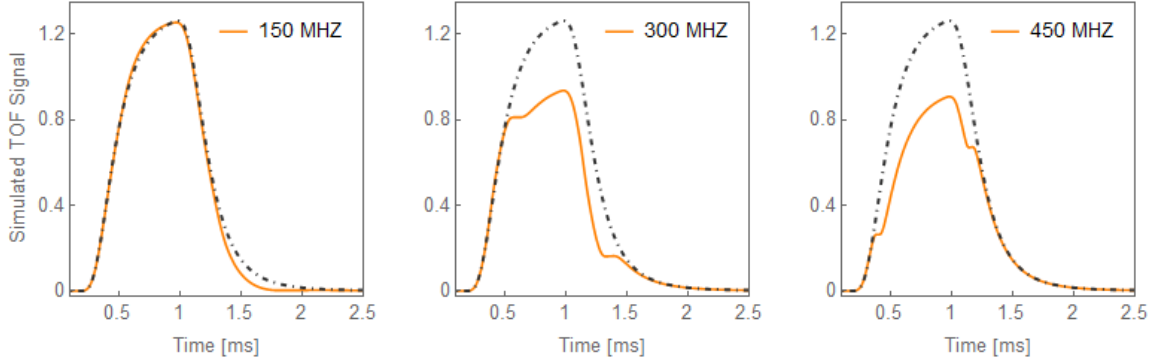


Figure 6.5: Simulated time-of-flight profiles, now assuming a stepwise yield function with temporal width equal to the characteristic diffusion time of the buffer gas cell. Note that the sharp features are now distributed across the entire time-of-flight distribution.

The effective detection length is taken to be 2.5 mm. We see that, because velocity and arrival time at the detector are well correlated, precise “notches” of molecules pumped from the test state are visible in the time-of-flight profile. Small increases in the instantaneous molecular flux are also visible, caused by pumping into the test state by molecules from the lower hyperfine level.

Compare this behaviour to the finite-width yield function in figure (6.5). At every instant in time there are now many different velocity classes arriving at the detector at once, some of which are bleached via the pump laser. As such, the sharp features of figure (6.4) are softened and distributed across the entire time-of-flight profile. The ledge-like features visible in the 300 and 450 MHz detuned cases are artefacts of the artificial yield function, which took the form

$$Y(t) = \begin{cases} 1/\tau_D & 0 \leq t \leq \tau_D \\ 0 & \text{otherwise.} \end{cases} \quad (6.17)$$

Here we set the width of the stepwise yield function to be the characteristic time for a molecule to diffuse the length of our buffer gas cell. The finite-width yield function chosen here broadens the overall time-of-flight profile, whilst keeping the integral of the distribution equal to 1.

We now attempt to reconstruct the velocity profile from the simulated data, using

the same yield function as equation (6.17). We define the difference signal

$$\mathcal{D}(\delta, t) dt = Y(t) * (\Delta(t) P(t) dt) (1 - B_\Omega(t)) \quad (6.18)$$

as the difference between the pumped and un-pumped time-of-flights, and the total bleaching as

$$\mathcal{T}(\delta) = \int_0^\infty \mathcal{D}(\delta, t) dt. \quad (6.19)$$

To determine the velocity profile, we bleach in turn different velocity classes using the pump beam, and then measure the total degree of bleaching $\mathcal{T}$. First note that, if the molecular source is thermal, the yield function is independent of the pump detuning and hence the velocity. Via Fubini's theorem,

$$\int_0^\infty Y(t) * (\Delta(t) P(t)) (1 - B_\Omega(t)) dt \quad (6.20)$$

$$= \int_0^\infty Y(t) dt \int_0^\infty (\Delta(t) P(t)) (1 - B_\Omega(t)) dt. \quad (6.21)$$

We see that the yield function contributes only an overall multiplicative factor to the resulting measured distribution.

We now evaluate $\mathcal{T}(v)$ and compare the results to the distribution we are trying to measure. The result of a simulated measurement is shown in figure (6.6), and is compared to the velocity distribution directly out of the cell and the profile at the detector. Qualitatively, we see that the measured distribution reproduces the profile at the detector rather well. The mean of the measured function $\mathcal{T}(v)$ is slightly biased towards higher velocities and is wider than the underlying distribution. We quantify these sources of systematic error in section (6.6). For now we remark that this method can rigorously remove the complications of the finite escape time of molecules from a source, and can provide a “good” measurement of the velocity distribution in the beam. Exactly what “good” means in this context will be defined in the following section.

6.6 Systematic errors in the bleaching measurement scheme

In section (6.5) we outlined a scheme to measure the velocity profile of a molecular beam by using the velocity-dependent rate of bleaching to our advantage. The simulated measurement provided a qualitatively good reproduction of the underlying

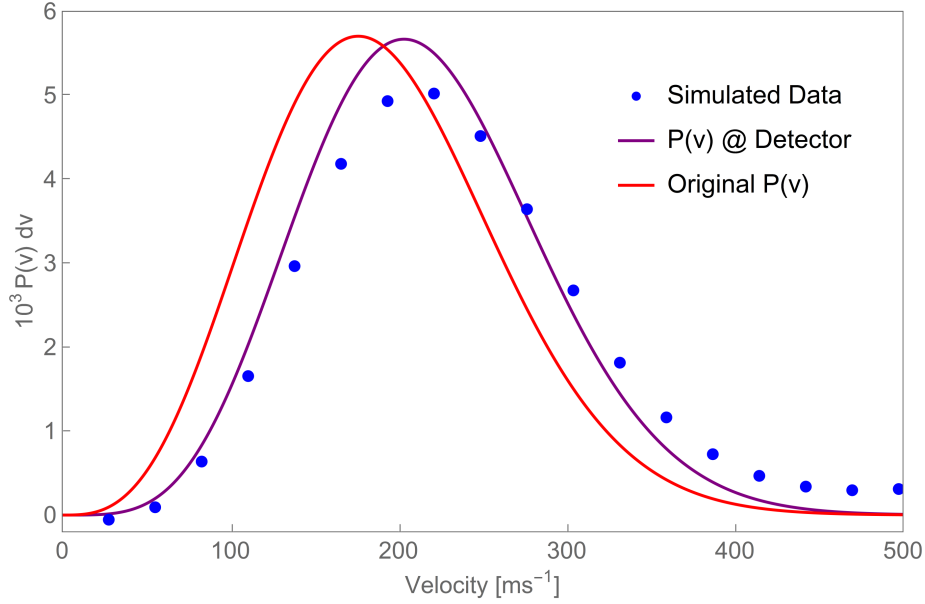


Figure 6.6: Comparison of $\mathcal{T}(\delta)$ with the velocity distribution out of the molecular source and the distribution at the detector.

distribution. We now wish to quantify the sources of error in such a measurement in order to remove them, correct for them, or allow for them in later analysis.

We begin by examining equation (6.20) in more detail. The right hand side contains three terms. The first, the integral over the source term $Y(t)$, contains information about the dynamics and lifetime inside the molecular source. Within this measurement formalism, we are able to rigorously remove this term as a constant, leaving behind terms where velocity and time are well correlated, as in figure (6.4). Suppose we attempt to measure some velocity v_0 . With the source terms removed and the distance between source and detector known, this is equivalent to asking for an arrival time t_0 . With this in mind, let us write the terms in equation (6.20) in a more transparent form:

$$\int_0^\infty Y(t) dt \int_0^\infty (\Delta(t) P(t)) (1 - B_\Omega(t)) dt \equiv \bar{Y} \int_0^\infty u(t) g(t - t_0) dt, \quad (6.22)$$

where the constant terms have been written as $\bar{Y}$, $\Delta(t) \times P(t) = u(t)$, and I have written the bleaching difference profile $1 - B_\Omega(t)$ as the square-integrable shift term

$g(t - t_0)$. A perfect measurement scheme amounts to the demand that

$$M(t_0) \equiv \int_0^\infty u(t)g(t - t_0) dt = u(t_0), \quad (6.23)$$

or that an attempted measurement of the velocity distribution in the time domain $u(t_0)$ returns the value that we expect.

We see immediately that, in order for equation (6.23) to hold, the bleaching profile must obey

$$1 - B_\Omega(t) \equiv g(t - t_0) = \delta(t - t_0), \quad (6.24)$$

where $\delta(t - t_0)$ is the Dirac delta function. This requirement obviously isn't one that we can physically experimentally realise! However, all isn't lost. Let's suppose that $g(t - t_0)$ has some characteristic width σ such that $g(\sigma) \ll g(0)$. Further, let's suppose that across the range $t_0 - \sigma \leq t \leq t_0 + \sigma$ the distribution $u(t) \approx u(t_0)$. Physically, this means that the characteristic width of the distribution we are trying to measure must be very much greater than the width of the bleaching profile we are using to measure it. In this case,

$$\int_0^\infty u(t)g(t - t_0) dt \approx u(t_0) \int_{t_0 - \sigma}^{t_0 + \sigma} g(t - t_0) dt = \bar{g}u(t_0), \quad (6.25)$$

where in the last step we have evaluated the integral and written it in the form of a constant $\bar{g}$. A measurement in this limit reproduces the required distribution up to a constant term, which we can remove by renormalisation in the analysis.

Experimentally, demanding that the bleaching profile be narrow is equivalent to requiring that the bleaching time $\tau_{\text{int}} \sim \Omega$ so as to minimise off-resonant contributions. In practice, this means that the difference signal we attempt to measure experimentally is rather small. Often we do not have the luxury of being able to measure small signals—our molecular flux may be weak or have significant statistical noise associated. In this case we must broaden the bleaching profile by increasing the laser power, and the special case of equation (6.25) no longer holds.

In the absence of this limiting behaviour, we return to equation (6.23). The integral here takes the form of a convolution between two square-integrable functions on the interval $[0, \infty)$. If the width of the bleaching profile is no longer negligible, performing the measurement scheme of equation (6.23) will produce a velocity distribution $\tilde{u}(t_0)$ with some characteristic width $W[\tilde{u}(t_0)] > W[u(t_0)]$, with the exact

form of $W[\tilde{u}(t_0)]$ depending on the details of the experiment performed. As an example, if we model the bleaching and velocity distributions as Gaussians of width σ_{bleach} and σ_{vel} , we expect to measure a velocity distribution with characteristic width $\sigma_{\text{measured}}^2 = \sigma_{\text{bleach}}^2 + \sigma_{\text{vel}}^2$.

There is another systematic effect that we must examine. In an ideal experiment, we would address a single ground state, bleaching the velocity class Doppler-shifted into resonance with our red-detuned pump laser. However, as is shown in figure (6.1) our toy system has two states within the ground state manifold separated by the X-state $v = 0, N = 0$ hyperfine splitting of $\Delta_{\text{HFS}} \sim 170$ MHz. This means that, in our ensemble of molecules, two velocity classes are pumped simultaneously. The molecules we wish to address are bleached normally, with population being removed from the test state $|g_1\rangle$ and redistributed through spontaneous decay into the states $|g_2\rangle$ and $|L\rangle$. However, faster moving molecules are also coupled to the laser on the $|g_2\rangle \rightarrow |e\rangle$ transition. This pumps population from $|g_2\rangle$ to $|g_1\rangle$, with the net effect being a measured increase in the observed $|g_1\rangle$ state population for these molecules. Within the molecular ensemble of the beam, there are two competing processes—one which reduces measured population, and one which enhances it.

This systematic is rather more difficult to quantify, but we can certainly signpost the conditions required to minimise its effect. Let's start by rewriting equation (6.18) for the four-level system in the slightly more suggestive square-integrable form introduced in equation (6.22):

$$\mathcal{D}(\delta, t) dt = Y(t) * (\Delta(t) P(t) dt) (g_1(t - t_1) - g_2(t - t_2)). \quad (6.26)$$

Here we have simply expressed the bleaching profile as the sum of two terms, with g_1 representing the depletion of $|g_1\rangle$ by bleaching and g_2 representing the enhancement of $|g_1\rangle$ via pumping. Let's assign g_1 and g_2 characteristic widths σ_1 and σ_2 respectively. If we carefully choose the laser intensity such that

$$|t_1 - t_2| \gg \sigma_1 + \sigma_2, \quad (6.27)$$

then we have no problems and we can remove this effect altogether by evaluating the modified form of equation (6.19),

$$\mathcal{T}(\delta, \tau) = \int_{\tau}^{\infty} \mathcal{D}(\delta, t) dt, \quad (6.28)$$

where $t_2 + \sigma_2 < \tau < t_1 - \sigma_1$. This choice effectively time-bins our data, with the lower limit of the integral chosen to remove the enhancement effect while still capturing

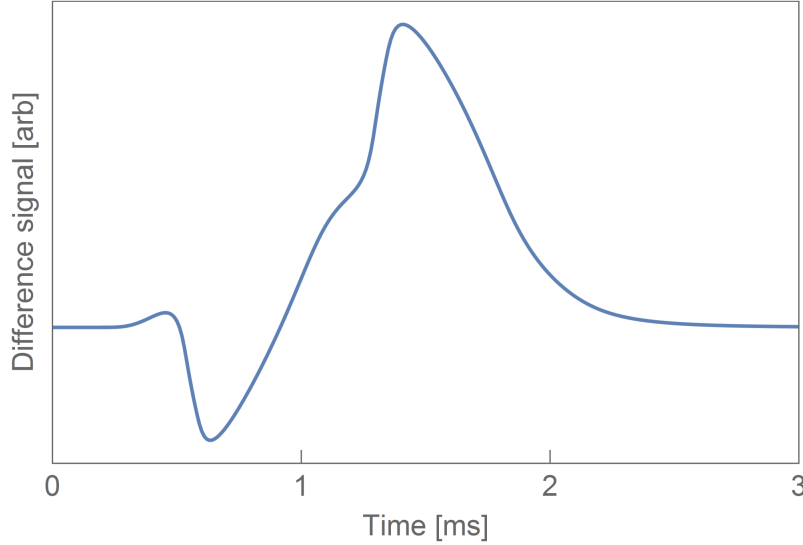


Figure 6.7: Difference signal $\mathcal{D}(150 \text{ MHz}, t)$ simulated for a bleaching laser power of 25 W m^{-2} . There are two competing processes here. The leftmost “dip” is caused by population being pumped into $|g_1\rangle$ from $|g_2\rangle$, whilst the rightmost “peak” is caused by bleaching from $|g_1\rangle$ to other states. The exact bleaching profile is obscured by the source function $Y(t)$; however, the convolution process should not move the position of the axis crossing at $t = 0.92 \text{ ms}$, as the convolving function is common to both the bleaching and pumping contributions. This makes the axis crossing an attractive choice for τ in equation(6.28).

the relevant bleaching.

Unfortunately, the width of the bleaching functions aren’t constant, and instead depend on the value of the detuning being measured. To illustrate this idea, let’s choose a Gaussian distribution to represent the bleaching profile⁷:

$$1 - B_\Omega(t) \sim \exp - \frac{(\delta_0 - \frac{f_0 x}{ct})^2}{2\sigma_f^2}. \quad (6.29)$$

Here δ_0 is the offset detuning set in the experiment, f_0 is the frequency of the transition we are driving, x is the free-flight distance of the beam, t is the arrival time measured on a detector, and σ_f is the fixed width of the distribution in frequency

⁷This isn’t strictly accurate, but a different choice of peaked function should still give the same dependence up to a numerical factor of order unity.

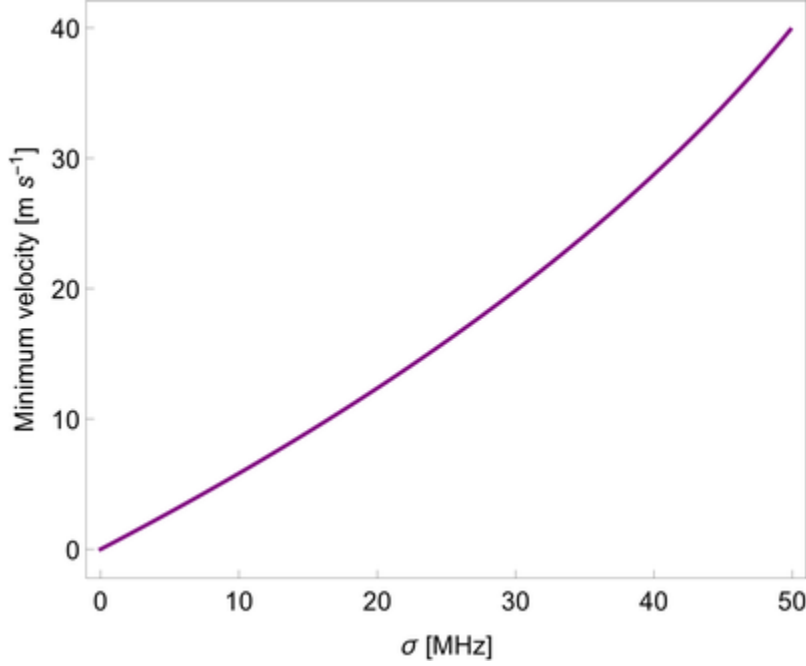


Figure 6.8: Minimum velocity that can be obtained using time-binning to correct for the $|g_2\rangle$ hyperfine state, obtained by solving equation (6.32) for $\Delta_{\text{HFS}} = 170.26$ MHz and evaluating the Doppler shift.

space. The full-width at half-maximum of equation (6.29) is found by solving the quadratic equation

$$\frac{(\delta_0 ct - f_0 x)^2}{2\sigma_f^2 c^2 t^2} = \ln 2 \quad (6.30)$$

for time; doing so, we obtain

$$\Delta t = \frac{2f_0 \sigma_f x}{c(\delta_0^2 - \sigma_f^2)\sqrt{\ln 4}}. \quad (6.31)$$

If we attempt to measure small velocities, we must set δ_0 to be small and hence Δt will be large. Condition (6.27) breaks down when the inequality fails⁸. Substituting the position of the peak time in equation (6.29) for t_1 , and repeating the analysis for t_2 , we obtain the expression for the minimum detuning required for the time binning

⁸This can also be seen by noting that, at this point, τ in equation (6.28) becomes undefined.

method to correct this systematic:

$$\frac{\Delta_{\text{HFS}}}{\delta_0^2} = \frac{2\sigma_f}{\sqrt{\ln 4}} \left(\frac{1}{\delta_0^2 - \sigma_f^2} + \frac{1}{(\delta_0 + \Delta_{\text{HFS}})^2 - \sigma_f^2} \right). \quad (6.32)$$

A plot of the minimum velocity that can be obtained whilst removing the confounding effect of $|g_2\rangle$ is shown in figure (6.8). We note that, even with a very broad bleaching profile of width 50 MHz in the frequency domain, the minimum velocity we can determine is still a very reasonable 40m s^{-1} . Using a lower power bleaching laser allows us to successfully explore the ultra-low velocity regions of our beam. We might also expect that, once we have removed the effect of $|g_2\rangle$, we would still have to worry about the detuning-dependent width (6.31) influencing our measurement. However, recall that the width of the bleaching distribution is constant in frequency; this effect is only relevant because we are attempting to remove a systematic effect in the time domain before evaluating the integrals.

If we know the bleaching profile $g(t - t_0)$, we can write down a better approximation of the underlying velocity distribution using functions of the measured distribution. Let's suppose that our measurement process has associated with it some systematic error $S(t_0)$, such that

$$M(t_0) = u(t_0) + S(t_0). \quad (6.33)$$

What happens if we analytically re-sample our measured data using the known bleaching profile? We will obtain a new measurement, $M_1(t_0) = \int_0^\infty M(t)g(t - t_0) dt$, with associated systematic error $S_1(t_0)$:

$$M_1(t_0) = M(t_0) + S_1(t_0). \quad (6.34)$$

Now, if $M(t_0) \approx u(t_0)$, and $M_1(t_0) \approx M(t_0)$, we should expect that $S(t_0) \approx S_1(t_0)$, and hence we can substitute equation(6.34) into equation(6.33) to obtain

$$u(t_0) \approx 2M(t_0) - M_1(t_0). \quad (6.35)$$

This forms a first-order correction to $M(t_0)$, and is based on the assumption that the systematic error is roughly independent of the details of the system we are trying to measure. Of course, this is not necessarily the case; for example, we might imagine that successive measurements increase the systematic error by a factor $\epsilon(t_0)$. To properly evaluate this system, we must use a second-order correction based on two

re-samplings:

$$M(t_0) = u(t_0) + S(t_0) \quad (6.36)$$

$$M_1(t_0) = M(t_0) + S(t_0) + \epsilon(t_0) \quad (6.37)$$

$$M_2(t_0) = M_1(t_0) + S(t_0) + 2\epsilon(t_0) \quad (6.38)$$

$$\implies u(t_0) = 3[M(t_0) - M_1(t_0)] + M_2(t_0). \quad (6.39)$$

We note that for both the first- and second-order corrections, we have assumed nothing about the width of the bleaching distribution or its form. However, the bleaching profile itself may well prove difficult to measure experimentally, and a theoretical line may be required instead if this method is pursued.

We now have three methods to attempt to remove any systematic errors in our measurement: first- and second-order re-sampling schemes and a time-binning scheme. We wish to evaluate the effectiveness of these methods in a quantifiable way, relative to the uncorrected data and our theoretical predictions. I have chosen three figures of merit for data processed by the three methods: the error in the mean value relative to the true value, the error in the distribution full-width at half-maximum relative to the true value, and the total error with respect to the theoretical curve, defined as

$$Q = \sqrt{\sum_j (\bar{M}(t_j) - T(t_j))^2 / \sum_j T(t_j)}, \quad (6.40)$$

where $\bar{M}$ is the data we wish to test and T is the theoretical line. If a measured, processed distribution matches theory perfectly, $\bar{M}(t_j) = T(t_j)$ and hence Q is zero. On the other hand, if our distribution is not a good match to the (in this case, known) true value at any point, this behaviour is captured in an increase in Q . The errors in the means and widths do not capture the global similarities between two distributions—for example, we can easily define a top-hat function and a Gaussian function with the same width and mean, yet one can hardly be said to be a good approximation of the other. The areas which contribute the most to Q can be found from the instantaneous error between theory and measurement, plots of which are shown in figure (6.11) as a function of pump laser power and velocity.

We first compare the “raw” data, computed via equation (6.19), with the time-binned data, obtained by judicious application of equation (6.28) with τ defined as the point at which bleaching and pumping exactly cancel. At low pump powers the time-binning process provides a better approximation than the raw data to the underlying velocity distribution as can be seen in figure (6.9). At high pump powers the

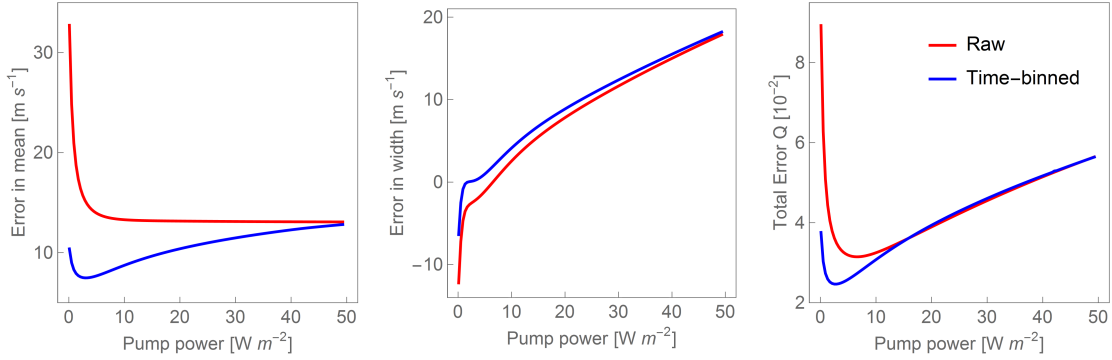


Figure 6.9: Three determinations of the error between measured data and theory for unprocessed (“raw”) and time-binned data. The time-binning process produces results closer to the true values of the mean and overall shape of the distribution for low pump powers, but overestimates the width with respect to the raw data.

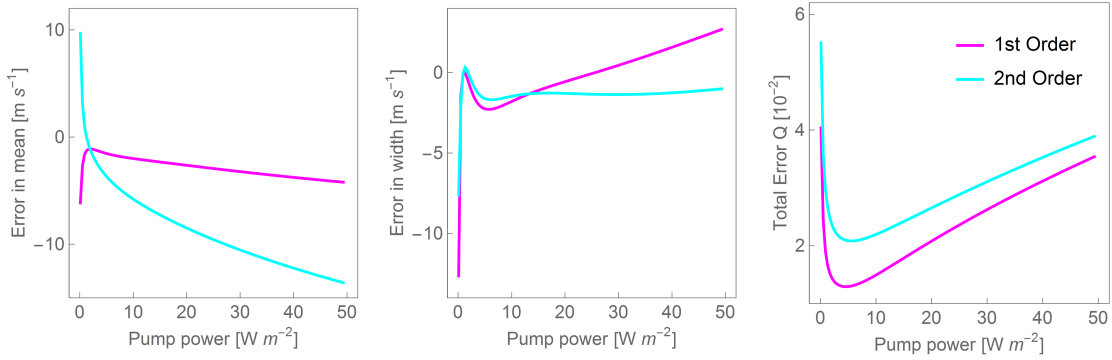


Figure 6.10: Three determinations of the error between measured data and theory for the first-order and second-order methods outlined in equations (6.35) and (6.39). The first-order scheme generally gives the most accurate representation of the true distributions of all three methods proposed in this section, with a minimum Q value of 1.29×10^{-2} .

accuracy of the two measurements converge. This convergence can be understood by realising that, at high pump power, we can no longer treat the bleaching and pumping as spectrally separate phenomenon—rather, the widths σ_1 and σ_2 of g_1 and g_2 increase to the point at which condition (6.27) fails.

The re-sampling schemes defined in equations (6.35) and (6.39) are in principle rather more accurate than the time-binned and raw data, as they aim to remove both our systematic effects rather than just the effect of the lower hyperfine state. Re-sampled data is obtained directly from the raw data and the theoretical bleaching profiles. The Q -value and errors in the mean and width for these schemes are plotted against pump power in figure (6.10). We see that both Q and the error in the mean is generally minimised using the first-order re-sampling scheme. The first order scheme also provides the most accurate measurement of the distribution width between 3.7 and 13.3 W m⁻², dropping to the second most accurate at high powers. At first glance, this method seems ideal—it takes our systematically biased data, and transforms it into data which reproduces our underlying system with great accuracy. However, note that we have cheated somewhat in using a *theoretical* curve to “clean up” experimental data. All is not lost however, as estimations of the bleaching profile can be determined experimentally once we have an approximate velocity profile from the raw data.

We can also examine the impact of the various error-correction schemes on individual velocity classes within our beam. In figure (6.11) contour plots of the instantaneous difference between theory and “measurement” are mapped for the different velocity classes and pump laser powers, with our figure of merit being

$$Q_{v,LP} = 10^2 [\bar{M}(t_j) - T(t_j)] / \sum_j T(t_j). \quad (6.41)$$

Recall from the earlier figure (6.6) that the bleaching scheme tended to overestimate the population in the high-velocity tail of the distribution, whilst underestimating the population near the peak. The tested distribution is peaked at ≈ 200 ms⁻¹. By mapping equation (6.41) over all laser powers, we can check to what extent this holds in both the high and low power limit for the cases of raw data, time-binned data, and first-order corrected data (left to right in figure (6.11) respectively). Examining the general features of all three contour plots, we see that in all cases the method continues to underestimate the peak and overestimate the population in the tail. However, there is a marked improvement in the case of first-order correction, which is subject to these two distortions significantly less than the raw and time-binned data. The time-binned data performs fractionally better in the very low (< 10 W m⁻²) power case, but at high intensity the raw and time-binned data are essentially indistinguishable.

Exactly which correction scheme is best depends on the nature of the experiment

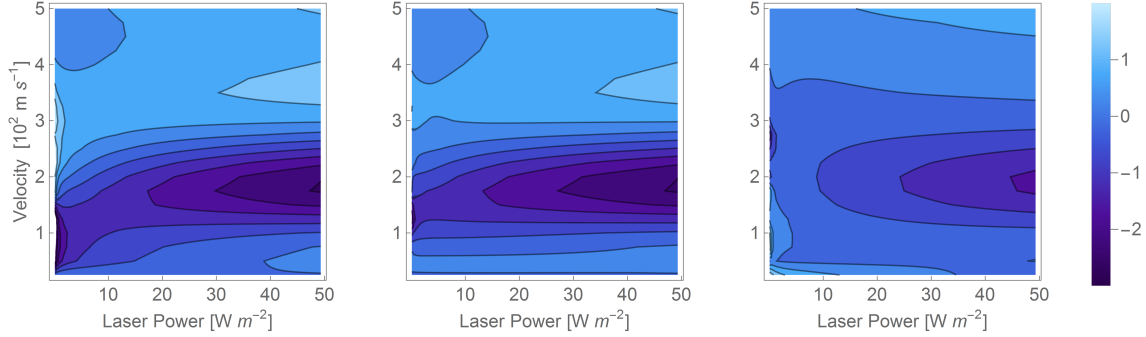


Figure 6.11: $100\times$ the instantaneous error between theory and measured data, defined as $10^2 [\bar{M}(t_j) - T(t_j)] / \sum_j T(t_j)$, for raw data (left), time-binned data (middle), and first-order corrected data (right). All schemes under-estimate the amplitude of the peak; however, this is minimised for the first order scheme. The time-binned and raw data also over-estimates the high velocity tail of the distribution, and error which is again reduced by the first-order correction.

being performed. If the goal is to extract information about the mean value of a fast velocity distribution and little is known about the internal structure of the molecule, then a low power pump and a time-binning scheme is appropriate. On the other hand, if the internal structure is well known and a detailed assessment of the very lowest velocities in the beam is needed, then re-sampling is more appropriate. If the means or widths need to be determined exactly, then careful control of pump power and a judicious choice of correction scheme will also yield satisfactory results. Ultimately, while there are systematic effects in this measurement scheme, their effect can be minimised as long as the molecular species is well understood.

6.7 Is the bleaching scheme viable?

We have proposed a scheme to measure the velocity distribution of a molecular beam by using the detuning-dependent transition rate between two internal molecular states. An experiment using a beam of known velocity distribution has been simulated. The internal states of the molecules were treated *via* a 4-level toy system, with the optical Bloch equations for the states solved exactly using the formalism of appendix (B.6). The measurement was shown to be rigorously independent of the details of the molecular source, and gave qualitatively good agreement with the

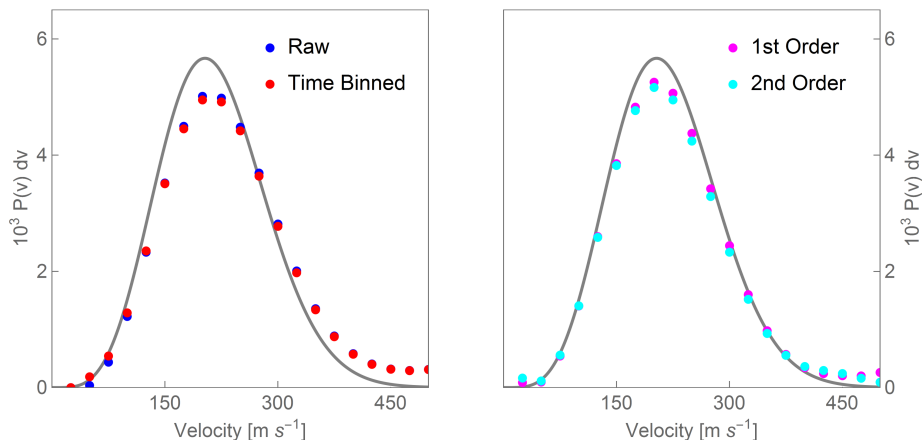


Figure 6.12: Raw, time binned, first-order re-sampled, and second-order re-sampled velocity distributions for 25 W m^{-2} , compared to theory (grey, solid line). Time binning does very little due to the comparatively high pump power. The first-order and second-order re-sampling schemes provide a better measure of the underlying distribution.

known distribution.

The systematic errors of the system were also examined, with the width of the bleaching distribution and the impact of other close-lying internal states both being potential problems. A simple time-binning scheme was proposed to remove the effect of unwanted internal states; this was shown to give a more accurate representation of the true distribution than the raw data for low pump power. A more complicated scheme based on re-sampling data with a known bleaching profile was also proposed. This second analysis method gave the best agreement with theory, but relied on detailed prior knowledge of the system in question. Comparisons of all three processing techniques with the theoretical curve are shown in figure (6.12).

We conclude that the bleaching scheme is a viable measurement option. A naive approach may induce unwanted bias, but with care the measurement can provide good quality data with systematics that are amenable to various simple analysis schemes. Using a low-power pump is important if little prior knowledge of the molecular system is available; conversely, if the system is already well understood then a high-power pump can be used to increase the difference signal $\mathcal{D}$, with the arising

errors treated analytically.

6.8 The velocity distribution after N collisions

Now we have a new technique for measuring velocity distributions, but how should we interpret our data? So far, we have been navigating by scaling arguments and experimental analysis. We know the number of collisions required in the second cell to within a factor of two, but are unable to make predictions as to the form of the resulting velocity distribution. In his seminal paper, Doyle [96] used as a sensible ansatz the effusive distribution, fitting it to his data and obtaining good agreement as long as the beam temperature is allowed to float. However, is this really what we expect? The traditional model for an effusive beam is one which arises from a large, low pressure, thermal cell, where molecules leave by diffusing through the aperture. It is not at all obvious that the same distribution should arise when we collide a hydrodynamic beam into a background and see what escapes from the other side.

In this section, we examine the evolution of the velocity distribution of a molecular beam under the action of collisions between it and some other distribution. We will ignore the specifics of the He–YbF interaction potential, instead modelling the colliding species as two rigid spheres whose dynamics can be parametrised from their momenta and the impact parameter b . Additionally, we assume that the elastic cross section of the interaction is much larger than the inelastic cross section, such that the dominant role of a collision is to change the particle momentum rather than the internal state. Further, we will operate in a density regime where the role of three-body collisions are negligible.

We begin by considering the interaction between a single helium atom and a YbF molecule. Using equation (2.46) to transform into the centre of mass frame, we can express the helium velocity $\tilde{\mathbf{v}}_{\text{He}}$ and the YbF velocity $\tilde{\mathbf{v}}_{\text{YbF}}$ in terms of the relative velocity $\tilde{\mathbf{v}}_{\text{r}} = \tilde{\mathbf{v}}_{\text{YbF}} - \tilde{\mathbf{v}}_{\text{He}}$ via

$$\tilde{\mathbf{v}}_{\text{YbF}} = \frac{m}{m+M} \mathbf{v}_{\text{r}} \quad (6.42)$$

$$\tilde{\mathbf{v}}_{\text{He}} = -\frac{M}{m+M} \mathbf{v}_{\text{r}}. \quad (6.43)$$

Within the centre of mass frame, the problem reduces to one in which a particle with velocity $\tilde{\mathbf{v}}_{\text{r}}$ scatters from a fixed point. If we define an axis $\hat{\mathbf{z}}$ along $\tilde{\mathbf{v}}_{\text{r}}$, we can cast the problem in a cylindrical co-ordinate system where the collision exhibits

azimuthal symmetry. The action of the collision is therefore to scatter the particle with velocity $\tilde{\mathbf{v}}_r = |\tilde{\mathbf{v}}_r|\hat{\mathbf{z}}$ into some angle χ in the $\hat{\mathbf{z}} - \hat{\mathbf{r}}$ plane such that the velocity after the collision is

$$\tilde{\mathbf{v}}_r^* = |\tilde{\mathbf{v}}_r|(\hat{\mathbf{z}} \cos \chi + \hat{\mathbf{r}} \sin \chi). \quad (6.44)$$

We will define post-collision quantities through the star superscript. Now, in a typical experiment we only care about the forward velocity of our beam. We will therefore project the momentum onto the $\hat{\mathbf{z}}$ axis; doing so, we obtain

$$\hat{\mathbf{z}} \cdot \tilde{\mathbf{v}}_r^* = \hat{\mathbf{z}} \cdot \tilde{\mathbf{v}}_r \cos \chi \quad (6.45)$$

$$\implies \hat{\mathbf{z}} \cdot \tilde{\mathbf{v}}_{\text{YbF}}^* = \hat{\mathbf{z}} \cdot \tilde{\mathbf{v}}_{\text{YbF}} \cos \chi \quad (6.46)$$

$$\implies \hat{v}_{\text{YbF}}^* = \hat{v}_{\text{YbF}} \cos \chi, \quad (6.47)$$

where, as we are only concerned with the axial projection, we have dropped the vector notation. Transforming both sides of equation (6.47) back into the lab frame, we find that

$$(v_{\text{YbF}}^* - V_C^*) = (v_{\text{YbF}} - V_C) \cos \chi \quad (6.48)$$

and, as there is no external force on the system, $V_C^* = V_C$. Simplifying equation (6.48) and solving for the lab-frame velocity after the collision, we obtain

$$v_{\text{YbF}}^* = \frac{Mv_{\text{YbF}} + mv_{\text{He}} + m \cos \chi (v_{\text{YbF}} - v_{\text{He}})}{m + M}. \quad (6.49)$$

As a useful sanity check, note that the collision which maximally changes the YbF velocity ($\cos \chi = -1$) reduces equation (6.49) to the form (5.6), and the minimally-changing collision ($\cos \chi = +1$) corresponding to the no scattering case gives $v_{\text{YbF}}^* = v_{\text{YbF}}$ as required.

We now need to calculate the probability that, given a collision has occurred, we scatter into some angle χ . We access this by first calculating the probability $P(b) db$ of a collision having an impact parameter b lie in the range $b \rightarrow b + \delta b$, then use the known relation between b and χ to obtain our final expression. From the azimuthal symmetry of the problem, $P(b)$ must be proportional to the cylindrical element $b db$,

$$P(b)db = A b db, \quad (6.50)$$

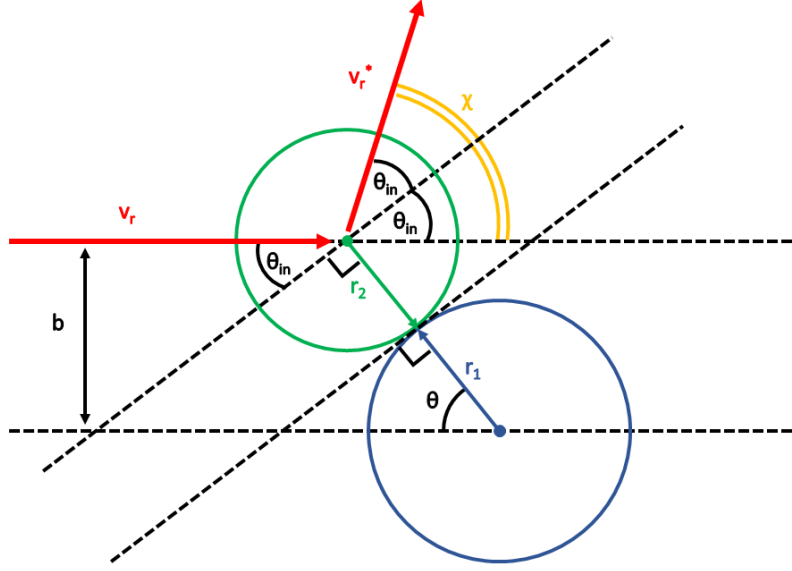


Figure 6.13: Geometry of the collision of two hard spheres in the centre of mass frame. The green particle enters the collision from the left before meeting the colliding centre, represented by the blue circle. We define an instantaneous plane perpendicular to the touching surface of r_1 and r_2 ; the scattering relative to this plane follows the usual elastic property $\theta_{\text{in}} = \theta_{\text{out}}$. The collision scatters v_r into the angle χ which can be easily seen to obey $\chi = 2\theta_{\text{in}}$, and $\theta_{\text{in}} = 90^\circ - \theta$. The angle $\theta = \arcsin(b/r_1 + r_2)$ follows via trigonometry.

where A is a constant of proportionality to be determined. From the normalisation condition and recalling that $0 \leq b \leq r_1 + r_2$,

$$\int_0^{r_1+r_2} P(b) db = A \int_0^{r_1+r_2} b db = 1 \quad (6.51)$$

$$\implies A = \frac{2}{(r_1 + r_2)^2} \quad (6.52)$$

$$\implies P(b) db = \frac{2b}{(r_1 + r_2)^2} db. \quad (6.53)$$

Now we must determine $b(\chi)$. Referring to figure (6.13), at the moment of collision we have

$$\sin \theta = \frac{b(\chi)}{r_1 + r_2}, \quad (6.54)$$

with $\theta = (\pi - \chi)/2$. From the chain rule,

$$P(b) db = P(b(\chi)) \frac{db}{d\chi} d\chi \quad (6.55)$$

and, inserting equation (6.54) into the derivative and simplifying using the double-angle formula, we finally obtain

$$P(\chi) d\chi = \frac{1}{2} \sin \chi d\chi. \quad (6.56)$$

Note that the mean scattering angle $\bar{\chi} = \int_0^\pi \chi P(\chi) d\chi = \pi/2$, from which we obtain the average change in forward velocity in a collision as

$$\left\langle \frac{d}{dN} v_{\text{YbF}} \right\rangle = \frac{m}{m+M} (v_{\text{He}} - v_{\text{YbF}}), \quad (6.57)$$

and we have therefore proved our assertion in section (5.2) that, on average, twice as many collisions are required in 3D than 1D to boost molecules by a given velocity.

We have obtained expressions for the post-collision YbF velocity as a function of the pre-collision YbF velocity, helium velocity, and scattering angle χ . The probability distribution for the scattering angle, $P_\chi(\chi) d\chi$ has also been determined. We now have everything we need to determine the form of the YbF velocity distribution following a collision with a background gas atom. To begin, consider some set of initial parameters $(v_{\text{YbF}}, v_{\text{He}}, \chi)$. Then, from equation (6.49) the post-collision velocity is known. If the initial helium and YbF velocity distributions $P_{v_{\text{YbF}}}(v_{\text{YbF}})$ and $P_{v_{\text{He}}}(v_{\text{He}})$ are known, then the probability of obtaining v_{YbF}^* from this combination of parameters is

$$P_{v_{\text{YbF}}^*}(v_{\text{YbF}}^*) dv_{\text{YbF}}^* = P_{v_{\text{YbF}}}(v_{\text{YbF}}) P_{v_{\text{He}}}(v_{\text{He}}) P_\chi(\chi) dv_{\text{YbF}} dv_{\text{He}} d\chi. \quad (6.58)$$

To obtain the total probability of obtaining v_{YbF}^* , we note that equation (6.49) acts as a constraint on the allowed permutations of $(v_{\text{YbF}}, v_{\text{He}}, \chi)$. Imposing this constraint and integrating over all allowed permutations, we find that

$$\begin{aligned} P_{v_{\text{YbF}}^*}(v_{\text{YbF}}^*) dv_{\text{YbF}}^* &= A \int_0^\pi d\chi \int_{-\infty}^\infty dv_{\text{YbF}} P_{v_{\text{YbF}}}(v_{\text{YbF}}) P_\chi(\chi) \\ &\quad \times P_{v_{\text{He}}} \left(\frac{[M+m]v_{\text{YbF}}^* - [m \cos \chi + M]v_{\text{YbF}}}{m(1 - \cos \chi)} \right). \end{aligned} \quad (6.59)$$

Here A is a constant of proportionality, chosen to fix the normalisation of $P_{v_{\text{YbF}}}^* dv_{\text{YbF}}^*$. Given some suitable initial velocity distributions, equation (6.59) can be applied iteratively to find the resulting distribution after some N collisions. As we are summing over all the possible collision combinations for each final velocity, we will refer to this method as the “permutation summing” method.

As a test to see if the method of equation (6.59) is sensible and valid, we have used it to analyse the two-stage beam source of CaH first shown in the original two-stage cell paper [96]. In figure (5) of that paper, the velocity distribution from a source with a 160 μm mesh aperture is measured and found to peak at $\approx 40 \text{ m s}^{-1}$. It is claimed that the resulting distribution is effusive, with fitted temperature of $3.6 \pm 0.6 \text{ K}$.

We begin our analysis by taking sensible ansatz functions for the initial CaH and He velocity distributions. As it only takes the helium $\approx (m + m)/m = 2$ collisions to thermalise in the second stage, we will assume that the helium distribution here can be taken to be the 1D thermal velocity distribution

$$P_{v_{\text{He}}}(v_{\text{He}}) = \sqrt{\frac{m_{\text{He}}}{2\pi k_B T}} \exp\left(-\frac{m_{\text{He}} v_{\text{He}}^2}{2k_B T}\right), \quad (6.60)$$

where $T = 1.8 \text{ K}$ is the measured temperature of the second stage. From the measured number density in the first stage, $\text{Kn} \approx 0.024$ and hence the CaH beam is close to being fully hydrodynamic. We assume that the CaH molecules are fully entrained in the helium beam from the first stage, and that in the absence of any further knowledge the He beam follows an effusive distribution at 2.5 K, with the temperature set from the measured thermalisation properties within the cell.

Next we must determine the range of collisions we wish to examine. In the absence of vents or inter-cell spacers, the maximum number density in the second stage may be calculated via the application of equation (2.13); taking the exit velocity to be the effusive helium beam velocity at 1.8 K, we find that the maximum number density is $n_{\text{max}} \approx 1.5 \times 10^{21} \text{ m}^{-3}$ and a maximum of ≈ 30 collisions are expected in the second stage.

We must also consider the action of collisions outside the cell, within the beam. As we are working in the effusive regime, the beam divergence is known. For a detector 3 mm from the source, as in Doyle’s experiment, we expect ≈ 1.1 forward-boosting collisions in the beam for every 10 in the second stage cell. We also note

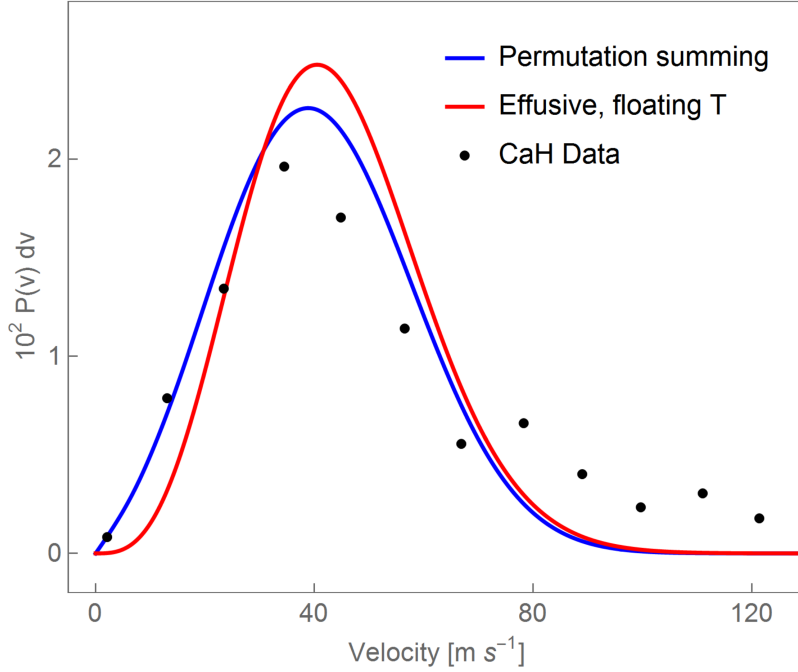


Figure 6.14: Result of applying the permutation-summing method of equation (6.59), with the number of collisions giving a best fit solution to the CaH data. It is compared to a fitted effusive beam distribution with the temperature as the free parameter.

that simply stating the expected number of collisions isn't enough—as we are working with distributions rather than means, we must sum over the contributions from all collision numbers, weighted by an appropriate probability distribution. As we know the mean number of collisions $\bar{N}$ within the beam and wish to know the probability that a molecule experiences N , we use a Poisson distribution for the weighting.

We have performed this process, the results of which are shown in figure (6.14) for 25 collisions in the second stage cell. Taking the ratio of the residual sum of squares for the permutation-summing and effusive models gives 0.58, showing that the permutation-summing curve is on average closer to the data than the effusive curve. However, it is difficult to say if this figure of merit is statistically significant due to the lack of error bars in the source material—we do not know if our model is predicting an exact distribution or a noisy signal. The number of collisions is somewhat higher than that predicted in [96] (an upper limit of 10 is set there) but our prediction isn't completely outlandish—solving equation (6.57) for this case suggests that we would require at least 14 collisions with the background gas to reduce the

forward velocity to 40 m s^{-1} , and to that we must factor in the reboosting outside the cell which is of the order of 10^{-1} for the first collision. Also note that our effusive fitting function is for that of an effusive beam, rather than a thermal cloud as in [96], where additionally both the temperature and amplitude are allowed to float. In the effusive distribution the temperature defines both the width and amplitude of the peak⁹ as the area under the curve must be normalised. Allowing the amplitude to float breaks this restriction, giving un-normalised fitting functions that are not in general probability distributions.

We have also assumed the forms of the velocity distribution from the first stage and the helium distribution in the second stage. Whilst both assumptions are reasonable given the flow rate, it is hard to test the model further without better knowledge of these distributions. However, it is also clear that the effusive fit describes the data to an even worse degree. Where the permutation-summing model has an edge is that it allows insight into the various processes ongoing in both the beam and the cell. For example, the final beam distribution arises from the trade-off between deceleration in the second stage, and re-acceleration in the beam. If we know the mean velocity of our molecules as they leave the first cell, the velocity at a downstream detector after the second stage follows by solving equation (6.57) inside the second cell, then using this solution as our initial molecular velocity in the beam. Performing this calculation, we find that

$$v(N_2, N_{c \rightarrow d}) = \bar{v}_f - \left[\bar{v}_f - v(0) \exp \left(-\frac{mN_2}{m+M} \right) \right] \exp \left(-\frac{mN_{c \rightarrow d}}{m+M} \right), \quad (6.61)$$

where v_f is the forward helium velocity from the second stage, $v(0)$ is the initial molecular velocity from the first stage, N_2 is the number of collisions in the second stage, and $N_{c \rightarrow d}$ is the number of collisions between the exit of the second stage and the detector. If the beam divergence is known (as it is in the effusive case), we may link N_2 and $N_{c \rightarrow d}$ using the continuity equation. In the limit of small changes to the forward velocity over the flight to the detector, we obtain the upper bound to the number density in the beam:

$$n_{c \rightarrow d} \leq N_2 \frac{r^2}{(r + z \tan \theta)^2}. \quad (6.62)$$

Here z is the distance to the detector and θ the divergence half-angle, which is known to be 60° for an effusive beam. We make use of equation (6.61) in the following section to interpret our data.

⁹The amplitude dependence arises from the cofactor $\bar{v}$.

6.9 Measuring beams of YbF using the optical bleaching method

Using the optical bleaching method laid out in section (6), we have obtained the forward velocity distributions of molecular beams produced from our two-stage source. We begin by examining the third cell configuration, with the extended second cell separated from the unextended first stage by 2 mm. The fine 170 μm mesh was applied to the side vents. To generate the pump and probe beams, two separate frequency-doubled diode lasers were first locked to the un-Doppler shifted ^{174}YbF Q(0) F = 1 transition within the molecular spectrum, and then the beam path of one laser was switched onto the co-axial path using flip-mounted mirrors. The co-axial laser, set at an intensity of 14 Wm^{-2} was pulsed on for 50 μs at a time, and the resonant time-of-flight profile obtained by performing LIF using the perpendicular beam at a detection region 5.5 cm from the cell exit. The co-axial laser frequency was then red-detuned by a fixed amount (usually 150–200 MHz), with the relative frequency between the co-axial and perpendicular beams set to within an instantaneous worst-case deviance of ± 10 MHz using a transfer cavity lock scheme. The source of this error was later found to be in the temperature feedback of one of the lasers, but this was not known at the time of the measurement.

In order to evaluate the velocity distribution, we use the time-binning method demonstrated in section (6.6) to remove the effects of the hyperfine structure as best as possible. The normalised difference signal is defined as

$$\Delta(\delta, t) = \frac{(\text{pump off} - \text{pump on})}{\int \text{pump off } dt}, \quad (6.63)$$

and the number of molecules $N(v) dv$ with velocities in the bin dv is given by the integral

$$N(v) dv = dv \int_{t_0}^{t_1} \Delta\left(\frac{vf_0}{c}, t\right) dt. \quad (6.64)$$

The time-binning scheme amounts to choosing t_0 and t_1 such that only molecules within our target quantum state contribute to the total integral. The typical form of $\Delta(\delta, t)$ is shown in the rightmost panel of figure (6.15). Molecules pumped from our target state at velocity $v = v_0$ contribute to the regions where $\Delta > 0$, whilst molecules pumped into F = 1 from F = 0 at velocity $v' = v_0 + \Delta_{\text{HFS}} c/f_0$ give rise to the regions with $\Delta < 0$. A full discussion is given in chapter (6), but in practice the time-binning method involves choosing t_0 such that only regions with $\Delta > 0$

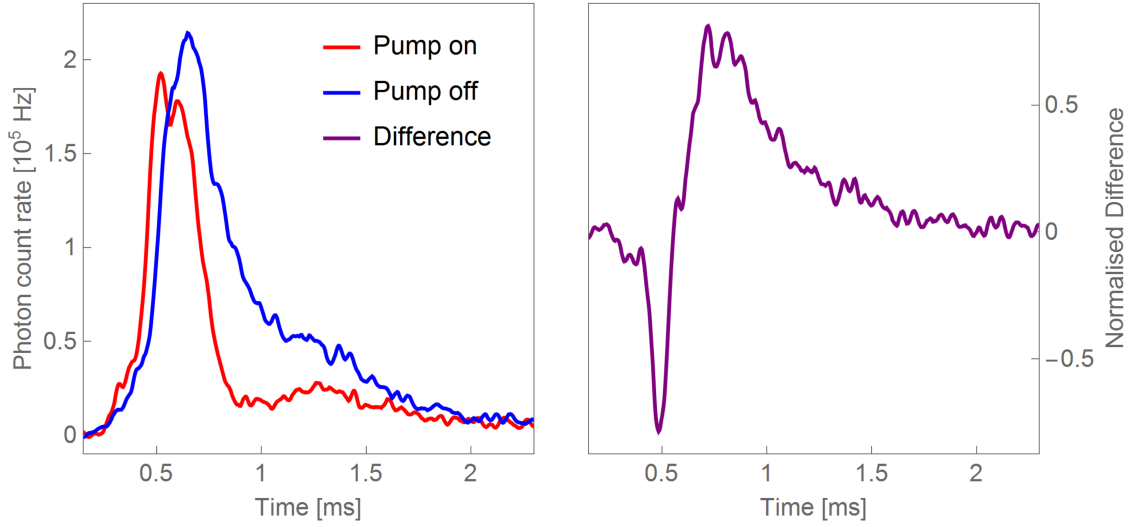


Figure 6.15: Comparison of the recorded time-of-flight distributions with the pump on and pump off for a (280 ± 10) MHz detuned pump laser (left panel), and the normalised difference signal $(\text{pump off} - \text{pump on}) / \int \text{pump off } dt$ at the same detuning (right panel).

contribute to the integral in equation (6.64).

Using this technique, we have obtained velocity distributions for helium flow rates of 2, 4, 6, and 8 SCCM from the third cell configuration, where the extended second stage is separated from the first stage by 2 mm. In figure (6.16) we show two contrasting distributions, obtained at 2 SCCM and 4 SCCM respectively. In this case, increasing the helium flow rate reduces the mean velocity of the distribution from $(172 \pm 9) \text{ m s}^{-1}$ to $(143 \pm 7) \text{ m s}^{-1}$. The means were calculated using the discrete integral

$$\langle v \rangle = \Delta v \sum_j v_j P(v_j), \quad (6.65)$$

from which the associated errors follow via the usual propagation techniques. Further increases to the helium flow rate were enough to increase the mean velocity to $\approx 160 \text{ m s}^{-1}$, as shown in figure (6.17). This behaviour can be understood from our discussions in section (6.8), where increasing the pressure in the second cell has diminishing returns on the amount of slowing provided whilst giving significant reboosting of the molecules in the beam. To this end, we have used equation

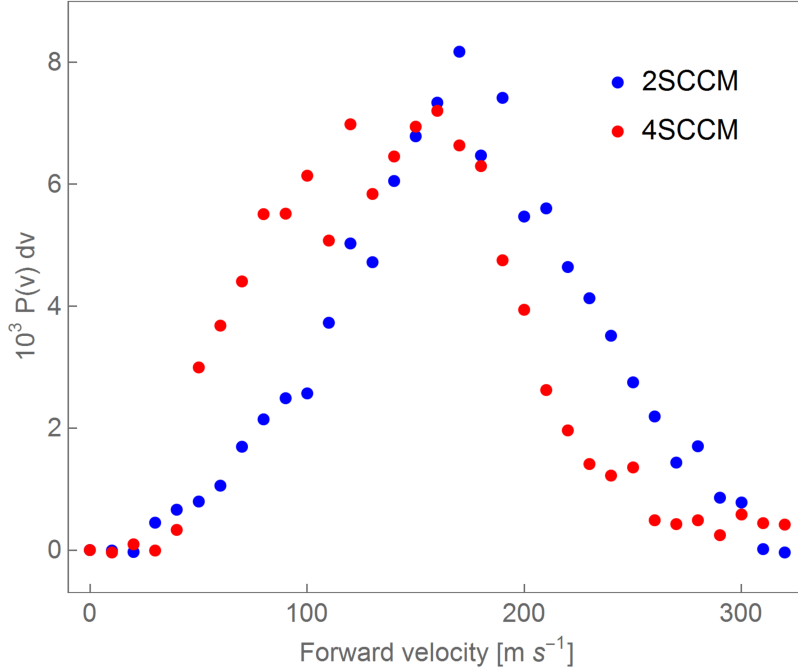


Figure 6.16: Velocity distributions obtained for helium flow rates of 2 SCCM and 4 SCCM using the bleaching technique.

(6.61) to perform a fit to the data. The YbF was assumed to be initially fully entrained in the helium flow such that $v(0) = \bar{v}_f$, giving three free parameters in the fit—the helium forward velocity, the number of collisions in the second stage, and the number of collisions in the beam. Further, taking inspiration from equation (2.13) we set both N_2 and $N_{c \rightarrow d} \propto dV/dt$, the helium flow rate. The fitting values are found to be $v_f = (249 \pm 69) \text{ m s}^{-1}$, $N_2 = (12.3 \pm 7.6) [\text{SCCM}^{-1}] dV/dt$, and $N_{c \rightarrow d} = (5.4 \pm 1.8) [\text{SCCM}^{-1}] dV/dt$.

Despite the uncertainties in the fit, we can infer some useful information from the procedure. The minimum mean velocity is reached around 4 SCCM, and the behaviour of the mean is fundamentally unexplainable using the theory of a one-stage source. The number of collisions in the second stage required to reduce the YbF forward velocity from v_0 to its effusive limit is 119 ± 14 , which from the fit occurs when the helium flow rate is ≈ 10 SCCM. However, by this point the number of collisions in the beam is expected to have increased markedly, with $N_{c \rightarrow d} \approx 54$ expected. In order to see lower velocities, we will have to reduce the number density in the beam, whilst maintaining the number of collisions in the second stage, which can be done

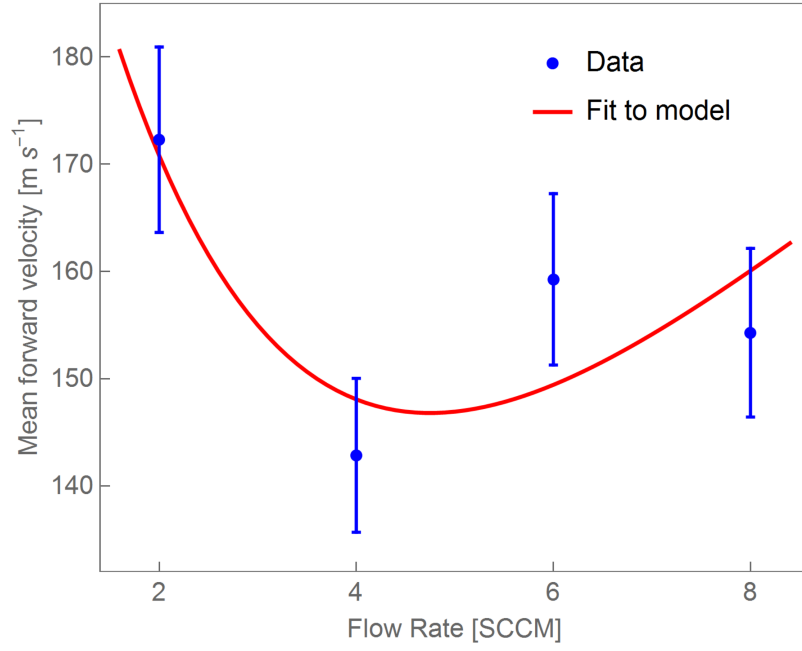


Figure 6.17: Mean velocities obtained from our measured distributions, as a function of helium flow rate. The fitting model is given in equation (6.61) and suggests that the final beam velocity is the result of interplay between deceleration in the second stage and re-acceleration after the second cell aperture.

by reducing the total helium flow and increasing the length of the second stage.

We have also measured the velocity distribution without the second stage; a plot of the distribution at 2 SCCM is compared to the distribution obtained using both stages in figure (6.18). The velocity distribution from the single-stage source is again bifurcated, a feature that we have seen previously in our work on the hybrid source. The mean of the single-stage distribution is $(169 \pm 5) \text{ m s}^{-1}$, which is consistent with two-stage mean velocity within error. Thus, at low flows and with the current set-up, collisions within the second stage act to thermalise the distinctly non-thermal distribution obtained from the first stage. The exact thermalisation process is currently unclear; the action of collisions with a thermal background will cause the shape of the velocity distribution to tend towards a Gaussian due to the central limit theorem. However, inserting the single-stage distribution shown in figure (6.18) as the initial YbF distribution in equation (6.59), we have found that for both thermal and effusive helium backgrounds it will take of the order of 50 collisions to fully thermalise. From our fitted values of N_2 and $N_{c \rightarrow d}$, the total number of collisions experienced by a molecule after leaving the first cell is $N_2 + N_{c \rightarrow d} = 35 \pm 16$, so this explanation for the difference in shape is feasible within the uncertainties involved.

The fast peak of the single-stage distribution can be understood by including the ablation process into our discussion. The fast peak has modal velocity $v_{\text{peak}} = 232 \text{ m s}^{-1}$, and is completely distinct from the slow peak. Now, at helium flows of 2 SCCM and ablation energies of 40mJ per shot, we can calculate the extent of the ablation plume using equation (3.17), taking the measured laser diameter of 1 mm and Yb reflectivity of $\approx 35\%$. Regardless of the helium flow regime, we find that the plume size is greater than the cell diameter, and we expect that the ablation process will affect the gas flow properties in the cell. Now, YbF molecules emitted towards the cell aperture will experience 68 collisions before leaving the cell; assuming an initial temperature of 2000 K ¹⁰ and a buffer gas temperature of 5 K, the final molecular temperature when leaving the cell will be $\approx 140 \text{ K}$. The thermal YbF velocity at this temperature is 123 m s^{-1} , which is less than the maximum supersonic helium velocity at 5 K of 230 m s^{-1} . Therefore, we might expect that the fast peak is formed of hot YbF molecules that have been swept from the cell by a pressure wave induced by the ablation process. Additionally, the molecules detected at v_{peak} have an average free-flight time of $213 \mu\text{s}$ to the detector, corresponding to a forward velocity of $v_f = x/t = 235 \text{ m s}^{-1}$; comparison to v_{peak} suggests that the molecules in

¹⁰This assumption is motivated by our earlier discussions of the temperature scale after ablation. If the temperature is significantly hotter, then this effect will only be exacerbated.

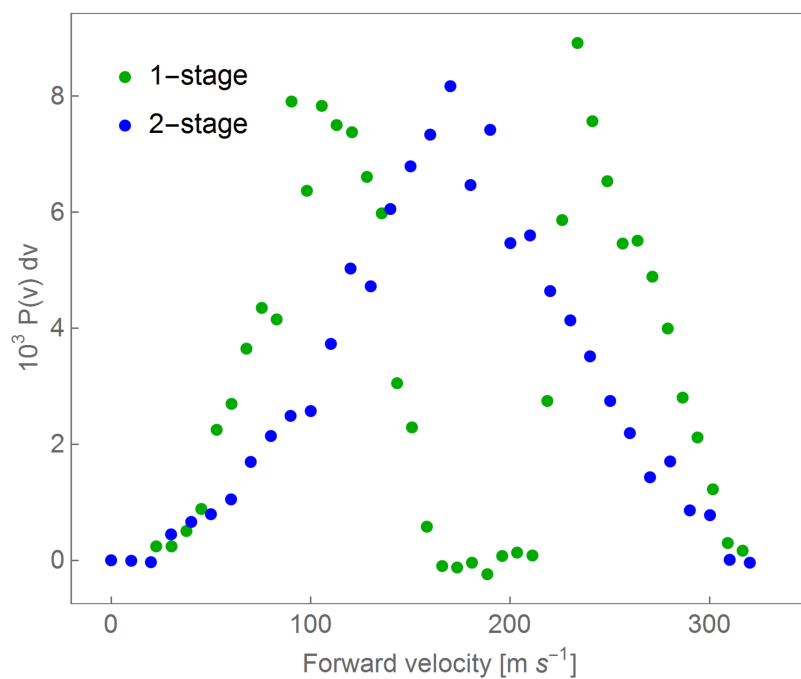


Figure 6.18: Velocity distribution from the single, unextended source (green) compared with the resulting distribution after the second stage, for a helium flow rate of 2SCCM.

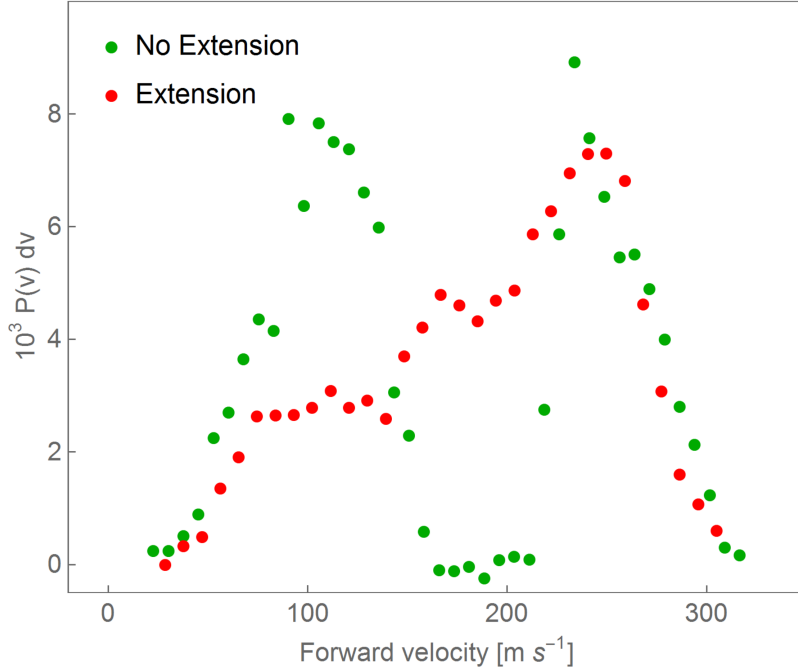


Figure 6.19: Velocity distribution from the single, unextended source (green) compared with the distribution from the extended first stage source (red). The helium flow rate in both cases was 2 SCCM.

the fast peak spend essentially zero time in the buffer gas cell.

Contrast this to the slow peak. We can estimate the number of collisions experienced by a YbF molecule as it diffuses to the exit as the ratio of the diffusion time, given by equation (2.69), to the average time between collisions, given by $\tau_c = \lambda/\bar{v}$. For a YbF molecule to diffuse from the target to the aperture therefore requires $\approx \tau_D/\tau_c = 326$ collisions with the background gas on average, more than enough to cool the molecules to the temperature of the buffer gas. Our interpretation is therefore that the unextended cell has two processes which contribute to its beam dynamics—a non-equilibrium process driven by a helium shock induced by ablation, followed by the slow diffusion of material to the aperture as usual.

We have also tested the extended first-stage cell, as used in configuration 2, and find further encouragement for this interpretation here. Plots of the unextended and extended cell velocity distributions obtained at 2 SCCM are shown in figure (6.19). We see again that the fast peak is present; if this peak were due to thermal effects,

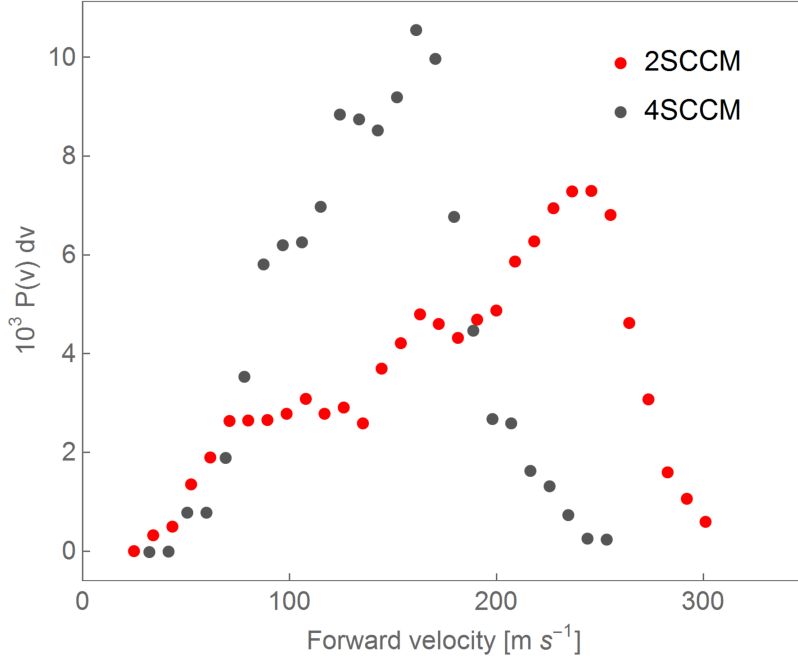


Figure 6.20: Velocity distribution from the extended source, measured at 2 SCCM and 4 SCCM helium flow rates. The fast peak, present for the unextended source, is completely suppressed in the 4 SCCM case, whilst it still remains for the lower 2 SCCM flow.

adding the extension should have suppressed its amplitude. The amplitude of the slow peak is suppressed by a factor of 2.4 compared to the unextended cell, which we may understand by noting that the extender adds 20 mm to the average distance a molecule must diffuse to reach the exit, from 15 mm to 35 mm. The length ratio $35/15 = 2.33$, arising from the increased surface area this extension provides, almost exactly matches the suppression in the peak yield.

The fact that the fast peak is not suppressed is somewhat surprising, as for flows above 3 SCCM we find that using the extender leaves only the slow peak. If a pressure wave is driving molecules from the cell, its energy will be dissipated once the thermal energy of the ablation is transferred to the buffer gas. The Mach number before the shock can be expressed in terms of the pressure differential across the wave via [124]

$$\text{Ma}^2 = \frac{(\kappa - 1) + (\kappa + 1)p_1/p_0}{2\kappa}, \quad (6.66)$$

where p_0 is the background pressure in the cell and p_1 is the pressure behind the shock. The shock will be fully dissipated when $\text{Ma} = 1$, or

$$p_1 = \frac{8}{7} p_0 \quad (6.67)$$

for an ideal gas. Applying the isentropic pressure-temperature relationship (2.25), we obtain the thermalisation condition

$$\left(\frac{8}{7}\right)^{2/5} T_0 \approx 1.055 T_0 = T_1. \quad (6.68)$$

Thus, as long as there are enough elastic collisions to satisfy equation (6.68), the effect of the pressure wave should be negligible. Applying equation (2.61) with an initial temperature of 2000 K subject to this constraint, we find that $N = 226$. With the extender, we expect 151 collisions at 2 SCCM, so the fact that we still have a fast peak is reasonable given this argument. Conversely, at 4 SCCM we expect ≈ 300 collisions within the extended first stage, and this effect should be negligible. Comparison of the measured distributions from the extended cell at 2 SCCM and 4 SCCM are shown in figure (6.20), and as expected the 4 SCCM case has no fast peak¹¹.

6.10 The final configuration—extending both cells

The bleaching method has allowed us to accurately measure the velocity distributions from our cell in the third configuration, and compare the results from this to the extended and un-extended single stage distributions. We have seen evidence that the dominant problem in the experiment is that the pressure in the second stage is too high, leading to an unfavourable number of re-boosting collisions in the beam. Further, we have found that the un-extended single stage produces rather unusual velocity distributions, and have accounted for this behaviour by considering the increase in cell pressure due to ablation. We finally turn to a fourth cell configuration, with extended first and second stages, and parametrise it using our bleaching scheme.

The two-centimetre first cell extender is used as before; additionally, we have constructed a new, extra-long insert that increases the length of the second stage to

¹¹Not shown in this section is the distribution from the unextended cell at 4 SCCM, which displays the same peak-splitting behaviour seen in the 2 SCCM case. In this case $N = 136 < 226$ collisions are expected, and the fast peak is not suppressed.

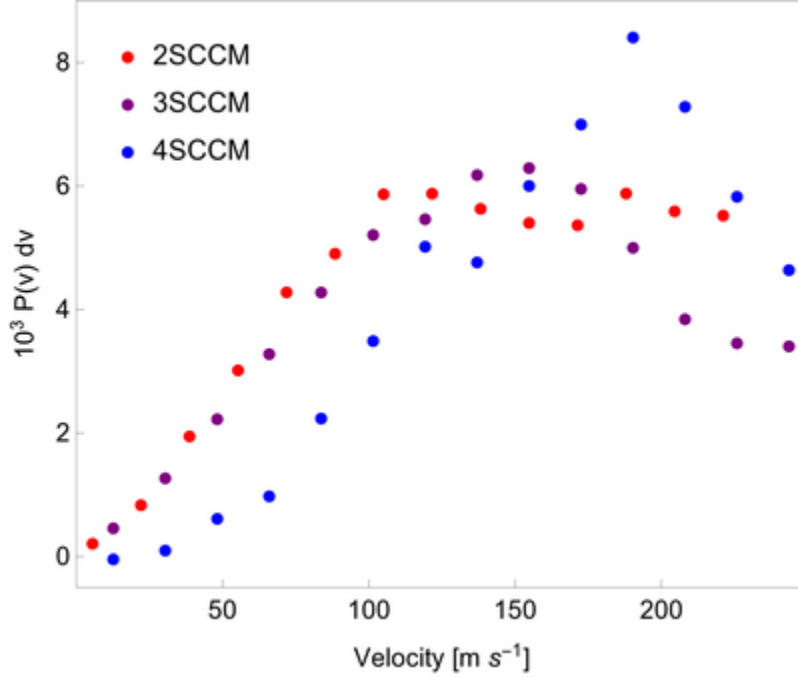


Figure 6.21: Velocity distribution from the fourth and final configuration, consisting of a 5 cm length first stage and a 4.5 cm length second stage cell separated by 2 mm.

4.5 cm. It is hoped that a combination of a long first stage, suppressing the pressure-gradient effects, and a long second stage, allowing a greater number of collisions at low pressure, will be sufficient to observe the slowest molecules to date. The pump power was 25 W m^{-2} , applied in a $50 \mu\text{s}$ time window as before, and the free-flight distance between cell and detector was increased to 22 cm.

The key results from this measurement are shown in figure (6.21). Due to unforeseen experimental circumstances, we were unable to capture the full distribution using the bleaching method, but have managed to obtain data up to and including the distribution peaks for the three flow rates considered here. We observe similar trends to those observed in section (6.8)—that the minimum peak velocities are obtained around 4 SCCM region—but have failed to bring the peak of any of the distributions below our previous best of 70 m s^{-1} shown in figure (5.21) using the third configuration. We can compare the 4 SCCM peak velocities from the extended first-stage source and the fourth-configuration source, obtaining $(129 \pm 5) \text{ m s}^{-1}$ and $(105 \pm 8) \text{ m s}^{-1}$ respectively, suggesting that the second stage in this configuration

is decelerating molecules by $\approx (24 \pm 9) \text{ m s}^{-1}$.

6.11 Comparison of bleaching and Doppler measurements

Our earlier work focussed on checking the validity of this scheme theoretically; based on this work, we used the bleaching technique to continue with the attempted parametrisation of the two-stage source. We would now like to test the measurements produced using this scheme with those from a Doppler-type measurement of the velocity distribution, in order to verify experimentally the validity of this technique. To do this, we will compare our measured distribution to one obtained through the measurement of the Doppler shift of the ^{174}YbF Q(0) line. In order to prevent optical bleaching in the measurement of the Doppler shift, the probe laser was inclined at an angle of 28° to the horizontal; as such, this technique measures the projection of the beam forward velocity onto the k-vector of the probe laser. The two velocity distributions measured using these techniques were obtained consecutively, in order to keep the experimental conditions as constant as possible between tests.

The measurements were performed 22 cm from the source. When the bleaching scheme was being performed, the pump power was fixed at 25 W m^{-2} , applied in a $50 \mu\text{s}$ time window as in the simulations. We used a helium flow rate of 3 SCCM, and the cell was in the fourth configuration as in section (6.10). We analyse the bleaching measurements using the time-binning method, as the two alternative correction methods require knowledge of the full distribution.

The measured velocity distributions are shown in figure (6.22). As in section (6.10), we were unable to obtain the full velocity distribution using the bleaching scheme, but were able to capture the low-velocity tail and the position of the peak. The peak velocities agree to within 5 m s^{-1} between the two measurement schemes, and the overall shape is comparable. However, the measurements using the bleaching scheme extend to zero velocity; in contrast, we were unable to obtain this resolution using the angled port scheme, possibly as a result of the calibration problem discussed earlier.

We conclude that the two schemes are in good agreement with one another, especially in the vicinity of the peak velocity. More particularly, we conclude that the optical bleaching scheme can indeed give accurate measurements of the velocity

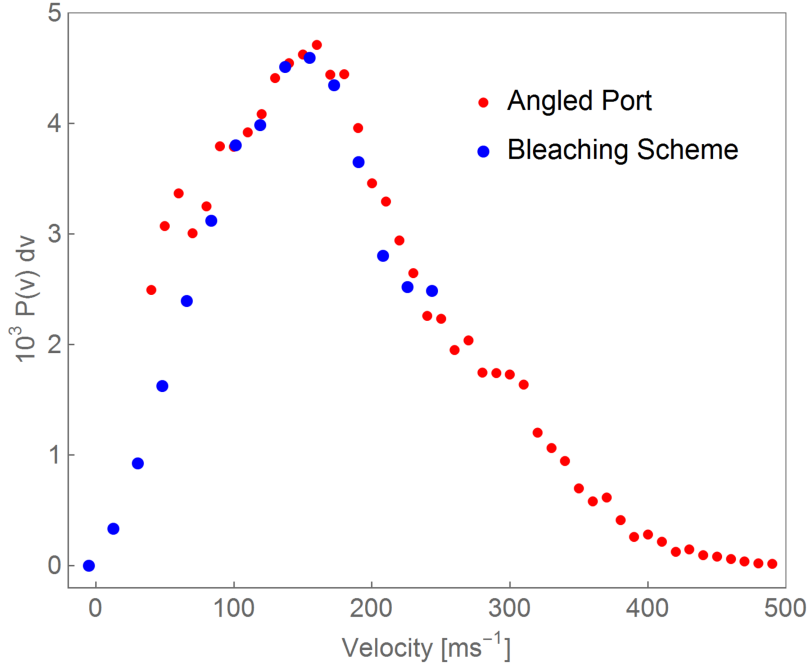


Figure 6.22: Comparison of the bleaching and angled probe schemes for a YbF beam produced by the two-stage source at 3 SCCM flow rate.

distribution of molecular beams.

6.12 Best-case flux and conclusion

This brings us up to date with our work on the two-stage source. Our best results were obtained using the third cell configuration, as shown in figure (5.21). Even though the source is not fully optimised, we have still seen significant population below 50 m s^{-1} . It would be useful to be able to compare the results from the hybrid and two-stage sources in terms of a molecular flux in the slowest possible case. As we have been unable to measure the beam divergence, we will instead use the known detector volume of $(3 \pm 1) \text{ mm}^3$ to define the detection solid angle. The beam intensity is maximised on-axis, so using the detection solid-angle will provide an upper limit to the molecular flux. Following the logic of section (3.10) as before, we obtain a characteristic total molecular flux in the ground ro-vibrational state of

$$\frac{N_m}{\Omega} = (6.8 \pm 0.7) \times 10^7 \text{ sr}^{-1} \text{ pulse}^{-1}, \quad (6.69)$$

and an absolute upper limit of $\approx 3 \times 10^8 \text{ sr}^{-1} \text{ pulse}^{-1}$ from the third configuration two-stage cell.

In designing and implementing the current two-stage molecular source, we were unable to obtain the ultra-low velocities found by Lu *et al* in [96]. There are a few possible reasons for this. First, YbF is a significantly heavier molecule than CaH so requires a great deal more collisions in the second stage to decelerate it from the hydrodynamic to effusive velocities required. One might simply expect, as we did initially, that increasing the helium flow rate is sufficient to compensate for this effect. However, doing so fundamentally changes the properties of the beam produced by the second stage. A well-optimised two-stage source operates in a regime that is close to effusive, with minimal collisions in the beam. Increasing the flow rate above this optimum will both increase the initial beam density and, because the divergence is minimised for intermediary flows, reduce the beam divergence. Collisions in this regime will tend to be forward-boosting to a greater extent than those in an effusive beam, and the symmetry between the two cases is broken.

Once we began running in the low helium flow regimes, the first stage cell was operating on the edge of its designed parameter space. This manifested itself in the interesting bifurcation of the velocity distribution, which we explained using a pressure-wave model. Whilst our intentions were good—a small cell maximises the extraction efficiency in the effusive regime—we took it a little too far and in the end were unable to compensate for this effect over the full range of flow rates required. A larger first-stage cell with a large aperture would be more suitable for the experiment performed.

Although we did not see the slowing we had hoped for in section (6.10), I believe that we were moving in the right direction at this point. There was a preponderance of evidence that lead us towards the double-extension, and seeing the peak velocity drop as a function of flow rate up to 4 SCCM only reinforces this view. However, increasing the lengths of both the first and second stages will tend to drastically reduce the overall flux—as we have seen, even in the third configuration with one extender, the total flux was decreased by a factor of ≈ 15 with respect to the hybrid source. In the effusive regime, the extraction efficiency from the source is the ratio of the aperture area to the internal surface area of the cell. If ζ_H (ζ_{2S}) is the internal surface area of the hybrid (2-stage) cell, the theoretical decrease in flux between the two cases is $\epsilon \approx \zeta_{2S}/\zeta_H$ which, evaluating both terms, gives $\epsilon \approx 1/14$, in good agreement with the measured change. So further increases in length to try to maximise

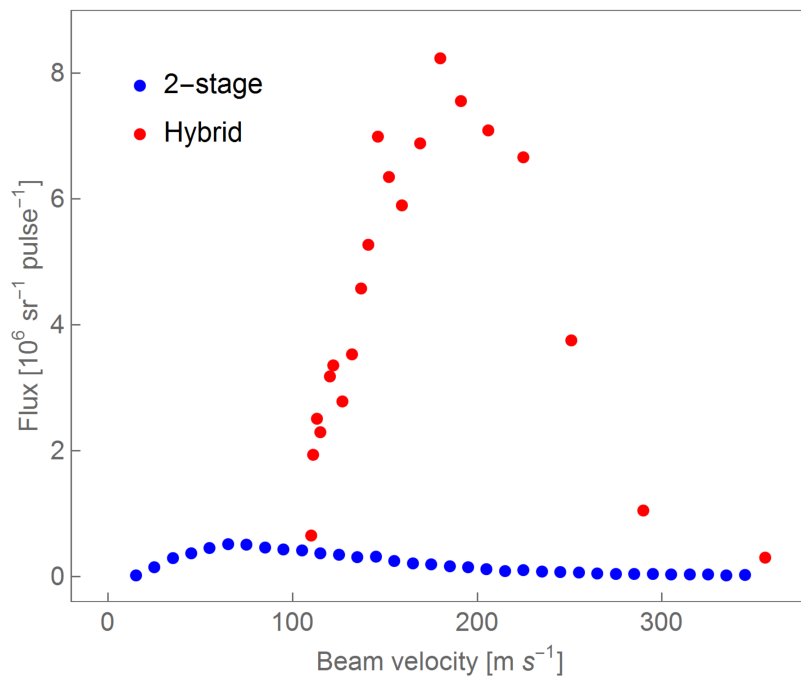


Figure 6.23: Slowest velocity distributions obtained from the two-stage and hybrid sources, in terms of the total molecular flux in each velocity interval. The data from the hybrid source was obtained at a helium flow of 10 SCCM, and the data from the 2-stage source was obtained using the third configuration (extended second stage, regular first stage) at 4 SCCM.

the number of collisions in the second stage without increasing the density may not prove to be beneficial.

The source parametrisation opened up an interesting line of research into the measurement of velocity distributions. Our initial attempt at characterisation, although sound in theory, was scuppered when the magnetic guide confined the helium buffer gas and hence led to forward-boosting of the distributions. Removing the guide and performing a direct measurement of the Doppler shift of spectral lines was found to be subject to velocity-dependent bleaching. Using a pulsed probe laser helped us to resolve our slowest measured distribution, but even this method proves fallible in the low signal-to-noise ratio regime due to the calibration problem. An improved scheme that used the previously problematic bleaching as a diagnostic was developed; immune to the calibration problem, it allows for direct measurements in the velocity regime and is robust even when the signal is extremely poor. We do not suggest discarding the Doppler shift technique as it is perfectly valid for intense beams of atoms and molecules—rather, we offer this new technique as a counterpoint that is specifically suited to a different intensity regime.

Molecular beams from two-stage sources remain an active area of research. A properly optimised beam represents a huge step towards our ultimate goal of a molecular fountain. Despite being unable to realise this goal, we have produced a source capable of beams with 47% of the total flux below 100 m s^{-1} , 12% below 50 m s^{-1} and a nonzero (0.34%) amount below 20 m s^{-1} . It is my belief that, knowing what we know now and with some small changes to the original design, a truly slow source for laser cooling YbF could be obtained using this method.

Chapter 7

Conclusion and outlook

7.1 Conclusion

In this thesis we have performed an exhaustive characterisation of two buffer gas sources of molecules. The first source was designed by Bulleid by solving the full Navier–Stokes equation using the computational fluid dynamics program Star-CCM+, with a predicted mean forward velocity of 120 m s^{-1} at helium flow rates of 60 SCCM and an extraction efficiency of 63%. The predicted molecular flux was thought to be of the order of $2 \times 10^{13} \text{ sr}^{-1} \text{ pulse}^{-1}$.

Our exploration of this hybrid source reveals a somewhat faster, less bright beam than was predicted computationally. Molecules leaving the cell are found to have thermalised after $500 \mu\text{s}$ in both the translational and rotational degrees of freedom to equilibrium values of the order $\approx 4 \text{ K}$. From measurements of the mean beam velocity as a function of time, we have concluded that the number of re-boosting collisions is negligible once the beam is more than 50 mm from the aperture.

We have measured both the instantaneous and total velocity distributions of ytterbium beams produced in this cell. The total distributions were measured from the Doppler-shift of the $^1\text{S}_0$ to $^3\text{P}_1$ transitions of the ^{172}Yb , ^{174}Yb , and ^{176}Yb isotopes. The peak velocities at all tested flows was found to lie in the 170 m s^{-1} – 190 m s^{-1} interval, with the corresponding mean velocities in the range 190 m s^{-1} – 220 m s^{-1} . None of the tested beams produced a significant number of molecules below 100 m s^{-1} . The instantaneous velocity distributions were inferred from the Yb spectral lineshape, and show that the velocity distribution at early times is broad and fast, before tending towards a narrow Gaussian character at later times.

Measurements of the confinement time within the hybrid source were performed by considering the difference between the free-flight and arrival times of the beam, and we have found that full thermalisation within the cell occurs on the $400\text{ }\mu\text{s}$ time scale at 10 SCCM of helium flow. We expect this to form a lower bound on the thermalisation time, as the cell pressure will be higher at higher flow rates. The beam divergence was also explored by measuring the absorption spectrum of a Yb beam. Whilst limited by the experimental shot noise, the angular full-width at half-maximum of $20^\circ \pm 5^\circ$ is compatible with the half-width predicted by Bulleid.

The characteristic flux from the cell has been determined from our measurements of the beam divergence and rotational temperature, along with a ray-tracing simulation of our experimental LIF optics. We find that YbF fluxes of $(2.10 \pm 0.34) \times 10^9\text{ sr}^{-1}\text{ pulse}^{-1}$ are typically obtained in the laboratory, with a best case three times greater than this. We have repeated this analysis for beams of Yb, finding typical fluxes of $(5.30 \pm 0.86) \times 10^9\text{ sr}^{-1}\text{ pulse}^{-1}$.

Having observed the decay of flux from our single stage source as a function of shot number, we performed a theoretical exploration of the thermal and mechanical properties of a repeatedly-ablated ytterbium rod. The temperature increase of the solid rod was observed at repetition rates above 10 Hz, with the formation of a liquid layer on the rod surface being postulated. If the target surface becomes wetted by molten metal, we expect a marked decrease in the yield due to inertial confinement at the solid-liquid interface. This provides one possible reason for the decrease in flux with increasing ablation rate, but even small changes to the metal properties can have a significant impact on the type and intensity of the ablation yield.

We next examined the variation in yield as the surface of the target becomes deformed by repeated ablation. As a hole is bored into the target by the laser, the number of photons striking the rod per unit surface area decreases and, as the ablation is a multi-photon process, there is a corresponding reduction in the yield. We predict that this will impact the measured flux on the scale of hundreds or thousands of shots, independent of the repetition rate, with the exact variation being a function of both the ablation energy and $1/e$ laser focus. Attempts to mitigate this effect by using non-Gaussian laser modes were unsuccessful, and we conclude that the optimal longevity is found in the Gaussian case. Finally, we examined the yield as a function of initial surface roughness and found that an initially smooth rod gives the best possible target longevity. In particular, once the height and length scales of

the surface roughness become comparable, the reduction in yield becomes significant.

Taking inspiration from our work on the hybrid source, a two-stage buffer gas cell has been designed and tested. A comparison of both the two-stage and hybrid sources at high flow rates was performed, from which we found the two-stage cell produced a greater number of molecules with forward velocities below 100 m s^{-1} . The thermalisation times for molecules in both sources was found to be comparable.

Next, we looked for efficient ways to rapidly explore the two-stage cell parameter space. Of particular interest was the number of slow molecules, which we wanted to rapidly map for a wide range of flow rates. Our approach was to construct a magnetic octupole guide, which would have the effect of greatly increasing the molecular free-flight time to the point at which it would dominate the time spent by molecules inside the source. Having carefully checked that the effect of non-adiabatic transitions in the guide would be negligible, we measured the slow fraction of molecules for three different cell configurations. Our best results were found when both the first and second stage cells were increased in length. However, we also noticed that the total flux measured at our distant detector was decreasing as a function of helium flow rate in a manner which suggested that a large number of collisions between helium and YbF in the guide were occurring. As this had the potential to cause significant forward-boosting of our beam, we removed the guide and attempted to directly measure the velocity distribution of beams produced from the extended second-stage cell.

As before, we determined the velocity distributions by measuring the Doppler shift in YbF spectral features using a co-axial laser beam. However, we also obtained strong evidence that this method can cause a velocity-dependent bias via the bleaching of the slowest molecules before they reach the detector. Using a pulsed co-axial probe laser we were able to correct for this effect, measuring our slowest velocity distribution to date in the process.

This measurement scheme, whilst useful in this instance, was found to be unreliable in the low signal-to-noise limit where one necessarily relies on extrapolation rather than data to determine the very slowest molecules. To solve this problem, we developed a new measurement scheme based on the optical bleaching of molecules in the region of a target velocity class. By integrating over all molecules bleached from a test state, we found that an accurate reconstruction of the velocity distribution of a molecular beam is possible. Crucially, as this measurement is performed directly in the velocity domain rather than the time domain, the extrapolation problem is

neatly sidestepped. This measurement scheme was used to parametrise molecular beams produced from a fourth cell configuration, with both the first and second stage extended simultaneously. We again saw evidence of slowing in the second stage, but were unable to reduce the peak velocity of the measured distributions below $\approx 100 \text{ m s}^{-1}$.

The typical flux from the two-stage source was found to be $(6.8 \pm 0.7) \times 10^7 \text{ sr}^{-1} \text{ pulse}^{-1}$, an order of magnitude worse than from the hybrid source. However, the significant slow fraction measured from the two-stage source makes it a far better candidate for potential laser cooling experiments. With small changes to the design and further optimisation, it is the belief of the author that the current molecular fraction of $\approx 12\%$ below 50 m s^{-1} could be significantly increased, with a corresponding knock-on effect on the small but nonzero fraction with velocities particularly amenable to laser deceleration and trapping below 50 m s^{-1} .

7.2 Outlook

We have made a significant step towards a beam source of molecules that could feasibly be used in laser slowing and cooling experiments. In the short term, further exploration of the parameter space in the third cell configuration is likely to be profitable, particularly if the inter-cell separation is scanned to fine-tune the pressure in the slowing cell. However, over the course of the exploration we have time and again found the need to extend both our cells, and have been plagued by weak signal and low signal-to-noise ratio. A long-term remedy to this would be to perform a significant redesign of the two-stage apparatus.

The re-design should firstly use a larger first-stage cell. As we saw in section (6.9), our current first-stage cell is inadequate at the very low flow regimes we ultimately used. With a larger cell volume, a larger aperture can also be used, allowing us to attain hydrodynamic enhancement and hence increase the molecular flux from the first cell.

Similarly, a longer second-stage cell will allow for a greater number of slowing collisions, without a corresponding increase in pressure and re-boosting collisions in the ensuing beam. The aperture from this second stage should also be expanded, as the relevant scale for effusive behaviour seems to be the mesh pore size rather than the macroscopic aperture that bounds it. If the second cell is operating in the effusive regime, then increasing the aperture size from A to A' will be accompanied by an

increase in the extraction efficiency of A'/A , further combating the low flux seen at present.

It is possible that the current method of YbF production is not optimal for the two-stage source. The chemistry behind the formation of YbF radicals is not well-understood, being described as “alchemy” in some sources. From measurements of the flux of both Yb and YbF beams, we can estimate the maximum efficiency of the formation process, obtaining $\approx 25\%$. As either a collaboration or a short project, a detailed study of the chemical formation of YbF could prove to be very beneficial to the work of the group, increasing the molecular yield by up to a factor of 4 and improving the reliability of our beam sources.

At present within the group, two new molecular sources are being tested. The first, consisting of a single stage neon beam, is offering promising results if the low-velocity tail can be effectively selected. The second is rather more radical, and involves the transverse laser cooling of a YbF beam produced from a hybrid-source-type cell. Initial data, obtained by Jongseok Lim, James Almond and Michael Trigatzis, has demonstrated the cooling of a small subset of the transverse velocities to an estimated 200 mK. The ultra-low divergence of the resulting beam, in conjunction with a forward beam velocity of the order of 150 m s^{-1} , allows the interaction length of the eEDM experiment to be increased. Although the method is currently in its infancy, it offers an interesting and practical bridge between the buffer gas source and the ultimate laser cooling goals.

Additional improvements to the experimental sensitivity are also being made to the eEDM apparatus. Having identified magnetic Johnson noise as a potential systematic error, the solid electric field plates were replaced with ones made from gold-plated glass to suppress this effect [98]. The detection scheme has also been recently re-examined, with an optical cycling scheme allowing each molecule to scatter an average of 12 photons and hence improve the counting statistics in the measurement [48].

Precision measurements of the eEDM remain an active and important field of study. The next 5–10 years promise to be hugely exciting, as advances in molecular sources drive the experimental shot-noise below a range of theoretical limits. It has been a pleasure to be involved, even in a small way such as this, with the process.

Appendices

Appendix A

Level structure in the $X^2\Sigma^+$ and $A^2\Pi_{1/2}$ manifolds of YbF

At the simplest possible level a molecule consists of a positively charged nucleus and a collection of negatively charged electrons, the combination of which forms a stable system via the electrostatic interactions of its constituents. The equations of motion of the constituents of this large, coupled system will in general be very complicated. However, certain simplifications exist that allow us to separate out the different classes of motion within the molecule, namely its rotational, vibrational, and electronic motions. Known as the Born–Oppenheimer approximation, the separation uses the fact that the electron mass m_e is far smaller than the nuclear mass m_n , allowing the electron to be accelerated at a much more rapid rate and to higher velocities than the nucleus. In general, the separation between the electronic, vibrational, and rotational energy levels— ΔE_E , ΔE_v , and ΔE_R —can be written as

$$\frac{\Delta E_v}{\Delta E_E} \approx \frac{\Delta E_R}{\Delta E_v} \approx \sqrt{\frac{m_e}{m_n}} \approx \frac{1}{100} \quad (\text{A.1})$$

This stratification of energy scales means that the various motions occur on very different timescales—we can write down the time-evolution of some $|\psi_n\rangle$ when it is an eigenfunction of the Hamiltonian, $H|\psi\rangle = E_n|\psi_n\rangle$:

$$|\psi_n(t)\rangle = e^{-i\frac{E_n}{\hbar}t} |\psi_n(0)\rangle, \quad (\text{A.2})$$

and hence the time scale over which phase accumulates within a state is inversely proportional to the energy. Thus, on the time scale of electronic motion governed by ΔE_E , the nucleus is essentially static. Similarly, on the time scale of vibrational

motion governed by ΔE_v , the rotational motion of the nucleus can be neglected.

In the limit of this behaviour, the wavefunction of the molecule can be decomposed into the simple product form

$$|\psi\rangle = |\psi_{\text{el}}\rangle |\psi_{\text{v},r}\rangle, \quad (\text{A.3})$$

where $|\psi_{\text{el}}\rangle$ is the electronic wavefunction, and $|\psi_{\text{v},r}\rangle$ is the nuclear wavefunction which contains the rotational and vibrational components. Within this approximation, the electrons follow the nuclear motion adiabatically—the electronic state is deformed by the nuclear motions without becoming mixed with other states. The vibrational and rotational motions can be separated because they are functions of different co-ordinates—the vibration depending on the internuclear displacement, and the rotation being a function of the Euler angles of the molecule. Thus, under the Born–Oppenheimer approximation we can separate the various motional components of the molecule and solve for them individually.

We can parametrise each molecular state according to its good quantum numbers. Which quantum numbers are good depend very much on the way in which the various types of angular momentum are coupled together by the molecular Hamiltonian. When certain interactions dominate, the coupling schemes simplify; these special cases are known as Hund’s coupling cases. For the $X^2\Sigma^+$ and $A^2\Pi_{1/2}$ manifolds of YbF, we are particularly interested in two coupling cases, which I will discuss below.

Hund’s case (a) arises when the orbital angular momentum $\mathbf{L}$ is strongly coupled to the internuclear axis $\boldsymbol{\lambda}$ through electrostatic forces, and the electron spin $\mathbf{S}$ is strongly coupled to $\mathbf{L}$ through the spin-orbit interaction. The projections of $\mathbf{L}$ and $\mathbf{S}$ onto $\boldsymbol{\lambda}$, Λ and Σ respectively, are well-defined even as $\mathbf{L}$ and $\mathbf{S}$ precess around $\boldsymbol{\lambda}$. The sum of the projections $\Omega = \Lambda + \Sigma$ defines a vector $\boldsymbol{\Omega} = \Omega \hat{\boldsymbol{\lambda}}$ along the internuclear axis; this couples to the angular momentum of the rotating nuclei, $\mathbf{N}$ to form a resulting total angular momentum $\mathbf{J} = \mathbf{N} + \boldsymbol{\Omega}$.

The precessions of $\mathbf{L}$ and $\mathbf{S}$ about $\boldsymbol{\lambda}$, assumed to be much faster than those of $\mathbf{N}$ and $\boldsymbol{\Omega}$ about $\mathbf{J}$, have two equal and opposite senses so that the projections are $\pm\Lambda$ and $\pm\Sigma$. Thus $\boldsymbol{\Omega}$ also has two senses, $\pm\Omega$; the degeneracy in Λ is called Λ -doubling, and the degeneracy in Ω is Ω -doubling. This degeneracy is lifted once the states are formed into parity-eigenstate superpositions, which are susceptible to the spin-orbit and rotational electronic Coriolis interactions (see pp. 328–331 of [91] for more information). The Hund’s case (a) basis forms a good representation of the

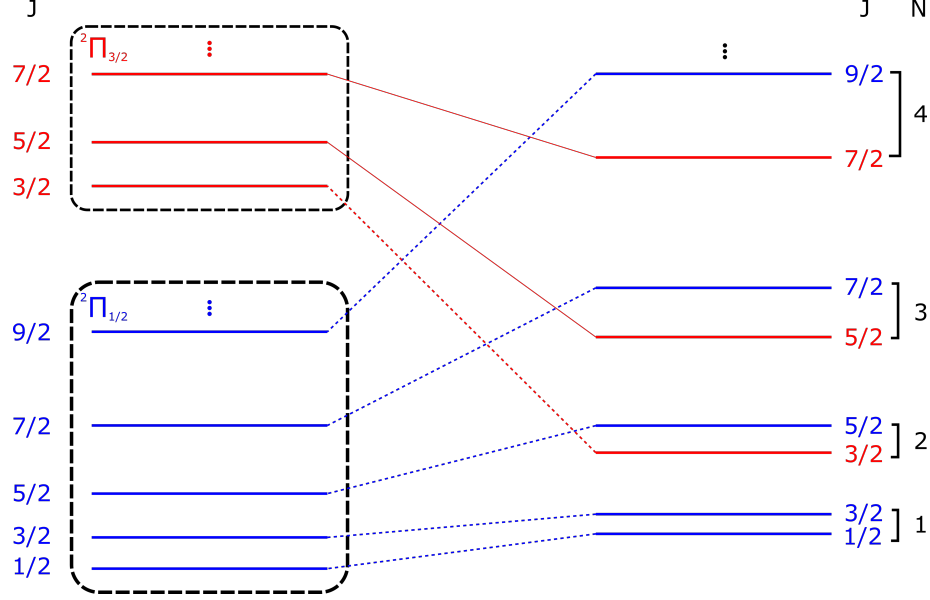


Figure A.1: Expansion of a $^2\Pi$ state into the Hund's case (b) basis under the formalism of equation (A.4). Image is based on figure 6.18 of [91].

A $^2\Pi_{1/2}$ state of YbF; its good quantum numbers are Λ , S , Σ , J , and Ω .

On the other hand, if the spin-orbit coupling is negligible then Hund's case (b) may be more appropriate. In this case $\mathbf{L}$ again precesses rapidly about $\mathbf{\Lambda}$, giving a well-defined projection $\Lambda = \mathbf{\Lambda} \cdot \hat{\mathbf{\Lambda}}$. $\mathbf{\Lambda}$ couples to the rotation $\mathbf{N}$ to form an intermediate angular momentum $\mathbf{R}$; $\mathbf{R}$ then couples to $\mathbf{S}$ to form a total angular momentum $\mathbf{J}$. As we will be using the case (b) description for our $X^2\Sigma^+$ ground state manifold where $\Lambda = 0$, $\mathbf{N} = \mathbf{R}$ giving us some redundancy in the labelling. By convention, we will typically label the angular momentum associated with rotations of the nucleus with the quantum number N . The good quantum numbers in a case (b) basis are Λ , N , S , and J .

We can expand case (b) wavefunctions in terms of the case (a) basis [125]; doing so, we obtain

$$|\Lambda, N, S, J, m_J\rangle = \sum_{\Omega, \Sigma} (-1)^{N-S+\Omega} (2N+1)^{1/2} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} \times |\Lambda, S, \Sigma, \Omega, J, m_J\rangle. \quad (\text{A.4})$$

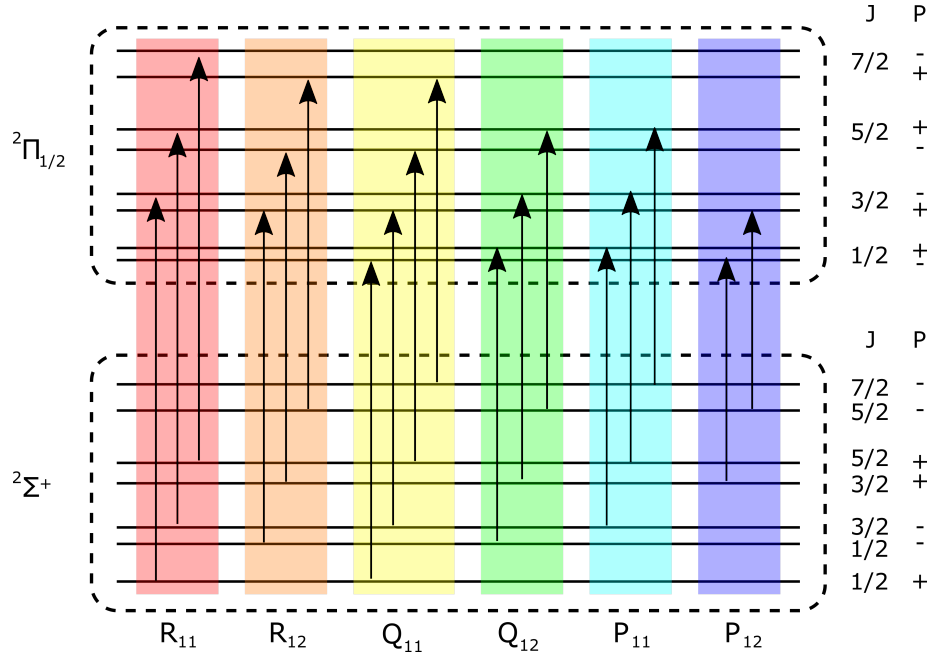


Figure A.2: Examples of the 6 classes of allowed transitions between the $X^2\Sigma^+$ and $A^2\Pi_{1/2}$ manifolds.

Although we do not do so here, this expansion allows us to compute the matrix elements for electronic transitions between the $X^2\Sigma^+$ and $A^2\Pi_{1/2}$ manifolds—see Appendix B of [48] for more details. It is however instructive to see the expansion of the $A^2\Pi$ state into a case (b) basis, where the familiar N is a good quantum number. The result of doing so is shown diagrammatically in figure (A.1).

We can characterise the different types of allowed transitions between the $X^2\Sigma^+$ and $A^2\Pi_{1/2}$ manifolds according to the change in the quantum number J . Transitions from $X^2\Sigma^+$ to $A^2\Pi_{1/2}$ where $\Delta J = +1$ are labelled with an R , those where $\Delta J = 0$ are labelled with a Q , and those with $\Delta J = -1$ are labelled with a P . As the spin-rotation coupling in the $X^2\Sigma^+$ state gives rise to 2 states with the same J but different N , we must also label each transition type according to its initial ground state. Hence there are a total of 6 allowed transition types [126]: R_{11} , R_{12} , Q_{11} , Q_{12} , P_{11} , and P_{12} . These transitions are illustrated for the first few states in the $X^2\Sigma^+$ and $A^2\Pi_{1/2}$ manifolds in figure (A.2). Throughout this thesis, I will use a slightly different transition-labelling convention in the style of [127]. We group the

P_{11} and Q_{12} transitions together and label them the “P-branch”, and the Q_{11} and R_{12} transitions are grouped and collectively labelled the “Q-branch”. This grouping simplifies the notation, as each transition in the group arises from the same rotational state in the ground state manifold, and connects to the same excited state. Transitions are specified uniquely by their ground state rotational quantum number N —for example, the transition $Q(1)$ labels both $Q_{11}(J = 3/2)$ and $R_{12}(1/2)$. The remaining two transitions, P_{12} and R_{11} are spectrally distinct, lying ≈ 1 THz to the red and ≈ 40 GHz to the blue respectively.

Finally, we must mention the additional angular momentum coupling that arises as a result of the nuclear hyperfine interaction. The fluorine nuclear spin is $\mathbf{I}$, with $|\mathbf{I}| = 1/2$, and the ytterbium nuclear spin is zero. In the $A^2\Pi_{1/2}$ manifold, $\mathbf{I}$ couples to $\mathbf{J}$ to give a total angular momentum $\mathbf{F}$, with quantum number F and magnetic projection quantum number m_F . This corresponds to Hund’s case (a_β). There will generally be 4 hyperfine components in the excited state manifold—two arising from the lifting of the Ω -degeneracy in each J -state, and two arising from the two possible values of $F = J \pm 1/2$ for each J . A similar situation arises in the $X^2\Sigma^+$ manifold, where $\mathbf{I}$ again couples to $\mathbf{J}$ to give $\mathbf{F}$ in a coupling scheme known as Hund’s ($b_{\beta J}$). Again we expect four hyperfine states F , as $J = N \pm 1/2$ can have two values, as can $F = J \pm 1/2$.

Appendix B

The optical Bloch equations

The material presented in these sections is based on the work of Loudon [103] and Cohen–Tannoudji [104] unless otherwise stated. I have also referred to the thesis of Graham Purves [105], whose work was an invaluable reference to me over the course of my studies.

B.1 The density matrix

The density matrix formalism extends the familiar “pure” states, described by a state vector $|\psi\rangle$, to statistical mixtures of states that may be found in an ensemble of particles. While pure states can be described by a state vector, these “mixed” statistical states cannot. However, such a state can be described by the density operator ρ . For a pure state ρ is defined as

$$\rho = |\psi\rangle \langle\psi|. \quad (\text{B.1})$$

We can always expand $|\psi\rangle$ in some basis set $\{|\phi_k\rangle\}$:

$$|\psi\rangle = \sum_{k=1}^N c_k |\phi_k\rangle, \quad (\text{B.2})$$

where the set of $c_k = \langle\phi_k|\psi\rangle$ are the expansion coefficients. Using this definition, ρ is given by the $N \times N$ matrix formed by the Kronecker product $|\psi\rangle \otimes |\psi\rangle$:

$$\rho = \begin{pmatrix} c_1 c_1^* & c_1 c_2^* & \cdots & c_1 c_N^* \\ c_2 c_1^* & c_2 c_2^* & \cdots & c_2 c_N^* \\ \vdots & \vdots & \ddots & \vdots \\ c_N c_1^* & c_N c_2^* & \cdots & c_N c_N^* \end{pmatrix}. \quad (\text{B.3})$$

The diagonals of equation (B.3) give the probability amplitudes for the states $\{|\phi_k\rangle\}$, while the off-diagonal terms give the coherences between pairs of states. Note that ρ is Hermitian and the sum of the diagonal elements is 1 via equation (B.2) with the normalisation condition $\langle\psi|\psi\rangle = 1$. This means that the number of independent variables in a density operator ρ of dimension $N \geq 2$ is $\frac{N(N+1)}{2} - 1$ rather than N^2 .

Mixed states are defined similarly to pure states, with the density operator now given by

$$\rho = \sum_j^M P_j |\psi_j\rangle \langle\psi_j|, \quad (\text{B.4})$$

where the set of probabilities $\{P_j\}$ describe the statistical distribution of the states $|\psi_k\rangle$, and the pure state is understood to be a specific case where $P_f = 1, P_{j \neq f} = 0$.

B.2 The Liouville equation

We can derive the temporal behaviour of the density matrix from the Schrödinger equation as follows. Consider a state $|\psi(t)\rangle$ whose time evolution is described by the unitary operator

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle. \quad (\text{B.5})$$

Via the uniqueness criterion, the initial condition for U must be

$$U(t_0, t_0) = 1. \quad (\text{B.6})$$

We now substitute equation (B.5) into the Schrödinger equation to obtain a differential equation for U :

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = H |\psi(t)\rangle \quad (\text{B.7})$$

$$\begin{aligned} \implies i\hbar \frac{\partial U(t, t_0)}{\partial t} |\psi(t_0)\rangle + i\hbar U(t, t_0) \frac{\partial |\psi(t_0)\rangle}{\partial t} = \\ |\psi(t_0)\rangle [HU(t, t_0)] + U(t, t_0) [H |\psi(t_0)\rangle]. \end{aligned} \quad (\text{B.8})$$

Substituting equation (B.7) into (B.8) and cancelling, we obtain

$$i\hbar \frac{\partial U(t, t_0)}{\partial t} = HU(t, t_0). \quad (\text{B.9})$$

We can solve equation (B.9) using the initial condition (B.6). Doing so, we obtain

$$U(t, t_0) = e^{-\frac{i}{\hbar} H(t-t_0)} \quad (\text{B.10})$$

Now, the density matrix is an operator. The expectation values of our operators (relating to experimental observables) should not be dependent on our choice of unitary transformation. We can write a general operator before the transformation as O and after as $\tilde{O}$. The correspondence of expectation values leads to

$$\langle \psi(t) | O | \psi(t) \rangle = \langle \psi(t_0) | \tilde{O} | \psi(t_0) \rangle \quad (\text{B.11})$$

$$\implies U \tilde{O} U^\dagger = O, \quad (\text{B.12})$$

as $U^\dagger U = 1$. As we know the functional form of U from equation (B.10), we can apply the chain rule on equation (B.12) and hence determine the behaviour of the operator O . Doing so yields

$$\dot{O} = \dot{U} \tilde{O} U^\dagger + U \dot{\tilde{O}} U^\dagger + U \tilde{O} \dot{U}^\dagger \quad (\text{B.13})$$

$$= -\frac{i}{\hbar} (H O - O H) + U \dot{\tilde{O}} U^\dagger \quad (\text{B.14})$$

$$\implies \frac{dO}{dt} = -\frac{i}{\hbar} [H, O] + \frac{\partial O}{\partial t}. \quad (\text{B.15})$$

Thus, substituting $O \rightarrow \rho$ and $\frac{\partial \rho}{\partial t} = -\gamma \rho$, we finally obtain¹ the equation of motion for the density matrix:

$$\dot{\rho} = \frac{i}{\hbar} [\rho, H] - \gamma \rho. \quad (\text{B.16})$$

This governing equation is known as the Liouville equation. Our remaining task is to determine the interaction Hamiltonian H , which will in turn determine the precise form of the density matrix and hence the behaviour of our molecule when interacting with light.

B.3 The light-matter interaction Hamiltonian

We seek the Hamiltonian for the interaction between an applied laser field and our atom or molecule. However, before we can write down its form we must first do a little book-keeping regarding our assumptions and definitions. We begin by noting that our statement of the problem already neglects a very important element—the

¹This last substitution is quite cryptic, and really arises because we are trying to shoehorn a quantum electrodynamic property (spontaneous decay) into a quantum mechanical process. If we compare our derived Liouville equation with the full Lindblad equation, we see that this substitution is necessarily true *in the special case that* $O = \rho$. For comparison with the Lindblad equation applied to spontaneous state transitions of this type, I recommend section 2.5 of [106].

quantum vacuum. Thus the full Hamiltonian consists of three systems—matter, light, and vacuum—along with the couplings and interactions between them.

Secondly, we stress that our treatment will be semi-classical. Our laser will be treated as a classical field whose properties are specified via a mode expansion. Due to its classical nature, the laser energy is parametrised by functions rather than operators, meaning that the contribution to the commutator in equation (B.16) is zero. Within this approximation, the total energy of the laser does not affect the time dynamics of the density matrix.

We also need to be clear about which system we are considering with our density matrix treatment. While the generalness of our approach makes equation (B.16) suitable for a quantum system of our choice, we will restrict our discussion to the internal states and coherences of our molecule. This lets us make some rather nice simplifications, as elements of the total Hamiltonian (such as molecular kinetic energy and laser-vacuum coupling) that act in different sub-spaces will not contribute to our dynamics and can therefore be ignored from the outset. The partitioning of the internal, electronic states and the external, momentum states can be made more rigorous by noting that the momentum typically changes on a time scale of milliseconds, while spontaneous decay destroys any coherence between the internal and external states over ten- or hundred-nanosecond time scales.

Under this particular set of assumptions and simplifications, we can write down the interaction Hamiltonian

$$H_I = H_{\text{int,m}} + H_{\text{m,L}} + H_{\text{m,V}}, \quad (\text{B.17})$$

where $H_{\text{int,m}}$ is the internal energy of the molecule, $H_{\text{m,L}}$ is the coupling between the molecule and the laser field, and $H_{\text{m,V}}$ is the interaction between the molecule and the vacuum field.

We can write out explicit forms for the three terms in equation (B.17) as follows. The internal energy is given by

$$H_{\text{int,m}} = \hbar \sum_{j=1}^M \omega_j |\phi_j\rangle \langle \phi_j|, \quad (\text{B.18})$$

as we note that $\langle \phi_q | H_{\text{int,m}} | \phi_q \rangle = \hbar \omega_q = E_q$, where $E_q \in \{E_1 \dots E_M\}$ is the energy of state q . The coupling between the molecule and the electric field of the laser $\mathbf{E}_L$

can be written as

$$H_{\text{m,L}} = -\mathbf{d} \cdot \mathbf{E}_{\text{L}}, \quad (\text{B.19})$$

with the molecular dipole moment $\mathbf{d}$ also appearing in the interaction between the molecule and the electric field operator of the vacuum:

$$H_{\text{m,V}} = -\mathbf{d} \cdot \mathbf{E}_{\text{V}}. \quad (\text{B.20})$$

We again stress that $H_{\text{m,L}}$ contains a classical laser field $\mathbf{E}_{\text{L}}$, while $H_{\text{m,V}}$ is a function of the quantum field $\mathbf{E}_{\text{V}}$. This subtlety leads to a difference in the mode expansion of the fields, which we address in the following section.

B.4 Mode expansion and the rotating wave approximation

We begin by considering the interaction between the molecule and the classical laser field. The molecular dipole operator between two internal states $|\alpha\rangle$ and $|\beta\rangle$ can be expressed as

$$\mathbf{d} = \mathbf{d}_{\alpha\beta} \left(|\alpha\rangle \langle\beta| + |\beta\rangle \langle\alpha| \right), \quad (\text{B.21})$$

where the operators $|\alpha\rangle \langle\beta|$ are the quantum state-changing operators that induce a transition from state $|\beta\rangle$ to state $|\alpha\rangle$ and vice versa. The driving laser field is taken to have a very narrow bandwidth such that a monochromatic description is appropriate:

$$\mathbf{E}_{\text{L}}(t) = \mathbf{E}_{\text{L}} \cos(\omega_{\text{L}} t). \quad (\text{B.22})$$

Substituting equations (B.21) and (B.22) into (B.19), and expanding the cosine into a sum of exponentials *via* Euler's formula, we obtain

$$H_{\text{m,L}} = -\frac{\mathbf{d}_{\alpha\beta} \cdot \mathbf{E}_{\text{L}}}{2} \left(|\alpha\rangle \langle\beta| + |\beta\rangle \langle\alpha| \right) \left(e^{i\omega_{\text{L}} t} + e^{-i\omega_{\text{L}} t} \right) \quad (\text{B.23})$$

$$= \frac{\hbar\Omega_{\alpha\beta}}{2} \left(|\alpha\rangle \langle\beta| e^{i\omega_{\text{L}} t} + |\alpha\rangle \langle\beta| e^{-i\omega_{\text{L}} t} + |\beta\rangle \langle\alpha| e^{i\omega_{\text{L}} t} + |\beta\rangle \langle\alpha| e^{-i\omega_{\text{L}} t} \right), \quad (\text{B.24})$$

where we have introduced the *Rabi frequency* for the transition:

$$\hbar\Omega_{\alpha\beta} = -\mathbf{d}_{\alpha\beta} \cdot \mathbf{E}_{\text{L}}. \quad (\text{B.25})$$

Now let us establish an energy hierarchy between the electronic states $|\alpha\rangle$ and $|\beta\rangle$, and set $E_{\alpha} = \langle\alpha| H_{\text{int,m}} |\alpha\rangle < E_{\beta}$. From the conservation of total energy, we expect

the transition $|\alpha\rangle \rightarrow |\beta\rangle$ to be accompanied with the absorption of a photon, and the transition $|\beta\rangle \rightarrow |\alpha\rangle$ to be accompanied by the emission of a photon. Although we have quite carefully and deliberately asserted that the laser field is entirely classical, we can still associate the $e^{-i\omega t}$ term with the creation of a photon, along with the converse for the conjugate. Discarding the “anti-resonant” terms that don’t follow this stipulation is known as the Rotating Wave Approximation; applying it gives the interaction potential we will use to model the interaction between laser and molecule:

$$H_{\text{m,L}} = \frac{\hbar\Omega_{\alpha\beta}}{2} \left(|\beta\rangle \langle\alpha| e^{i\omega_{\text{L}}t} + |\alpha\rangle \langle\beta| e^{-i\omega_{\text{L}}t} \right). \quad (\text{B.26})$$

We now turn to the expansion of $H_{\text{m,V}}$. The exact mathematics behind the derivation of the spontaneous decay rate adds little to the discussion; instead, we will demonstrate why this Hamiltonian might be responsible for decays from the excited state into vacuum modes, and leave the details to the interested reader.

Following Loudon, we expand the vacuum field in terms of the creation and annihilation operators $a_k^\dagger$ and a_k , and substitute for the dipole operator:

$$H_{\text{m,V}} = i\hbar \left(|\alpha\rangle \langle\beta| + |\beta\rangle \langle\alpha| \right) \sum_k g_k \left(a_k e^{-i\omega_k t} - a_k^\dagger e^{i\omega_k t} \right). \quad (\text{B.27})$$

Here g_k is a function of ω_k that contains various constants relating to the quantisation volume and dipole moment of the transition. The state vector for the combined field–molecule system can be written as

$$|n_k, \phi\rangle = |n_k\rangle \otimes |\phi\rangle, \quad (\text{B.28})$$

where n_k labels the number state of the photon field and ϕ labels the inner state of the molecule. For decay processes, we are interested in the transition from an excited state $|\beta\rangle$ to a lower-energy state $|\alpha\rangle$ mediated by the creation of a photon of frequency ω_k . Using the usual relationship between the creation operator and the photon number state

$$a_k^\dagger |n_k\rangle = \sqrt{n_k + 1} |n_k + 1\rangle \quad (\text{B.29})$$

we obtain the transition matrix element:

$$\langle n_k + 1, \alpha | H_{\text{m,V}} | n_k, \beta \rangle = -i\hbar g_k e^{i\omega_k t} \sqrt{n_k + 1}. \quad (\text{B.30})$$

From Fermi’s Golden Rule, the transition rate between $|\beta\rangle$ and $|\alpha\rangle$ into the mode ω_k must be given by the modulus squared of equation (B.30). Defining this rate as $\Gamma_{\beta,\alpha,k}$, we find that

$$\Gamma_{\beta,\alpha,k} \propto g_k^2 (n_k + 1) = \Gamma_{\text{stim}} + \Gamma_{\text{spon}}. \quad (\text{B.31})$$

We see that equation (B.31) consists of two parts. The first, Γ_{stim} , is proportional to the number of photons in the mode ω_k , and is responsible for stimulated emission processes. The second is constant with respect to photon number, and is responsible for spontaneous emission. Integrating Γ_{spon} over all vacuum modes will yield the total spontaneous emission rate for the transition $|\beta\rangle \rightarrow |\alpha\rangle$. Thus we see that $H_{\text{m,v}}$ is responsible for the redistribution of population from high-energy to low-energy states and, in the following, we will group its contribution into an overall damping term Γ , related to γ in equation (B.16).

B.5 Optical Bloch equations for a 3-level system

The simplest possible form of the optical Bloch equations is that of the two-level system². However, a typical molecule will have a manifold of internal states due to the vibrational and rotational couplings. Furthermore, there are no totally forbidden transitions between vibrational energy levels due to the Franck–Condon principle. Even in a carefully chosen molecule, population will eventually be lost to these dark states. This complexity makes the two-level description a poor approximation to the physical system we wish to consider. In this section, we derive the optical Bloch equations (OBEs) for the three-level Λ system. Although still unable to capture exactly the dynamics of a real molecule, the Λ system has the advantage of being able to model leaks to and repumping from dark states. As such, it forms a useful toy model for describing the coarse dynamics of our system.

We define the three-level system as follows. The three levels are internal states of the molecule, labelled as $|e\rangle$, $|g_1\rangle$, and $|g_2\rangle$, with energies $E_e > E_{g_1}, E_{g_2}$. The states $|e\rangle$ and $|g_1\rangle$ are connected by a laser field of frequency ω_{e,g_1} , and the states $|e\rangle$ and $|g_2\rangle$ by a laser field of frequency ω_{e,g_2} . The total spontaneous decay rate from the excited state is Γ , with decays proceeding along the $|e\rangle \rightarrow |g_1\rangle$ channel with probability $r \leq 1$.

In appendix (B.4) we discussed the roles of both the laser and vacuum fields, deriving the Hamiltonian for the molecule–laser coupling in the rotating wave approximation and justifying “parcelling” the molecule–vacuum coupling into the total decay rate

²Technically, the simplest form is the one-level system; however, in this case the laser cannot couple electronic states. Nothing ever changes in this system, making the one-level case the Bingley, North Yorkshire of molecular physics.

Γ . The total Hamiltonian for our Λ system is therefore

$$H_I = H_{\text{int},m} + H_{e \leftrightarrow g_1, L} + H_{e \leftrightarrow g_2, L}, \quad (\text{B.32})$$

where the coupling between the laser and the level pair $|e\rangle$ and $|g_j\rangle$ is defined *via* equation (B.26):

$$H_{e \leftrightarrow g_j, L} = \frac{\hbar \Omega_{e, g_j}}{2} (|e\rangle \langle g_j| e^{i\omega_{e, g_j} t} + |g_j\rangle \langle e| e^{-i\omega_{e, g_j} t}). \quad (\text{B.33})$$

The Hamiltonian H_I can be expressed in in the matrix representation:

$$H_I = \hbar \begin{pmatrix} \omega_e & (\Omega_{e, g_1}/2)e^{-i\omega_{e, g_1} t} & (\Omega_{e, g_1}/2)e^{-i\omega_{e, g_2} t} \\ (\Omega_{e, g_1}/2)e^{i\omega_{e, g_1} t} & \omega_{g_1} & 0 \\ (\Omega_{e, g_1}/2)e^{i\omega_{e, g_2} t} & 0 & \omega_{g_2} \end{pmatrix}. \quad (\text{B.34})$$

Similarly, we can write out the explicit form of the 3-level density matrix:

$$\rho = \begin{pmatrix} \rho_{e,e} & \rho_{e, g_1} & \rho_{e, g_2} \\ \rho_{g_1, e} & \rho_{g_1, g_1} & \rho_{g_1, g_2} \\ \rho_{g_2, e} & \rho_{g_2, g_1} & \rho_{g_2, g_2} \end{pmatrix}. \quad (\text{B.35})$$

The equations of motion for the elements $\rho_{\alpha, \beta}$ of the density matrix are given by equation (B.16); we can expand the commutator and use the properties of matrix multiplication to obtain

$$\dot{\rho}_{\alpha, \beta} = \frac{i}{\hbar} [\rho, H]_{\alpha, \beta} - \Gamma_{\alpha, \beta} \rho_{\alpha, \beta}, \quad (\text{B.36})$$

where

$$[\rho, H]_{\alpha, \beta} = \sum_{\nu} \left(\rho_{\alpha, \nu} H_{\nu, \beta} - H_{\alpha, \nu} \rho_{\nu, \beta} \right), \quad (\text{B.37})$$

and the decay term $\Gamma_{\alpha, \beta}$ is given by

$$\Gamma_{\alpha, \beta} = \frac{\Gamma_{\alpha} + \Gamma_{\beta}}{2}. \quad (\text{B.38})$$

We can now write down explicit forms for the equations of motion of our populations:

$$\begin{aligned} \dot{\rho}_{e, e} = & + \frac{i}{2} \Omega_{e, g_1} (\rho_{e, g_1} e^{i\omega_{e, g_1} t} - \rho_{g_1, e} e^{-i\omega_{e, g_1} t}) \\ & + \frac{i}{2} \Omega_{e, g_2} (\rho_{e, g_2} e^{i\omega_{e, g_2} t} - \rho_{g_2, e} e^{-i\omega_{e, g_2} t}) - \Gamma \rho_{e, e}, \end{aligned} \quad (\text{B.39})$$

$$\dot{\rho}_{g_1, g_1} = - \frac{i}{2} \Omega_{e, g_1} (\rho_{e, g_1} e^{i\omega_{e, g_1} t} - \rho_{g_1, e} e^{-i\omega_{e, g_1} t}) + r \Gamma \rho_{e, e}, \quad (\text{B.40})$$

$$\dot{\rho}_{g_2, g_2} = - \frac{i}{2} \Omega_{e, g_2} (\rho_{e, g_2} e^{i\omega_{e, g_2} t} - \rho_{g_2, e} e^{-i\omega_{e, g_2} t}) + (1 - r) \Gamma \rho_{e, e}. \quad (\text{B.41})$$

As ρ is Hermitian, we have three independent coherences:

$$\begin{aligned}\dot{\rho}_{e,g_1} = & - \left(i(\omega_e - \omega_{g_1}) + \frac{r\Gamma}{2} \right) \rho_{e,g_1} \\ & + \frac{i}{2} \Omega_{e,g_1} e^{-i\omega_{e,g_1}t} (\rho_{e,e} - \rho_{g_1,g_1}) - \frac{i}{2} \Omega_{e,g_2} e^{-i\omega_{e,g_2}t} \rho_{g_2,g_1},\end{aligned}\quad (\text{B.42})$$

$$\begin{aligned}\dot{\rho}_{e,g_2} = & - \left(i(\omega_e - \omega_{g_2}) + \frac{(1-r)\Gamma}{2} \right) \rho_{e,g_2} \\ & + \frac{i}{2} \Omega_{e,g_2} e^{-i\omega_{e,g_2}t} (\rho_{e,e} - \rho_{g_2,g_2}) - \frac{i}{2} \Omega_{e,g_1} e^{-i\omega_{e,g_1}t} \rho_{g_1,g_2},\end{aligned}\quad (\text{B.43})$$

$$\begin{aligned}\dot{\rho}_{g_2,g_1} = & - i(\omega_{g_2} - \omega_{g_1}) \rho_{g_2,g_1} \\ & + \frac{i}{2} \Omega_{g_1,e} e^{-i\omega_{e,g_1}t} \rho_{g_2,e} - \frac{i}{2} \Omega_{g_2,e} e^{-i\omega_{e,g_2}t} \rho_{e,g_1}.\end{aligned}\quad (\text{B.44})$$

We could, in theory, use equations (B.39–B.44) as presented here. However, it contains rapidly-oscillating transients due to the laser field which make the problem rather tricky for computation. Instead, we transform our coherences into a set of cunningly chosen co-rotating frames:

$$\rho_{e,g_1} = \bar{\rho}_{e,g_1} e^{-i\omega_{e,g_1}t} \quad (\text{B.45})$$

$$\rho_{e,g_2} = \bar{\rho}_{e,g_2} e^{-i\omega_{e,g_2}t} \quad (\text{B.46})$$

$$\rho_{g_2,g_1} = \bar{\rho}_{g_2,g_1} e^{-i(\omega_{e,g_1} - \omega_{e,g_2})t} \quad (\text{B.47})$$

Substituting these “slow” variables into (B.39–B.44) and simplifying, we obtain the most familiar form of the 3-level OBEs:

$$\dot{\rho}_{e,e} = + \frac{i}{2} \Omega_{e,g_1} (\bar{\rho}_{e,g_1} - \bar{\rho}_{g_1,e}) + \frac{i}{2} \Omega_{e,g_2} (\bar{\rho}_{e,g_2} - \bar{\rho}_{g_2,e}) - \Gamma \rho_{e,e}, \quad (\text{B.48})$$

$$\dot{\rho}_{g_1,g_1} = + \frac{i}{2} \Omega_{e,g_1} (\rho_{g_1,e} - \rho_{e,g_1}) + r\Gamma \rho_{e,e}, \quad (\text{B.49})$$

$$\dot{\rho}_{g_2,g_2} = + \frac{i}{2} \Omega_{e,g_2} (\rho_{g_2,e} - \rho_{e,g_2}) + (1-r)\Gamma \rho_{e,e}, \quad (\text{B.50})$$

$$\dot{\rho}_{e,g_1} = - \left(\frac{r\Gamma}{2} - i\delta_{e,g_1} \right) \rho_{e,g_1} + \frac{i}{2} \Omega_{e,g_1} (\rho_{e,e} - \rho_{g_1,g_1}) - \frac{i}{2} \Omega_{e,g_2} \rho_{g_2,g_1}, \quad (\text{B.51})$$

$$\begin{aligned}\dot{\rho}_{e,g_2} = & - \left(\frac{(1-r)\Gamma}{2} - i\delta_{e,g_2} \right) \rho_{e,g_2} + \frac{i}{2} \Omega_{e,g_2} (\rho_{e,e} - \rho_{g_2,g_2}) \\ & - \frac{i}{2} \Omega_{e,g_1} \rho_{g_1,g_2},\end{aligned}\quad (\text{B.52})$$

$$\dot{\rho}_{g_2,g_1} = + i(\delta_{e,g_1} - \delta_{e,g_2}) \rho_{g_2,g_1} + \frac{i}{2} \Omega_{g_1,e} \rho_{g_2,e} - \frac{i}{2} \Omega_{g_2,e} \rho_{e,g_1}, \quad (\text{B.53})$$

where we have defined the laser detunings from resonance as

$$\delta_{e,g_1} = \omega_{e,g_1} - (\omega_e - \omega_{g_1}), \quad (\text{B.54})$$

$$\delta_{e,g_2} = \omega_{e,g_2} - (\omega_e - \omega_{g_2}). \quad (\text{B.55})$$

This formalism can be extended by analogy to address more complex systems. In general, the detunings and Rabi frequencies will be functions of time—in the lab, we might consider changing the laser frequency or power in order to create a desired effect. Somewhat surprisingly, even in this case the system admits an exact solution, which we present in the following section.

B.6 Exact solutions for the optical Bloch equations with time-dependent parameters

We begin by noting that equations (B.48–B.52) can all be written in the form

$$\dot{\rho}_j = \sum_k R_{j,k} \rho_k. \quad (\text{B.56})$$

For the sake of simplicity I have changed the labelling scheme from one which explicitly states the levels contributing to $\rho_{\alpha,\beta}$ to one which just assumes that the level pairs form some ordered, countable set $\{\alpha\alpha, \alpha\beta, \alpha\gamma \dots \beta\alpha \dots\}$. In this formalism, each element can be labelled with a single index. $R_{j,k}$ is the coupling coefficient for each density matrix element, and is in general a function of time, as are the density matrix elements themselves.

The form of equation (B.56) is evocative of a matrix equation. In fact, in fixing a labelling scheme we open up the possibility of defining a vector representation of our density matrix elements:

$$\boldsymbol{\rho} = (\rho_1, \rho_2, \rho_3 \dots). \quad (\text{B.57})$$

Once we have defined the order of the elements in $\boldsymbol{\rho}$, we can write down a corresponding coupling matrix $\mathbf{R}$ whose rows are formed from the coefficients $R_{j,k}$ in (B.56). We are left with a rather nice, compact form for the optical Bloch equations:

$$\dot{\boldsymbol{\rho}} = \mathbf{R} \boldsymbol{\rho}. \quad (\text{B.58})$$

To illustrate the point, we consider the three-level OBEs of equations (B.48–B.52). We define our density vector as

$$\boldsymbol{\rho} = (\rho_{e,e}, \rho_{g_1,g_1}, \rho_{g_2,g_2}, \rho_{e,g_1}, \rho_{e,g_2}, \rho_{g_1,e}, \rho_{g_1,g_2}, \rho_{g_2,e}, \rho_{g_2,g_1}) \quad (\text{B.59})$$

from which the rather large 9×9 coupling matrix $\mathbf{R}$ is given in Appendix (C) for the sake of clarity.

To proceed, we now expand $\boldsymbol{\rho}$ in terms of the eigenvectors of $\mathbf{R}$. The eigenvector set $\{\mathbf{u}_j\}$ is defined as

$$\mathbf{R}\mathbf{u}_j = \lambda_j \mathbf{u}_j, \quad (\text{B.60})$$

and the expansion of ρ is given by

$$\boldsymbol{\rho} = \sum_j c_j \mathbf{u}_j, \quad (\text{B.61})$$

where the set of expansion coefficients c_j are to be determined. Substituting equation (B.61) into (B.58) and applying (B.60), we obtain

$$\sum_j \left(\dot{c}_j \mathbf{u}_j + c_j \dot{\mathbf{u}}_j \right) = \sum_j c_j \lambda_j \mathbf{u}_j. \quad (\text{B.62})$$

The equality in equation (B.62) must be true on a term by term basis. Considering a single term and simplifying, we obtain the linear first-order differential equation:

$$\dot{\mathbf{u}}_j = \left(\lambda_j + \frac{\dot{c}_j}{c_j} \right) \mathbf{u}_j. \quad (\text{B.63})$$

Integrating both sides of equation (B.63) we find that

$$\mathbf{u}_j(t) c_j(t) = \mathbf{A}_j e^{\int_0^t \lambda_j(s) ds}. \quad (\text{B.64})$$

The constant vector $\mathbf{A}_j$ can be determined by evaluating equation (B.64) at $t = 0$ where the value of the integral in the exponent is zero. Hence

$$\mathbf{u}_j(t) c_j(t) = \mathbf{u}_j(0) c_j(0) e^{\int_0^t \lambda_j(s) ds}, \quad (\text{B.65})$$

and the elements of the density matrix are therefore given by

$$\boldsymbol{\rho}(t) = \sum_j \mathbf{u}_j(0) c_j(0) e^{\int_0^t \lambda_j(s) ds}. \quad (\text{B.66})$$

Equation (B.66) has some useful properties. The initial conditions completely specify the expansion coefficients, with the transient behaviour captured in the exponent. While even modest-sized systems will require the eigenvectors and eigenvalues to be calculated numerically, this is a task that can be performed efficiently with minimal

computing power.

Finally we note that the formalism above fails when $\mathbf{R}$ and $\boldsymbol{\rho}$ are functions of both time and position. In this case, as our positions can be parametrised as $\mathbf{r} = \mathbf{r}(t)$ we must apply the chain rule to find the total derivative. This gives the “hydrodynamic” derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla, \quad (\text{B.67})$$

where $\mathbf{v}$ is the instantaneous velocity vector of the molecule in question. However, it is often the case that any spatial inhomogeneity experienced by the molecule will occur over much longer characteristic times than the internal, electronic time scales induced by the electric field. For example, the characteristic Rabi cycle of a transition might be of the order of a microsecond or less, while the diameter of the laser is typically of the order of a millimetre. The approach outlined in this section is valid when $\mathbf{v} \cdot \nabla \rho \ll \partial_t \rho$. Linearising this equation and defining a characteristic length ζ and time τ , we obtain the condition $\zeta/\tau \gg |v|$; taking $\tau \approx 10^{-6} \text{ s}$ and $\zeta \approx 10^{-2} \text{ m}$, we find that this criterion holds by two orders of magnitude for typical experimental velocities of $v \leq 250 \text{ m s}^{-1}$.

B.7 Steady state solutions of the OBEs

We are often more concerned with the steady state solutions to the OBEs, rather than the intricacies of the transient behaviour. For example, when calculating the optical force on a molecule we may choose to do so with the detuning (and hence, molecular velocity) assumed to be constant. We would then solve for the steady state populations as a function of detuning, and finally let the velocity vary slowly with time to obtain the force.

The method outlined in appendix (B.6) offers one way to calculate the steady state behaviour of the system. We can take the limit in equation (B.66) to obtain

$$\boldsymbol{\rho}(\infty) = \sum_j \mathbf{u}_j(0) c_j(0) e^{\int_0^\infty \lambda_j(s) ds}, \quad (\text{B.68})$$

and then evaluate the eigenvalue integrals $\int_0^\infty \lambda_j(s) ds$. Note that, in order for the steady state to exist, the eigenvalues corresponding to the non-zero eigenvectors must all be square-integrable.

On the other hand, if the coefficients of the coupling matrix $\mathbf{R}$ are slowly-varying or constant, accurately evaluating the numerical integrals in (B.68) can become computationally expensive. A more efficient and exact scheme is to directly set the time derivative in (B.58) equal to zero to obtain

$$\mathbf{R}\boldsymbol{\rho} = \mathbf{0}, \quad (\text{B.69})$$

where $\mathbf{0}$ is the null vector. The common way to solve equations of the form of (B.69) is to apply the inverse of $\mathbf{R}$ to both sides and solve for $\boldsymbol{\rho}$; however, note that $\mathbf{R}^{-1}\mathbf{0} = \mathbf{0}$ via the properties of the null vector. Thus, as we have set the problem up, we can only retrieve the trivial solution $\boldsymbol{\rho} = \mathbf{0}$

Equation (B.69) is actually something of a trap. As it stands, the system is underdetermined by virtue of the population conservation law

$$\sum_j \rho_{j,j} = 1. \quad (\text{B.70})$$

As an example, let's try and solve the simpler system of $(x, y, z) = (1, 0.3, 0.7)$, without using the conservation law $x + y + z = 2$. We attempt to solve the system of equations

$$\begin{pmatrix} 0 & 7 & -3 \\ 3.5 & 0 & -5 \\ 0.3 & -1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \quad (\text{B.71})$$

to retrieve the values of (x, y, z) . We can eliminate y from the system using normal simultaneous equation methods to obtain

$$\begin{pmatrix} 2.1 & -3 \\ 3.5 & -5 \end{pmatrix} \begin{pmatrix} x \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \quad (\text{B.72})$$

however, we are left with two equations that are multiples of each other! The most that we can say is that $x = \frac{10}{7}z$. To lift this requirement, we replace one of the equations in (B.71) with the conservation law. Replacing the second equation leads to

$$\begin{pmatrix} 0 & 7 & -3 \\ 1 & 1 & 1 \\ 0.3 & -1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 2 \\ 0 \end{pmatrix}, \quad (\text{B.73})$$

which solves nicely and correctly obtains (x, y, z) . We can use this principle to solve for the steady state population of $\boldsymbol{\rho}$ by defining a new coupling matrix $\tilde{\mathbf{R}}$, obtained by replacing one row (say row q) in $\mathbf{R}$ with equation (B.70). Then

$$\boldsymbol{\rho}(\infty) = \tilde{\mathbf{R}}^{-1}\boldsymbol{\sigma}, \quad (\text{B.74})$$

where $\sigma = (0, 0, \dots, 1, \dots)$ is the vector whose only nonzero element is at position q . We can use this method to obtain an analytic expression for the excited state population in the steady- or quasi-steady state—for example, the two-level system yields

$$\rho_{e,e}^{\text{two-level}}(\infty) = \frac{\Omega^2}{\Gamma^2 + 4\delta^2 + 2\Omega^2}, \quad (\text{B.75})$$

with the ground state population following from equation (B.70). Similar, but rather more complicated, expressions can be obtained for the three-level system³:

$$\rho_{e,e}^{\text{three-level}}(\infty) = \frac{4r(r-1)(\delta_{e,g_1} - \delta_{e,g_2})^2 \Omega_{e,g_1}^2 \Omega_{e,g_2}^2}{\sum_{i=0}^3 c_{2i} \Omega_{e,g_1}^{2i}}, \quad (\text{B.76})$$

$$\rho_{g_1,g_1}^{\text{three-level}}(\infty) = \frac{\sum_{j=0}^2 b_{2j} \Omega_{e,g_1}^{2j}}{\sum_{i=0}^3 c_{2i} \Omega_{e,g_1}^{2i}}, \quad (\text{B.77})$$

where the co-factors $\{b_j\}$ and $\{c_i\}$ are given by

$$b_0 = (r-1)r\Omega_{e,g_2}^2 \left[4r^2\Gamma^2(\delta_{e,g_1} - \delta_{e,g_2})^2 + (4\delta_{e,g_1}(\delta_{e,g_2} - \delta_{e,g_1}) + \Omega_{e,g_2}^2)^2 \right], \quad (\text{B.78})$$

$$b_2 = 4(r-1)(2r-1)(\delta_{e,g_1} - \delta_{e,g_2})\Omega_{e,g_2}^2 - (1 + 2(r-1)r)\Omega_{e,g_2}^4, \quad (\text{B.79})$$

$$b_4 = r(r-1)\Omega_{e,g_2}^2, \quad (\text{B.80})$$

$$c_0 = b_0, \quad (\text{B.81})$$

$$\begin{aligned} c_2 = & 4(r-1)r(\delta_{e,g_1} - \delta_{e,g_2})^2 \left[(r-1)^2\Gamma^2 + 4\delta_{e,g_2}^2 \right] \\ & + 4(\delta_{e,g_1} - \delta_{e,g_2}) \left[(r-1)(3r-1)\delta_{e,g_1} + (2-3r)r\delta_{e,g_2} \right] \Omega_{e,g_2}^2 \\ & - (r^2 - r + 1)\Omega_{e,g_2}^4, \end{aligned} \quad (\text{B.82})$$

$$c_4 = 8(r-1)r(\delta_{e,g_1} - \delta_{e,g_2})\delta_{e,g_2} - (r^2 - r + 1)\Omega_{e,g_2}^2, \quad (\text{B.83})$$

$$c_6 = r(r-1). \quad (\text{B.84})$$

While the analytic forms of the steady-state populations are rather unwieldy, they do allow us to point out some interesting properties and differences between the two- and three-level system. Scanning the laser detuning δ in equation (B.75) across $\delta = 0$ produces a sharp resonance in the excited state population. This is in contrast to

³Note that this method isn't computationally efficient. Analytically calculating the inverse of a matrix via Gauss–Jordan elimination proceeds on time scales of the order $\mathcal{O}(n^3)$, where n is the size of that matrix. The size of our coupling matrix scales as $n = L^2$, where L is the number of levels in our system. So we should be prepared for significant (at least $\mathcal{O}(L^6)$) scaling. Anecdotally, I've found that the method becomes cumbersome for $L > 5$.

equation (B.75), which has zero excited state population when $\delta_{e,g_1} = \delta_{e,g_2}$. The coherences in the three-level system result in a dark state when both lasers are equally detuned, a process known as coherent population trapping.

The intensity of the driving field is proportional to the square of the Rabi rate. In the case of very high intensity driving fields, we can write down the maximum population in the excited state for both the two- and three-level systems. Equation (B.75) is maximised for $\delta = 0$; taking the limit $\Omega \rightarrow \infty$ yields $\rho_{e,e}^{\text{two-level}}(\infty) \rightarrow 1/2$. For the three-level system, the excited state population is maximised when $\delta_{e,g_1} = -\delta_{e,g_2}$ and $\delta_{e,g_1} = \Omega_{e,g_1}/2$. Substituting these values in with $\Omega_{e,g_1} = \Omega_{e,g_2}$, we find that $\rho_{e,e}^{\text{three-level}}(\infty) \rightarrow 1/3$. In both cases, the high intensity limit finds population equally shared amongst all the levels in the system.

This result can be generalised using a simple rate equation model. Suppose we drive population between G states in the ground state manifold, g , and E states in the excited state manifold, e , at a total rate R , and that decays proceed from the manifold of excited states back to the manifold of ground states with total rate Γ . We assume that some level of mixing occurs within the manifold of ground states such that all populations here are equal, and the same for the excited states. In practice this mixing may arise from many sources, for example external fields (such as the Earth's magnetic field), molecular collisions, polarisation modulation schemes, and so on. The total population in the system must be conserved, hence

$$E e(t) + G g(t) = 1. \quad (\text{B.85})$$

The rate equation for the excited population is

$$E \dot{e}(t) = -\Gamma E e(t) + R(g(t) - e(t)), \quad (\text{B.86})$$

so that, evaluating the system at steady state and substituting equation (B.85) into (B.86) we obtain

$$E e(\infty) = \left(\frac{E}{E+G} \right) \left(\frac{\Gamma G E}{R(G+E)} + 1 \right)^{-1}. \quad (\text{B.87})$$

Taking the limit of $R \rightarrow \infty$ in (B.87), we find that, in the high intensity limit, the total population is shared equally amongst all states. For the specific case of $E = 1$ and $G = 2$ discussed above, $\lim_{\Omega \rightarrow \infty} e(\infty) = 1/3$, in agreement with the full quantum treatment.

B.8 The maximum photon scattering rate

In many practical applications, we are most interested in the rate at which photons are scattered from a laser beam into free space via the process of spontaneous decay. For example, the process of conventional laser deceleration proceeds with an atom or molecule absorbing energy (and hence, momentum) from a laser beam with a well defined beam direction, and then re-radiating that energy into a randomly-oriented mode in free space. Averaging over all possible directions, we can show that each spontaneous decay process removes $p = \hbar k$ momentum from the particle we are attempting to cool, where k is the laser wave vector.

The instantaneous photon scattering rate must be given by the product of the spontaneous decay rate Γ and the excited state population $\rho_{e,e}$. For a fixed set of detunings, $\rho_{e,e}$ is a monotonically increasing function of the intensity. Hence, the maximum scattering rate is taken by evaluating the asymptote

$$\Gamma_{\text{eff}} = \Gamma \lim_{\Omega \rightarrow \infty} \rho_{e,e}(\infty). \quad (\text{B.88})$$

We have already evaluated $\rho_{e,e}$ in equation (B.87) above, and found that connecting multiple low-energy states to a single excited state reduces the excited state population according to $\lim_{\Omega \rightarrow \infty} \rho_{e,e}(\infty) = 1/(E + G)$. Thus, if we are to maximise the scattering rate of our system, we must be careful not to drive population from a manifold of ground states to a single excited state.

We have also rather brushed aside the role of detuning in this discussion. However, the asymptotic behaviour of $\rho_{e,e}$ is a strong function of the detunings in such a system. We have obtained a rather ungainly expression for the three-level excited state population in equation (B.76); thankfully, equations of this type simplify somewhat in the special case where all Rabi rates are equal, and spontaneous decay is equally likely to proceed from the excited state to any of the levels in the ground-state manifold:

$$\rho_{e,e}^{\text{three-level}}(\infty) = \frac{\Omega^2}{(\frac{\Gamma}{\sqrt{2}})^2 + 4(\delta_1^2 + \delta_2^2) - \Omega^2 + 2\frac{\Omega^4}{(\delta_1 - \delta_2)^2}}. \quad (\text{B.89})$$

A similar expression exists for the four-level “tripod” system with three levels in the ground state manifold:

$$\rho_{e,e}^{\text{four-level}}(\infty) = \frac{\Omega^2}{(\frac{\Gamma}{\sqrt{3}})^2 + 4(\delta_1^2 + \delta_2^2 + \delta_3^2) - 8\Omega^2 + Q(\delta_1, \delta_2, \delta_3)\Omega^4}, \quad (\text{B.90})$$

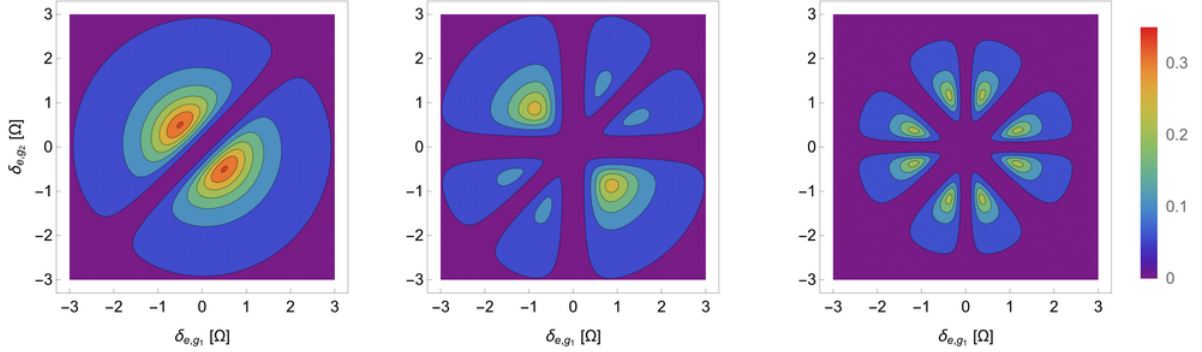


Figure B.1: The maximum steady-state excited state population for the three-level, four-level and five-level systems as functions of the free detunings. The detunings are determined via symmetry arguments to be of the form $\{\delta_1, \delta_2\}$, $\{0, \delta_1, \delta_2\}$, and $\{\delta_1, -\delta_1, \delta_2, -\delta_2\}$ for the three-, four-, and five-level systems respectively, as discussed below. We set $\Omega_{e,g_i} = \Omega_{e,g_j} \gg \Gamma$ and $r = 1/n_g$. The detuning of the driving lasers is measured in units of the Rabi rate Ω . The zeroes are caused by transfer of population into the coherent dark states formed when $\delta_{e,g_i} = \delta_{e,g_j}$.

where the cofactor in the denominator is given by

$$Q(\delta_1, \delta_2, \delta_3) = \frac{((\delta_1 - \delta_2)^2 + (\delta_2 - \delta_3)^2 + (\delta_3 - \delta_1)^2)^2}{(\delta_1 - \delta_2)^2 (\delta_2 - \delta_3)^2 (\delta_3 - \delta_1)^2}. \quad (\text{B.91})$$

To maximise the excited state population, we must minimise the denominator with respect to the various detunings. The first detuning-dependent term, $\sum_j \delta_j^2$ is a measure of the absolute distance from resonance of the lasers. It is minimised by setting the total detuning as small as possible. Counterbalancing that is the cofactor of Ω^4 , which diverges strongly when the detunings co-incide. The tension between these terms is what sets the optimum set of detunings for the system. The two terms also both have an implicit symmetry, depending as they do on the square of the detunings. Thus we might expect that a symmetric pairing of levels with detunings $\delta_i = -\delta_j$ would arise; indeed, referring to the explicit forms in table (B.1) we find this to be true.

Ground state levels	Maximum excited state population	Optimum detunings δ/Ω
1	$1/2$	0
2	$1/3$	$\pm 1/2$
3	$1/4$	$0, \pm\sqrt{3}/2$
4	$1/5$	$\pm 0.371, \pm 1.167$
5	$1/6$	$0, \pm 0.678, \pm 1.429$

Table B.1: Optimum detunings required for the maximum scattering rate to be obtained for special cases of the two-level, Λ , tripod, and five- and six-level systems. In all cases we have a single excited state, $\Omega_i = \Omega_j \forall i, j$ and $\Gamma_{e, g_i} = \Gamma_{e, g_j} \forall g_i, g_j$. The factors for the five- and six-level systems have been determined numerically.

B.9 Concluding the optical Bloch equations

We have seen how the Liouville equation arises as the density matrix equivalent of the Schrödinger equation, and have applied it to the light-matter coupling Hamiltonian, deriving an explicit form of the 3-level optical Bloch equations. We have considered the approximations involved in this derivation, rigorously where possible, and noted some useful schemes for obtaining analytic forms for both the transient and steady state behaviour of the populations and coherences. The steady state solutions for the coupling of many levels in the ground state manifold to a single excited state have been addressed, and the critical detunings required to maximise the scattering rate have been evaluated for the 2- through 6-level systems.

These methods are extensively used in simulating pump-probe experiments in chapter (6) and elsewhere in the thesis.

Appendix C

Coupling matrix for the 3-level optical Bloch equations

Following from the discussion in appendix (B.6), for a density vector of the form

$$\rho = (\rho_{e,e}, \rho_{g_1,g_1}, \rho_{g_2,g_2}, \rho_{e,g_1}, \rho_{e,g_2}, \rho_{g_1,e}, \rho_{g_1,g_2}, \rho_{g_2,e}, \rho_{g_2,g_1})$$

we can define a 9×9 coupling matrix $\mathbf{R}$, given by:

$$\mathbf{R} = \begin{pmatrix} -\Gamma & 0 & 0 & \frac{i}{2}\Omega_{e,g_1} & \frac{i}{2}\Omega_{e,g_2} & -\frac{i}{2}\Omega_{e,g_1} & 0 & -\frac{i}{2}\Omega_{e,g_2} & 0 \\ r\Gamma & 0 & 0 & -\frac{i}{2}\Omega_{e,g_1} & 0 & \frac{i}{2}\Omega_{e,g_1} & 0 & 0 & 0 \\ (1-r)\Gamma & 0 & 0 & 0 & -\frac{i}{2}\Omega_{e,g_2} & 0 & 0 & \frac{i}{2}\Omega_{e,g_2} & 0 \\ \frac{i}{2}\Omega_{e,g_1} & -\frac{i}{2}\Omega_{e,g_1} & 0 & -\frac{r\Gamma}{2} + i\delta_{e,g_1} & \frac{(r-1)\Gamma}{2} + i\delta_{e,g_2} & 0 & -\frac{i}{2}\Omega_{e,g_1} & 0 & -\frac{i}{2}\Omega_{e,g_2} \\ \frac{i}{2}\Omega_{e,g_2} & \frac{i}{2}\Omega_{e,g_1} & 0 & 0 & 0 & -\frac{r\Gamma}{2} - i\delta_{e,g_1} & \frac{i}{2}\Omega_{e,g_2} & 0 & 0 \\ -\frac{i}{2}\Omega_{e,g_1} & 0 & 0 & 0 & -\frac{i}{2}\Omega_{e,g_1} & \frac{i}{2}\Omega_{e,g_2} & i(\delta_{e,g_2} - \delta_{e,g_1}) & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{i}{2}\Omega_{e,g_2} & 0 & \frac{(r-1)\Gamma}{2} - i\delta_{e,g_2} & 0 \\ -\frac{i}{2}\Omega_{e,g_2} & 0 & \frac{i}{2}\Omega_{e,g_2} & 0 & 0 & 0 & 0 & \frac{i}{2}\Omega_{e,g_1} & \frac{i}{2}\Omega_{e,g_1} \\ 0 & 0 & 0 & -\frac{i}{2}\Omega_{e,g_2} & 0 & 0 & 0 & \frac{i}{2}\Omega_{e,g_1} & i(\delta_{e,g_1} - \delta_{e,g_2}) \end{pmatrix}$$

This explicit form of $\mathbf{R}$ is not used in the remainder of the discussion, but is included here both for the sake of completeness and as an aid to anyone who wishes to use this thesis as a reference.

Appendix D

Elastic collisions of point particles with “flat” walls

D.1 Motivation

If we are to model the trajectories of noble gas atoms in an effusive-limit buffer gas cell, we must be able to describe the interaction between the atoms and the cell walls. Naively, we might assume that the walls are flat and the process proceeds with atoms ricocheting within the volume like balls on a snooker table. This is obviously not true as we should expect some level of inhomogeneity on the atomic scale, whether from grain boundaries in crystalline structures, local depth variations from deposited surfaces, or otherwise.

In the following, we develop a simple theory for the dispersal of atomic momentum after interaction with a surface. We consider the case where the surface is flat on average, with some stochastic roughness occurring over a well-defined length and depth scale.

D.2 Macro-smoothness, micro-lengths, and micro-roughness

We must first assess what it means for a surface to be smooth. Clearly, the question of smoothness is equivalent to a statement about the scale on which we measure the surface. Gravel is smooth in comparison to, say, the Himalayas, but is rough in comparison to sandpaper. Roughness requires two separate scales, one of

which parametrises the length over which surface variations occur, and one of which parametrises the magnitude of these variations. I will define these parameters as the micro-length, a , and micro-roughness z respectively.

In the following, I will make a distinction between the gross and fine scales of the surface. On the macro-scale, the surface will be assumed to be smooth, whilst on some micro-scale it will be rough. Smoothness of the macro-scale is determined by two axioms: firstly, that the characteristic roughness micro-length is much smaller than the characteristic macro-scale lengths, and that the local roughness perturbations are distributed with equal probability about the position of the mean surface.

A point particle striking the wall will interact with the local, micro-scale geometry therein. Suppose we divide our wall into micro-length elements, each with some well-defined gradient. Then, as long as the micro-length is much smaller than the macro-scales, even small changes in the particle trajectory will cause the particle to interact with a different wall element. The macro-scale that parametrises the trajectory length scale is the mean free path, λ . In the limit that $\lambda \gg a$ the wall-scattering process becomes highly sensitive on the initial trajectory conditions, and the particle effectively performs a random sampling of the available wall elements.

D.3 Stochastic micro-geometries and scattering angle probabilities

The way in which the wall roughness is defined requires some attention. In the following, I will assume that the local surface is randomly generated according to some probabilistic distribution. In the limit $\lambda \gg a$, we expect there to be a very large number of available surface elements per unit macro-scale. This allows us to invoke the central limit theorem and assume that the probabilistic distribution is normal.

Let's define the wall geometry by first generating a set of random points, then joining those points with straight lines. If the probability distribution used to generate these points is normal, then the probability of a given point x having some height $h(x)$ above or below the mean surface position is

$$P(h) dh = \frac{1}{z\sqrt{\pi}} \exp \left[-\frac{h^2}{z^2} \right] dh, \quad (\text{D.1})$$

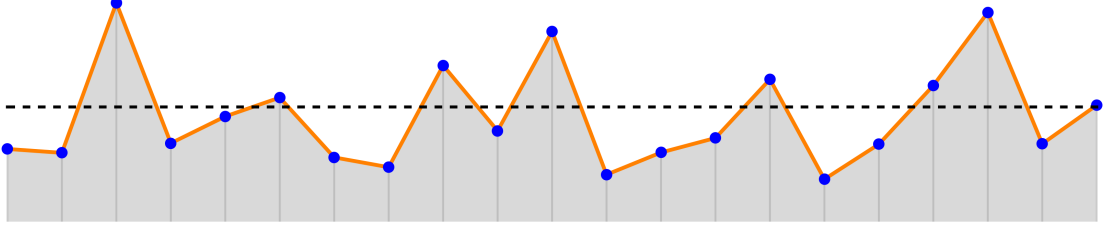


Figure D.1: Example of a number of surface elements generated stochastically, according to a normal distribution. The grey area represents the wall, defined by randomly generated points in blue, while the orange line is the wall boundary. The black dotted line is the mean wall position, and may be considered to reflect the wall on the macro-scale.

where z is the micro-roughness scale defined earlier. The gradient G of the line segment between two adjacent points separated by the micro-length is

$$G = \frac{h(x+a) - h(x)}{a}. \quad (\text{D.2})$$

Now, the probability of obtaining a given G must be the probability of obtaining some specific values of $h(x)$ and $h(x+a)$, summed over all permutations that give $h(x+a) - h(x) = aG$. Hence

$$P(G) dG = a \int P(h) \times P(h - aG) dh. \quad (\text{D.3})$$

Substituting equation (D.1) into equation (D.3) and performing the integral, we find that

$$P(G) dG = \frac{a}{z\sqrt{2\pi}} \exp \left[-\frac{a^2 G^2}{2z^2} \right] dG, \quad (\text{D.4})$$

as required.

In general, we are interested in the change in trajectory once a particle strikes the wall. We will define these trajectories through their angle with the macro-surface, shown as the black dotted line in figure (D.1). If the collision between the particle and the wall is elastic, the initial angle, θ_i will map deterministically onto the output angle θ_o when we know the angle between the micro- and macro-surfaces, θ_s . The geometry for such a scattering event is shown in figure (D.2). We immediately note two relations linking the various angles involved. First, from the elasticity condition,

$$\theta_o = \theta_i + 2\theta_w, \quad (\text{D.5})$$

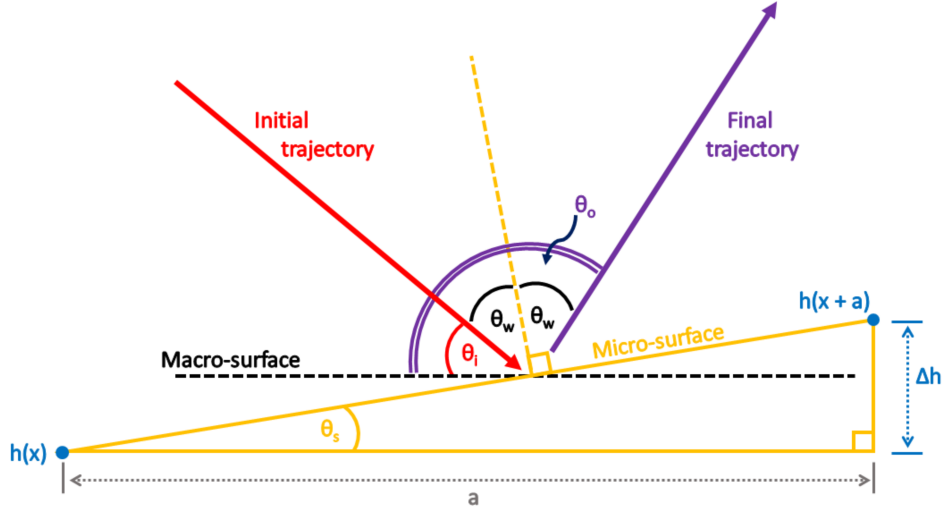


Figure D.2: Scattering of an initial trajectory, parametrised by some θ_i , from a wall micro-surface. The on-average flat macro-surface forms the reference for the angles θ_i , surface angle θ_s , and the output angle, θ_o . The colour scheme used here for the macro- and micro-surfaces is consistent with figure (D.1).

where θ_w is the angle conserved by the elastic scattering process. Secondly, using the normal to the micro-surface,

$$\theta_w + \theta_i + \theta_s = \frac{\pi}{2}. \quad (\text{D.6})$$

Substituting equation (D.5) into equation (D.6) to eliminate θ_w , we find that

$$\theta_s = \frac{\pi - (\theta_i + \theta_o)}{2}. \quad (\text{D.7})$$

To connect θ_s and G , note that the gradient can be written as

$$G = \frac{\Delta h}{a} = \tan \theta_s = \tan \left[\frac{\pi - (\theta_i + \theta_o)}{2} \right] \quad (\text{D.8})$$

through the application of equation (D.7).

We now use the random sampling property that is induced by the assumption $\lambda \gg$

a to connect the probability of a surface element having some gradient with the probability of a final trajectory having some angle θ_o . Substituting equation (D.8) into (D.4) and using the chain rule to change the integral element, we obtain

$$P_s(\theta_o|\theta_i) d\theta_o = -\frac{a}{\sqrt{2\pi}z (\cos[\theta_i + \theta_o] - 1)} \exp\left(-\frac{a^2}{2z^2} \tan^2\left[\frac{\pi - (\theta_i + \theta_o)}{2}\right]\right) d\theta_o, \quad (\text{D.9})$$

the probability distribution for a final trajectory to proceed at an angle θ_o to the macro-surface, given an initial trajectory angle θ_i .

D.4 The surface scattering probability

The derivation of equation (D.9) assumes that all θ_i are equally likely to strike a given micro-surface element, regardless of its angle θ_s . This obviously is not true as if the trajectory and the surface are parallel the particle can never get closer to the wall, and hence can never meet. The parallel conditions are

$$\theta_i = -\theta_s \quad (\text{D.10})$$

$$\theta_i = \pi - \theta_s. \quad (\text{D.11})$$

Applying equation (D.7) we can rewrite these conditions in terms of θ_o :

$$\theta_o - \theta_i = +\pi \quad (\text{D.12})$$

$$\theta_o - \theta_i = -\pi. \quad (\text{D.13})$$

Conditions (D.12) and (D.13) must define the extrema of the probability distribution, as trajectories with angles not satisfying $-\pi \leq \theta_o - \theta_i \leq \pi$ must originate from *within* the micro-surface element and hence be unphysical. Similarly, we also know that the probability must be maximised when the surface is perpendicular to the trajectory, giving a third condition:

$$\theta_o - \theta_i = 0. \quad (\text{D.14})$$

We know that the probability of a trajectory striking a given wall element should scale as the projection of the trajectory onto that element, so we are looking for a suitable sinusoid. Invoking conditions (D.12–D.14), we see that the appropriate unit-area sinusoid is

$$P_a(\theta_o|\theta_i) d\theta_o = \begin{cases} \frac{1}{4} \cos\left[\frac{\theta_o - \theta_i}{2}\right] d\theta_o & -\pi \leq \theta_o - \theta_i \leq \pi \\ 0 & \text{otherwise.} \end{cases} \quad (\text{D.15})$$

Thus, we have found the probability of striking a surface element with a given θ_s , written in terms of the input and output angles. The total probability distribution for a point particle scattered from the surface is then

$$P(\theta_o|\theta_i) d\theta_o = A P_s(\theta_o|\theta_i) P_a(\theta_o|\theta_i) d\theta_o, \quad (\text{D.16})$$

or, in words, the probability of a particle scattering from a given micro-surface element, *and* the probability that the micro-surface has some angle θ_s with respect to the mean macro-surface. Here A is a normalisation constant, which must be introduced as the product of two unit-integrable functions is not guaranteed to also be unit-integrable.

D.5 Observed angles and higher order scattering

We are interested in the case where a particle with $0 \leq \theta_i \leq \pi$ strikes the macrosurface, undergoes scattering, then leaves the surface with some θ_o . In order for a final trajectory to be observed, $0 \leq \theta_o \leq \pi$. Now, conditions (D.12) and (D.13) bound not just P_a , but also P . Inputting the physically meaningful range of θ_i , we find that P may be non-zero on the interval¹ $-\pi \leq \theta_o \leq 2\pi$. Physically, this means that some trajectories are scattered inwards, towards the surface rather than away from it, as can be seen when, for example, $\theta_s > \pi/4$ and $\theta_i > \pi/4$. These trajectories will undergo further scattering events with the micro-surface before they finally re-emerge on the interval $0 \leq \theta_o \leq \pi$.

To take this into account, we perform two processes. In the first, we make use of the periodicity of the angular co-ordinates to map P onto the interval $(0, 2\pi)$. Then, we take the components of P that have $\pi < \theta_o < 2\pi$ and scatter them again, generating some new P_1 on $(0, 2\pi)$. We iterate this process for $P_1, P_2, \dots P_{n-1}$ until, for some n , the component of P_n on $\pi < \theta_o < 2\pi$ is effectively zero. When this has occurred, because of probability conservation, all the population has been redistributed onto $0 \leq \theta_o \leq \pi$ and P_n is the scattering distribution we would experimentally measure if we integrated over all time².

¹It will be useful later in the analysis, when dealing with re-reflections within the micro-surface, to consider the expanded range $0 \leq \theta_i \leq 2\pi$. In this case $-\pi \leq \theta_o \leq 3\pi$, but otherwise the following discussion here is unchanged.

²Particles which are scattered inwards will be retained by the surface while all the extra scattering events take place, so we would expect them to re-emerge at later times than ones which have only one scattering event.

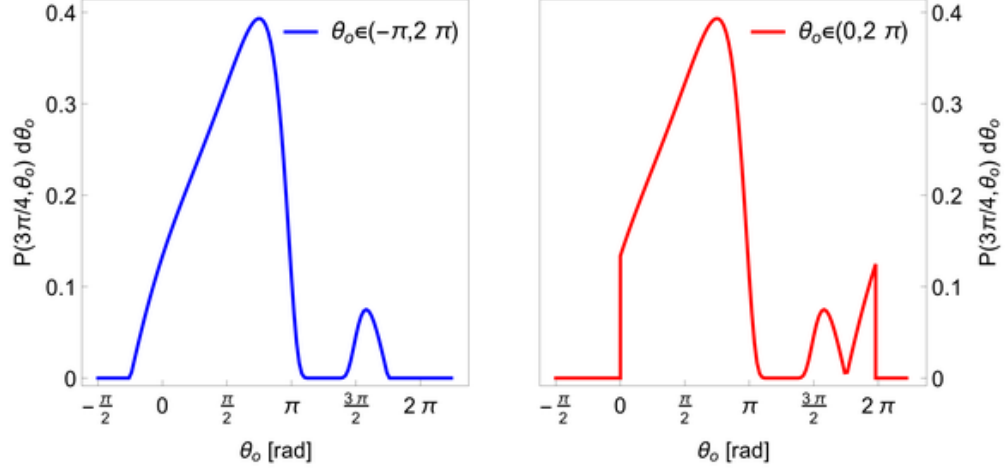


Figure D.3: Two plots showing the initial, raw distribution $P_a(3/4, \theta_o)$ defined on $\theta_o \in (-\pi, 2\pi)$ (blue), and the periodically mapped function defined on $\theta_o \in (0, 2\pi)$ (red). Note that we have used the periodicity to map the region with $-\pi \leq \theta_o < 0$ onto $\pi \leq \theta_o < 2\pi$.

We have performed these processes computationally as follows. First, we determined the set of distributions Q found by mapping the functions $P(\theta_o|\theta_i) d\theta_o$ over various values of $\theta_i \in (0, 2\pi)$. Then, as the interval $(-\pi, 0)$ is the same as $(\pi, 2\pi)$ by symmetry, the contributions with $\theta_o \in (-\pi, 0)$ and $\theta_o \in (\pi, 2\pi)$ are summed for each $P \in Q$, with this sum being arbitrarily attributed to the interval $\theta_o \in (\pi, 2\pi)$. This defines a new set of functions $G_0 \in H_0$, with each G_0 being bounded on both $\theta_i \in (0, 2\pi)$ and $\theta_o \in (0, 2\pi)$.

We now have a family of distributions $G_0(\theta_i, \theta_o) \in H_0$ which describe the probability of redistribution of a given $\theta_i \in (0, 2\pi)$ into the range $\theta_o \in (0, 2\pi)$. For each $G_0(\theta_i, \theta_o)$, we now want to iteratively re-scatter trajectories with $\theta_o \in (\pi, 2\pi)$. To do this, first we define a function

$$\Upsilon(y) = \begin{cases} 1 & 0 \leq y \leq \pi \\ 0 & \text{otherwise.} \end{cases} \quad (\text{D.17})$$

Now we define a function $G_1(\theta_i, \theta_o)$ where one additional re-scattering process on the surface has occurred:

$$G_1(\theta_i, \theta_o) = \Upsilon(\theta_o)G_0(\theta_i, \theta_o) + \int_{\pi}^{2\pi} G_0(\theta_i, \theta_j)G_0(\theta_j, \theta_o) d\theta_j. \quad (\text{D.18})$$

Observe that G_1 has two components. The first part of the sum retains all parts of G_0 for which $0 \leq \theta_o \leq \pi$. Added to this we have the contribution of re-scattering from each $\pi < \theta_o < 2\pi$, weighted by the appropriate probability amplitude and summed over all possible θ_j . The iterative contribution is given by

$$G_n(\theta_i, \theta_o) = \Upsilon(\theta_o)G_{n-1}(\theta_i, \theta_o) + \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_j)G_{n-1}(\theta_j, \theta_o) d\theta_j, \quad (\text{D.19})$$

and, in general, we should expect to repeat the iteration until “almost all” of the population has been scattered from the interval $(\pi, 2\pi)$ into $(0, \pi)$. I’ll address the convergence of G_n rigorously in the next section; meanwhile, the result of applying transformation (D.19) repeatedly onto $G_0(\theta_i, \theta_o) = P(\pi/10|\theta_o)$ is shown in figure (D.4). For now, note that transformation (D.19) does indeed transfer population from $(\pi, 2\pi)$ into $(0, \pi)$.

D.6 Square-integrability and convergence of G_n

I’ve introduced the iterative transformation (D.19) in a slightly loose way. Before moving on, we should show that the set of distributions $G_n \in H_n$ are indeed probability distributions—namely, that they are square-integrable, normalised with unit area—and also, that the transformation (D.19) is convergent.

The set of G_n can be shown to be probability distributions with unit area via induction as follows. Suppose that, for the set H_{n-1} , we have

$$\int_0^{2\pi} G_{n-1}(\theta_i, \theta_o) d\theta_o = 1 \quad (\text{D.20})$$

for all θ_i . Then the area under $G_n(\theta_i, \theta_o)$ is

$$\begin{aligned} \int_0^{2\pi} G_n(\theta_i, \theta_o) d\theta_o &= \int_0^{2\pi} \left(\Upsilon(\theta_o)G_{n-1}(\theta_i, \theta_o) \right. \\ &\quad \left. + \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_j)G_{n-1}(\theta_j, \theta_o) d\theta_j \right) d\theta_o. \end{aligned} \quad (\text{D.21})$$

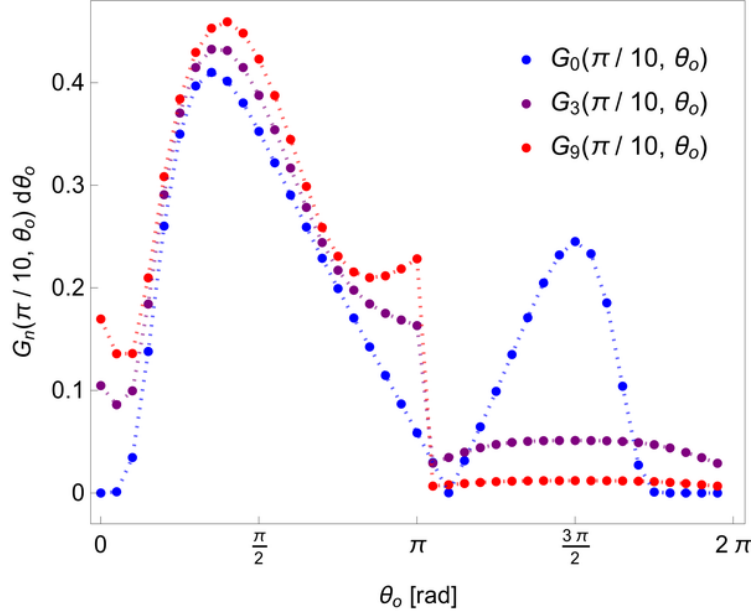


Figure D.4: Numerically computed evolution of G_n for increasing n , with $\theta_i = \pi/10$ and $z = a = 1$. The population on the interval $\theta_o \in (\pi, 2\pi)$ is directed back into the surface, so undergoes repeated scattering events from the surface according to transformation (D.19). The dotted lines connecting the simulated data points are guides to the eye, and as such should not be taken as being indicative of the underlying distribution, especially in regions where the gradient is rapidly-changing.

Using definition (D.17) the first term gives

$$\int_0^{2\pi} \Upsilon(\theta_o) G_{n-1}(\theta_i, \theta_o) d\theta_o = \int_0^\pi G_{n-1}(\theta_i, \theta_o) d\theta_o. \quad (\text{D.22})$$

The second term is somewhat trickier. By applying integration by parts, we obtain

$$\begin{aligned} & \int_0^{2\pi} \int_\pi^{2\pi} G_{n-1}(\theta_i, \theta_j) G_{n-1}(\theta_j, \theta_o) d\theta_j d\theta_o \\ &= \int_0^{2\pi} \left[G_{n-1}(\theta_j, \theta_o) \int_0^{\theta_j} G_{n-1}(\theta_i, \theta_k) d\theta_k \right]_{\theta_j=\pi}^{\theta_j=2\pi} d\theta_o \\ & - \int_0^{2\pi} \int_\pi^{2\pi} \frac{\partial}{\partial \theta_j} G_{n-1}(\theta_j, \theta_o) \cdot \left(\int_0^{\theta_j} G_{n-1}(\theta_i, \theta_k) d\theta_k \right) d\theta_j d\theta_o \end{aligned} \quad (\text{D.23})$$

Now, from the first term on the right of equation (D.23),

$$\begin{aligned} \int_0^{2\pi} \left[G_{n-1}(\theta_j, \theta_o) \int_0^{\theta_j} G_{n-1}(\theta_i, \theta_k) d\theta_k \right]_{\pi}^{2\pi} d\theta_o &= \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_j) d\theta_j \\ &= \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_o) d\theta_o, \end{aligned} \quad (\text{D.24})$$

where we have used both the unit-integral requirement of equation (D.20) along with the independence of $\int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_j) d\theta_j$ on the integration variable. For the second term on the right of equation (D.23), we can switch the order of the integrals using Fubini's theorem:

$$\int_0^{2\pi} \int_{\pi}^{2\pi} \frac{\partial}{\partial \theta_j} G_{n-1}(\theta_j, \theta_o) \cdot \left(\int_0^{\theta_j} G_{n-1}(\theta_i, \theta_k) d\theta_k \right) d\theta_j d\theta_o \quad (\text{D.25})$$

$$= \int_{\pi}^{2\pi} \left(\int_0^{2\pi} \frac{\partial}{\partial \theta_j} G_{n-1}(\theta_j, \theta_o) d\theta_o \right) \left(\int_0^{\theta_j} G_{n-1}(\theta_i, \theta_k) d\theta_k \right) d\theta_j. \quad (\text{D.26})$$

Focussing now on the partial derivative term in equation (D.25),

$$\int_0^{2\pi} \frac{\partial}{\partial \theta_j} G_{n-1}(\theta_j, \theta_o) d\theta_o = \frac{d}{d\theta_j} \int_0^{2\pi} G_{n-1}(\theta_j, \theta_o) d\theta_o = \frac{d}{d\theta_j} 1 = 0, \quad (\text{D.27})$$

where we have invoked the requirement of equation (D.20) to evaluate the integral, and used the fact that it must be unity *regardless* of θ_j . Thus

$$\int_0^{2\pi} \int_{\pi}^{2\pi} \frac{\partial}{\partial \theta_j} G_{n-1}(\theta_j, \theta_o) \times \left(\int_0^{\theta_j} G_{n-1}(\theta_i, \theta_k) d\theta_k \right) d\theta_j d\theta_o = 0 \quad (\text{D.28})$$

and, combining the result of equations (D.22) and (D.24), we finally find that

$$\begin{aligned} \int_0^{2\pi} G_n(\theta_i, \theta_o) d\theta_o &= \int_0^{\pi} G_{n-1}(\theta_i, \theta_o) d\theta_o + \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_o) d\theta_o \\ &= \int_0^{2\pi} G_{n-1}(\theta_i, \theta_o) d\theta_o. \end{aligned} \quad (\text{D.29})$$

Thus, as long as all the G_0 functions are square-integrable with unit area, all the G_n must also be normalised by induction.

For the transformation (D.19) to be convergent, we require that the population

on $(\pi, 2\pi)$ decreases as the number of iterations increases. From the normalisation condition on $(0, 2\pi)$, this is equivalent to the demand

$$\delta = \int_0^\pi G_{n-1}(\theta_i, \theta_o) d\theta_o - \int_0^\pi G_n(\theta_i, \theta_o) d\theta_o \leq 0. \quad (\text{D.30})$$

The equality holds in the limit of convergence. By using equation (D.19) to expand for G_n ,

$$\begin{aligned} \delta = \int_0^\pi \left(G_{n-1}(\theta_i, \theta_o) - \Upsilon(\theta_o) G_{n-1}(\theta_i, \theta_o) \right. \\ \left. - \int_\pi^{2\pi} G_{n-1}(\theta_i, \theta_j) G_{n-1}(\theta_j, \theta_o) d\theta_j \right) d\theta_o. \end{aligned} \quad (\text{D.31})$$

By using the properties of $\Upsilon(\theta_o)$, the first two terms in the sum of equation (D.31) cancel, leaving

$$\delta = - \int_0^\pi \int_\pi^{2\pi} G_{n-1}(\theta_i, \theta_j) G_{n-1}(\theta_j, \theta_o) d\theta_j d\theta_o. \quad (\text{D.32})$$

Now, if $G_0 \in H_0$ are positive definite, so too are G_1 as all the terms in transformation (D.19) must be greater than zero. This must then be true for all $G_m \in H_m$, so that the product under the double integral in equation (D.32) must also be positive definite. The integral of a positive-definite function is positive definite, therefore

$$\int_0^\pi \int_\pi^{2\pi} G_{n-1}(\theta_i, \theta_j) G_{n-1}(\theta_j, \theta_o) d\theta_j d\theta_o \geq 0 \implies \delta \leq 0, \quad (\text{D.33})$$

and we have proved that repeated application of (D.19) drives population convergently into $(0, \pi)$. As the population on $(0, \pi)$ tends to 1, δ tends to zero as can be seen after the application of Fubini's theorem on (D.32):

$$\delta = - \int_\pi^{2\pi} G_{n-1}(\theta_i, \theta_j) \left(\int_0^\pi G_{n-1}(\theta_j, \theta_o) d\theta_o \right) d\theta_j. \quad (\text{D.34})$$

Then, if all the population is in $(0, \pi)$ (convergence),

$$\begin{aligned} \int_0^{2\pi} G_{n-1}(\theta_j, \theta_o) d\theta_o &= \int_0^\pi G_{n-1}(\theta_j, \theta_o) d\theta_o = 1 \\ \implies \int_\pi^{2\pi} G_{n-1}(\theta_j, \theta_o) d\theta_o &= 0. \end{aligned} \quad (\text{D.35})$$

Evaluating the inner integral in equation (D.34) first and then applying (D.35) twice,

$$\begin{aligned}\delta &= - \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_j) \left(\int_0^{\pi} G_{n-1}(\theta_j, \theta_o) d\theta_o \right) d\theta_j \\ &= - \int_{\pi}^{2\pi} G_{n-1}(\theta_i, \theta_j) \times 1 d\theta_j = 0.\end{aligned}\tag{D.36}$$

We conclude that applying transformation (D.19) on a valid initial probability distribution (having unit area and being positive definite) produces another valid probability distribution, and that a greater or equal amount of population in this new distribution lies in the interval $(0, \pi)$.

D.7 Sequential scattering and the Knudsen cosine law

We have justified the key properties of the $G_n \in H_n$, showing that they produce valid probability distributions and that the population of those distributions on $(\pi, 2\pi)$ tends to zero as $n \rightarrow \infty$. Because of this second property, the limiting distribution $G_{\infty}(\theta_i, \theta_o)$ is nonzero only on $(0, \pi)$ and hence must correspond to the distribution that would be measured in an experiment (if the arrival time of particles at a hypothetical detector were ignored, of course). We associate $G_{\infty}(\theta_i, \theta_o)$ with the distribution after a single scattering event from the *macro-surface*, as the many rescattering processes that lead to the generation of G_{∞} occur must locally within the micro-surface.

Computationally, we would discretise the functions $G_{\infty}(\theta_i, \theta_o)$ into intervals of θ_i and θ_o ; an example of this was shown earlier in figure (D.4), where a fixed value of $\theta_i = \bar{\theta}_i$ was chosen, and the various integrals calculated in the discrete limit over some set of $\theta_{o,j}$. Extending the iteration limit to infinity is also not practically possible, so we should choose a large but finite n and monitor the sequentially generated G_n to ensure sufficient convergence. In the following we will label the converged functions as $G_{\infty}(\theta_i, \theta_o)$, but it should be understood that this is not necessarily the formal infinite limit and may have been determined numerically.

Once the set of $G_{\infty} \in H_{\infty}$ have been determined, they form an analogue to the Green's functions for a differential equation—for each θ_i is an associated distribution in the independent variable θ_o . If we have an initial distribution $F_0(\theta_i)$, we can integrate the contribution from each θ_i to obtain the distribution after scattering once

from the macro-surface, $F_1(\theta_o)$:

$$F_1(\theta_o) = \int_0^\pi F_0(\theta_i) G_\infty(\theta_i, \theta_o) d\theta_i. \quad (\text{D.37})$$

If we wish to consider a second scattering event from a different macro-surface (as may happen when the gas is confined in a cell, for example), we can treat $F_1(\theta_o)$ as a new initial distribution³ and feed it into an analogue of equation (D.37). In general, the angular distribution after m collisions with the macro-surface is

$$F_m(\theta_o) = \int_0^\pi F_{m-1}(\theta_i) G_\infty(\theta_i, \theta_o) d\theta_i. \quad (\text{D.38})$$

We are interested in how rapidly a specific molecular trajectory with a well-defined initial angle loses its orientation. Scattering from the surface will change both the mean and the width of the angular distribution. If the surface is perfectly smooth, then we expect the mean to change according to the usual laws of elastic reflection, $\theta_o = \pi - \theta_i$, and sequential macro-scattering events will give distributions whose means alternate between these values. Conversely, if it is rough then the distribution will broaden and the behaviour of the mean is not obvious.

We have tested the evolution of narrow angular distributions under repeated macro-surface scattering for a variety of surface roughness parameters, a/z . The set of discretised G_∞ were generated as discussed previously, and then the macro-surface functions F_m were found through the repeated application of equation (D.38). An example of this is shown in figure (D.5) for $a/z = 5$, with an initial distribution given by

$$F_0(\theta_i) = \begin{cases} \frac{1}{\delta} & \pi/4 \leq \theta_i < \pi/4 + \delta \\ 0 & \text{otherwise,} \end{cases} \quad (\text{D.39})$$

where $\delta = \pi/20$ is the frequency of data points used in our discretisation. We chose this F_0 as it has unit area and a narrow, well-defined width, although I can see no reason why the following arguments would not hold for other narrow functions with the same integral properties. The repeated scattering action broadens the distribution, and shifts the mean towards the centre of the range $\theta_o = \pi/2$. The distribution also becomes increasingly symmetrical about $\theta_o = \pi/2$, as we can see by directly comparing F_1 and F_{30} in figure (D.5). This behaviour—of broadening, symmetrising, and re-forming the mean—is consistent with all tested roughnesses, $1 \leq a/z \leq 5$,

³Just to be clear, as we are considering different scattering events we are free to relabel θ_o from F_{m-1} as θ_i in F_m .

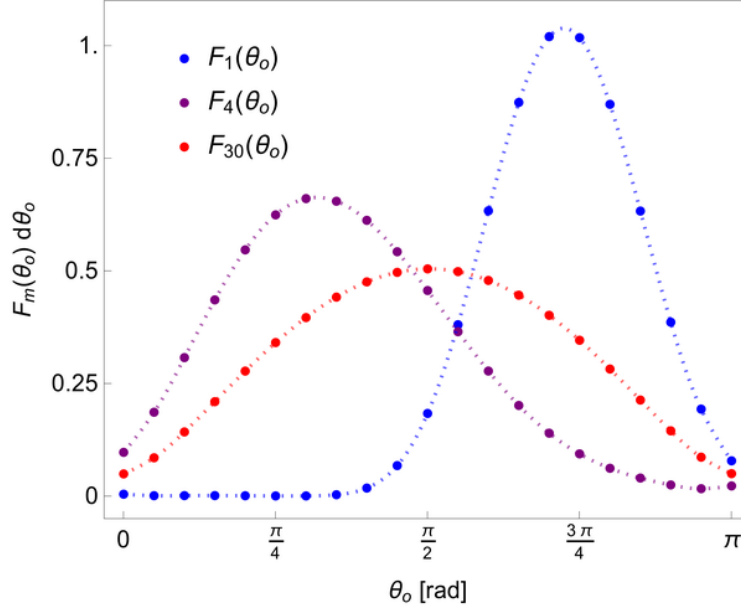


Figure D.5: Numerically determined F_m for a surface roughness $a/z = 5$, and a discrete delta function F_0 centred at $\theta_i = \pi/4$. The data is shown through the points, while the dotted line is a guide to the eye generated through interpolation.

and all initial mean angles for our F_0 distributions of equation (D.39).

Asking how many macro-collisions m are required for the initial distribution to lose its orientation is equivalent to asking how large m must be before F_m is the same *for all* θ_i in a given $F_0(\theta_i)$. If this condition holds then all information about the initial θ_i must have been lost, and the various initial velocity components must have become completely mixed. As a measure for this, we have calculated the residual sum of squares (RSS) between our numerically determined F_m distributions—specifically, between distributions with the same m but different mean θ_i , using as our reference the set of F_m with $\theta_i = \pi/2$. We wish to compare the RSS to some other meaningful scale, consistent across all our distributions, to determine when they begin to lose their distinguishability. As all the F_m are defined on $(0, \pi)$ and have unit area, then the characteristic amplitude f_m of the distributions will be of the order $f_m \approx 1/\pi$. We define the indistinguishability point (IP) as the number of collisions required such that $\text{RSS} < 1/\pi$. A plot of the IP for three different surface roughnesses is shown in figure (D.6). We see that increasing the ratio a/z , and hence decreasing the surface roughness, increases the typical IP values for all initial mean angles, $\langle \theta_i \rangle$. This means

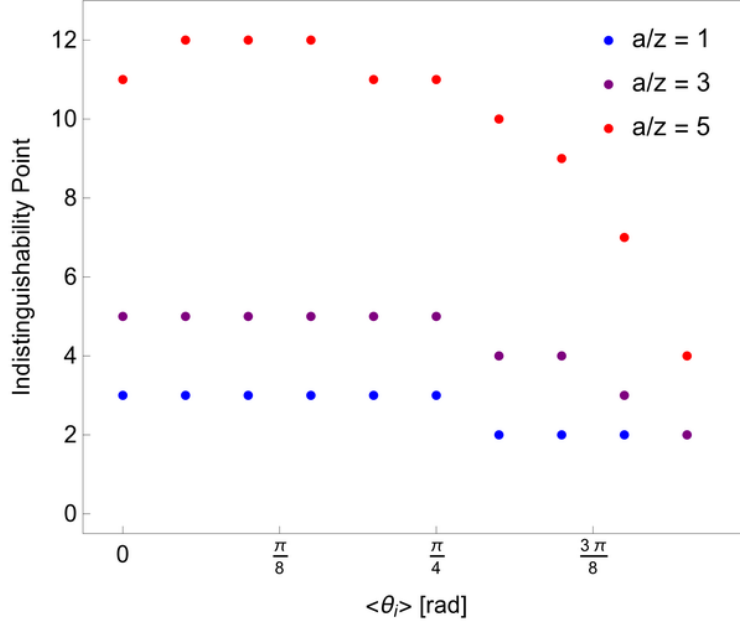


Figure D.6: Indistinguishability point, determined by calculating the RSS between our F_m with mean initial angle θ_i and the F_m with initial angle $\pi/2$. The IP follows by determining when the RSS drops below the threshold $1/\delta$.

that trajectories scattered from smoother surfaces take longer on average for their orientations to become completely lost, as we would intuitively expect.

Next we should consider the functional form that our distributions eventually converge to. In their work “Knudsen’s cosine law and random billiards” [128], Feres and Yablonsky showed that Knudsen’s assumption of a cosine-scattering dependence from a surface held for a range of micro-geometries. The explicit form of Knudsen’s cosine law, re-written in our co-ordinate system which is defined relative to the surface parallel rather than the surface normal, is

$$F_\infty(\theta_o) = \begin{cases} \frac{1}{2} \sin(\theta_o) & 0 \leq \theta_o \leq \pi \\ 0 & \text{otherwise.} \end{cases} \quad (\text{D.40})$$

In particular, they were interested in a range of highly structured, pore-type geometries, and performed their simulations on a periodically generated surface. This is in contrast to the random model proposed here, where the surface is assumed to be highly disordered on the micro-scale with no periodicity. As part of their work, they

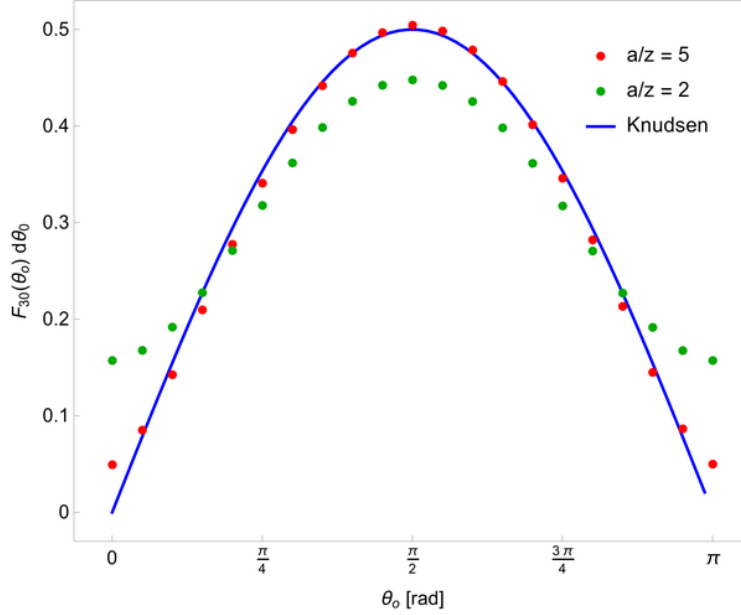


Figure D.7: Functional forms of $F_{30}(\theta_o)$ obtained for $a/z = 2$ and $a/z = 5$, using in both cases the narrow $F_0(\theta_i)$ of equation (D.39). Both cases converge somewhat to the cosine law of equation (D.40), although the convergence is clearly better in the case with lowest surface roughness, $a/z = 5$.

also showed that the Knudsen cosine law arose following sequential macro-scattering events, rather than just after a single scattering process on the micro-surface. However, they also noted that this behaviour did not hold for all their choices of micro-geometries. We wish to examine our random system, under many macro-collisions, and see if it also follows this seemingly fundamental law.

Explicit forms for the macro-scattering function after 30 macro-collisions, $F_{30}(\theta_o)$, are compared to the Knudsen law of equation (D.40) in figure (D.7). Both roughnesses show some characteristics of the cosine law, having peaked maxima at $\theta_o = \pi/2$, but the behaviour close to the extrema, $\theta_o = 0$ and $\theta_o = \pi$, is more varied. In general, the rougher surfaces have a higher probability of scattering particles along the directions of the extrema than the smoother surfaces. This is because the larger micro-roughness surfaces often have local gradients which differ greatly from those of the macro-surface, supporting these scattering processes. Note that, as we have already shown that all our tested F_∞ with the same surface roughness converge to the same function independent of initial angle, the convergence to cosine-like func-

tions must be true regardless of $\langle\theta_i\rangle$. Even if the final function F_∞ is not of a similar form to the Knudsen model, it must still be symmetric about $\theta_o = \pi/2$, as can be inferred intuitively from the symmetry of the macro-surface.

We can make this discussion more quantitative by again invoking the residual sum of squares, this time between the Knudsen law of equation (D.40) and the F_m distributions for various surface roughnesses. A plot of the natural logarithm, $\ln(\text{RSS})$, of this residual sum of squares for three a/z values is shown in figure (D.8). We have invoked the logarithm as it makes comparing both the initial and long-term convergence properties for the various roughnesses a little easier. We see that, as I asserted earlier, smoother surfaces converge more slowly but more faithfully towards the cosine distribution. Also note that the previously discussed indistinguishability point occurs when $\ln(\text{RSS}) < -\ln(\pi) \approx -1.14$. From our simulations, $\ln(\text{RSS})$ converges to ≈ -1.077 for $a/z = 4$, and ≈ -1.406 for $a/z = 5$, so the functions F_∞ are good approximations to the cosine law beyond $a/z \gtrsim 5$. Finally, we point out that the number of collisions required to reach a converged distribution is not a linear function of a/z . For this particular choice of F_0 , we have computed the number of collisions required for convergence—specifically, when the gradient between successive $\ln(\text{RSS})$ values is less than 10^{-2} . We find that, for $a/z = 1$ through 5, the required number of collisions for convergence (N_{cc}) is 2, 4, 8, 15, and 28 respectively. This suggests that

$$N_{\text{cc}} \approx K^{a/z}, \quad (\text{D.41})$$

where $K \approx 2$ is a constant. This gives us a useful rule of thumb for the required number of collisions for convergence to the asymptotic form, F_∞ , although we note that the exact value of K may well depend on $\langle\theta_i\rangle$, as we saw in figure (D.6). Averaging over a set of equiprobable initial $\langle\theta_i\rangle$, with $\langle\theta_i\rangle \in (0, \pi)$, we find that $N_{\text{cc}} = 2, 4, 8, 15$, and 26 for $a/z = 1$ to 5 respectively, and $K \approx 2$ is still appropriate⁴.

Finally, let's consider what an appropriate range of values for a/z would be for scattering on a surface. If we imagine the surface as being formed via the sequential deposition of atoms onto some substrate, then an a/z greater than or equal to 1 would be appropriate. For our magnetic guide system, the ratio of the tetragonal lengths of the unit cell forms a useful lower limit; for neodymium magnets, the lattice scales are given in [129] as 8.8 and 12.2 angstroms respectively, giving a lower limit to a/z again of order unity.

⁴Performing a fit in Mathematica with K the only floating variable gives $K = 1.93 \pm 0.01$.

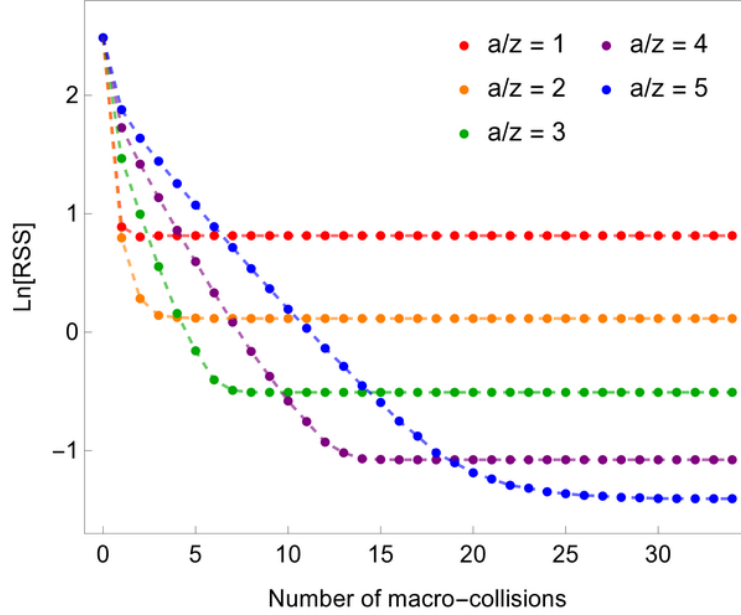


Figure D.8: Natural logarithm of the residual sum of squares, calculated between the computed F_m functions and the Knudsen law of equation (D.40). The lines connecting the data points form guides to the eye, and are particularly useful for seeing the behaviour close to zero macro-collisions.

D.8 Conclusion

We have modelled the interaction of a point particle with a wall under the assumption that the wall, while smooth and flat on average, has some small-scale local structure which contributes to the dissipative scattering process. We have modelled this structure as being random, and obtained expressions for the local wall gradient under the assumption that the micro-structure is normally distributed. We have additionally considered the probability that a scattering event occurs from a given micro-surface element, given an initial trajectory angle θ_i , by considering the projection of this trajectory onto the surface element.

A scheme has been developed to handle the repeated scattering of particles from the rough micro-surface. This scheme has been shown mathematically to produce valid probability distributions, and to convergently re-distribute population from trajectories directed into the macro-surface to those directed outwards from it. This scheme was used to numerically determine the converged scattering probabilities af-

ter a single macro-collision, G_∞ , for a range of surface roughnesses.

Finally, we applied the computed G_∞ distributions to determine the action of repeated scattering processes on the macro-surface. We have observed the convergence towards a universal F_∞ regardless of the mean initial angle $\langle\theta_i\rangle$, and found that this distribution is symmetric and, for smooth walls, sinusoidal in character. We have examined the convergence properties for our various roughnesses and initial angles, obtaining a useful rule of thumb expression for the number of macro-collisions required for convergence.

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