

THESIS

Buffer gas cooling and mid-infrared spectroscopy of polyatomic molecules

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Abstract

This thesis reports buffer gas cooling, beam formation, and state-selective absorption spectroscopy of polyatomic molecules, focusing on the trioxane molecule, $\text{C}_3\text{H}_6\text{O}_3$. The molecules are injected from room temperature into a cryogenically-cooled cell containing a buffer gas of helium or neon. They are detected inside the cell by state-selective mid-infrared wavelength modulation spectroscopy using a quantum cascade laser. We recorded trioxane spectral features from both the Q- and R-branches of the ν_5 vibrational band, between 977.1 and 978.6 cm^{-1} . We resolved spectral features as narrow as 6 MHz , and observed molecules with temperatures as low as $7.4 \pm 0.3\text{ K}$. We estimate the density of cold trioxane in the cell to be $5 \times 10^{21}\text{ m}^{-3}$. After characterising the molecules inside the cell, we extracted a beam of trioxane from the cell and detected it using a mass spectrometer. We studied in detail the parameters that affect the beam and learned how to produce beams with high flux. We attempted to detect molecules in a single state in the beam using laser absorption, and have tentatively observed a signal by this method. The work shows that quite complex molecules can be cooled to low temperature using this method, either inside a cell or in a beam, and shows the enormous simplification of the spectrum that occurs at these low temperatures, enabling high resolution spectroscopy of complex species. An interesting application of the work is to produce cold beams of chiral molecules and use these to measure the parity-violating energy difference between chiral enantiomers arising from the weak interaction. The progress made in this thesis are the first important steps in this direction.

Declaration

I declare that this thesis is my own work. Where I have used the work of others the sources are appropriately referenced and acknowledged.

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Publications and conferences

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Contents

1	Introduction	9
1.1	Why molecules and why cold?	9
1.2	Cooling of molecules	12
1.3	Buffer gas cooling	13
1.4	Parity violation	16
1.5	Spectroscopic methods for complex molecules	21
1.5.1	Wavelength and frequency modulation spectroscopy methods	22
1.5.2	Cavity-enhanced spectroscopy	22
1.6	Future experiment	25
1.7	In this thesis	26
2	Cryogenic source of complex molecules	28
2.1	Overview of the experiment	28
2.2	Cryogenic apparatus	31
2.2.1	Cold cell	31
2.2.2	Molecular source	32
2.2.3	Beam chamber	32
2.2.4	Heat loads	33
2.3	Details specific to helium buffer gas	34
2.4	Details specific to neon buffer gas	36
2.5	Laser system	37
2.5.1	Quantum cascade laser	37
2.5.2	Noise reduction	40
2.5.3	Frequency calibration	40
2.5.4	Measurement of the laser linewidth	43

2.5.5	Remaining issues with the spectroscopic system	45
2.6	Data acquisition system	45
2.7	Mass spectrometer	46
3	Trioxane molecular structure	47
3.1	Trioxane energy levels	48
3.2	Trioxane roto-vibrational spectrum	51
3.2.1	Notation	54
3.3	Strength of the trioxane lines	54
4	Production and spectroscopy of cold trioxane	56
4.1	Theory of buffer gas cooling	56
4.1.1	Cooling time and length	57
4.2	Wavelength Modulation Spectroscopy	62
4.2.1	WMS theoretical principles	62
4.2.2	Impact of WMS parameters on the molecular spectrum	66
4.3	Trioxane ν_5 Q- and R- branch spectra	69
4.4	Characterisation of molecules	75
4.5	Saturation	75
4.6	Power broadening	76
4.7	Trioxane in-cell density	76
4.8	Sub-Doppler spectroscopy	79
4.8.1	Interaction of 2-level system with pump and probe fields	80
4.8.2	Mollow treatment of interaction of two level system with a pump and probe fields	82
4.9	Sub-Doppler spectroscopy results	86
4.9.1	Reproducibility	87
5	Beam formation and detection	90
5.1	Theory of molecular beam creation	90
5.1.1	Helium buffer gas beam properties	93
5.1.2	Neon buffer gas beam properties	93
5.1.3	Choice of buffer gas	95
5.2	Characterising a trioxane beam with helium as buffer gas	95

5.2.1	Helium flow	96
5.2.2	Trioxane capillary position	98
5.2.3	Trioxane flow	100
5.2.4	Different aperture sizes	101
5.2.5	Optimised values and conclusions	101
5.3	Characterising a trioxane beam with neon as the buffer gas	102
5.3.1	Neon flow	102
5.3.2	Trioxane flow	104
5.3.3	Trioxane capillary position	105
5.3.4	Time	107
5.3.5	Optimised values and conclusions	108
5.4	Cluster formation	108
5.5	Choice of buffer gas	109
5.6	State-selective detection by absorption spectroscopy	110
5.6.1	Absorption spectroscopy in the beam	110
5.6.2	Absorption and signal-to-noise enhancement in the beam	111
5.6.3	Results	116
6	Conclusions and outlook	118
6.1	Conclusions	118
6.2	Outlook	121
6.2.1	Improvements to the setup	121
6.2.2	Chiral molecules	125
	Bibliography	126

Chapter 1

Introduction

The aim of the work reported in this thesis was to produce beams of cold polyatomic molecules and detect them state-selectively using laser absorption in the mid-infrared. While there are many motivations of cooling down molecules, and producing cold beams of complex molecules, a particular motivation of the current work was to create a source of molecules for measuring the parity-violating energy difference between left- and right-handed enantiomers of chiral molecules. So far, despite efforts over many decades, there was no successful measurement of this effect. This chapter presents some of the applications of cold molecules. It outlines the methods used to cool and detect them, with a particular focus on buffer gas cooling, laser spectroscopy, and parity violation. I also highlight a few achievements in buffer gas cooling of cold molecules and producing cold beams of complex molecules.

1.1 Why molecules and why cold?

The main advantage, and also the biggest drawback of using molecules in a variety of experiments is their complex energy-level structure. The presence of vibrational and rotational degrees-of-freedom in addition to the translational ones gives more experimental flexibility but also provides challenges in cooling and manipulation.

The presence of internal electric dipole moments in molecules and the possibility of manipulating them with external fields means that the molecules can facilitate anisotropic, long-range interactions. The large set of molecular internal states allows flexibility for an experimenter to engineer the system needed for a particular purpose [1]. For applications in quantum simulation and information processing, ultracold molecules can exhibit coherence times similar to that of ultracold atoms [2]. Their usefulness is additionally amplified by the fact that they can be coupled to solid-state systems, allowing for scalability and integration into quantum systems based on other

techniques. These features are very advantageous if applied for example in quantum computing. Quantum computing can be useful for many tasks, including large integer factorisation [3], solving linear systems of equations [4], and many-body simulation [5]. Molecules could be utilised in almost all parts of the quantum computing system, including photon sources [6], qubits and quantum memories [7]. Different types of cold molecules have been hailed as possible qubits. One idea is to use ultracold polar molecules trapped in an array or a lattice [8]. An example of a qubit, in that case, is the molecule's electric dipole moment that can be externally oriented along or against an electric field. The qubits can be individually addressed and the interactions between qubits can be facilitated via dipole-dipole interaction [9, 10]. Symmetric-top molecules (like CaOCH_3) have been also proposed as potential candidates for qubits [2].

Strong correlations between molecules can help in the synthesis of quantum materials, in which quantum effects manifest over a wide range of energies and length scales. Examples of such materials are Bose-Einstein condensates (BEC), degenerate Fermi gases, and optical lattices [11]. Ultracold atoms can be used for simulation of some phenomena of condensed matter physics, however, they have no long-range interactions that can lead to understanding a range of phenomena in quantum many-body physics. The dipole-dipole interaction between molecules provides the required long-range interaction. For example, cold polar molecules can help in answering various questions about many-body quantum correlations [12]. Cooling molecules up to the degree where the quantum regime manifests is very challenging and provides a major obstacle in the creation of quantum materials from molecules [13]. The creation of ultracold polar molecules near quantum degeneracy using Feshbach resonances to magneto-associate molecules from cold atoms has proven to be a pathway to overcome this obstacle [14]. For example in 2015 a gas of bosonic NaRb was achieved, with a density of molecules in the absolute ground state close to being high enough to observe quantum phenomena [15]. Recently, a group from the university of Boulder, Colorado, has demonstrated the production of a degenerate Fermi gas of polar KRb molecules. Such a system can be used for a wide variety of applications, for example to probe many-body correlation by measuring local density fluctuations [16].

The rotational and vibrational states of molecules usually have long lifetimes, and so the transitions between them can be very narrow and can be used to probe many fundamental questions using precise spectroscopy of molecules. In hot samples, however, the width of the lines is affected by Doppler, collisional, and transit time broadening. Additionally, the rich internal structure of molecules leads to very dense spectra. Cooling of molecules reduces Doppler broadening and decongests the spectra by reducing the number of populated states, allowing for better spectroscopic resolution. Using slow beams increases interaction time further increasing the resolution. With such high resolution it becomes possible to search for a possible time-variation of fundamental constants, such as the fine-structure constant that determines the strength of the electroweak interaction.

While the value of the constant is measured to 2.3×10^{-10} [17] relative uncertainty, it is still an open question whether the value is time-dependent. A constraint on the possible time-variation of the fine-structure constant has been made using a beam of slow, cold hydroxyl radicals [18]. Extremely sensitive measurement of the electron-to-proton mass ratio was performed by spectroscopy of two nearly degenerate vibrational levels in a cold K⁸³Rb molecule produced by photoassociation [19]. High precision spectroscopy with cold molecules can also probe other fundamental questions in a tabletop experiment. For example, slow molecules are excellent objects to use in the detection of time-reversal symmetry violation by measurement of the electron electric dipole moment (EDM) [20]. The EDM hails from the time (T) violation, which can be thought of as equivalent to a charge-parity (CP) violation. CP violation is needed to explain the matter-antimatter asymmetry in the universe [21]. Different theories, including standard model and theories beyond the standard model, have placed different bounds on the magnitude of CP violation and therefore the electron electric dipole moment [22]. Measuring the value of the electron EDM can help provide evidence for or against possible extensions of current theories. The best upper limits on the electron EDM have been made using beams of YbF [23] and ThO [24, 25] molecules cooled to a few kelvin, as well as trapped HfF⁺ ions at room temperature [26]. Measurements using ultracold molecules will lead to even greater sensitivity [27]. Another area of interest is an observation of spin-dependent and spin-independent parity-violating effects in molecules. As this is very important for this thesis it will be covered in detail in Section 1.4.

Molecules participate in a variety of important and interesting chemical reactions, and precise state engineering can lead to monitoring each step in a reaction, from approach trajectories, energy potentials, reaction intermediates and finally emerging products [28, 29]. So far chemical reactions for cold molecules have been studied in crossed supersonic molecular beams that ensure narrow and well-known velocity distributions. Vibrational and rotational state selection in molecular beams was performed by a DC or an AC field, which allows engineering the reaction up to some degree [30]. In supersonic beams there are still a lot of collisions between the molecules and the molecules are very fast in the laboratory frame [31]. An improvement over that is a hydrodynamic or an effusive molecular beam that has a lower velocity in the laboratory frame and with lower gas densities it has limited collisions [32, 33]. Additionally, laser slowing and trapping of molecules can give more control over molecular degrees-of-freedom [34]. In ultracold molecules, the fine and hyperfine structure can be manipulated to extend control over the chemical reaction [35, 36]. Cold beams of molecules can reproduce low-density environments present in space. More than 100 molecular species have been so far observed in the interstellar dust, characterised by low temperatures (around 50 K) and low number density (approximately from 10^{12} to 10^6 cm⁻³). Recreating such an environment can help in cross-checking the spectroscopic measurements taken in the interstellar dust. Observing chemical reactions in these conditions can reveal how complex molecules are created in low energy

environments [37].

1.2 Cooling of molecules

In this section, a few established methods of cooling molecules will be outlined. First, the methods can be separated into direct and indirect ones. Indirect methods create molecules from constituent atoms. Examples are photoassociation and magnetoassociation. In photoassociation, a bound state is created between two atoms after they absorb a photon of a certain wavelength [14]. Molecules that have been created this way include Rb_2 [38], LiK [39], and KRb [40]. Magnetoassociation is a method in which loosely-bound molecules are formed from atoms by tuning through a Feshbach resonance. For atoms with differing magnetic moments, the external magnetic field can be applied to tune through their Feshbach resonances, thus producing species from two different atoms. Examples of molecules created by that method are Cs_2 [41], RbCs [42, 43], NaK [44], and NaRb [15]. Indirect methods have a few shortcomings: they can be used only to create a restricted set of molecules and additional steps are required to move the molecules produced to the ground state.

Supersonic beams are a direct way of cooling molecules. In this method, the molecules of interest are seeded in a high flux of inert gas and extracted to the vacuum via a nozzle. The mixture of gases cools adiabatically because of the rapid expansion into the vacuum. The species of interest have a narrow spread of velocities in their internal frame but a high speed in the laboratory frame. A supersonic beam results in a high flux of molecules. The technical challenge with the supersonic beam is keeping a low pressure in the system with a high influx of gas, which requires complex pumping setups. Pulsed supersonic beams, which only emit short pulses of gas, largely avoid this problem. The development of this direct cooling method started with beams where the molecule of interest was directly seeded into the carrier gas, for example from an oven. The molecular beams produced with this method included rubidium, potassium, bromine, iodine, chlorine and more. The development of seeding the beam by laser ablation of a target in a flow of a carrier gas allowed to develop beams of refractory metals like Cu_2 [45]. This method was later expanded to indirect production of molecules in the supersonic beam: the molecules were created via the reaction of the molecules produced by laser ablation with the impurity gas added to the supersonic carrier. That allowed to produce beams of molecules like YF and YO [46], which in turn led to development of beam of a YbF [23] used for precision measurement of the electron EDM, described in Section 1.1. The next generation of experiments for measurement of electron EDM, like ACME measurement using ThO [24, 25], started using buffer gas cooling, which is another example of a direct cooling method, and the method used in this thesis.

Direct cooling methods can be used for a wider range of molecules. An example of a direct

cooling method is buffer gas cooling which can, in theory, be applied to any molecule, as the process of cooling is independent of the molecule's internal state. In this method, the molecules of interest collide with a cold buffer gas, usually helium or neon, and thermalise to the temperature of the buffer gas. As long as the molecules can survive the collisions, they can be cooled by this method. The final temperature of the molecules is restricted to the temperature of the buffer gas. For example for the three most popular buffer gases - helium, neon and argon - the temperatures achieved can be as low as 1 K, 15 K, and 40 K respectively. For some applications, therefore, buffer gas cooling is enough to bring molecules to the desired temperature. Even in cases where much lower temperatures are needed, buffer gas cooling is often the first step of a multi-step cooling process. As buffer gas cooling is at the heart of this thesis it will be discussed in detail in Section 1.3.

Laser cooling of molecules can be another step to bring molecules down to ultracold temperatures. This was first developed for diatomic molecules [47], but has recently been applied to more complex species. For example, the Sisyphus cooling method was utilised to cool SrOH [48]. Some proposals extend the method to even more complex molecules, like alkaline earth monoalkoxide radicals that have favourable Franck-Condon factors for laser cooling [49].

1.3 Buffer gas cooling

Buffer gas cooling is a relatively new method that is currently being adopted by many groups working in the field of cold molecules. The technique is perfect for reducing the translational temperature of molecules, and additionally, it can cool internal degrees of freedom. In this section, I will distinguish between buffer gas cooling in the cell and the production of a molecular beam, presented in Figure 1.1. I make that distinction because of different technical challenges and a differing molecular environment produced in each of these cases. My discussion will focus on polyatomic molecules.

Buffer gas cooling relies on mixing the molecules of interest with a pre-cooled buffer gas inside a cold cell. The molecules thermalize to the temperature of the buffer gas. In the buffer gas cell, even accounting for a loss of species due to freezing to the cell walls, the molecules can be observed at a relatively high density as the observation regions are usually quite close to the molecular delivery regions. Because collisions are required for thermalisation they still contribute to the line broadening in the molecular spectrum [50]. Delivery methods of species of interest to the buffer gas cell can be grouped into three kinds: laser ablation, beam loading, and capillary filling, illustrated in Figure 1.2.

In laser ablation, shown in Figure 1.2a, a solid-state precursor is ablated with a pulsed laser, and the molecules produced are cooled by the buffer gas [52]. This method can only be applied to molecules that have a suitable solid precursor, but can be used to create radicals. For

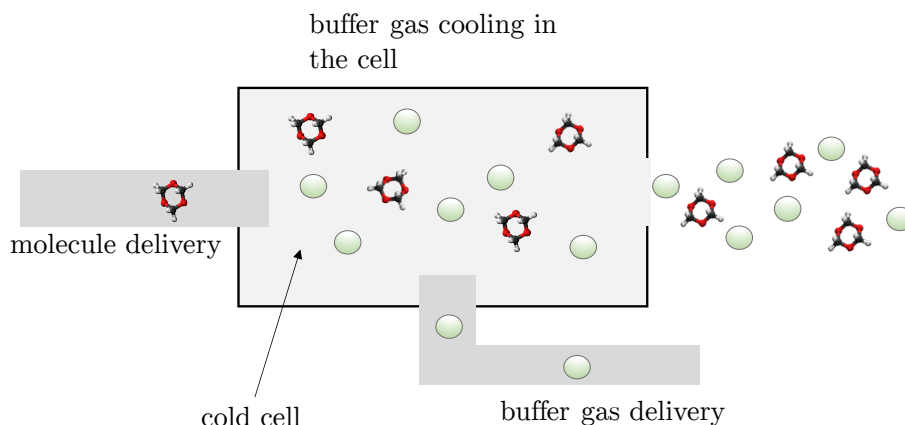


Figure 1.1: A view of the buffer gas cell with the molecule and buffer gas (green disks) inlets, demonstrating buffer gas cooling in the cold cell and molecules extracted to the buffer gas beam.

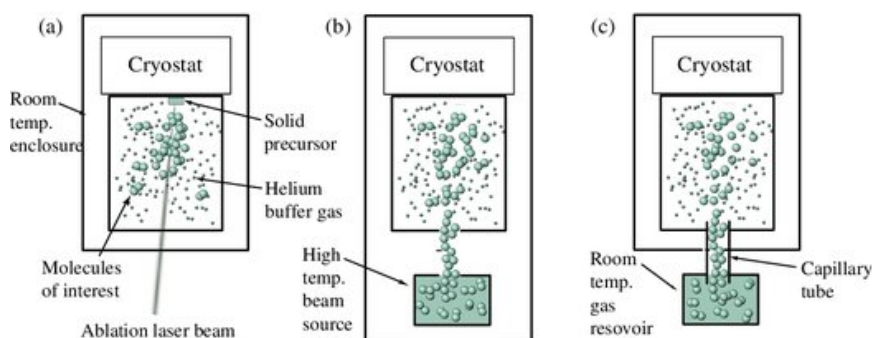


Figure 1.2: A cut-through of a buffer gas cell with different ways of introducing molecules into the cell demonstrated. a) ablation b) beam loading c) capillary filling. Reproduced with permissions from [51].

some molecules, the yield of ablation product is either low and/or hard to predict and may suffer from a lack of specificity in molecules produced. The ablation process can be a significant heat load on the cold cell. In beam filling the beam of molecules is produced away from the cold cell [53]. This method is demonstrated in Figure 1.2b. The beam flows into the cell via an aperture and then mixes with the buffer gas. This method makes management of heat loads on the cold cell easier but results in quite small fluxes. It also suffers from the problem that the buffer gas escapes through the aperture needed for beam loading, and collisions between the molecules and the escaping buffer gas can prevent the beam from entering the cell. The outflow of the buffer gas through the delivery aperture must be low enough to allow the species into the cell. The number density of the buffer gas inside the cell, on the other hand, must be high enough to allow for efficient thermalisation. In the capillary filling method molecular vapour flows into the cell from an outside source via a capillary

reaching directly into the cold cell [54], as shown in Figure 1.2c. This method cannot be used to produce radicals since they would all stick to the capillary walls or react to other products before reaching the cell. The method results in a specific molecule delivered to the cell but can only be applied to molecules that have high vapour pressure or can be oven heated to produce more vapour. The capillaries are prone to clog and might suffer from small flux. Because the capillary has to be kept close to room temperature to prevent freezing of molecules inside, it can pose a significant heat load on the cold cell (Section 2.2.4).

There are a number of groups that perform buffer gas cooling and study complex molecules in the buffer gas cell. For example, the Doyle group at Harvard University, reported microwave spectroscopy of enantiomers of 1,2-propanediol, $\text{CH}_3\text{CHCH}_2\text{OH}$, cooled to 7 K [55]. A study of cold naphthalene, C_{10}H_8 , in a cold cell was performed via laser-induced fluorescence at 308 nm, and the temperature of the sample was detected to be 6 K [56]. Recently, microwave spectroscopy of a buffer-gas cooled sample of lemon-oil allowed the determination of some of its 25 constituents like limonene, $\text{C}_{10}\text{H}_{16}$, β -pinene, $\text{C}_{10}\text{H}_{16}$, and ethanol, $\text{C}_2\text{H}_5\text{OH}$ [57]. Frequency comb spectroscopy of the CH stretch mode (3 μm) has been performed on buffer gas cooled vinyl bromide, CH_2CHBr , adamantane, $\text{C}_{10}\text{H}_{16}$, and diamantane, $\text{C}_{14}\text{H}_{20}$, with measured rotational and translational temperatures between 10 - 20 K [58]. Di Sarno et al. used a 1.5 μm laser to perform Lamb-dip (or sub-Doppler) spectroscopy on acetylene, C_2H_2 , cooled to 20 K inside a buffer gas cell. The laser was stabilised by referencing it to a Rb/GPS clock. The resulting full-width-half-maximum (FWHM) of the Lamb feature was established to be 820 ± 40 kHz [59]. Successful cooling and cavity-enhanced frequency comb spectroscopy of fullerene, C_{60} , with argon as a buffer gas has been reported. The temperature of the molecules was measured to be 150 K [60].

Buffer Gas beams

If an aperture is installed in a buffer gas cell the molecules can follow the flow of the buffer gas out of the cell, forming a molecular beam. There are three parameters that describe the quality of the beam: the forward velocity of the species in the beam ($v_{||,s}$), the temperature in the moving frame (T_F), and the flux of molecules (ϕ). A perfect beam is slow (low $v_{||,s}$), cold (low T_F) and bright (high ϕ). Achieving a beam that covers these three requirements is very challenging. For example, the slowest beams are created with low buffer gas flows, where there are no collisions in the vicinity of the beam aperture to increase the velocity. With a low flow, however, the molecules diffuse to the cell walls faster than they are extracted from the cell which results in small molecular flux. This signifies the biggest challenge with the molecular beam: when the buffer gas flow is low, slow beams are formed in a collision-free environment where high vacuum can be maintained, but this comes at the price of low beam brightness. Additionally, the molecular beam expands as it propagates away from the source, making the density of molecules in the beam lower, and making observation at long distances

harder. A low brightness makes optical detection of molecules in the beam a challenge, and for this reason, amongst others, there have been very few reports of molecular beams of complex molecules. A beam of YbOH molecules was observed via absorption spectroscopy just outside the cold cell, and the reported extraction was about 10% of molecules from the cell [61]. A helium buffer gas beam at 2 K was used as a source of molecules for Sysiphus cooling of SrOH [48]. Carbon cluster production (from C_3 to C_{12}) has been observed in the buffer gas beam via Fourier-transform infrared spectroscopy between 2.5 and 10 μm . The observation was performed 20 mm from the cell aperture [62] and the beam had enhanced extraction from the cell because of the high buffer gas flow used (40 sccm). Beams of ND_3 [63], CH_3F , and CF_3CCH [64] were successfully produced and loaded into electrostatic beam guides. A buffer-gas cooled beam of NH_3 molecules was created and detected via resonance enhanced multiphoton ionisation (REMPI) and time-of-flight mass spectroscopy (TOF-MS) at 51 mm from the cell aperture [65]. In 2014 David Patterson and John Doyle reported the creation and subsequent Fourier Transform microwave spectroscopy of benzonitrile, $\text{C}_6\text{H}_5\text{CN}$, in a buffer gas beam. The detection was performed 50 mm from the cell aperture and the number density of benzonitrile molecules reported at that point was $n_{\text{molecule}} = 6 \times 10^9 \text{ cm}^{-3}$ which corresponds to a flux of $\phi = 10^{15} \text{ molecules s}^{-1}$. The rotational temperature of the molecule determined in the experiment was 5 K. They additionally reported the creation of beams of anisole, $\text{CH}_3\text{OC}_6\text{H}_5$, aminobenzonitrile, $\text{H}_2\text{NC}_6\text{H}_4\text{CN}$, and fluorobenzene, $\text{C}_6\text{H}_5\text{F}$. They also attempted to create and observe beams of acetone, $(\text{CH}_3)_2\text{CO}$, and 1,2-propanediol, $\text{CH}_3\text{CHCH}_2\text{OH}$, but were unsuccessful, probably due to clustering of the molecules that removed the monomers from the beam [66].

1.4 Parity violation

The first effect that can be attributed to parity violation (PV) was observed in experiments that measured the decay products of a K meson. The K meson is a quark-antiquark state with parity of -1 . The decay of the meson was observed to yield two types of products, one with parity of -1 (conserved) and one with parity of $+1$ (not conserved). The initial theories suggested that the K meson can exist in two different initial states, but no proof of that was found. Instead, it was discovered that the parity is violated in this interaction. The violation was connected with the weak interaction that causes the K meson decay [67].

Shortly after this observation, it was shown that parity violation affects the rate of a transition between two states. When a transition rate between a state and its mirror state is compared, one can note that there is a small difference. This led to an experiment performed in 1957 that studied the β -decay of the ^{60}Co nuclei [68]. The experiment showed that the direction of electrons emitted in the decay, presented in Figure 1.3, depended on the orientation of the spin of the nucleus, which confirmed the existence of a parity-violating effect. The β -decay of cobalt is

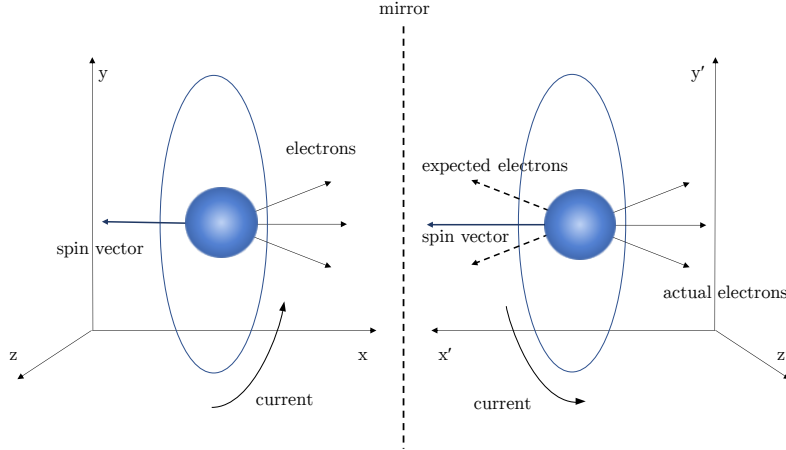


Figure 1.3: Image showing the direction of electrons observed in β -decay of the ^{60}Co nucleus, and its mirror reflection. The electrons are emitted preferentially in one direction, which violates parity symmetry.

mediated by a charged W boson which changes the charge of the nucleus. This observation of parity violation can therefore be applied only to processes caused by a weak force that changes the charge of their constituents. Theoretical studies of the weak interaction, and especially its unification with the electromagnetic force, predicted many interesting phenomena, one of which was the presence of an uncharged force carrier, the Z^0 boson, a particle that mediates weak interactions that do not cause the charge to change [69]. The Z^0 boson couples to the electron and the coupling is determined by the electron's helicity. Helicity is the product of electron spin and velocity, which is a quantity that changes with a mirror reflection, therefore any interaction mediated by the Z^0 boson will be parity violating [70]. Because this boson mediates an electron-nucleus interaction it is beneficial to assign a weak charge Q_W to the nucleus. Precise measurement of this quantity is one of the main aims of the parity violation measurements in neutral atoms. PV effects can be divided into nuclear spin-dependent (NSD) and nuclear spin-independent (NSI) effects. The part of the interaction that depends on the nuclear spin is much harder to measure than the spin-independent counterpart.

PV measurements in atoms

The presence of the weak force in the interaction between an electron and a nucleus means that the parity-violating effects should also be present in the charge conserving processes in neutral atoms. Indeed, these effects are present and their experimental detection is a way to test parity violation in the weak interaction. To observe the PV effect a few types of experiments are performed. One of them is to compare the rate of transitions between two pairs of states, one being the mirror image of another. The problem with such a measurement is that the difference is extremely small.

The asymmetry is defined as

$$A_{\text{RL}} = \frac{P_L - P_R}{P_L + P_R}, \quad (1.1)$$

where P_L, P_R are transition rates for two states and their mirror states respectively [71]. The theoretical value of the asymmetry is calculated to be of order 10^{-15} , which is extremely difficult to measure with current techniques. There are however a few enhancement effects that can be used to increase this value to 10^{-6} which is much easier to measure. The fact that asymmetry is proportional to the cube of atomic number Z^3 means that it can be more easily observed in heavy atoms. The problem with this approach, however, is the fact that the heavier the atom gets the more complex structure it has, which makes it harder to determine the transition rates theoretically. Another method measures the rate for transitions that are strictly forbidden in the absence of parity violation. This is the preferred method for a lot of experiments because it allows the use of atoms with a well-known structure, like Cs or Tl [72]. The transitions of choice were strongly forbidden M1 transitions between states of the same parity. Because there is no electromagnetic dipole moment between the two states, the transition is forbidden but the weak interaction creates a small dipole moment that makes such transitions possible.

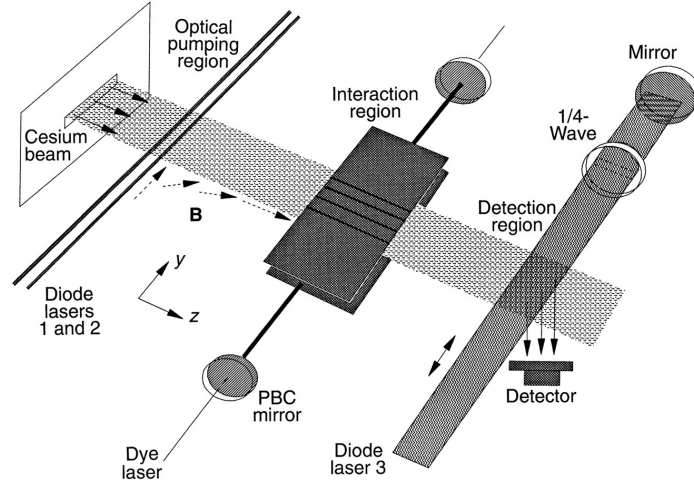


Figure 1.4: JILA Cs experimental apparatus showing a molecular beam passing through interaction and detection regions. The spin polarisation of the molecules is defined in the interaction region where B is along the z -axis and E is along the x -axis. The handedness of the region is changed by flipping each of the field axes. Reproduced with permissions from [73].

An example of such an experiment is one performed on Cs atoms in JILA where the difference in transition rates was directly observed [73]. In the experimental setup, shown in Figure 1.4, the mirror images of the states are created by spin polarizing the beam in two opposite directions. The atoms were pumped into the desired state and then the fluorescence caused by the decay from this state was detected. This experiment uses a transition between the 6S and 7S states of Cs.

Both states have the same parity, hence there is no electric dipole moment between them and the transition is strictly forbidden. The weak interaction causes the mixing of some of the 6P state with both S states creating a transition amplitude of A_{PNC} . It is an extremely small value, making it very hard to measure experimentally. To enhance the effect, the group in JILA placed Cs atoms in a DC electric field which created a Stark-induced additional mixing of P and S states. This gives an additional amplitude A_{E} to the transition. A_{PNC} and A_{E} interfere to produce a signal which is proportional to the product of the two quantities and is experimentally measurable. When the value of A_{PNC} is modulated by changing the parity-violating conditions it can be separated from A_{E} . The value of Q_{W} was determined from this measurement. The JILA experiment remains the most precise experiment to measure nuclear spin-independent parity violation in atoms. The experiment also succeeded in measuring the anapole moment of the Cs nucleus which is a nuclear spin-dependent quantity.

Another type of measurement searches for a rotation in the polarization plane of light passing through a sample of neutral atoms. This type of experiment uses an allowed magnetic-dipole transition, so the light is detected mainly by transmission. This type of experiment can be performed for Bi [74], Tl [75], and Pb [76]. PV effects scale rapidly with atomic number Z , which makes these heavy atoms suitable for the measurement. These experiments were successful in detecting an optical rotation of light which is caused by spin-independent parity violation effects.

Parity violation in chiral molecules

After the detection of spin-dependent parity violation in neutral atoms, experimental efforts turned to study chiral molecules. This type of molecule is a perfect system to study weak nuclear force-induced spin-independent parity violation as they naturally provide two identical systems of opposite handedness, eliminating the need to introduce it in the experimental setup. Because every nucleon contributes to this effect it is larger than the spin-dependent effect but does not lead to mixing of forbidden and allowed states that is the main enhancement mechanism present in the spin-dependent effect [77].

The main path of studying the parity violation in chiral molecules is to detect the differences in absorption line frequencies between two enantiomers. These differences correspond to the shift in the energy levels caused by the weak force. In a molecule the electron wavefunction can have significant amplitude at the nuclei, which means that there is a small, but significant, probability of finding the electron in the nucleus. The electron then interacts with nucleons via the weak force which will add a small perturbation to the energy levels. This shifts the energy levels differently for the two enantiomers. Because of that shift the transition energy for right-handed ($h\nu_{\text{R}}$) and left-handed ($h\nu_{\text{L}}$) enantiomers will be different [78]. The parity-violating energy difference is proportional to Z^5 , where Z is the nuclear charge. This makes the effect more pronounced in chiral molecules with a heavy

stereogenic center, and it was recently shown that some chiral molecules can exhibit energy shifts of order 100 MHz [79]. This is still an extremely small value hence the experiments need to be able to have a precision high enough to detect such a shift. If both enantiomers were measured together it would be impossible to resolve their spectral lines, so it is necessary to use chiral molecules in their enantiopure form. This provides an additional requirement for the chosen molecule, and it also must be available in large (gram) quantities and have a simple and known electronic structure. Many groups are studying the creation of these kinds of molecules with some suitable candidates being chiral analogues of methyltrioxorhenium [80], trisulfane [81], 1,2-dithiine [82] and many others.

Experiments on parity violation in chiral molecules can be conducted with rotational [83], rovibrational [84], Mössbauer [85], and NMR [86] spectroscopy. There is additionally a separate kind of experiment conducted by the M. Quack group in ETH Zurich that researches transitions between the achiral excited state and the chiral ground state of the molecule. This method requires careful preparation of states in a well known and well-resolved energy level structure of the chiral molecule. No measurement has been done so far but steady progress is being made in reaching experimental conditions that will be sufficient to measure the parity-violating effect with this method.

A promising pathway of detecting the parity-violating energy difference is probing rovibrational transitions in the mid-infrared part of the optical spectrum, which is pursued in this project [87]. This type of experiment can provide sensitivities high enough to be able to resolve energy differences on a scale of a hundred MHz.

Biomolecular homochirality

Detection of PV effects in chiral molecules will be a great clue towards the explanation of biomolecular homochirality: the property of organic molecules that shows a preference towards one selected chirality. For example in living organisms almost all amino acids are levorotatory (left-handed) and sugars are dextrorotatory [88]. This was first observed by Pasteur and since then there was no satisfying explanation to the origin of this chiral selectivity. The theories that try to provide an origin to the discrepancy can be broadly divided into ones that search for an evolutionary reason for the difference and ones that provide an explanation using chemical or physical principles.

The former theories state that the organic molecules of each handedness were encountered in the primordial soup. In there RNA developed that could use either of the forms, but RNA using a right-handed one was more “successful”, creating an evolutionary bias towards one handedness. These theories are currently tested by experiments trying to develop a RNA that can use the left-handed form and compare its effectiveness to the commonly encountered RNA [89].

There is also a number of theories that search for the origin of the biomolecular homochirality in chemical and physical principles. Some theories suggest that under restrictive conditions

some chemical reactions may involve homochiral channels [90, 91]. These theories, however, show a weakness in proposing conditions that have never been present on Earth. Another theory claims that some chemical reactions can be sensitive to parity-violating energy differences in their reactants and after a long enough sequence of reactions can yield products with only one chirality [92]. This theory is very promising, however, a PV energy difference has never been observed in chiral molecules. Any measurement of this effect will, therefore, give credibility to this theory and possibly increase our understanding of biomolecular homochirality.

Parity violation measurement in molecules

As discussed in a previous section nuclear spin-dependent parity violation (NSD-PV) was detected in ^{133}Cs atoms and nuclear spin-independent parity violation is being researched in chiral molecules. However one has to remember that the NSD-PV is a sum of two contributions: Z^0 exchange and anapole moment, where Z^0 exchange couples electrons to nucleons, and anapole moment creates nucleon-nucleon coupling. A new kind of experiment utilizing diatomic molecules is underway now to measure the nuclear anapole moment with higher precision [93]. The effect coming from the anapole moment is enhanced in diatomic molecules because it scales with an inverse of the splitting between energy levels. Diatomic molecules have large moments of inertia which means that their rotational energy levels are very closely spaced, which enhances the PV effect. To observe them one considers a forbidden transition between molecular states of the same parity. This transition becomes weakly allowed because of a weak force acting between those levels. The transition rate, in this case, is very small and to be able to detect it experimentally the forbidden state is mixed with an allowed state by placing the molecules in an electric field. Then the molecules are placed in a magnetic field which creates level crossings that can be sensitively detected. Currently experiments are conducted on molecules like ^{199}HgH [94] and are prepared for ^{138}BaF [95] amongst many others. Laser cooled polyatomic molecules are explored as possible systems for studying spin-dependent parity violation due to the possibility of high resolution and control of their internal states. Closely-spaced, opposite-parity doublet states present in these molecules can be brought to degeneracy by application of a magnetic field, enhancing the contribution of the parity violation effects to these molecular transitions. To combine it with enhancement stemming from a heavy nucleus, molecules like RaOH and YbOH are considered [96].

1.5 Spectroscopic methods for complex molecules

Because of the low number density of molecules in the buffer gas cell, and even lower density in the buffer gas beam, direct laser absorption signals can be too small to detect amid the noise. A number of techniques can be utilised to lower the noise and/or increase the absorption such that

molecules can be observed.

1.5.1 Wavelength and frequency modulation spectroscopy methods

Wavelength modulation spectroscopy (WMS) is a very powerful technique for noise reduction that works by moving the signal from a high- to a low-noise region. As this is the technique used in this thesis it will be described in more detail in Section 4.2.

In frequency modulation spectroscopy the phase of the laser is modulated at high frequency. The modulation results in the creation of side-bands which produce beat notes at the modulation frequency. In the absence of an absorber the phases of the odd-order side-bands have the same magnitude, but opposite sign. That means that the beat notes due to the positive and negative side-bands cancel each other out. Interaction with an absorbing sample however changes the relative phases of the side-bands, causing imbalance and therefore modulation of power. This creates a beat signal at high frequency where $\frac{1}{f}$ noise is reduced. Even when the signal is demodulated and shifted to DC it still conserves its low noise property and therefore can give much more sensitive absorption readings.

1.5.2 Cavity-enhanced spectroscopy

Increasing detection sensitivity by the introduction of a cavity is a very popular method in experiments that use molecules in the gas phase. Increased interaction path-length due to light making multiple trips in the cavity allows the detection of samples with low molecular density and is therefore widely utilised in the molecular beam and buffer gas cooling studies. Detection sensitivity depends on the relative fraction of intensity ($I_0 - I$) to the incident intensity I_0 . The absorption of a molecular sample follows the Beer-Lambert law

$$I = I_0 \exp[-\sigma(\nu)CL], \quad (1.2)$$

where C is molecular concentration, L is the length of interaction and $\sigma(\nu)$ is the absorption cross-section at frequency ν . We can see that simply increasing absorption length is going to increase absorbed intensity. The intra-cavity power buildup for a cavity with a finesse F can be expressed as

$$\kappa = \frac{P}{P_0} = \frac{F}{\pi}, \quad (1.3)$$

where P is the power inside of the cavity and P_0 is the input laser power. The finesse of a cavity constructed from mirrors of reflectance R is defined as

$$F = \frac{4R}{(1 - R)^2}. \quad (1.4)$$

For a transition that is not saturated increasing the power inside the cavity, and therefore the intensity of the light interacting with the sample will increase the amount of absorption. The

simplest example of a cavity is a Fabry-Perot resonator that consists of two mirrors with radii of curvature R_1 and R_2 separated by a distance D . Light entering the cavity will form a standing wave, which results in some frequencies interfering destructively and some constructively. Transmission of frequencies that interfere constructively happens at

$$\nu_n = \frac{nc}{2D}, \quad (1.5)$$

where n is an integer. From that we can define the change in the frequency between two transmitted frequencies as the free spectral range of a cavity

$$\nu_{\text{FSR}} = \frac{c}{2L}. \quad (1.6)$$

Only certain laser frequencies will be coupled to the cavity. To perform scans with a laser coupled to a cavity the length of the cavity can be scanned. A major problem in cavity-enhanced spectroscopy is the conversion of frequency noise of the laser into amplitude (intensity) noise. This problem can be minimised if the central frequency of the laser is in perfect resonance with the center of the cavity mode, which can be achieved by locking the laser to the cavity.

Cavity-ring down

Cavity ring-down spectroscopy measures the rate of decay of the power inside a cavity [97]. This approach benefits from the cavity enhancement and also provides immunity from shot-to-shot laser intensity fluctuations. The method compares the decay time of the cavity with and without molecules. When the molecules are present, and are resonant with the light, the additional absorption in the cavity increases the cavity decay rate. The cavity is scanned to be able to record a range of frequencies to form a molecular spectrum.

Cavity-ring down spectroscopy has been performed on a molecular buffer gas beam [98]. An acetylene molecular beam was interrogated at a distance of 1 cm from the cold cell by a 1.5 μm stabilised narrow-linewidth diode laser coupled to a cavity. The spectral feature linewidth is reported to be 100 MHz and the number density of molecules is reported to be 1.6×10^{12} molecules per cm^3 .

Frequency comb spectroscopy

Frequency comb spectroscopy combines the advantages of an optical frequency comb, with its broad spectral range and high resolution, with the high sensitivity obtained by high finesse cavity enhancement. The technique of frequency comb spectroscopy is based on the interrogation of a gas sample of molecules with a spectrum that consists of discrete and narrow frequency modes (frequency comb). The comb is characterised by a repetition rate f_{rep} and a carrier envelope frequency offset f_{ceo} . The frequencies of the comb modes can be therefore written as $f_n = nf_{\text{rep}} + f_{\text{ceo}}$ [99], shown in Figure 1.5. For enhanced sensitivity, comb lines are matched with resonant frequency modes of a

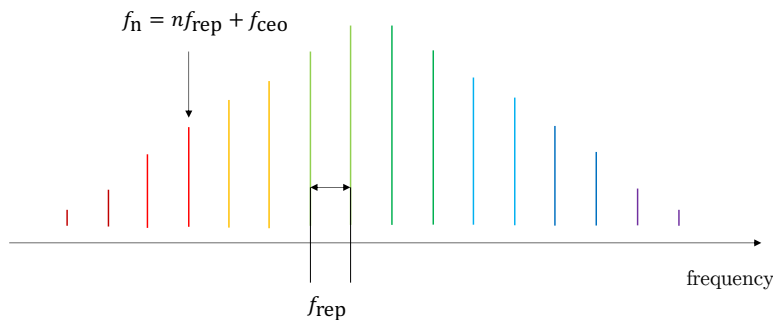


Figure 1.5: Frequency comb schematics.

high finesse optical cavity filled with molecules of interest. The comb's light after passing through a sample is collected by a spectrometer. There are few choices of spectrometer techniques used with frequency combs: direct frequency comb spectroscopy [100], Ramsey-comb spectroscopy [101], Fourier transform [102], and dual-comb spectroscopy [103]. Each of these methods has its drawbacks and advantages for different applications but discussion of those is beyond the scope of this thesis. References are provided for a reader that wants to learn more. Generally, one wants to choose the spectrometer with the resolution better than the comb line spacing to be able to resolve each line. In this way, the comb's linewidth will determine the instrumental line-shape, and in the case of very narrow comb modes make it negligible [104]. To ensure stability the comb can be referenced to a stable comb at a different frequency [105], self-stabilised [106] or be externally stabilised to an atomic clock [107].

Frequency combs have been established in many spectral regions, including mid-infrared. A group from Université Paris 13 had established a frequency comb at 10.3 μm with a repetition rate of 250 MHz, and an FWHM of a comb line of 0.2 Hz with a 10 MHz resolution bandwidth. In mid-IR direct creation of ultrashort pulses remains a challenge, hence these combs are produced by down-conversion or a sum-frequency generation of a near-IR comb [108].

Cavity-enhanced frequency-comb spectroscopy has been applied to cold molecules both in supersonic beams and in buffer gas cells. The Ye group at JILA reports recording a broadband spectrum at 3.3 μm of several complex molecules (nitromethane, CH_3NO_2 , naphthalene, C_{10}H_8 , hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$, and adamantane, $\text{C}_{10}\text{H}_{16}$) inside a buffer gas cell. The linewidth of the comb was measured to be 50 kHz and allowed the probing of molecular spectral features with a linewidth of 33 MHz [60].

NICE-OHMS

NICE-OHMS stands for noise immune cavity-enhanced optical-heterodyne molecular spectroscopy and it is a technique that combines frequency modulation spectroscopy with cavity en-

hancement [109]. First, to make sure that the frequency of the laser matches the cavity mode the laser is locked to the cavity. The laser light is modulated at a frequency ν_{mod} , with the magnitude of the frequency high enough such that the side-bands are away from the cavity modes. This locks the central frequency of the laser to the cavity mode. Then, a second modulation signal is applied to the laser at $\nu_m = n \times \nu_{\text{FSR}}$ where n is an integer. This allows for the implementation of the FMS method and making sure that the FM modulation frequency is a multiple of the locking frequency allows both carrier and side-bands to enter the cavity. Scanning the cavity will not be a problem as ν_m will be simultaneously scanned. Laser frequency shifts affect all the modes of the FM spectrum in the same way, hence as mentioned in Section 1.5.1, from the principle of the FM spectroscopy it will cancel out. This will make the method immune to frequency-amplitude noise conversion while reaping all the benefits of the cavity enhancement [110]. A few applications of NICE-OHMS were demonstrated on gaseous samples, for example, ammonia detection at 1532 nm [111] or Doppler-free saturation spectroscopy of acetylene at 1.5 μm [112].

1.6 Future experiment

The source developed in this thesis is intended as one of the three components of a future experiment to detect the effect of parity violation in chiral molecules, with other components being a chiral molecule with a strong PV effect, and a spectroscopic system with high enough sensitivity to resolve the effect.

As discussed in earlier sections of the introduction the future experiment will probe a transition in the mid-infrared region, to observe transitions with natural linewidth of about 1 Hz. To be able to resolve spectral lines this narrow, the experiment has to reduce, or completely remove, all sources of broadening and be able to access spectral features not obscured by any other spectral lines. The solution to that is explored in this thesis: to conduct the experiment using a source of cold molecules. In cold molecules the population moves to lower energy levels and the spectrum is de-congested. Additionally, cold molecules have reduced Doppler broadening. If the molecules are extracted into a molecular beam the broadening effects will be further reduced, with collisional broadening disappearing in a collision-less environment of the beam.

Performing the experiment on a molecular beam presents an additional advantage: the beam can be probed at large distances. With this a Ramsey interferometry setup can be used in this system, which can lead to sensitivity high enough to resolve the PV effects. This kind of sensitivity requires high frequency stability, which for quantum cascade lasers at 10 μm is researched for example by the Université Paris 13. In their experiments they lock the laser to a primary frequency standard, achieving a relative frequency stability lower than 2×10^{-15} between 1 and 100 s. Additionally, with this method, the laser absolute frequency is known with an uncertainty below 10^{-14} [108]. After

passing through the Ramsey interferometer the molecules can be detected using a cavity-enhanced method. The experiment should be performed on each of the enantiomers separately, which will reduce systematic effects.

This brings us to the final component of the experiment: a chiral molecule with a large PV effect that can be produced in an enantiopure form in large quantities. Work on such molecules, and especially its production in bulk, is in progress.

The three components of the future experiment to detect parity violation in chiral molecules are developed separately, and after showing that they are suitable for the intended purpose a future experiment will be assembled from these building blocks. This thesis aims to demonstrate that it is possible to create a source of cold, complex molecules and perform mid-infrared spectroscopy on the cold sample.

1.7 In this thesis

The overall aim of this experiment is to create a source of cold complex molecules for measuring the parity-violating energy difference between the enantiomers of chiral molecules. The work is envisioned as the first step in that journey, namely the creation of a method that cools complex molecules and directs them into a molecular beam. It expands on the methods described in Section 1.3 to create a robust, bright, and cold buffer gas beam of large molecules. Additionally in the project, we utilise a novel quantum cascade laser to conduct a precise measurement of long-lived rotational states of rigid trioxane molecules in the mid-infrared. This will contribute to proving how powerful cooling is for spectroscopic resolution. I hope that the data gathered will show that performing rotational spectroscopy on a sample of buffer-gas-cooled molecules can be a step towards achieving the precision required for performing this challenging measurement. This thesis attempts to add to the list of molecules for which the buffer gas beam was created and optically observed. By cooling the molecules to low temperature, I am able to record absorption spectra in the mid-infrared with a resolution of 5 MHz. I also aim to demonstrate detection of a molecular beam far away from the cell (145 mm and 235 mm), which is the critical step needed for high precision spectroscopy. To detect molecules I use wavelength modulation spectroscopy and explore other avenues like cavity enhancement and laser locking.

In Chapter 3 I calculate the internal energy level structure of trioxane and its transition frequencies. I theoretically show how cooling influences the population of rotational levels and obtain the integrated strength of the transition to be able to calculate the molecular density in the cold cell and the buffer gas beam. Chapter 4 shows wavelength modulation spectroscopy data of trioxane performed inside the cold cell, where the spectrum is resolved up to 6MHz. This chapter also includes attempts to measure even narrower, sub-Doppler, spectral features of trioxane. Chapter 5 reports

the production and optimization of a beam of trioxane molecules detected on a mass spectrometer, and describes trials of mid-infrared absorption spectroscopy of this beam. A tentative spectroscopic signal is observed in the molecular beam at a distance of 145 mm from the cold cell.

This thesis is intended as a guide and manual for all researchers tasked with building a buffer gas source. Despite a number of buffer gas beams being used in research groups around the world the processes inside the cell and parameters that impact the creation of the buffer gas beam are not fully explored yet. I hope that this thesis will help to shine a light on some potential issues and solutions. To achieve this Chapter 2 describes the experimental setup used, while Chapter 5 outlines how various parameters such as buffer gas flow, capillary distance from the cell, and the flow of the species influence the cooling of the molecules and the formation of a molecular beam.

Cryogenic source of complex molecules

2.1 Overview of the experiment



No	Part name
1	cryocooler
2	high pressure helium lines connecting to compressor
3	cryocooler legs
4	30 K stage
5	7 K stage
6	30 K bobbin
7	steel bellows
8	7 K bobbin
9	copper block
10	cold cell
11	helium delivery line
12	PEI attachment
13	trioxane capillary
14	needle valve
15	trioxane glass tube
16	beam exit aperture flange
17	observation region inside cold cell
18	observation region 145 mm from beam exit aperture
19	observation region 235 mm from beam exit aperture
20	molecular beam
21	charcoal cryopump
22	radiation shield
23	line leading to rotary pump
24	turbomolecular pump
25	pressure gauge
26	helium line leading to flow controller
27	mass spectrometer
28	molecular shutter

Table 2.1: Components of the vacuum and the cold system, as shown in Figure 2.1.

The apparatus is designed to cool molecules to a few kelvin through collisions with a buffer gas in a cryogenically-cooled cell. Figure 2.1 and Table 2.1 show the components of the vacuum and the cryocooling systems that are used in the experiment. At the heart of the apparatus is a Sumitomo SRP-082B2 50 MHz two-stage pulse tube cryo-refrigerator that will also be referred to as the cold head (part 1). It has a first stage cooling capacity of 40 W at 45 K, and second stage cooling capacity of 1 W at 4.5 K. With low heat loads, the first stage can reach temperatures as low as 30 K, which is the case in this system, and this stage will be henceforth referred to as the 30 K stage (part 4). The second stage has to dissipate heat loads from the room temperature capillary and direct-line-of-view openings and as a result its temperature is 7 K. In the rest of this thesis, this stage will be referred to as the 7 K stage (part 5). The power and high-pressure helium gas needed to operate the cold head is supplied by a Sumitomo F-70H helium compressor (part 2). The temperatures on both stages are monitored via calibrated LakeShore thermistors. The cold cell (part 10) is mounted on the 7 K stage and thermalizes to the temperature of that stage. To bring the cell to the level of windows machined in the vacuum chamber a 50 mm thick copper block (part 9) is placed between the cell and the 7 K stage. Copper has very good thermal conductivity and the presence of the block does not impede thermalisation. Aluminium radiation shields are connected to the 30 K stage of the cold head and surround the cold cell preventing room temperature radiation from heating the cell (part 22). Four openings are machined in the shields to allow for optical access, beam extraction and access for the molecular capillary. The cold head is placed inside a vacuum chamber, evacuated to a pressure of 5×10^{-6} mbar. The pumping is performed in two stages: first, a rotary pump (part 23) reduces the pressure to 2×10^{-2} mbar and then an Oerlikon Turbovac turbomolecular pump (part 24) brings it down to the base pressure. The pressure is monitored via an Oerlikon Leybold Vacuum D-50968 pressure gauge (part 25) mounted on a KF25 port close to the turbomolecular pump. When heating the system to refresh the charcoal cryopumps the pressure cannot exceed 10^{-1} mbar as it can easily damage the turbomolecular pump. To allow for optical access to the system two KF25 window ports (part 17) were machined in the vacuum chamber that accommodate 1-inch windows. The windows used on the system need to have a high transmission for 10 μm radiation, therefore ZnSe windows are used. The windows have an anti-reflection coating and provide about 95% of transmission at this wavelength. To deliver the buffer gas to the cell a steel capillary connects the system to the gas bottle (part 26). After entering the vacuum system, the capillary is connected to copper bobbins (part 6 and 8) that are anchored to the cold stages, so that the gas can thermalise to temperature of these stages. Most of the heat load carried by the flow of room temperature buffer gas into the system is deposited on the 30 K stage. The bobbin configuration depends on the choice of the buffer gas and is discussed in more detail in Sections 2.3 and 2.4. The flow of helium is controlled by an MKS GE50A Digital Mass Flow Controller, which operates in a range between 1-20 sccm of gas flow. The gas flow can be adjusted with a precision of

0.4 sccm. Several heaters with a total heating power of 15W are attached to the 30 K stage. They allow for fast heating of the system to room temperature. Any wires that go inside the vacuum system, both to thermistors and heaters, are heat sunk to the 30 K stage to reduce the heat load on the 7 K stage.

2.2 Cryogenic apparatus

2.2.1 Cold cell

Figure 2.2 shows the main parts of the cold cell. The cold cell is made from a copper cube with side length of $l_{\text{cell}} = 50$ mm. An empty space is created inside the cube by drilling 20 mm diameter holes through five of the six faces, as illustrated in Figure 2.2b. One of the sides has a polyetherimide (PEI) flange (part 12) where a gas capillary can be inserted to deliver the molecules of interest. PEI is a good thermal insulator, so the capillary can be held at a very different temperature to the cold cell without excessive heat load. On the opposite side is an aluminium flange (part 16) with a small aperture machined through, which serves as the exit aperture for beam production. The aperture is machined into a flange to allow for fast and easy change of the aperture. To ensure that there are no leaks, indium seals are used to seal the flanges to the body of the cell. Two of the faces of the cell have ZnSe windows for the optical investigation of the gas inside the cell (part 17). To minimise the coating of the windows with the molecules used in the experiment, the windows are placed on steel extensions that increase the distance between the center of the cell and the windows. The buffer gas inlet is placed on the bottom of the cell (part 11). To minimise the eddies from the flow of neon there is no channel machined on the sixth face of the cold cell, directly above the buffer gas delivery line.

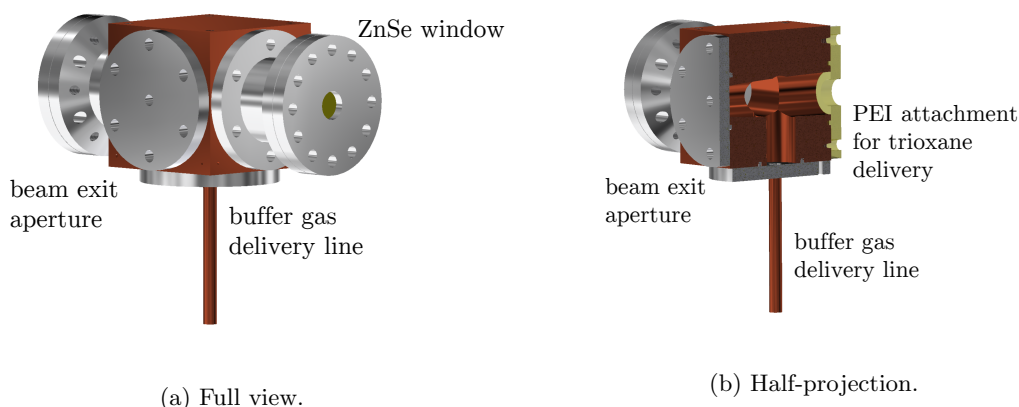


Figure 2.2: Full view and a half projection of the cold cell.

2.2.2 Molecular source

The species of interest are delivered to the cold system via a capillary. This method of introducing molecules is called capillary filling. The method can be applied to molecules that have appreciable vapour pressure at room temperature (usually a few mbar). The molecule delivery system consists of a glass tube (part 15) filled with the molecules in the solid-state. The pressure of the tube is monitored with a Leybold Thermovac TTR 91 pressure gauge, fixed to a KF16 flange at the end of the tube. The pressure is monitored to make sure that no atmospheric gases made their way into the tube, and if that's the case, the tube is pumped down before running. The molecular vapour can leave the tube via a steel capillary (part 13), and the flow of the vapour is controlled by a needle valve (part 14) and a tap. To take subsequent measurements with and without the molecules (signal and background) a shutter valve (part 28) is installed after the needle valve. The capillary enters the vacuum system via an o-ring seal in a custom KF25 flange. This seal allows the capillary to be moved so that its position inside the cold cell can be adjusted without breaking vacuum. This method is very prone to small leaks if a piece of debris gets lodged in under the o-ring or the o-ring gets scratched, but it enables the optimisation of the best position of the capillary in the cell. After the optimum position is determined the capillary will be fixed in place with a Swagelok joint that will prevent any leaks. The end of the capillary is machined from copper. To prevent molecules from freezing inside, blocking the capillary, it has to be kept at a temperature above 0°C, so a heating wire is wound along the length of the capillary and the temperature of the end of the capillary is monitored with a Thorlabs TH10K thermistor. We determined empirically that 0°C is optimal for preventing clogging, with capillary quickly blocking below that temperature. To reduce the heat load from the capillary on the cell the PEI flange is attached to the wall that the capillary enters through. The diameter of the opening in the PEI attachment is slightly larger than the outer diameter of the capillary. This small gap reduces the thermal contact, but also allows the buffer gas to escape, which is undesirable.

2.2.3 Beam chamber

The molecules injected through the capillary become entrained in the flow of buffer gas which carries them through the exit aperture to form a molecular beam. This beam then passes through a vacuum tube with a mass spectrometer mounted at the end. Optical observation of the molecular beam is facilitated by two sets of windows: one machined in the vacuum chamber, 145 mm from the beam aperture (part 18) and the other in the beam chamber, 235 mm from the aperture (part 19). The beam chamber has a radius of 250 mm.

2.2.4 Heat loads

To assess heat loads in the experimental setup we cooled the system without any room temperature inserts, that is without trioxane capillary and buffer gas delivery line. The trioxane capillary has to deliver room temperature molecules straight to the cell hence we expect it will put a heat load on the 7 K stage. The buffer gas delivery system, dissipating the majority of the heat on the 30 K stage, should not have much impact on the 7 K stage. In this setup the temperatures measured on 7 K and 30 K stages with no room temperature inserts are respectively 5.5 K and 28.5 K.

The next step was to measure the temperatures with re-connected buffer gas delivery line. In this case the 30 K stage thermistor measured 30.6 K. Referring to the heat map [113] that specifies how the temperatures vary with the heat loads, and is supplied with the Sumitomo cryo-refrigerator, this corresponds to about 8W of heat load on the 30 K stage and about 1 W at the 7 K stage. The possible source of the heat load on the 30 K stage are four large openings machined in the top of the radiation shield, close to the 30 K stage.

The final step was to introduce the room temperature capillary back into the system. This has increased the 7 K stage and cold cell temperature to 6.8 K. From the heat map this corresponds to a heat load on the 7 K stage of about 2.5W. To reduce the heat load from the openings in the radiation shield we installed a secondary radiation shield around the original one, with two openings offset in such a way that there is no line-of-sight between the cold head and the outside world. This has reduced the 30 K stage temperature to 27.8 K but did not affect the 7 K stage temperature. The new temperature of the 30 K stage corresponds to about 6W of heat load. This can be attributed to heat load from room temperature radiation, room temperature thermistors anchored to 30 K stage, and the buffer gas delivery line.

To investigate the heat load on the 7K stage, which from the heat map is about 3 W [113], we need to calculate the heat load from the openings in the radiation shield that allow for optical access, trioxane line access and molecular beam exit. To calculate the radiative power of a body Q_r we use the Stefan-Boltzmann equation

$$Q_r = \varepsilon \sigma A T^4. \quad (2.1)$$

In this equation ε is the emissivity of a body ($0 \leq \varepsilon \leq 1$), σ is a constant $\sigma = 5.67 \times 10^{-12}$ W cm⁻²K⁻⁴, A is the area of the body in question, and T is the temperature of the body. We assume that four openings are at room temperature, each is 1 inch in diameter and they behave as perfect black bodies, ($\varepsilon = 1$). This results in a radiative power of 0.85 W. The same calculation can be done for the trioxane capillary made from a copper pipe ($\varepsilon = 0.05$) with the outside diameter of 0.8 cm, kept at 0°C. We assume that we can treat the capillary as a cylinder of some length h . For $h = 2$ cm the heat load from the capillary is around 0.01 W. The combination of heat loads from

the openings and the capillary explain only a small part of heat load placed on the 7 K stage.

Additional heat loads are placed on the cold cell when running the experiment. The main sources are the flow of trioxane and the flow of the buffer gas. Trioxane molecules that travel to the cold cell walls and freeze on them increase the cell temperature. Low flows of buffer gas should see it fully thermalised to the 30 K stage temperature after traveling through the 30 K bobbin, minimising heat load on the 7 K stage. With higher flows of helium the buffer gas might not be fully thermalised in the 30 K bobbin before reaching the cold cell, thus placing some extra heat load on the 7 K stage. We see that with both helium and neon buffer gases. With helium the added heat loads from the trioxane and buffer gas beam increase cold cell temperature by 1-2 K, and with neon the increase can be as much as 7 K.

2.3 Details specific to helium buffer gas

Helium is an inert, monatomic gas with atomic number 2. At 4 K helium has a substantial vapour pressure of about 700 mbar (525 Torr or 7×10^4 Pa) so even at this temperature it can be efficiently used as a buffer gas. The high vapor pressure means that helium will not freeze to cold surfaces, so the use of coconut charcoal cryopumps is necessary to keep the pressure around the molecular beam low. The coconut charcoal traps helium inside its porous structure, acting as an efficient cryopump when cooled to cryogenic temperature.

Cryopumps

In the experimental system the charcoal cryopump (part 21) is a copper cylinder with a diameter of 200 mm and a height of 500 mm, surrounding the cold cell, with the inside covered by the activated coconut charcoal. The cylinder is closed at the bottom to increase the area available for charcoal. The cylinder is fixed to the 7 K cold stage and thermalises to its temperature. The cylinder has machined openings for the probe laser, the molecular capillary, and the molecular beam. The granular coconut charcoal is glued using Loctite Stycast 2850FT to the inside of the cylinder. We can characterise the pumping speed S (usually given in liters per second l/s) of the cryopumps with the equation

$$S = \frac{Q}{p_v}, \quad (2.2)$$

where Q is the throughput flow in the system and p_v is the working pressure, that is pressure measured when the system is cold and the helium is flowing. Putting the above equation in terms of the quantities of our system with the flow of helium f given at reference conditions of 1 atm we get

$$S = \frac{f}{p_v}. \quad (2.3)$$

For the 12 sccm of helium flow the working vacuum pressure was measured to be 2.9×10^{-5} mbar which gives pumping speed of about 7000 l/s. To increase pumping the outside of the cylinder was also covered with charcoal but no change in the working pressure was observed. This shows that the majority of the pumping is done in the area surrounding the molecular beam. The higher the temperature of the charcoal pump, the less efficient the pumping is, with 9.5 K observed as a threshold value where the helium is released from the cryopump. A significant technical challenge in our system is to provide efficient cryopumping with quite high temperatures on the cold stage (7 - 8 K). Over time the charcoal slowly saturates with helium decreasing the efficiency of pumping and causing degradation of the molecular beam. The experiment needs then to be brought back to room temperature to release all of the helium. Every year the charcoal should be replaced as with time it loses its cryopumping properties. This might be due to degradation of the thermal contact between the charcoal and the copper cylinder, or due to the charcoal becoming permanently coated with layers of the molecules used in the experiment. High flows of buffer gas (> 4 sccm) place an additional heat load on the cold stage, hence the temperature of the cold stage has to be constantly monitored while running the experiment to not exceed 10 K. If that happens helium is rapidly released from the cryo-sorbs and the pressure increase overwhelms the mass spectrometer and the turbomolecular pump.

Cooling the helium

To ensure that the helium gas reaches the temperature of the 7 K stage, the gas passes through a series of bobbins. A bobbin is a length of copper tube wound on a copper cylinder. The bobbin is attached to the cold stage, thermalising to its temperature, provided a good thermal connection is ensured. Buffer gas passing through the copper tube thermalises with the tube walls. To ensure efficient thermalization the copper tube is wound around the central cylinder about 10 times which provides about 630 mm thermalization length. Helium first passes through a bobbin anchored to the 30 K stage (part 6) and then through one attached to the 7 K stage (part 8). A length of steel bellows (part 7) allows for gas flow between the bobbins. Steel is used to decrease thermal contact between the two stages. Two steps of cooling of the buffer gas ensure that the majority of the heat load is dissipated on the 30 K stage.

Capillary

The capillary enters the cell through the PEI attachment and an outflow of helium is allowed through the space between the capillary and the PEI.

2.4 Details specific to neon buffer gas

Neon is a noble, monatomic gas with an atomic number 10. It has no substantial vapour pressure below 15 K hence it cannot be used to bring the species to temperatures as cold as helium. The upside of working with neon is that any cold surface (< 15 K) acts as a cryopump. It is therefore much easier to use a high flow of neon without having the pressure too high to destroy a molecular beam. The need to keep neon above 15 K, and simultaneously have colder surfaces that serve as a cryopump, means that the thermal connections in the system have to be designed carefully.

Thermal separation

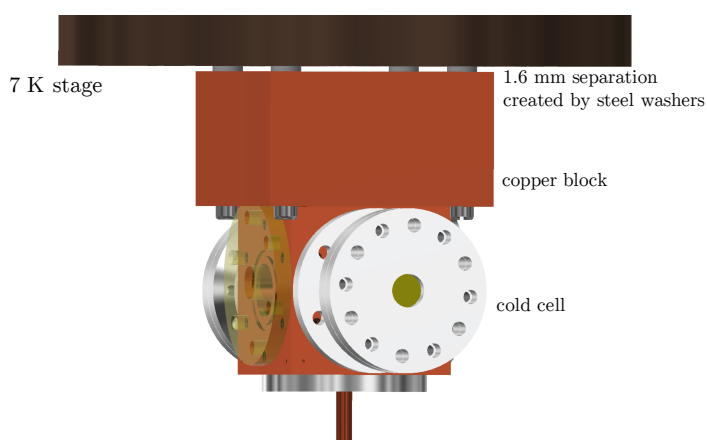


Figure 2.3: Cold cell adjusted for the neon buffer gas. The cell is thermally disconnected from the 7 K plate with steel washers.

To prevent the neon freezing inside the cold cell, the cell cannot be kept at the temperature of the 7 K stage, so a thermal separation needs to be created between the cell and the cold plate. To make sure that we have an adequate vapour pressure of neon we maintain the cell temperature at 17 K. To do that 4 steel washers with a thickness of 1.6 mm were placed on the screws linking the cold cell and the 7 K stage, which is illustrated in Figure 2.3. The steel washers provide the thermal separation needed to bring the cell to about 17 K. To have full control over the cell temperature we also attached a small heating resistor to the cold cell that allows us to increase its temperature above 17 K. Sheets of copper cooled to 7 K act as efficient cryopumps for neon, without the need for charcoal. The saturation of the cryopumps was not observed to be a problem and the lifetime of the source is limited by other factors. To cool neon to 17 K it first passes through two bobbins anchored to the 30 K stage which allows it to thermalise to that temperature. Then neon is delivered directly to the cold cell and by collisions with the cell walls is cooled to 17 K.

Cryopumps

With the neon as a buffer gas any cold (< 15 K) surface acts as a cryopump. With the flow of 18 sccm of neon we have recorded the guard pressure of 5×10^{-6} mbar. From Equation 2.3 we can calculate that these numbers correspond to about 61 000 l/s pumping speed.

Capillary

The capillary was surrounded with a layer of Kapton tape that sealed the space between the PEI attachment and the capillary which resulted in increased molecular extraction to the beam.

2.5 Laser system

2.5.1 Quantum cascade laser

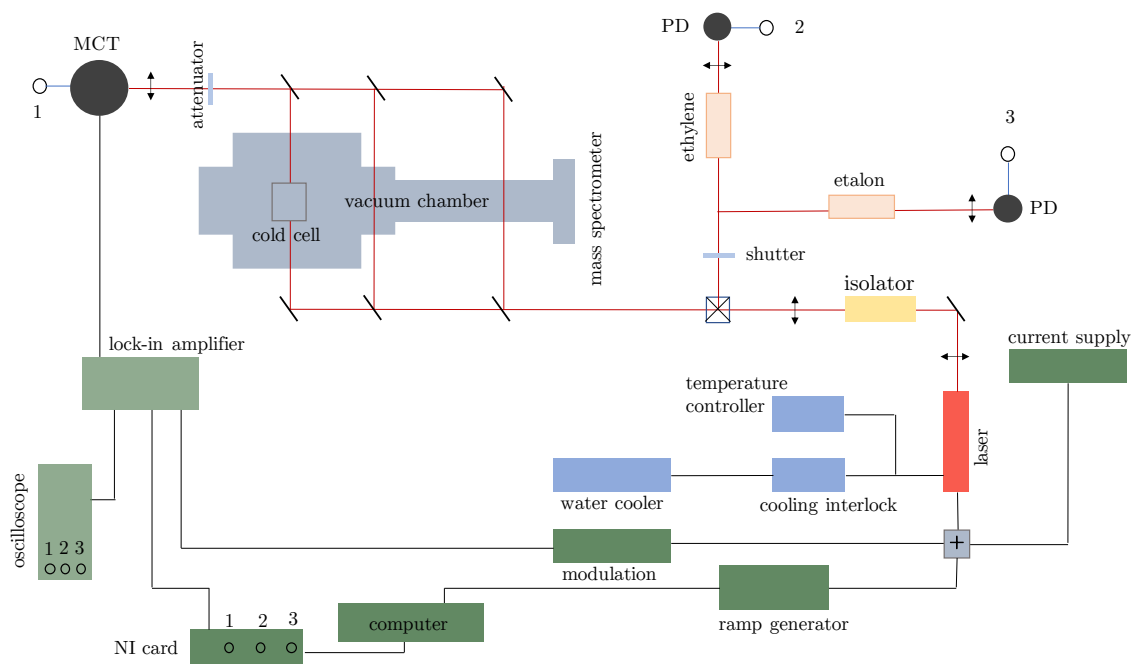


Figure 2.4: Schematic of the laser system in the experimental setup showing the components of the WMS system and the paths used for absolute and relative frequency reference. The outputs of the MCT, and two photodiodes are marked respectively with numbers 1,2 and 3, and their inputs are marked with the same number on the NI card and oscilloscope.

The laser used for probing molecules is an Alpes Laser distributed-feedback quantum cascade laser (QCL), with a wavelength of 10 μm and about 7 mW of power. The laser system is shown in Figure 2.4. During the course of this project the power of the laser decreased which was

attributed to the slow death of the diode. QCLs are very susceptible to diode damage from radiation back-reflected to the laser hence an isolator needs to be placed after the laser, that prevents the retro-reflected radiation from reaching the laser. This back-reflection is also a source of noise, minimised by the presence of the isolator. The beam leaving the laser is diverging hence a very long focal length (600 mm) lens is placed after the isolator. This lens produces a well collimated laser beam. A beam knife-edge measurement set a radius of the laser beam close to the cold cell at $r_l = 2$ mm. A very big problem in mid-infrared systems is etaloning, which occurs whenever optical cavities form between optical elements. The solution to this problem is to arrange all the flat elements (lenses, windows) at a slight angle to each other. Additionally, some etalons are caused by mirrors in the system. These can be washed out by vibrating the mirror at high speed. We found that a good way to induce the vibrations is to mount a small fan on top of the mirror mount, and then break off one blade of the fan to deliberately unbalance it.

After leaving the laser, the beam is focused by an aspheric lens and passes through an isolator to reduce retro-reflected radiation from reaching the laser. After the isolator, a long focal length lens (600 mm) is used to collimate the beam. Then the laser beam is separated into two branches by a 50-50 beamsplitter. The first path is used for interrogation of the molecules in the cold system. With the system of flip-mirrors the beam can be directed to go through the cold cell or to interact with the molecular beam at two different distances from the cold cell. Because about 50% of the power is lost in the isolator and 50% subsequently is split between the two branches, about 1.5 mW of power is passing through the cold cell when we take transmission through the windows into account. After passing through the cold system the laser is focused onto a liquid nitrogen cooled MCT detector. An MCT (mercury cadmium telluride) detector allows for very low noise detection of the infrared radiation when cooled with liquid nitrogen. The liquid nitrogen has to be manually refilled and a full refill is enough for a day of data-taking. The signal from the detector is sent to a lock-in amplifier and the lock-in output can be recorded on either oscilloscope or the computer. Because the lock-in has a limited input voltage the power reaching the MCT detector is attenuated to provide a MCT output signal just below the maximum allowed voltage. The second branch separated by the beamsplitter is used for calibration. Using a flip-mirror the laser can be either directed to pass through a cell containing ethylene, or an etalon. Each of the calibration paths has its photodiode. The ethylene cell is not fully vacuum-tight and needs to be evacuated and refilled with ethylene gas every few days. While the signals from one of the legs of the calibration path and from the MCT can be recorded simultaneously we observed that it leads to an increase of the noise in the MCT signal, most notably from etaloning. We therefore installed a shutter in the calibration path so that we can rapidly chop the laser beam in the calibration path on and off.

The QCL probe laser is controlled with a custom-made current supply. The laser can operate between 10 and -30 °C, with the output wavelength and power dependent on the temperature.

Figures 2.5 and 2.6 show how the wavenumber and output power depend on the current and temperature of the diode. The temperature of the laser is controlled by an Alpes Lasers TC3 temperature controller and cooling is provided by a circulating chilled water through the base of the laser. To prevent the laser from operating when the cooling water is not running a cooling interlock is applied. The frequency of the laser can be adjusted either by changing the current I_{laser} supplied by the current driver (fast control) or by adjusting the temperature of the diode T_{laser} with a temperature controller (slow control). The laser frequency is scanned with a voltage ramp provided by a function generator that also serves as a trigger for the data recording. The ramp voltage V_{ramp} determines the frequency range of the scan, with the maximum of 5 V corresponding to a scan of 800 MHz. The modulation, with frequency $f_{\text{modulation}}$ and amplitude $\delta_{\text{modulation}}$, needed for the WMS spectroscopy, is supplied by a function generator to the laser and the lock-in amplifier simultaneously. Wavelength modulation spectroscopy is a technique that reduces noise in the spectroscopy signals. It does that by moving a DC signal to a much higher frequency, by supplying a modulation signal to a laser. The same modulation signal is then send to the lock-in amplifier, to serve as a reference. The modulated laser beam, after passing through the molecular sample is detected by an MCT and the output signal is delivered to a lock-in amplifier. The lock-in samples the signal at the frequency supplied by the reference. The output of the lock-in amplifier is proportional to the signal at the reference frequency. A more in-depth description is provided in Section 4.2. The modulation and the ramp are voltage sources and have to be converted into current sources to be delivered to the QCL. Because the laser has only one input, the signals from the current supply, modulation and ramp generator are added and delivered to the laser.

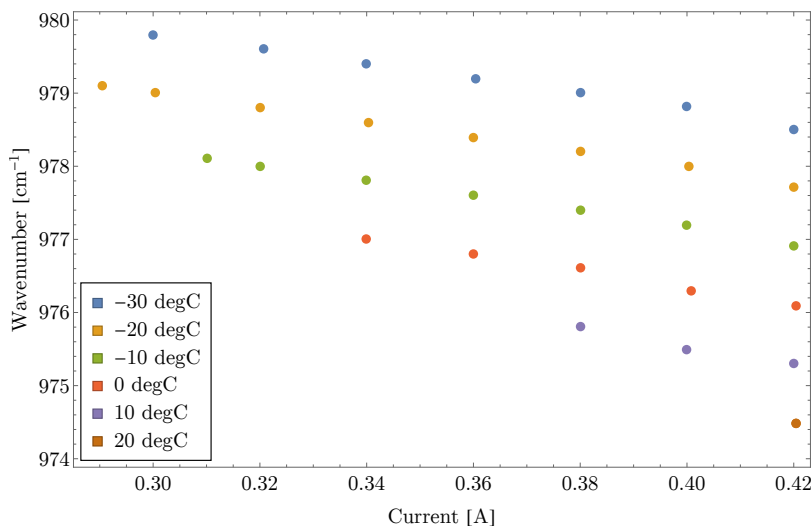


Figure 2.5: Laser output wavenumber as a function of supplied current and diode temperature. Graph reproduced from [114].

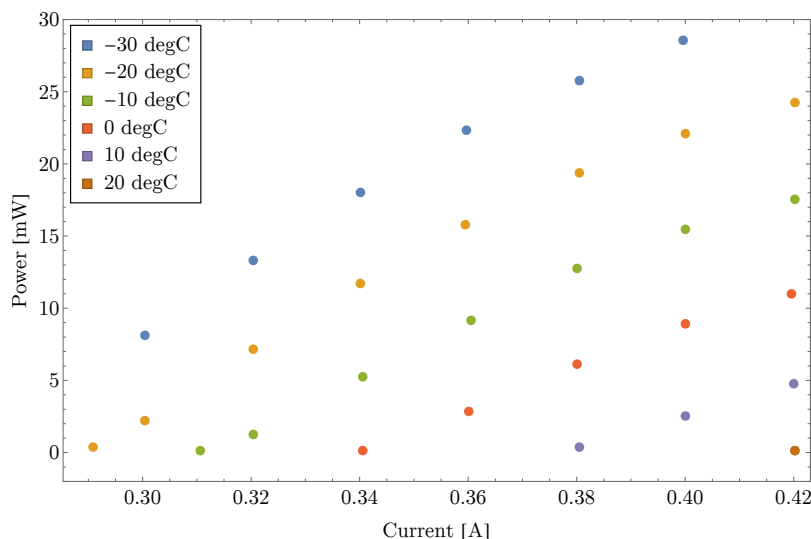


Figure 2.6: Laser output power as a function of supplied current and diode temperature. Graph reproduced from [114].

2.5.2 Noise reduction

The QCLs are very susceptible to current noise, which has to be minimised to observe small absorption signals. To minimise the noise we made sure that any cables connecting the laser with its power supply, diode current driver, modulation and the ramp are as short as possible. Additionally, it is best to place all components on the same optical table. Making sure that all of the aforementioned components have the same ground also reduces the noise. The diode current driver is home-built and designed specifically to minimise the noise. Additionally we can use a 50 Hz notch filter after the MCT output that substantially reduces the noise. With very strong in-cell signals (signal-to-noise ratio of 100) the 50 Hz filter was not needed, but it was found to be helpful when trying to perform molecular spectroscopy in the beam. When taking data with the filter we have to make sure that the scan rate is slow enough that the trioxane spectral features aren't affected by the filter.

2.5.3 Frequency calibration

The QCL spans a range of frequencies, that cover many trioxane transitions. Additionally the laser frequency can be scanned, with a set scan range. To be able to determine the laser's absolute frequency and the width of a scan we need to have an absolute frequency reference and relative frequency calibration with respect to that reference.

After the isolator, the laser is split into a detection and calibration path. The beam in the calibration path passes through a gas cell filled with ethylene and ethylene spectroscopic features can be observed

at the same time as trioxane in the cold cell. The knowledge of the frequencies of observed ethylene transitions allows the absolute frequency to be determined. Figure 2.7 shows the ethylene transitions between 978 and 979 cm^{-1} , with transition frequencies and strength of the lines obtained from the Hitran database [115]. Comparing the observed ethylene transition with the theoretical spectrum in Figure 2.7 determines the absolute frequencies at those particular points in the scan. In Figure 2.7 the frequencies of trioxane transitions in this spectral range are marked with pink lines. Identifying the ethylene transitions closest to these lines and moving the laser to their vicinity we are able to locate the trioxane features.

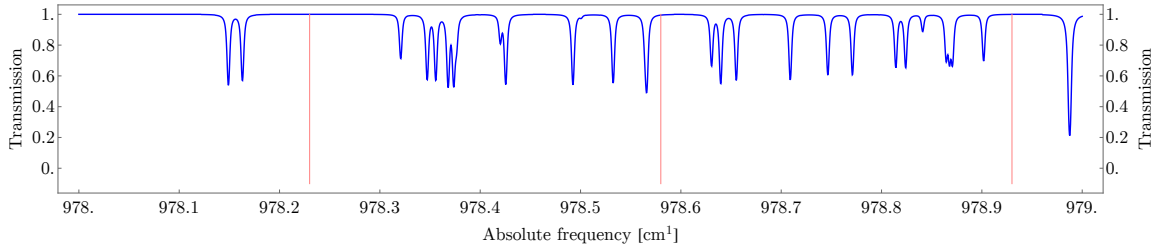


Figure 2.7: Ethylene spectrum in the range between 978 and 979 cm^{-1} . The vertical pink lines show central frequencies of three trioxane transitions $R(3, K)$ at 978.23 cm^{-1} , $R(4, K)$ at 978.58 cm^{-1} and $R(5, K)$ at 978.93 cm^{-1} . The notation used here will be explained in the next chapter. The ethylene lines are used for absolute frequency calibration of the trioxane spectra.

During each scan, a voltage ramp V_{ramp} is applied to the laser that scans its frequency by some unknown value in time t_{scan} . We assume that the voltage increase is linear, so the frequency scanned is also linear in time. All spectra are recorded as a function of time, which later needs to be converted to a frequency measurement. In the experiment we use solid germanium (Ge) etalon, with refractive index of 4 at 11 μm . This type of etalon has relatively high finesse in the infrared without the need for any coatings. The free spectral range of the etalon f_{fsr} is 490 MHz. We record the etalon spectrum at the same time as the trioxane spectrum. Figure 2.8b shows a scan of the etalon with $t_{\text{scan}} = 25$ s.

The transmission of an etalon is given by an Airy function

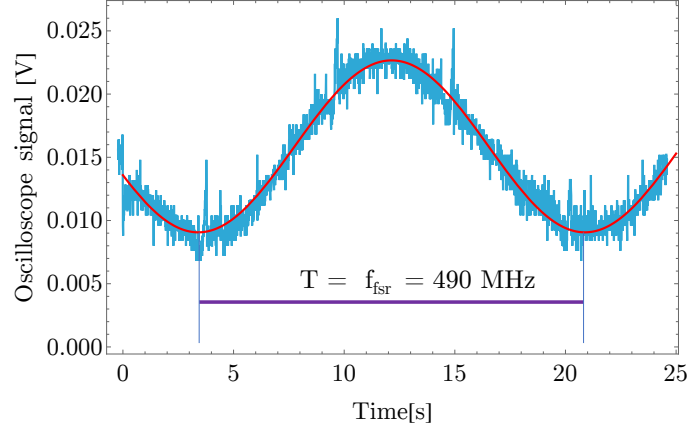
$$\text{Airy}(\delta) = \frac{1}{1 + F \sin^2(\frac{\delta}{2})}, \quad (2.4)$$

where

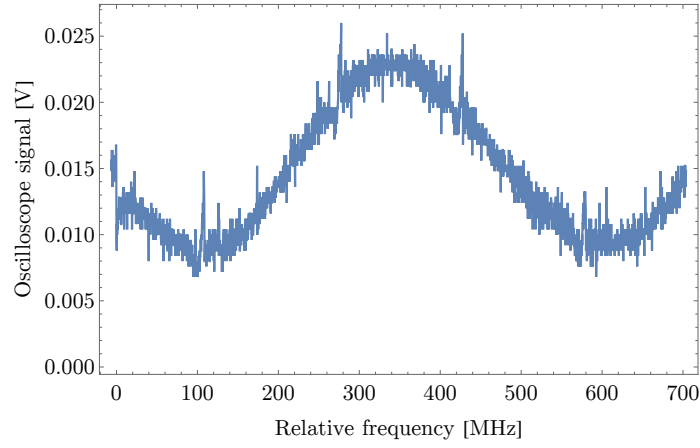
$$\delta = 2\pi \frac{f}{f_{\text{fsr}}}. \quad (2.5)$$

In this equation f is the frequency of the light and F is the coefficient of finesse of the etalon. We assume a linear scan,

$$f = f_0 + \alpha t, \quad (2.6)$$



(a) Scan of etalon in time. Time of scan is equal to 25s. The etalon data are fitted with Equation 2.7 (red). The free spectral range and therefore the period is marked with the purple line.



(b) Scan of etalon with the time axis converted to the frequency axis

Figure 2.8: Scans of etalon in time and in frequency demonstrating relative frequency calibration using a Ge etalon with a free spectral range of 490 MHz.

where f_0 is the frequency at $t = 0$ and α is the quantity to determine. So the Equation 2.4 can be re-written

$$\text{Airy}(t) = \frac{1}{1 + F \sin^2(\pi\alpha(t - t_0)/f_{\text{fsr}})}. \quad (2.7)$$

Equation 2.7 is fitted to data with 3 free parameters, F , t_0 and α . t_0 is related to f_0 and can be obtained from the absolute frequency reference. The fit will provide α , which is the parameter needed for frequency calibration. Figure 2.8b shows the same etalon scan but with the time axis converted to the frequency using the method described above.

2.5.4 Measurement of the laser linewidth

At the MHz and sub-MHz scales that this experiment is aiming to probe, the linewidth of the laser becomes important. No data was available to us about the QCL linewidth hence we measured it experimentally. To measure the linewidth the laser frequency was set to be in the middle of an ethylene spectral feature. If the laser was a constant in frequency, a constant lock-in amplifier output voltage would be recorded. Any changes to the voltage observed would signify internal drifts of frequency.

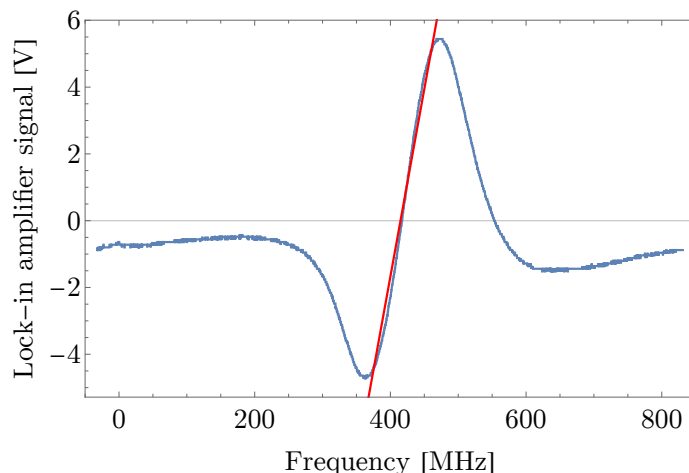


Figure 2.9: Calibration of the drift of the laser using the gradient of the spectral feature. The laser frequency is set to the centre of the spectral feature where the lock-in amplifier signal is equal to zero. Any shift of the laser frequency will move it away from the central frequency of the spectral feature (i.e. the zero-crossing) causing non-zero reading. The linear fit shown in red can be used to convert recorded voltage to frequency shift of the laser.

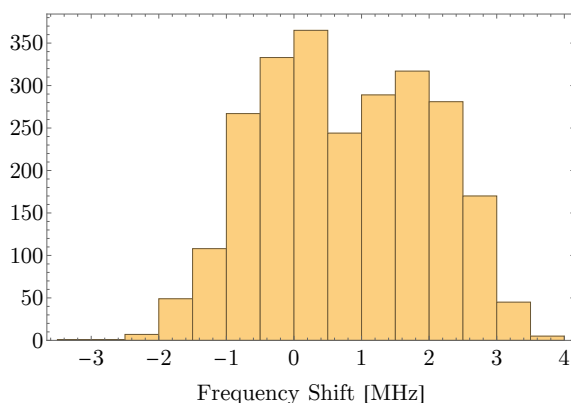


Figure 2.10: Histogram of the laser frequency shifts within 1 s.

Figure 2.9 shows a typical spectral feature of ethylene acquired by WMS spectroscopy, with axes

switched such that frequency is on the y -axis. The spectral lines have Gaussian lineshapes, and the lock-in amplifier takes the first derivative of this, producing a steep gradient that crosses zero at the line centre. The frequency axis in Figure 2.9 has been calibrated by recording the transmission of an etalon with a known free spectral range at the same time, as explained in Section 2.5.3. We fitted a linear function, shown with red in Figure 2.9, to the gradient of the line between the maximum and minimum of the Gaussian derivative. This gives a conversion between the voltage recorded by the lock-in amplifier and the frequency shift of the laser. The laser frequency is set to the centre of the spectral feature, where the lock-in amplifier output is equal to zero. Any shift in the laser frequency will move the laser to a different part of the spectral feature and hence produce a change in the lock-in amplifier output. We have recorded the lock-in amplifier output at different timescales ranging from 1 ms to 100 s and with the linear fit from Figure 2.9 converted it to frequency in MHz. For each timescale, a histogram of the magnitude of the shift was recorded. As an example, a histogram of laser behaviour for 1 s is shown in Figure 2.10. Zero in the plot is the central frequency of the transition. As the laser frequencies roughly follow a Gaussian distribution an FWHM was calculated for each of the data sets. The FWHM is then taken as a linewidth. Figure 2.11 shows the laser linewidth vs the timescale of the measurement.

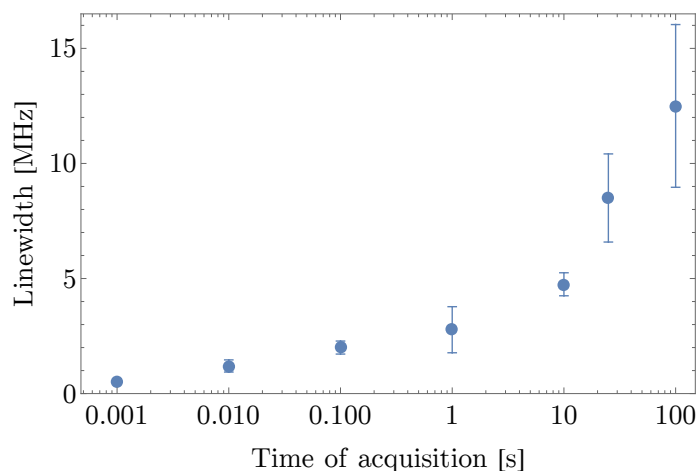


Figure 2.11: Average laser linewidths for different timescales. The x -axis is on a logarithmic scale. The errors are taken as the standard deviation of a number of measurements for a given time of acquisition.

From the measurement, it can be seen that the linewidth increases with the timescale. For 1 s, the linewidth is 2.8 ± 1 MHz. Any features with a width below that will be obscured. If the spectral feature is scanned in 1 ms the laser linewidth would be 0.5 ± 0.1 MHz and the contribution to the broadening will be decreased - it is preferable to scan the laser quickly to avoid spectral broadening due to the laser linewidth. The time of the scan over the spectral feature cannot be arbitrarily small due to the low-pass filter in the lock-in amplifier. The low pass filter consists of a capacitor that by

charging and discharging performs an average of the signal. If the charging time of the capacitor (time constant) is too small then the noise would not be rejected efficiently. Looking at the linewidth data there is one particular timescale that is good for both the lock-in amplifier and the laser: 100 ms. The QCL linewidth at this timescale is 2 ± 0.3 MHz.

2.5.5 Remaining issues with the spectroscopic system

While the WMS gets rid of a part of the noise, there are still some effects that obscure the signals produced by the molecules. The etaloning, retro-reflection, and the beam walking contribute the most to the noise present in the signal. Etaloning produces a background on which the signal is overlaid. It tends to be the same from scan to scan and it can be subtracted in data post-processing. Retro-reflection is minimised by using an optical isolator. Beam walking is a more complex problem that hails from the fact that the optical elements (especially lenses) in the laser beam are not ideal. When the laser beam is recorded on the MCT it has to pass through a lens to be focused on the active region and ensure that the radiation is collected in the most efficient way. The optical table with optical elements and detectors is not connected to the vacuum chamber. Before reaching the lens the beam passes through the vacuum chamber that is shaking due to the cryocooler vibrations. The beam has to pass through ZnSe windows on the chamber and with the chamber shaking the position of the beam on any of the windows can also change. If windows have non-uniform thickness or coating this can cause a subtle change in the beam's direction. This subsequently can cause the laser beam to change position on the focusing lens and be differently positioned on the active region. Because the movements of the chamber are not periodic, the noise that the beam walking adds to the beam cannot be subtracted. On the small scales, this noise is dealt with by the WMS and additional averaging is performed to bring the level of the noise down.

The scan origin shifts its frequency in time. The laser wavelength is adjusted by changing the current supplied to the diode and adjusting the diode temperature. The drift in the scan origin might be due to the fluctuations in the temperature of the diode. To make sure that all the scans start from the same frequency, data from the ethylene cell and the cold cell are recorded simultaneously. Later the positions of the ethylene features are used to adjust the frequency between the scans. This step is vital, especially for scans averaging the data over long periods of time, to observe small absorption in the molecular beam.

2.6 Data acquisition system

To start with, only small volumes of data were recorded, hence a 4-channel oscilloscope was used to record data from the lock-in, ethylene, and etalon. When a need for averaging and

scan post-processing arose in order to observe a molecular beam, a home-written C# software was used. The hardware was interfaced with a computer via a NI USB 6251 card. The trigger for the NI card was supplied from the ramp generator. The software allows recording large sets of data at high sampling rates.

2.7 Mass spectrometer

The experiment uses a HALO residual gas analysis (RGA) Hiden Analytical quadrupole mass spectrometer with an RC interface and MassSoft software (part 27). The mass spectrometer is sensitive to masses up to 300 amu and has a high sensitivity for HV and UHV applications. The sampling rate is set to 2 Hz. The mass spectrometer is placed on the end of the beam chamber on a 150 ISO flange. The spectrometer can be damaged if the vacuum pressure is too high, so it is interlocked to the pressure gauge such that it automatically turns off if the pressure exceeds 5×10^{-5} mbar. Quadrupole spectrometers consist of four cylindrical rods, arranged in two parallel pairs. Each pair is connected and a voltage difference is applied between both pairs. For a given difference only ions with a certain mass-to-charge ratio will reach the detector, as the other ions will fall into unstable trajectories and will not reach the detector. The mass spectrometer either operates at fixed voltage, so that only ions with a chosen mass-to-charge ratio are recorded, or it scans through a voltage difference allowing to obtain a mass spectrum. In the experiment, we use both of these modes, the first one to observe the amount of trioxane in the beam and the other to determine the presence of clusters.

Chapter 3

Trioxane molecular structure

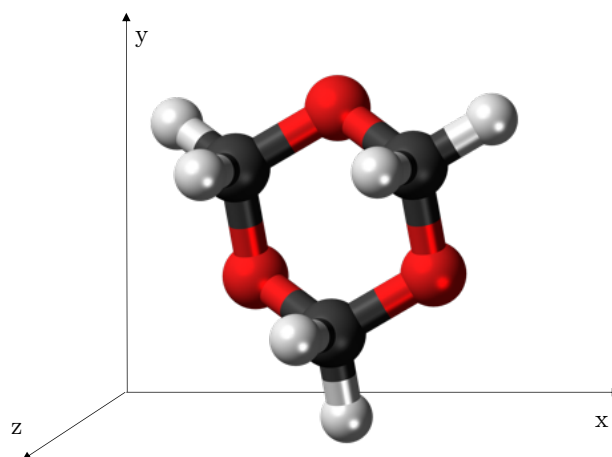


Figure 3.1: Molecule of 1,3,5 Trioxane [116].

The molecule used throughout this thesis is 1,3,5-trioxane ($\text{C}_3\text{O}_3\text{H}_6$; Figure 3.1). Trioxane is a stable cyclic trimer with a small number of vibrational modes and negligible internal vibrational relaxation. Its ν_5 vibrational band has strong transitions at $10\text{ }\mu\text{m}$, which enables us to develop the mid-infrared experimental techniques. The trioxane is treated as a precursor to a chiral molecule that will be used for detecting parity violating effects. Trioxane will have a similar size to any chiral molecule considered for this measurement [80,81], which means that any cooling methods developed should be translatable to chiral molecules. Additionally, trioxane is cheap and relatively safe when handled with care which makes it a good molecule to work with on a daily basis. The chemical properties of trioxane are relatively well known because of the extensive research about trioxane as a potential source of formaldehyde for industrial applications like the production of pesticides or disinfectant agents [117]. This chapter focuses on calculating energy levels and the spectrum of trioxane to later compare with experimental results. Here an expression for the strength of the

trioxane transitions will be derived which can be used to extract the trioxane density from the measurement of its spectrum.

3.1 Trioxane energy levels

1,3,5 trioxane has 3-fold symmetry, meaning that a rotation by $\frac{2\pi}{3}$ around the molecular axis (in Figure 3.1 the z -axis), leaves the molecule unchanged. It follows that when the rotation is performed the molecular moments of inertia in that plane (I_x and I_y) cannot change, which is possible only when they are equal ($I_x = I_y = I_B$). This defines trioxane as a symmetric top molecule. Its rotational motion consists of rotation about the molecular axis, here defined as z -axis (with associated momentum P_z and moment of inertia $I_z = I_C$), and precession of this axis along with the total angular momentum P .

The energy of rotation W can be written as

$$W = \frac{P^2}{2I_B} + P_z^2 \left(\frac{1}{2I_C} - \frac{1}{2I_B} \right). \quad (3.1)$$

Both total angular momentum and angular momentum along the z -axis are quantized hence the energy becomes

$$W = J(J+1) \frac{\hbar^2}{2I_B} + K^2 \left(\frac{\hbar^2}{2I_C} - \frac{\hbar^2}{2I_B} \right). \quad (3.2)$$

where K can take the values $K = -J, -J+1, \dots, J-1, J$. We can define rotational constants $B = \frac{\hbar^2}{2I_B}$ and $C = \frac{\hbar^2}{2I_C}$ and the expression simplifies to

$$W = BJ(J+1) + (C-B)K^2. \quad (3.3)$$

When the molecule rotates the centrifugal force pulls atoms apart, hence the moments of inertia of the molecule increase, and the constants B and C decrease. This changes slightly the energy of the levels so the formula must include the correction terms

$$W = BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4. \quad (3.4)$$

Figure 3.2 shows all the energy levels for the ground and excited ν_5 vibrational mode for J between 16 and 20. Figure 3.3 focuses on the energy levels involved in the transitions used for the current experimental work, namely the Q branch transitions with $K = 16$ and 17. Trioxane, as a symmetric top, has no dipole moment parallel to the molecular axis. The angular momentum in that direction will not change when the molecule interacts with light, hence we can establish a selection rule of $\Delta K = 0$. We are interested in the transitions between the ground and the excited level of the ν_5 vibrational band. We observe transitions in Q, P, and R-branches for which $\Delta J = 0, \pm 1$ with the

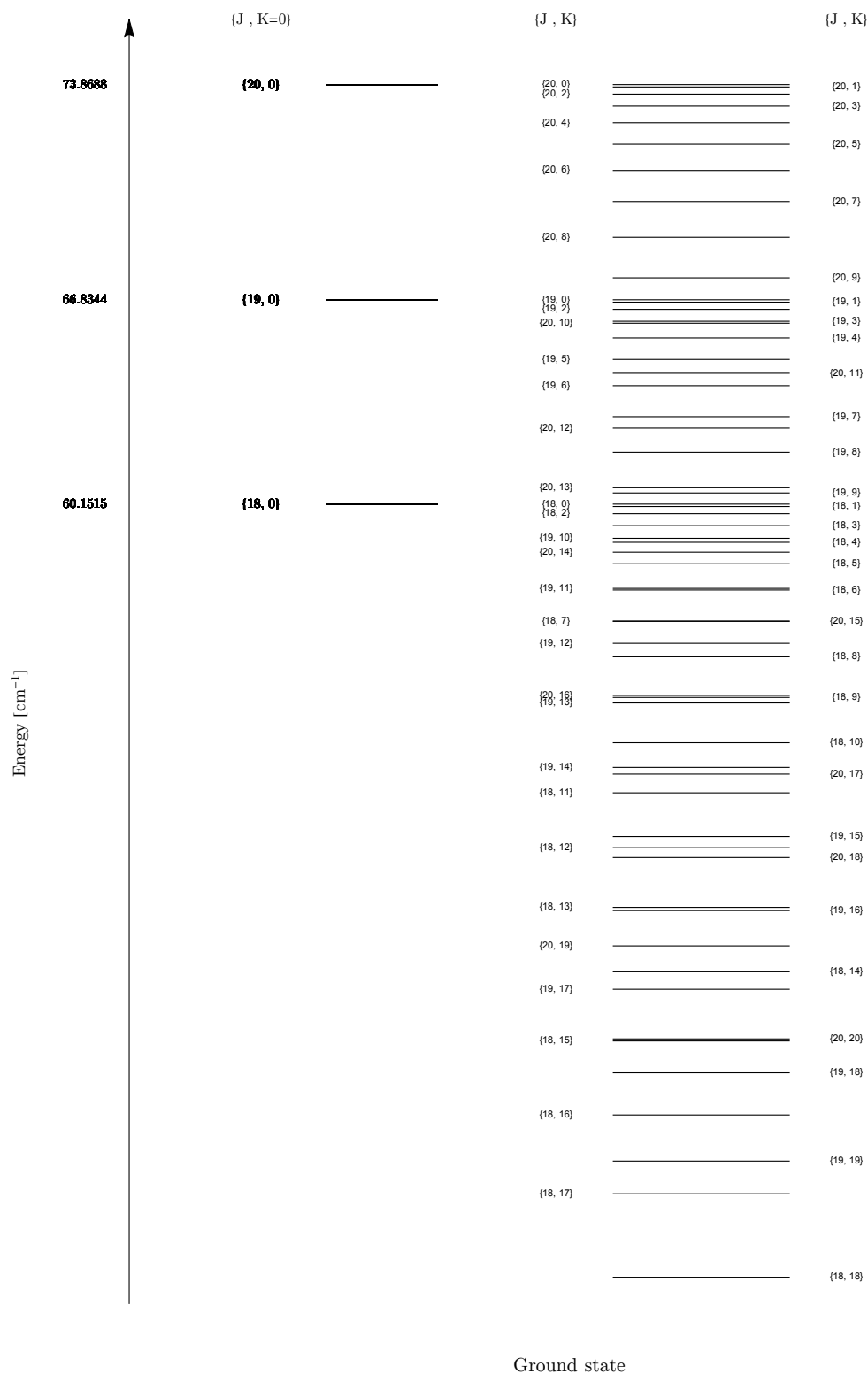


Figure 3.2: Trioxane energy levels between $J = 16$ and $J = 20$ for the ground vibrational state of the molecule. States with $K = 0$ are highlighted.

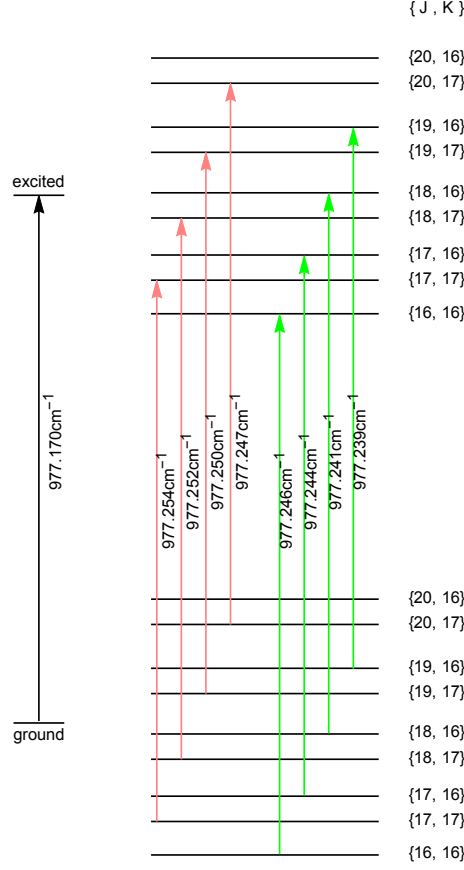


Figure 3.3: Energy level diagram of trioxane for J between 16 and 20 with $K = 16$ and 17. Transitions between levels with $K = 16$ and 17 are denoted respectively by green and red arrows. The labels “ground” and “excited” correspond to zero and one quantum of vibrational energy in this mode.

band origin at 977.170 cm^{-1} . The expression for transition frequencies in the Q-branch is given by

$$\begin{aligned}
 f = & (B^{\text{excited}} - B^{\text{ground}})J(J+1) \\
 & + (C^{\text{excited}} - C^{\text{ground}} - B^{\text{excited}} + B^{\text{ground}})K^2 \\
 & - (D_J^{\text{excited}} - D_J^{\text{ground}})J^2(J+1)^2 \\
 & - (D_{JK}^{\text{excited}} - D_{JK}^{\text{ground}})J(J+1)K^2 \\
 & - (D_K^{\text{ground}} - D_K^{\text{excited}})K^4.
 \end{aligned} \tag{3.5}$$

Equation 3.5, along with the selection rules allows us to calculate a molecular spectrum. Molecular constants for the ν_5 vibrational band of trioxane are experimentally obtained by our collaborator from Université Paris 13, Benôit Darquié. We use these constants here to determine transition frequencies.

3.2 Trioxane roto-vibrational spectrum

Equation 3.5 only gives the frequencies of transitions. To have a more complete picture it is good to consider the intensities of each of them. To do that let's consider a molecule undergoing a transition between any ground state m to any excited state n . The rate of the transition for a monochromatic light source (laser) is given by

$$p_{m \rightarrow n} = \rho S(\nu_0, \nu) B_{m \rightarrow n}, \quad (3.6)$$

where ρ is radiation density, $S(\nu_0, \nu)$ is the normalized lineshape centered at ν_0 and $B_{m \rightarrow n}$ is the Einstein coefficient of absorption. The reverse transition will have a rate ,

$$p_{m \leftarrow n} = \rho S(\nu_0, \nu) B_{m \leftarrow n} + A_{m \leftarrow n} \quad (3.7)$$

where $B_{m \leftarrow n}$ is the Einstein coefficient of induced emission and $A_{m \leftarrow n}$ is the Einstein coefficient of spontaneous emission. It can be shown that both Einstein B coefficients are equal and are given by

$$B_{mn} = \frac{4\pi^3}{3h^2\epsilon_0} |\langle n | \mu | m \rangle|^2, \quad (3.8)$$

where μ is the dipole moment operator. In the experiment where the laser propagates through the molecular sample, we are interested in the net change in the power in a supplied radiation field. We want to know the power that the sample of N molecules undergoing $m \rightarrow n$ transitions in the beam with the volume of interaction V will absorb if the energy needed to undergo this transition is $h\nu_{mn}$. Induced emission will also be happening at the same time and emits photons in the same direction as the incident laser beam. The spontaneous emission is random in direction and only a small amount of power will be in the direction of the propagation hence we can disregard it in the calculation. The net change in the power supplied is therefore

$$\Delta P = P_{m \leftarrow n} - P_{m \rightarrow n} = V(N_n - N_m) B_{mn} \rho S(\nu_0, \nu) h\nu, \quad (3.9)$$

where N_m, N_n are the number of molecules in each state. If the region of interaction with the sample has cross-section A and we consider the change in power when the laser propagates a small distance Δx we can re-express the above as

$$\Delta P = -A \Delta x (N_m - N_n) B_{mn} \rho S(\nu_0, \nu) h\nu. \quad (3.10)$$

The radiation density can be expressed as the power supplied divided by the speed of light and the cross-section of the interaction region A

$$\rho = \frac{P}{cA}. \quad (3.11)$$

Taking an infinitesimal element Δx we arrive at the differential equation

$$\frac{dP}{dx} = -(N_m - N_n) B_{mn} \frac{P}{c} S(\nu_0, \nu) h\nu. \quad (3.12)$$

The solution to this equation is

$$P = P_0 e^{-(N_n - N_m) B_{mn} \frac{1}{c} S(\nu_0, \nu) h \nu}. \quad (3.13)$$

Writing $P = P_0 e^{-\alpha x}$ we can identify a coefficient of absorption

$$\alpha_{mn} = (N_m - N_n) B_{mn} \frac{1}{c} S(\nu_0, \nu) h \nu. \quad (3.14)$$

We can assume that the laser does not change the populations appreciably so that they are close to thermal equilibrium. In that case, we can use the Boltzmann law to relate the populations of both levels giving

$$\alpha_{mn} = N_m (1 - e^{-h\nu_{mn}/kT}) B_{mn} \frac{1}{c} S(\nu_0, \nu) h \nu. \quad (3.15)$$

At a wavelength of 10 μm and a temperature below 10 K, $h\nu_{mn} \gg kT$ and so the exponential is much smaller than 1 and can be neglected. In this case

$$\alpha_{mn} = N_m B_{mn} \frac{1}{c} S(\nu_0, \nu) h \nu. \quad (3.16)$$

Expressing N_m as a total number of molecules multiplied by a fraction of molecules that are present in lower state we obtain an absorption coefficient

$$\alpha_{mn} = \frac{4\pi^3 \nu N F_m}{3ch\epsilon_0} S(\nu_0, \nu) |\langle m | \mu | n \rangle|^2, \quad (3.17)$$

where F_m is the fraction of molecules in the ground state. As the pressure in the cold cell in the experiment is extremely low the main contribution to the lineshape function is the Doppler broadening. The normalized lineshape function is

$$S(\nu_0, \nu) = \sqrt{\frac{mc^2}{\pi kT \nu_0^2}} \exp\left(-\frac{mc^2(\nu - \nu_0)^2}{2kT \nu_0^2}\right). \quad (3.18)$$

It is useful in discussion of line strengths to talk about the integrated line strength

$$I = \int_{-\infty}^{\infty} \alpha_{mn} d\nu. \quad (3.19)$$

Hence the integrated line strength can be calculated to be

$$I = \int_{-\infty}^{\infty} \frac{4\pi^3 \nu N F_m}{3ch\epsilon_0} \sqrt{\frac{mc^2}{2\pi kT \nu_0^2}} \exp\left(-\frac{mc^2(\nu - \nu_0)^2}{2kT \nu_0^2}\right) |\langle m | \mu | n \rangle|^2 d\nu. \quad (3.20)$$

To keep with the convention used in the literature we are going to use wavenumber $\tilde{\nu}$ in cm^{-1} instead of the frequency ν . The wavenumber and frequency are connected according to the equation

$$\nu = 100c\tilde{\nu} \quad (3.21)$$

where the 100 is used to convert from m^{-1} to cm^{-1} and will be omitted in the following equations. This gives an expression

$$\begin{aligned} I &= \int_{-\infty}^{\infty} \frac{4\pi^3 \tilde{\nu} N F_m}{3h\epsilon_0} \sqrt{\frac{m}{2\pi kT \tilde{\nu}_0^2}} \exp\left(-\frac{mc^2(\tilde{\nu} - \tilde{\nu}_0)^2}{2kT \tilde{\nu}_0^2}\right) |\langle m | \mu | n \rangle|^2 d\tilde{\nu} \\ &= \frac{4\pi^3 \tilde{\nu}_0 N F_m}{3ch\epsilon_0} |\langle m | \mu | n \rangle|^2. \end{aligned} \quad (3.22)$$

The fraction of molecules in any particular state is given from Boltzmann law by

$$F_m = \frac{N_m}{N} = \frac{g_m e^{-E_m/kT}}{\sum_i g_i e^{-E_i/kT}}, \quad (3.23)$$

where g_m is the degeneracy of the state m and E_m is the energy of this state.

To obtain F_m one has to remember that we observe the transition from a rotational state of the ground vibrational state to a rotational state of the excited vibrational state. Hence we have to take into account the fraction of molecules in particular rotational state $F_{J,K}$ in a ground vibrational state F_V . The total fraction of molecules in the state is therefore

$$F_m = F_V F_{J,K}. \quad (3.24)$$

For a given vibrational state n_v with an energy of $\hbar\omega_0(n_v + \frac{1}{2})$ the fraction of population in this vibrational state is

$$F_V = \frac{e^{-\hbar\omega_0(n_v + \frac{1}{2})/kT}}{\sum_n e^{-\hbar\omega_0(n + \frac{1}{2})/kT}} = e^{-n_v \hbar\omega_0/kT} (1 - e^{-\hbar\omega_0/kT}). \quad (3.25)$$

The degeneracy of any rotational state is $(2J+1)$, hence the fraction of molecules $F_{J,K}$ in the given rotational state is

$$F_{J,K} = (2J+1) \frac{e^{-E_{J,K}/kT}}{\sum_{J,K} (2J+1) e^{-E_{J,K}/kT}}. \quad (3.26)$$

The dipole moment $|\langle m | \mu | n \rangle|$ for a transition with $\Delta J = 0, \pm 1$ and $\Delta K = 0$ is given by [118]

$$|\langle m | \mu | n \rangle|^2 = \frac{\mu^2 K^2}{J(J+1)} \quad (\Delta J = 0), \quad (3.27)$$

$$|\langle m | \mu | n \rangle|^2 = \frac{\mu^2 ((J+1)^2 - K^2)}{(2J+1)(J+1)} \quad (\Delta J = +1), \quad (3.28)$$

$$|\langle m | \mu | n \rangle|^2 = \frac{\mu^2 (J^2 - K^2)}{J(2J+1)} \quad (\Delta J = -1), \quad (3.29)$$

where μ is the dipole moment of this vibrational mode. Therefore the full expression for an integrated line intensity is

$$I = e^{-n_v \hbar\omega_0/kT} (1 - e^{-\hbar\omega_0/kT}) (2J+1) \frac{e^{-E_{J,K}/kT}}{\sum_{J,K} (2J+1) e^{-E_{J,K}/kT}} \frac{4\pi^3 N \tilde{\nu}_0}{3ch\epsilon_0} |\langle m | \mu | n \rangle|^2. \quad (3.30)$$

We are interested in the vibrational ground level with $n_v = 0$. Therefore the first exponential of the 3.30 is equal to 1. The next term can be approximated to be close to 1 hence we are left with

$$I_{J,K} = (2J+1) \frac{e^{-E_{J,K}/kT}}{\sum_{J,K} (2J+1) e^{-E_{J,K}/kT}} \frac{4\pi^3 N \tilde{\nu}_0}{3ch\epsilon_0} |\langle m | \mu | n \rangle|^2. \quad (3.31)$$

3.2.1 Notation

Through the majority of this thesis the notation $branch(J, K)$ will be used. In this case J signifies the ground level. As mentioned earlier for each J there exist $K = J, J - 1, \dots, -J + 1, -J$ levels. All allowed transitions have $\Delta K = 0$. Because the levels with the same $|K|$ are degenerate when talking about transitions with a specific value for K we will refer to the absolute value. If we refer to a spectrum that shows all K lines for a given J transition, for example all K lines for $J = 3$ transition of the R branch, we will use notation $R(3, K)$.

3.3 Strength of the trioxane lines

To assess the number density of trioxane in the cold cell we can utilise Equation 3.31 to obtain N . For that, however, we need to know the value of the transition dipole moment μ for this transition. Our collaborator, Prof. Trevor Sears from Stony Brook University, has calculated the values for the integrated intensity and the transition dipole strength for the whole band using the software Gaussian. The result of this calculation is $\mu = 5.80 \times 10^{-31} \text{ C m}$.

Now we can progress to calculating the intensity of a spectral line at 7 K from Equation 3.31. This is going to be used in Section 4.7 to determine the number density of trioxane from the direct spectrum. For example, for $Q(15, 15)$ the integrated line strength is equal $I_{15,15} = 2.2 \times 10^{-22} \text{ cm}^{-1} \text{ molecule cm}^2$. There is a note about unit convention: Equation 3.31 has units of molecule $\text{m}^{-1} \text{ cm}^{-1}$ because N in that equation is the number of molecules, not the number density. Writing out N as nV where V is the volume we can shift integrated line density into a unit which now becomes molecule $\text{m}^2 \text{ cm}^{-1}$. In the numerical calculation, we have taken lines with J between 1 and 200 and have calculated the partition function as the sum of partition functions for Q-, P-, and R-branches. The dipole moment of singular transition was calculated using Eq. 3.27. Now we can explicitly see how cooling down the molecules increases the strength of the lines. If we compare the result for 7 K with the result for 293 K: $I_{15,15} = 3.1 \times 10^{-23} \text{ cm}^{-1} \text{ molecule cm}^2$, we see that the line increased by about order of magnitude.

Trioxane spectrum with an assigned fractional population Figure 3.4 shows the calculated spectrum for the ν_5 vibrational mode, with the Q branch ($\Delta J = 0$) in blue, P branch ($\Delta J = +1$) in orange and R branch ($\Delta J = -1$) in purple, with the assigned populations of the ground state for this transition at 7 K. Additionally, to show how the cooling of the molecules simplifies the spectrum, the Q branch is shown in Figures 3.5a and 3.5b for temperatures of 7 K and 300 K respectively. It is immediately visible that the majority of the molecular population at 7 K has moved to lower levels hence the spectrum is less congested.

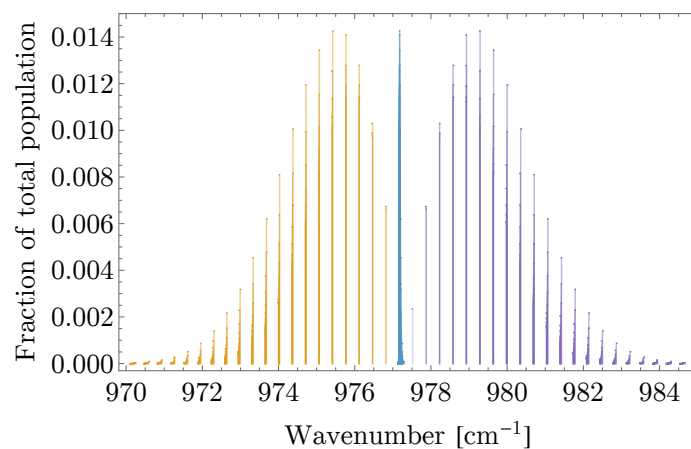


Figure 3.4: Spectrum of the ν_5 vibrational mode of trioxane at 7 K. The height of the lines is taken as the fraction of the population in the state.

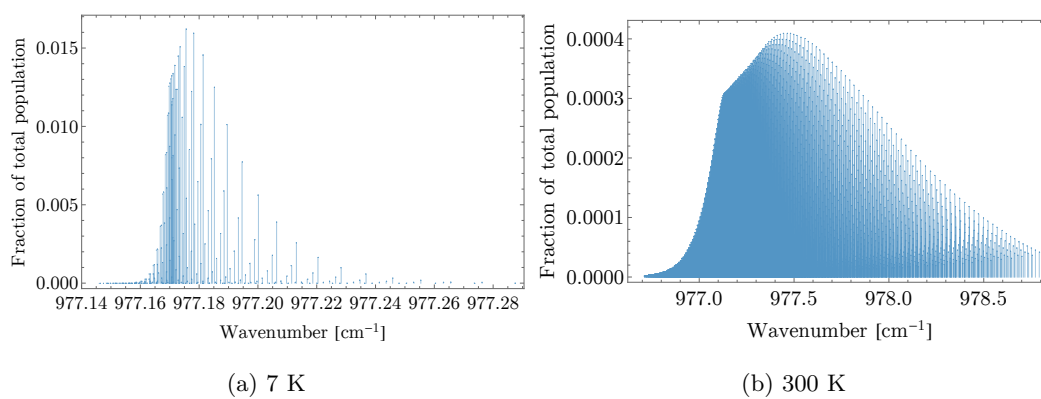


Figure 3.5: Fraction of total population for various lines of Q-branch of ν_5 vibrational line at different temperatures.

Chapter 4

Production and spectroscopy of cold trioxane

In this chapter, we will discuss the processes of cooling and detection of trioxane molecules. First, the principles of buffer gas cooling will be outlined and thermalisation of the molecules will be discussed. Then, wavelength modulation spectroscopy (WMS), used for investigation of molecules in the cold cell will be outlined, and the impact of WMS parameters on molecular spectra will be discussed. Here, the spectra recorded for Q- and R-branches of the ν_5 vibrational band of cold trioxane will be presented and used to extract the temperature of molecules in the cell. Additionally, the number density of trioxane molecules in the cell will be calculated from direct absorption data. This analysis is based on the calculations presented in Chapter 3. Finally, we will discuss how the power of the laser affects the width and amplitude of the trioxane features and will discuss whether the transition is saturated .

4.1 Theory of buffer gas cooling

In the buffer gas cooling method molecules are cooled by collisions inside a cold cell. The cell is placed in a vacuum and kept at the temperature of a few kelvin with a cryocooler. The buffer gas, cooled to temperature of T_{B0} , and a hot molecule of interest at an initial temperature T_{S0} are delivered to the cell and allowed to mix. The collisions of the hot molecule of interest with the cold buffer gas cause thermalization of the former to a temperature T_{SF} which is close to that of the buffer gas.

Cold cell characteristics We are going to consider a cubic cold cell with length, width, and depth all equal to l_{cell} , with a beam exit aperture with a radius r_{aperture} . The flow of buffer gas used

for cooling is between 1-20 sccm¹.

At a temperature of several Kelvin elastic scattering is still in the classical regime. The classical collision-cross section to a good approximation scales as the square of the molecular radius. The trioxane molecular radius is about 3 Å and YbF is about 2 Å. The YbF-He scattering cross-section is measured experimentally, so observing the similarity in radii we will assume throughout this thesis that the collision-cross section of trioxane with the buffer gas beam is equal to the YbF-He scattering cross-section $\sigma = 2.6 \times 10^{-19} \text{ m}^2$ [119].

Buffer gas used In this experiment, we have attempted beam production using two different buffer gases, helium and neon. The gases have different physical properties and pose different technical challenges, while also having distinct advantages.

4.1.1 Cooling time and length

In the cold cell, the molecule of interest with mass m_S undergoes a number of collisions N_c with buffer gas atoms of mass m_B , each one lowering its temperature, down to the final temperature of T_{SF} . The cooling of the molecules can be modelled with the equation [120]

$$T_{SF} = (T_{S0} - T_{B0})e^{-\frac{N_c}{\kappa}} + T_{B0}, \quad (4.1)$$

where T_{S0} is the initial temperature of the species of interest, T_{B0} is the temperature of the buffer gas, and κ is defined as

$$\kappa = \frac{(m_S + m_B)^2}{2m_S m_B}. \quad (4.2)$$

Because the process of cooling is incremental, it is beneficial to calculate whether the molecules are fully thermalised by the time they reach the detection region to make sure that the laser interrogates fully thermalised molecules. The first thing that needs to be calculated is the density of buffer gas molecules in the cold cell. The gas is delivered to a cold cell with a flow f . After leaving the pipe it can be modelled by a flow of gas through an aperture, in this case the beam exit aperture with an area A_{aperture} and radius of r_{aperture} :

$$f = \frac{1}{4} n_B \bar{v}_B A_{\text{aperture}}, \quad (4.3)$$

where n_B is the buffer gas number density, and $\bar{v}_B$ is the mean velocity of the buffer gas atoms. From that the n_B can be extracted:

$$n_B = \frac{4f}{\bar{v}_B A_{\text{aperture}}} = \frac{4f}{\pi r_{\text{aperture}}^2} \sqrt{\frac{\pi m_B}{8kT_{B0}}}. \quad (4.4)$$

The flow of buffer gas, f , is controlled using a flow controller, so the buffer gas density inside the cell can be determined. Knowing this, and the mean velocity, we can calculate the mean free path

¹1 sccm is equivalent to 4.5×10^{17} molecules per second at standard conditions of 0°C and 1 atm

λ for the molecule of interest in the buffer gas. We cannot use the standard equation for the mean free path $\lambda = \frac{1}{n\sigma}$ since this is only appropriate when the buffer gas atoms are stationary. To account the fact that both species are moving, we use a correction factor which is the ratio of the molecular velocity $\bar{v}_s$ to the relative velocity of the buffer gas atoms and molecules $\bar{v}_{\text{rel}}$ [121]

$$\lambda = \frac{1}{n\sigma} \frac{\bar{v}_s}{\bar{v}_{\text{rel}}}. \quad (4.5)$$

The relative velocity is given by

$$\bar{v}_{\text{rel}} = \sqrt{\frac{8kT_{\text{B0}}}{\pi\mu}}, \quad (4.6)$$

where

$$\mu = \frac{m_S m_B}{m_S + m_B} \quad (4.7)$$

is the reduced mass. Using equations 4.4 and 4.6 we can calculate λ to be

$$\lambda = \frac{A_{\text{aperture}} \bar{v}_B}{4f\sigma \sqrt{1 + \frac{m_S}{m_B}}}. \quad (4.8)$$

We assume that $\frac{m_S}{m_B}$ is much larger than 1 which gives the final form

$$\lambda = \frac{A_{\text{aperture}} \bar{v}_B}{4f\sigma \sqrt{\frac{m_S}{m_B}}}. \quad (4.9)$$

There are two regimes describing the movement of the molecules in the cell. In the first one, referred to as random walk, the majority of the molecules are entrained in the buffer gas. The molecular movement is dominated by the random motion and the thermalization length l_r is given by

$$l_r = \lambda \times \sqrt{N_c}. \quad (4.10)$$

In the other regime, called direct expansion, the majority of the molecules have high speed, ballistically moving through the cell. In this case the thermalization length is given by

$$l_d = \lambda \times N_c. \quad (4.11)$$

This happens for example when hot (room temperature) molecules enter the cold cell. There is a possibility for the molecules to be in a regime intermediate between those two when the majority of motion is caused by molecules being entrained in the buffer gas flow but with the velocity of molecules still being a significant component. While discussing the molecular movement through the buffer gas, one has to consider it separately from the flow of the buffer gas itself. With increasing buffer gas flow the outflow through the exit hole increases and the molecules of interest are extracted faster from the cell. So while with high helium flow the molecules thermalise faster and exhibit more random motion they also might be extracted faster from the cell resulting in less cooling.

The molecules in the cell take time to thermalise t_t . This quantity is defined as the time of one collision multiplied by the number of collisions needed to reach T_{SF} . The time of one collision is a mean free path divided by the relative velocity of the buffer gas and the molecule of interest

$$t_t = t_c \times N_c = \frac{\lambda}{\bar{v}_{\text{rel}}} \times N_c. \quad (4.12)$$

The final thing to consider is the diffusion of the species of interest to the walls of the cell. If the trioxane diffuses to the cell walls and freezes, it can no longer contribute to the experiment. In the interest of efficient cooling and minimization of the loss of trioxane, the thermalization time must be smaller than the diffusion time which can be obtained from the equation [120]

$$\tau_{\text{diff}} = \frac{16}{9\pi} \frac{A}{n_B \sigma} \bar{v}_B. \quad (4.13)$$

Cold cell in the system In the experiment the cold cell is kept at 7 K. It has dimensions $l_{\text{cell}} = 50$ mm, and the beam aperture has a radius $r_{\text{aperture}} = 1$ mm. The aperture walls have a thickness of 3 mm.

Helium buffer gas In this section, we calculate values for the buffer gas density and thermalization length and time for trioxane molecules ($m_S = 90$ amu) in a helium buffer gas ($m_B = 4$ amu). The helium flow used in this experiment is between 1-8 sccm. Flow above that value causes the pressure in the system to be too high (1×10^{-5} mbar) to create the molecular beam. Flows between 1-8 sccm correspond to number densities in the cell from 3×10^{21} to $2.4 \times 10^{22} \text{ m}^{-3}$.

The helium gas passes through a pipe wound around a bobbin which is thermally anchored to the 7 K plate. We can assume that the buffer gas effectively thermalises to the temperature of the bobbin ($T_{B0} = 7$ K). To calculate how many collisions are needed for trioxane to cool down from room temperature ($T_{S0} = 293$ K) close to T_{B0} we use Eq. 4.1.

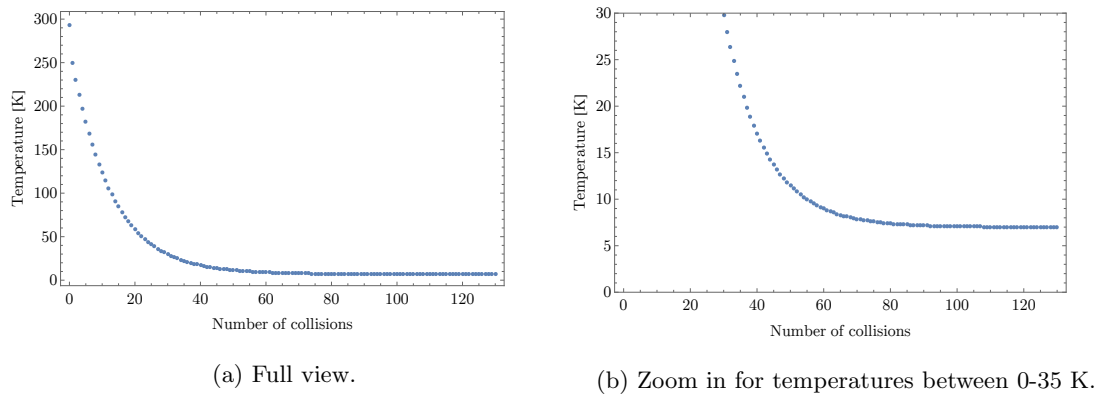


Figure 4.1: Temperature of trioxane vs number of collisions with helium buffer gas. The molecules are cooled from room temperature 293 K by thermalising with the buffer gas at 7 K.

Figure 4.1 shows the evolution of the temperature of trioxane with the number of collisions. We can easily notice that after about 100 collisions the molecules effectively thermalise to T_{B0} . For 1 sccm the mean free path of trioxane is 0.3 mm. The distance between the observation region and the trioxane capillary is 25 mm. We have discussed two regimes of molecular movement in the cell, and now we are going to consider distances travelled by molecules of interest in the cell in each of them. In direct expansion, where molecules travel in one direction dictated by the helium flow, they undergo on average 83 collisions and thermalise to about 10 K. If we assume that the molecules are governed only by the random walk, the molecules undergo about 800 collisions, and therefore are fully thermalised when observed.

The typical experimental procedure is to start the flow of trioxane to the cold cell when the laser scan starts. Laser scans can take from 100 ms to 25 seconds. The thermalisation time for trioxane is calculated to be 0.1 ms, shorter even then the shortest scan. Thus, there is no need to allow additional time at the beginning of the scan for molecules to thermalize. For trioxane molecules in 1 sccm of helium flow, the diffusion time to the walls is calculated to be 6 ms. We have to ensure that the molecules will be extracted from the cell in a time shorter than the diffusion time but longer than the thermalization time to efficiently create a molecular beam. The properties of buffer gas cooling of trioxane with helium are summarised in Table 4.1. This and other considerations for creating a beam will be discussed in Section 5.1

Helium					
beam exit aperture radius	$r_{\text{aperture}}[\text{mm}]$	1		2	
buffer gas flow	$f[\text{sccm}]$	1	8	1	8
buffer gas number density	$n_B [\text{m}^{-3}]$	3×10^{21}	2.4×10^{22}	7×10^{20}	6×10^{21}
number of collisions to thermalize	N_c	100	100	100	100
buffer gas beam temperature	$T_B[\text{K}]$	7	7	7	7
mean free path	$\lambda [\text{mm}]$	0.27	0.03	1.07	0.13
thermalisation length - direct	$l_d[\text{mm}]$	27	3.3	107	13
thermalisation length - random	$l_r[\text{mm}]$	2.7	0.33	10.7	1.3
time of one collision	$t_c[\text{ms}]$	0.13	0.02	0.54	0.07

Table 4.1: Summary of properties of buffer gas cooling with helium for different aperture sizes and flows.

Neon buffer gas We now repeat the calculations from the previous section for trioxane in neon ($m_B = 20$ amu) buffer gas. Any cold (< 15 K) surface acts as a cryopump for neon, and with that requirement neon has to be kept at temperature above $T_{B0} = 17$ K. The area of cold surfaces in

the experiment is larger than the area of charcoal adsorbers, and we can assume that neon will be pumped more efficiently than helium. From that we can expect that we can run the experiment with flows between 1-20 sccm, corresponding to number density in the cell between 4×10^{21} and $8 \times 10^{22} \text{ m}^{-3}$. Figure 4.2 shows the change of temperature of trioxane with the number of collisions. We can see that, for molecules starting from room temperature $T_{S0} = 293 \text{ K}$, about 30 collisions are required to reach 17 K. Note that we are assuming the collision cross section of trioxane with neon is the same as that with helium

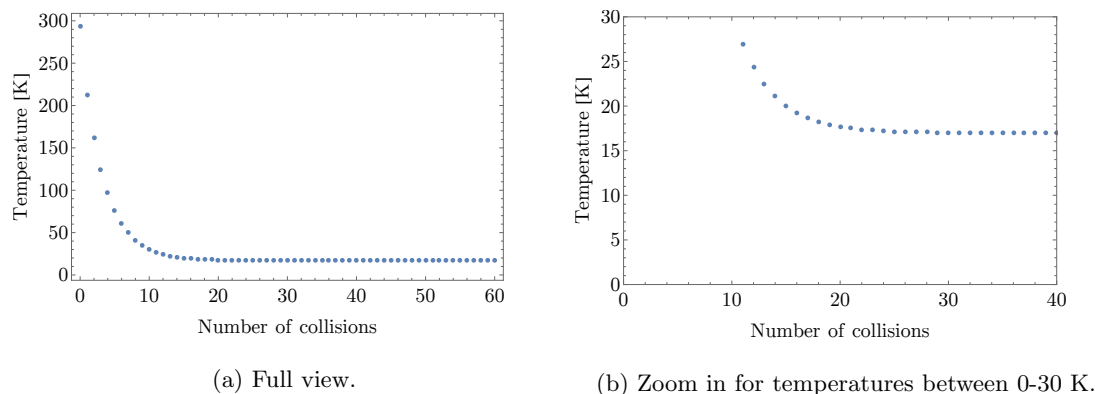


Figure 4.2: Temperature of trioxane vs number of collisions in neon buffer gas. The initial temperature of trioxane was 293 K and the temperature of the neon buffer gas is 17 K.

The mean free path of trioxane in neon with 1 sccm of flow is 0.4 mm, hence the thermalization length in the direct regime is 12 mm and in the random walk regime is 2.1 mm. The thermalization time with that flow of neon is 0.05 ms.

The mean free path of trioxane in neon with 20 sccm of flow is 0.02 mm, hence the thermalization length in the direct regime is 0.6 mm and in the random walk regime is 0.1 mm. The thermalization time with that flow of neon is 0.002 ms. Even with the low flow of neon, the trioxane is fully thermalised before reaching the detection region.

Experiments with different apertures To facilitate the extraction of molecules to the molecular beam the aperture was replaced with a new one with $r_{\text{aperture}} = 2 \text{ mm}$. The change of the aperture affects the neon number density in the cell, which now for 1 sccm is 1×10^{21} and $2 \times 10^{22} \text{ m}^{-3}$. So while the number of collisions needed for trioxane to thermalise stays constant the thermalization length and time will change. For 1 sccm neon flow the thermalization length in the direct regime is 46 mm and if molecules perform random walk is 8.4 mm. With 20 sccm however, the thermalization lengths are respectively 2.3 and 0.4 mm, which mean that the molecules would be fully thermalised in the observation region. Thermalization times for both 1 and 20 sccm are still in the millisecond range. The properties of buffer gas cooling of trioxane with neon are summarised in Table 4.2. With

the bigger aperture the measurement of the temperature of the molecules will determine in which regime the molecules are. For both helium and neon we have tried a small, 0.5 mm diameter in radius aperture but observed no extraction of molecules to the beam, most probably due to fast clogging with trioxane molecules, hence it won't be included in the discussion.

Neon					
beam exit aperture radius	$r_{\text{aperture}}[\text{mm}]$	1		2	
buffer gas flow	f [sccm]	1	20	1	20
buffer gas number density	n_B [m^{-3}]	4×10^{21}	8×10^{22}	1×10^{21}	2×10^{22}
number of collisions to thermalize	N_c	30	30	30	30
buffer gas beam temperature	T_B [K]	17	17	17	17
mean free path	λ [mm]	0.4	0.02	1.5	0.08
thermalisation length - direct	l_d [m]	12	0.6	46	2.3
thermalisation length - random	l_r [m]	2.1	0.1	8.4	0.4
time of one collision	t_c [ms]	0.05	0.002	0.2	0.01

Table 4.2: Summary of properties of buffer gas cooling with neon for different aperture sizes and flows.

4.2 Wavelength Modulation Spectroscopy

To investigate the molecules we use a spectroscopic technique called wavelength modulation spectroscopy. In this method a lock-in amplifier is used to detect small signals obscured by noise, frequently much bigger in amplitude. The main source of noise in electronics is so-called $\frac{1}{f}$ noise, inversely proportional to frequency. A DC signal is difficult to detect because this is where the noise is largest, but if the signal is modulated at a high frequency it is shifted to the place where the noise is much smaller. Figure 4.3 shows how the noise depends on the frequency. The lock-in amplifier is used to isolate the signal at the modulation frequency with a much lower noise.

4.2.1 WMS theoretical principles

A lock-in amplifier is a device used to extract signals with constant frequency from random noise. The input signal and reference are supplied to the lock-in and then compared. If both occur at the same frequency the lock-in produces an output signal, otherwise no output is present. Let's assume that a sinusoidal reference at a frequency Ω is supplied to the lock-in amplifier where A_m is the amplitude of modulation:

$$V_R(t) = A_m \sin(\Omega t). \quad (4.14)$$

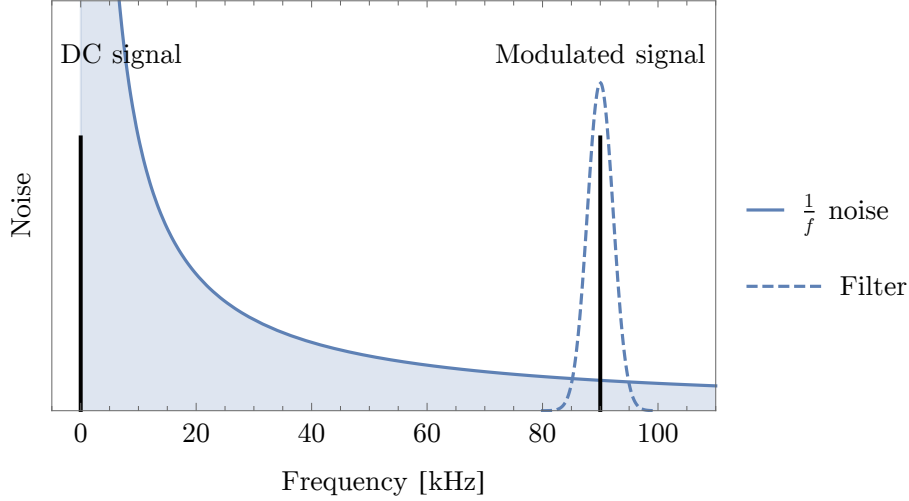


Figure 4.3: Noise spectrum (blue curve) of an electronic device, showing the initial signal and the modulated signal moved to the higher frequency.

The input signal is also a sinusoidal function with some frequency ω , expressed as

$$V_s(t) = V_0 \sin(\omega t + \phi), \quad (4.15)$$

where ϕ is a set phase relationship between the signal and reference. The reference and the input are multiplied inside the lock-in

$$V_{\text{lock}} = V_s(t)V_R(t) = V_0 A_m \sin(\omega t + \phi) \sin(\Omega t) = \frac{1}{2} V_0 A_m \{\cos[(\omega - \Omega)t + \phi] - \cos[(\omega + \Omega)t + \phi]\}. \quad (4.16)$$

If the signal frequency is not equal to the reference then the time average of V_{lock} is equal to zero and the lock-in amplifier does not produce any output. If however $\omega = \Omega$ then the expression for V_{lock} can be given as:

$$V_{\text{lock}} = \frac{1}{2} V_0 A_m \{\cos[\phi] - \cos[2\Omega t + \phi]\}. \quad (4.17)$$

In this case the lock-in amplifier signal V_{lock} contains a DC component and a component at twice the modulation frequency, demonstrated in Figure 4.3. The DC signal lies in the region of high noise and the modulated signal is moved to a region with a much lower noise. The low-pass filter is used to filter out the signal at the 2Ω frequency leaving the DC component as an output.

Figure 4.4 shows a simple block diagram of a lock-in amplifier, each part is named and marked with a setting that can be adjusted.

Detection of the signal In this experiment the aim is not to detect the presence of a sinusoidally varying signal but rather a change in this signal. We consider a modulated signal interacting with some system and then reaching the detector, in this case frequency modulated laser light passing through an absorbing sample of gas and then falling on the photodiode. The photodiode will respond

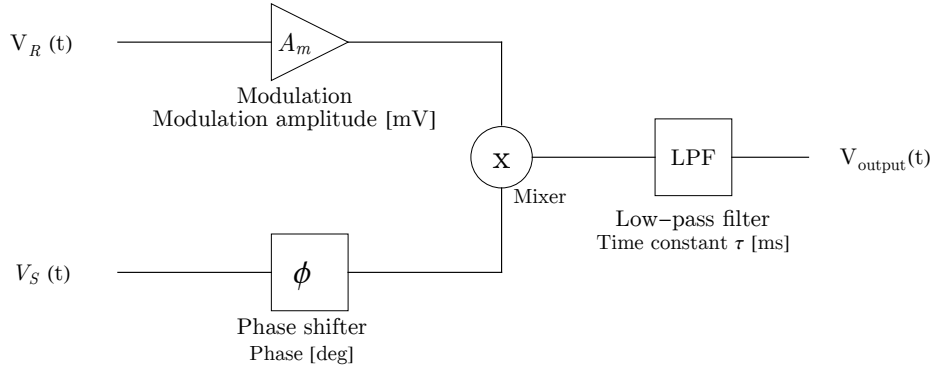


Figure 4.4: Internal block diagram of lock-in amplifier.

to changes in light intensity by producing a voltage proportional to the change. In the case of light passing through a gas sample a change like that might be due to a spectral feature. The light at the frequencies causing the transition will be attenuated thus giving a varying voltage in the detector. We can assume that the detector is set-up in such a way that the detection of attenuation of light produces positive output voltage. This will be the lock-in amplifier input signal. The lock-in output signal is proportional to the derivative of the change in the input signal, and will show changes in the voltage supplied by a detector. Figure 4.5 shows a theoretical detector output voltage with five regions of the signal highlighted, and the output voltage of a lock-in amplifier corresponding to these regions. The output voltage increases with the increase of the slope, up to the maximum point of the transition where the slope is zero. Then the slope is negative hence the lock-in amplifier, sensitive to the sign of the slope, produces a negative output signal. We can see that the result is the first derivative of the spectral feature. Some lock-in amplifiers provide an option to choose an output signal proportional to a higher derivative of the input signal.

Parameters and their influence on lock-in operation

Phase We want to maximize the output signal, which is the DC component of V_{lock} . We can see that it is dependent on the relative phase between the signal and the reference. The aim is to find the value for which $\cos(\phi)$ is equal 1, and therefore the output signal is maximum. The most precise way to find a ϕ value for which the output is maximum is to minimize the signal and then flip the phase by 90° .

Sensitivity Sensitivity is a different name for the gain of the amplifier. It can be set up depending on the needs of the experiment.

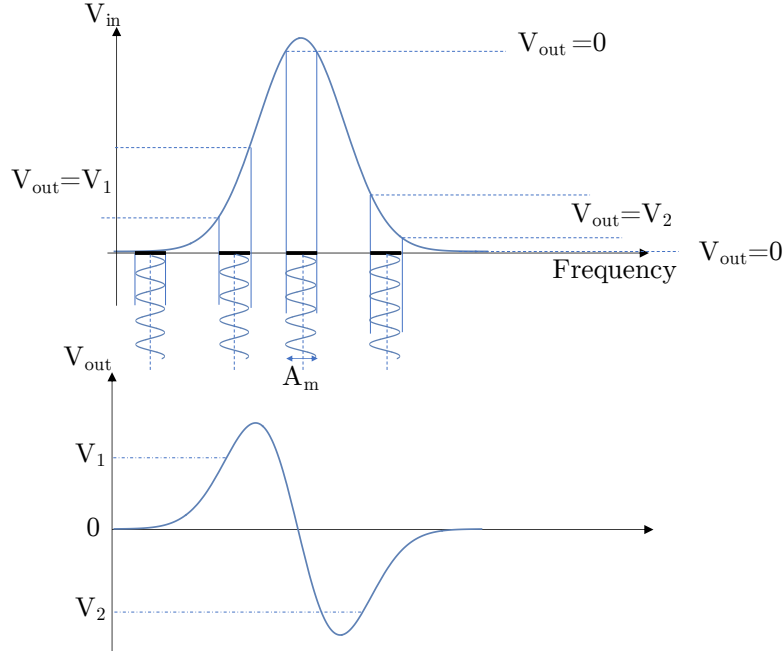


Figure 4.5: The lock-in response to change in the input signal. In the frequency domain the modulation amplitude determines the frequency range of the lock-in amplifier demodulation. The output signal is proportional to the slope of the input signal.

Time constant For the discussion of the meaning of the time constant we first have to discuss a low pass filter that is used to attenuate the AC part of the signal. A low-pass filter in the simplest form is an RC circuit that only allows signals above some threshold frequency to pass through. It reduces the noise by limiting higher frequency signals from making it into output signal. The RC circuit consists of a resistor and capacitor in series (Figure 4.6).

For an RC circuit, we can define the transfer function $T(\omega)$, a ratio of the output signal to the input signal

$$T(\omega) = \left| \frac{V_{\text{output}}}{V_{\text{input}}} \right| = \frac{1}{\sqrt{1 + (\omega\tau)^2}}, \quad (4.18)$$

where ω is the frequency of the supplied signal, and $\tau = RC$ is the time constant. For signals at high frequency, the output voltage is very small. For low frequencies V_{output} is almost equal to V_{input} , making this RC circuit a low-pass filter.

In a lock-in amplifier, the time constant is an adjustable parameter, and increasing the time constant increases the effectiveness of noise filtering. A time constant that is higher than the time taken to scan over a spectral feature, however, can contribute to artificially broadening spectral features or even averaging over them completely. As a rule of thumb, the time constant should be set to a tenth of the time it takes to scan through a spectral feature.

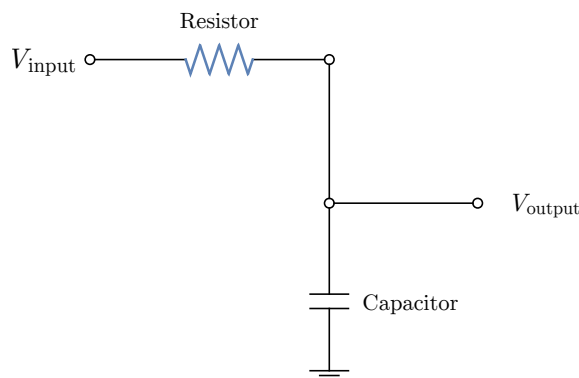


Figure 4.6: Circuit diagram of a RC filter.

Amplitude In the lock-in amplifier the signals are mixed in the time domain but to filter out the DC component the resulting V_{lock} is transformed to the frequency domain via Fourier transform. When the modulation is in the time domain (for example when supplied with the reference signal, as in the beginning of the section) it has units of mV, but when considered in a frequency domain it has units of frequency (MHz). As shown in Figure 4.5 the modulation amplitude that is supplied A_m in a frequency domain determines what frequency range of the input signal is modulated. This is one of the control parameters. If the amplitude is too small the output, will be also small. If the amplitude is too big, small changes in the slope will be unresolved causing a distortion in the signal.

4.2.2 Impact of WMS parameters on the molecular spectrum

WMS spectrum

Figure 4.7 shows an example of a wavelength modulation spectrum of a trioxane spectral feature. In this spectrum the amplitude is proportional to the density of molecules and the width of the feature is proportional to the square root of the translational temperature. To achieve signals with a high signal-to-noise ratio and a width that accurately represents the temperature of the molecules the WMS parameters need to be optimised.

Modulation amplitude

Figure 4.8 shows the temperature inferred from the WMS spectrum for various modulation amplitudes. For these data, there was 3 sccm of trioxane and 1 sccm of helium. The temperature was calculated by fitting the $R(0,0)$ line of the R-branch (see later) with a derivative of a Gaussian, with standard error of the fit reported. With the cell temperature of 7 K, we expect the width of the features to be around 6 MHz. The lowest modulation amplitude was chosen to be close to that value (4.8 MHz) and we can expect that the shape of the spectral feature is not distorted too

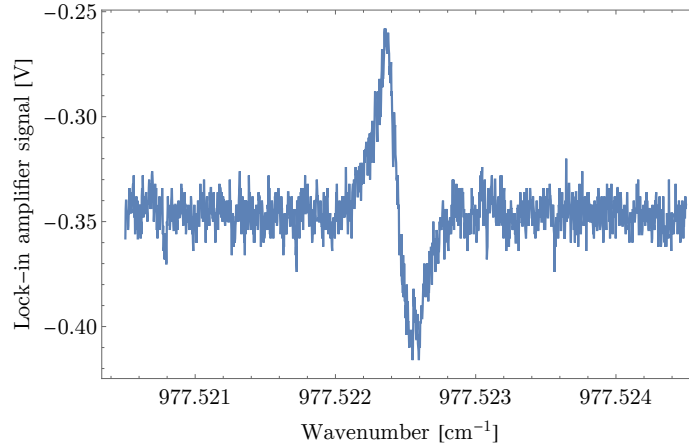


Figure 4.7: Example of a wavelength modulation spectroscopy spectrum.

badly, so temperatures obtained from fitting are close to the real temperature of the trioxane in the system. On the plot, the inferred temperature is 9 K, close to the cell temperature. With increasing modulation amplitude the inferred temperature of the molecules increases. The system is over-driven and the spectral features are artificially widened, so fitting results in incorrect temperatures.

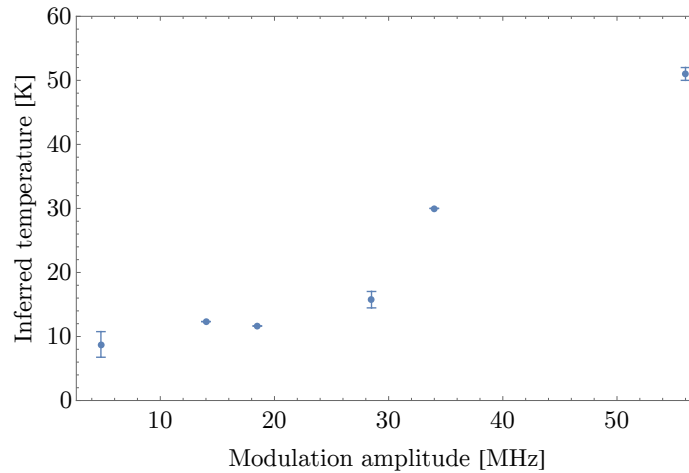


Figure 4.8: Inferred temperature of the molecules with the increasing WMS modulation amplitude. The error in the data is taken as the standard error of the fit.

Time constant

As a way of measuring the impact of the time constant on spectral features, we have investigated how the width and amplitude of the feature depend on the time taken to scan through the feature. Figure 4.9 shows how the amplitude and width of a $R(1,0)$ transition depend on the chosen time constant. Increasing the time constant slightly increases the amplitude of the spectral

features. The width of the spectral features also increases with the time constant.

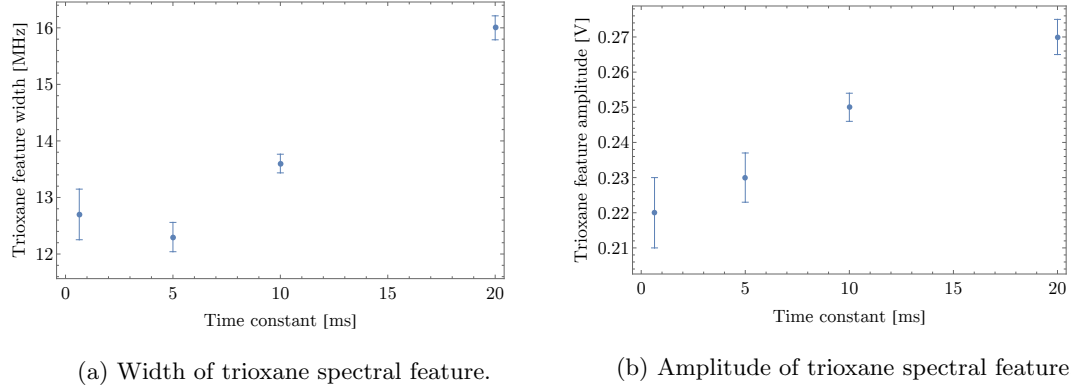


Figure 4.9: Amplitude and width of trioxane spectral features as a function of the WMS time constant. a) Width of the line versus the time constant b) Amplitude of the line vs time constant. The error is taken as the standard error of the fit to the data.

Modulation frequency

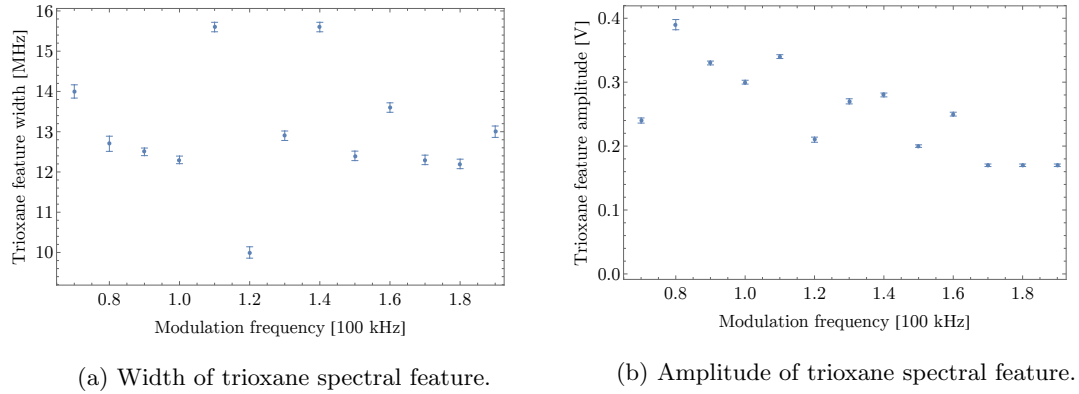


Figure 4.10: Changes in width and amplitude of trioxane spectral line measured in 1s scan with change in WMS modulation frequency. The error in the data is taken as the standard error of the fit.

Figure 4.10 shows how the width and amplitude of a $R(1,0)$ transition depends on the modulation frequency. We can see that the modulation frequency does not affect the width. There is a clear trend, however, present while looking at the trioxane feature amplitude with changing modulation frequency. Decreasing the modulation frequency increases the trioxane amplitude. The maximum amplitude is measured when the modulation frequency is equal to 80 kHz, and this value is therefore used to take all the data measured in the cell and in the beam.

Phase

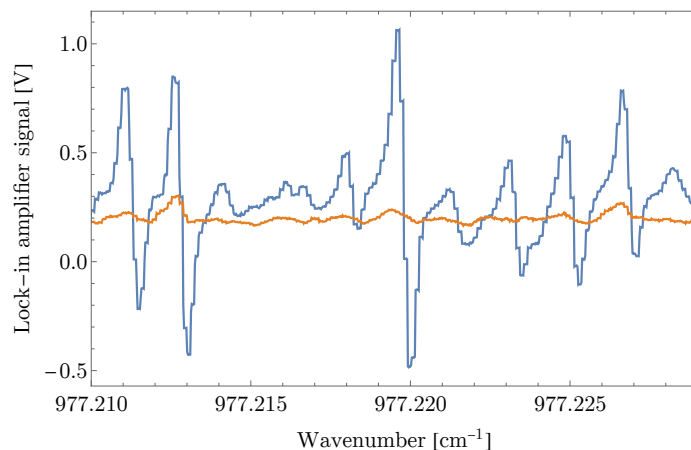


Figure 4.11: Wavelength modulation spectroscopy signal and reference out of phase (orange) and in-phase (blue). The molecular signal is visible as the first derivative of the Gaussian function.

From Equation 4.17 it can be observed that when the signal and reference are 90 degrees out of phase such that $\cos(\phi) = 0$ the lock-in amplifier does not produce any output. Similarly, when the two are in phase so that $\cos(\phi) = 1$ the output is maximised. This is illustrated by Figure 4.11, showing a measurement of a part of a Q-branch between $Q(13, 12)$ and $Q(14, 14)$ both in and out of phase. When both the signal and reference are in phase the output is maximised, and the molecular signal, present as a first derivative of a Gaussian function, is visible.

4.3 Trioxane ν_5 Q- and R- branch spectra

Using in-cell WMS spectroscopy we were able to record a number of trioxane transitions from both the Q- and R-branches of the ν_5 vibrational mode.

Q-branch

Figure 4.12 shows both the measured and theoretical spectrum of the trioxane Q-branch between 977.232 cm^{-1} and 977.256 cm^{-1} , which corresponds to the transitions between $Q(17, 17)$ and $Q(19, 16)$. Figure 4.13 shows the same spectrum with labelled transitions for reference. This region is good for observation of the Q-branch because it is not very congested and is characterised by strong spectral features. Additionally, this region has a suitable ethylene transition nearby to calibrate the absolute frequency of the spectrum. We have fitted the data with the spectra calculated using pGopher for 10, 15, and 20 K and have observed the best agreement with the 15 K calculation, which is shown in purple on Figure 4.12. We have demonstrated that all the lines are fully resolved

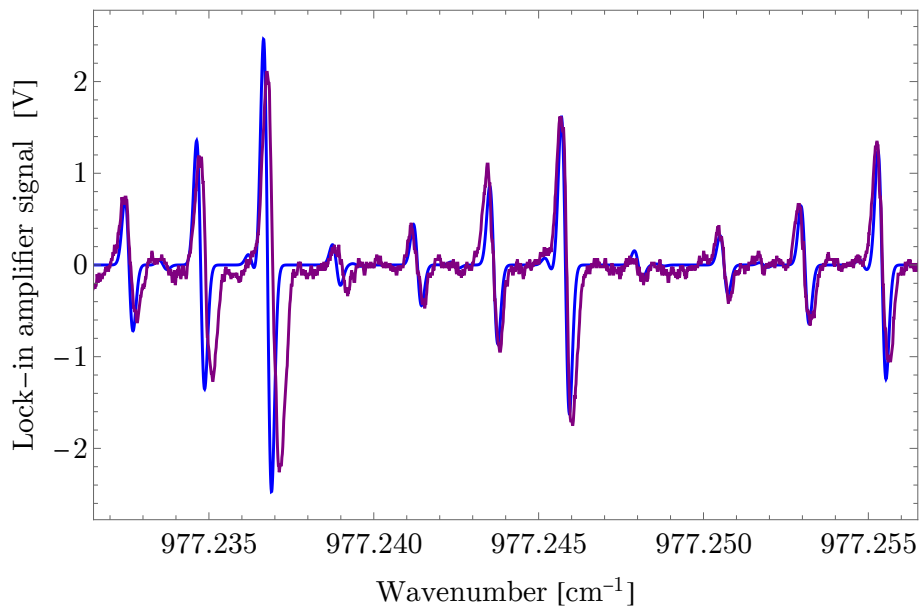


Figure 4.12: Q-branch WMS spectrum (blue) with an overlaid calculated spectra at 15 K (purple).

and with good signal-to-noise ratio. The transition wavenumbers are calculated using the method described in Chapter 3, and they agree well with the experimental results. Figure 4.14 shows the Gaussian-broadened spectrum retrieved from pGopher for the same frequency range, and the same inferred temperature, as the spectrum presented in Figure 4.13.

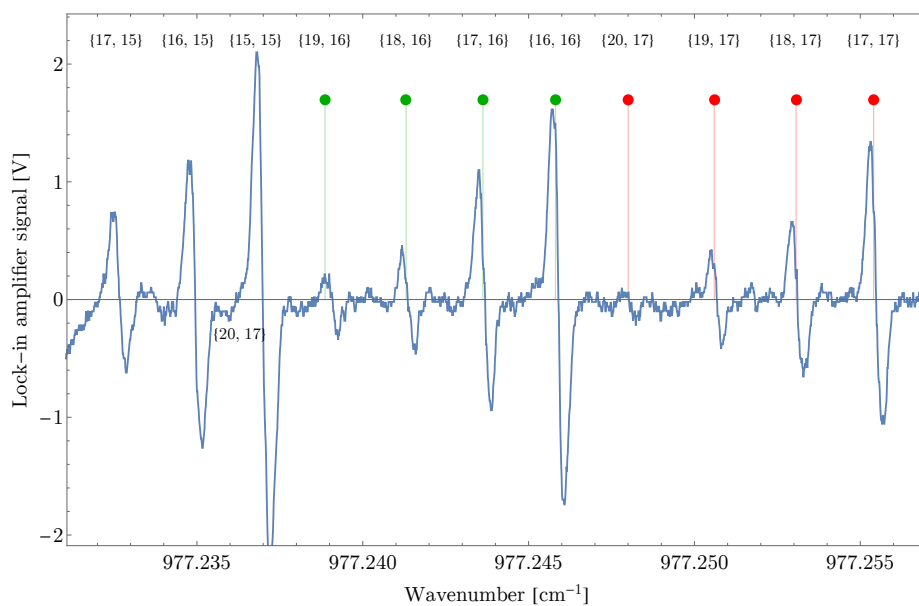


Figure 4.13: Q-branch WMS spectrum (blue) with assigned transition labels in the form of (J, K) . The red and green markers correspond to the arrows on Figure 3.3. The positions of the markers are calculated theoretically. The line $Q(20, 17)$ can barely be resolved.

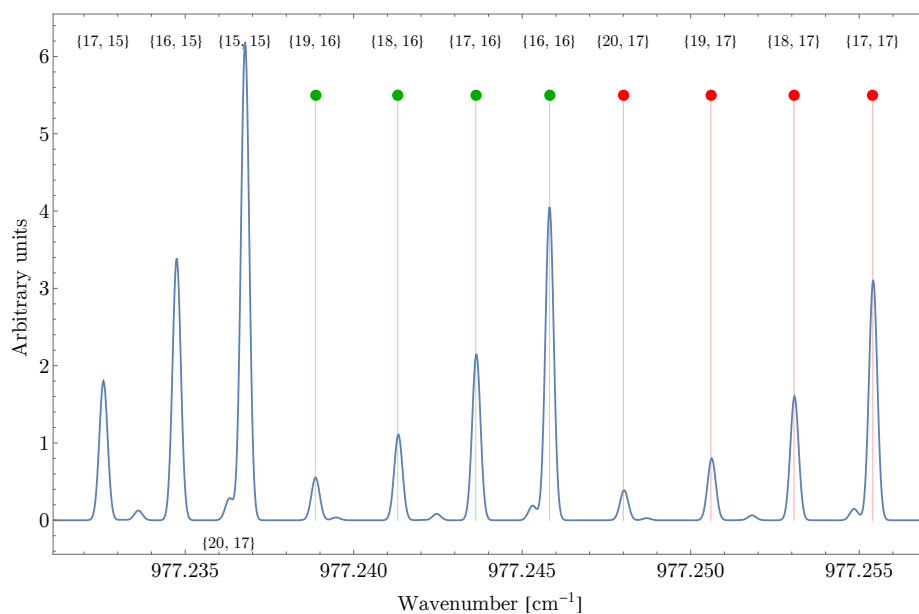


Figure 4.14: Doppler-broadened Q-branch pGopher spectrum covering the same frequency range as Figure 4.13 with assigned transition labels in the form of (J, K) . The spectrum is produced for a temperature of 15 K. The red and green markers correspond to the arrows in Figure 3.3. The positions of the markers are calculated theoretically.

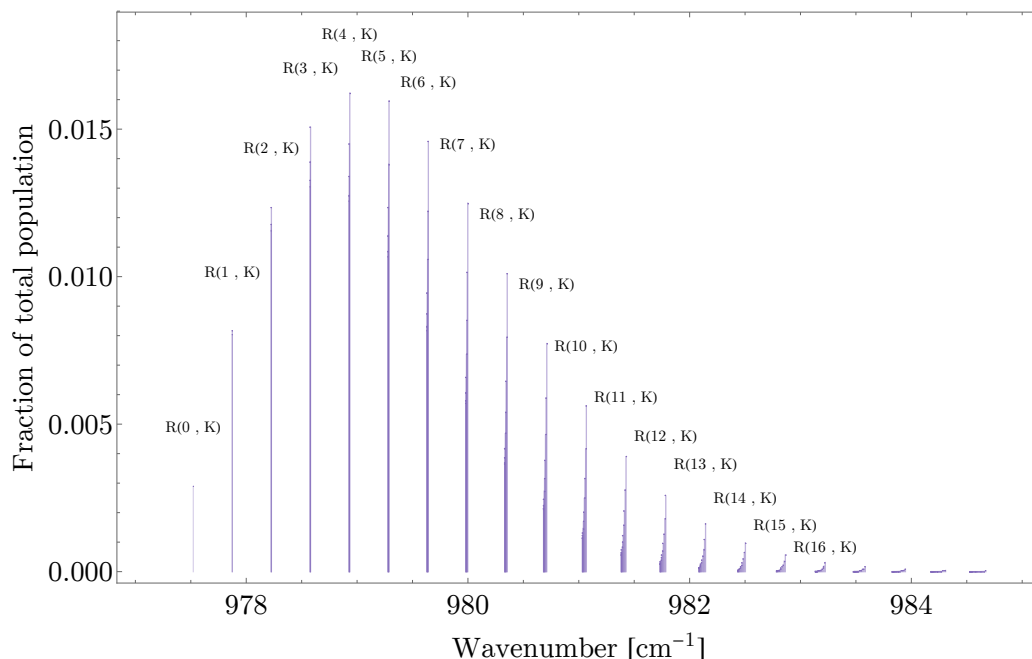
R-branch

Figure 4.15: Theoretical calculation of R-branch spectra with marked spectral features.

Figure 4.15 shows the theoretically calculated spectrum of the R-branch of the ν_5 vibrational transition in trioxane.

We recorded first four transitions of the R-branch using WMS spectroscopy inside a cold cell. We have explored only a few J lines from this branch because we were limited by the spectral range of the quantum cascade laser. Spectra of $R(0, K)$, $R(1, K)$, $R(2, K)$, and $R(3, 0)$ lines are shown in Figures 4.16, 4.17, 4.18 and 4.19 respectively. The main component contributing to the width of the lines is Doppler broadening. WMS spectroscopy produces spectra as first derivatives of the spectral features hence the spectra are fitted with the sum of derivatives of Gaussians. WMS allows to resolve all K -lines in the spectra, with smallest distance between lines of 11 MHz.

These spectra have different signal-to-noise ratio because of optical setup changes between measurements that affect etaloning and beam walking, the two most dominant noise contributions. The $R(1, K)$ transition amplitudes for each K line do not follow the values predicted by the theory. According to Equation 3.27, we expect a $K = 0$ to $K = 1$ intensity of ratio about $\frac{4}{3}$, however the $K = 1$ line is consistently significantly weaker. The possible reason for this discrepancy is spin-statistics, which was not accounted for in the theoretical calculations but might play a role in determining the relative strengths. It is possible to implement spin statistics in the calculation and see whether the discrepancy of the size of the $K = 0$ and $K = 1$ line is reproduced, but this is outside the scope of this thesis.

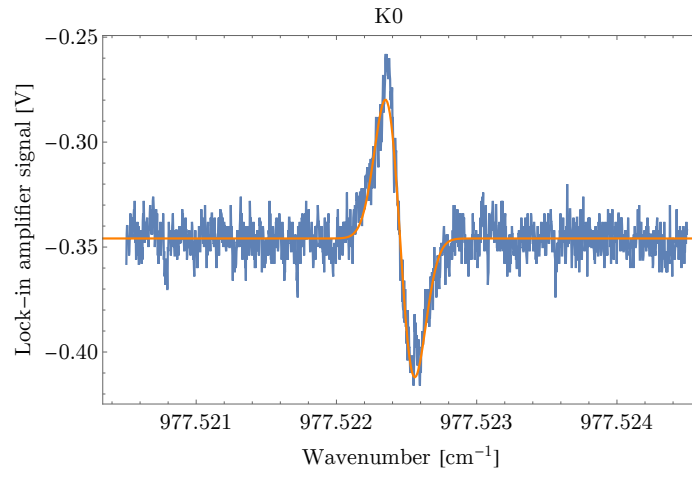


Figure 4.16: WMS spectrum of $R(0, K)$ transition (blue) fitted with the derivative of a Gaussian function (orange).

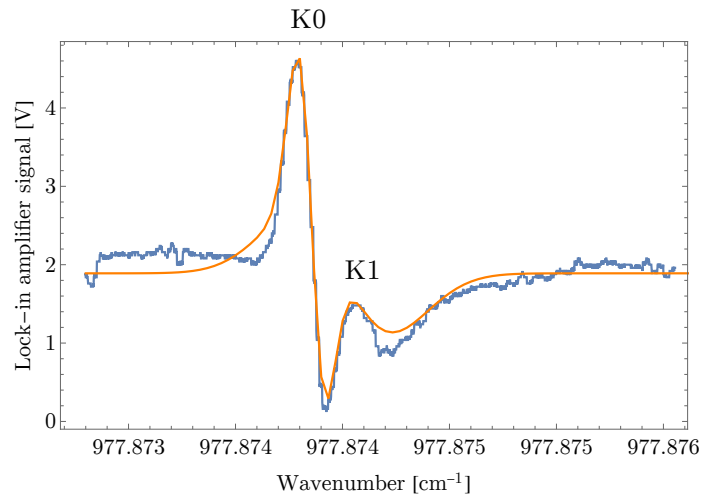


Figure 4.17: WMS spectrum of $R(1, K)$ transition (blue) fitted with a sum of two Gaussian-derivative functions (orange).

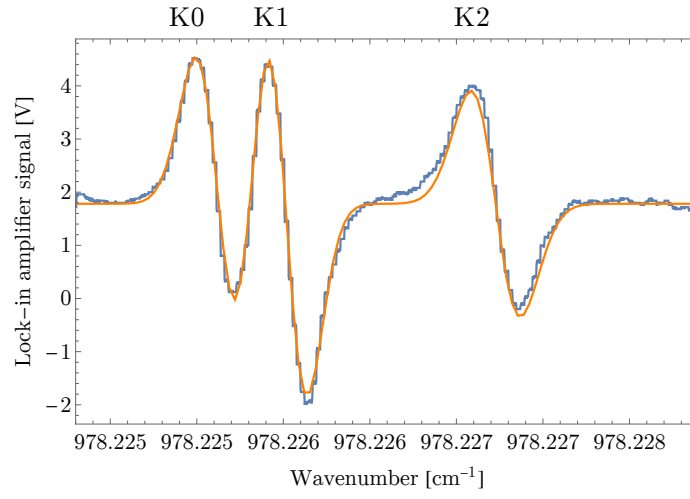


Figure 4.18: WMS spectrum of $R(2, K)$ transition (blue) fitted with a sum of three Gaussian-derivative functions (orange).

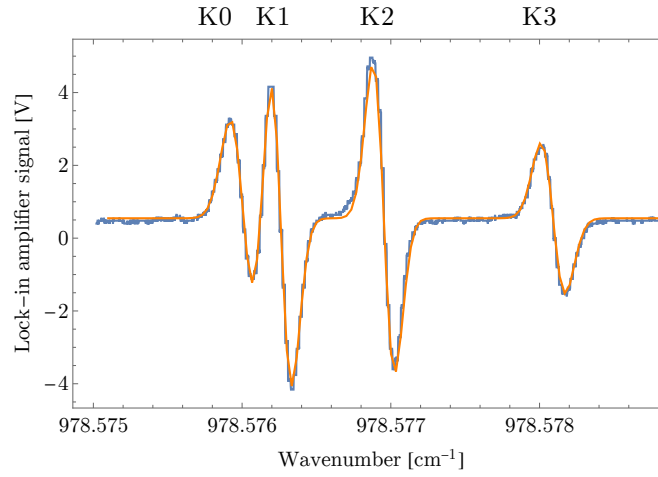


Figure 4.19: WMS spectrum of $R(3, K)$ transition (blue) fitted with a sum of four Gaussian-derivative functions (orange).

4.4 Characterisation of molecules

Helium

The lowest recorded temperature of the molecules with helium buffer gas is 7.4 ± 0.3 K, observed in a measurement of $R(0,0)$ transition, an example of which is shown in Figure 4.16. This observation is consistent with cell temperatures of 7 K. For the majority of the scans, however, the temperatures recorded are closer to 11 K. The temperature of the molecules is highly dependent on the amount of trioxane delivered to the cell, the helium flow, and the position of the capillary inside the cell. Discussion of these parameters is included in Sections 5.2.3, 5.2.1 and 5.2.2 respectively. Observing the molecules at very low temperatures requires small trioxane flows, which in turn gives quite a small signal-to-noise ratio. The high flow of trioxane increases the cell temperature resulting in an increase of the final temperature of the molecules. Usually, we opt for higher trioxane flows (3 sccm and above) that causes an increase in the amplitude of the spectral features making the observation of molecules easier but produces hotter molecules.

Neon

When neon is used as a buffer gas the coldest temperatures of the molecules are 21.3 ± 0.2 K, which is consistent with the cell temperature of 20 K. Because the final temperature of molecules depends on the thermalisation of the neon with the cold cell the temperatures of the molecules measured are highly dependent on the neon flow into the cell. While the temperature of the molecules is much higher than in the case of the helium buffer gas all the observed lines in R-branch and high J -numbers (> 10) of the Q-branch were easily resolved, which makes neon suitable for spectroscopy of trioxane molecules.

4.5 Saturation

An important parameter in the optical probing of molecules is the saturation parameter. In the limit of large intensity, and therefore saturation parameter (over-saturation), the population of the excited state reaches half of the total population, as derived in Section 4.8 from the interaction of a two level system with light. Figure 4.20 shows the dependence of the amplitudes of spectral features on the laser power. The data shows the amplitude of the $R(3,0)$ transition. Each data point was taken with the same flow and WMS parameters. The data are fitted with the function

$$\rho(s) = A_{\max} \frac{P/P_{\text{sat}}}{1 + P/P_{\text{sat}}}, \quad (4.19)$$

where $A_{\max}$ is a signal at an infinite power and P_{sat} is the value of the power where the signal reaches half its maximum value. The best fit line is shown in Figure 4.20 and gives a saturation power of

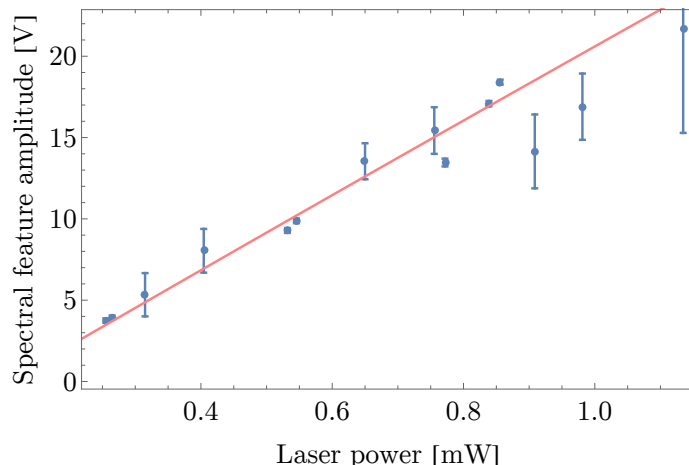


Figure 4.20: Amplitudes of the $R(3,0)$ transition versus the laser power. The errors are root mean square errors of the fit. The data are fitted with Equation 4.19.

$P_{\text{sat}} = 20.4 \pm 4.1$ mW. In the experimental setup so far the maximum power that interacts with the sample about 2-3 mW, which means that increasing the power will favourably contribute to the experiment.

4.6 Power broadening

Figure 4.21 shows the dependence of the width of the spectral features on the power delivered to the cold cell. We express the power as the percentage of the maximum power $P_{\text{max}} = 1.1$ mW. The data was recorded with 1 sccm helium flow and 3.5 sccm trioxane flow. We can see that there is no change in the inferred temperature with the increase of the laser power. This is consistent with the fact that the spectrum is dominated by Doppler broadening and other kinds of broadening will not be resolved. The power broadening will be however important when considering a sub-Doppler spectrum where the saturated-absorption feature width is not Doppler broadened.

4.7 Trioxane in-cell density

Direct absorption spectrum measurement

To determine the number density of trioxane in the cold cell we recorded the direct absorption spectrum of the Q-branch between 977.235 cm^{-1} and 977.255 cm^{-1} . This is shown in Figure 4.22. The direct absorption was obtained by recording the laser intensity on the MCT, without using wavelength modulation spectroscopy. The MCT produces a negative voltage inversely proportional to the signal, so a higher intensity corresponds to a lower voltage. Without using WMS

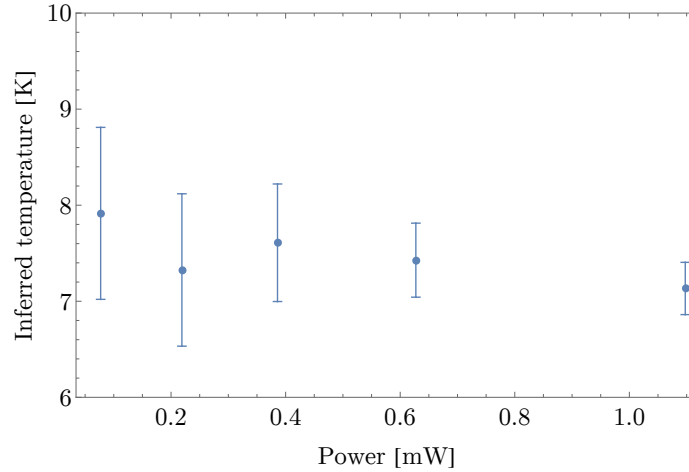


Figure 4.21: Width of the $Q(15,15)$ transition versus power of the laser (blue), where 100% corresponds to 1.1 mW. The data are fitted with a linear fit, shown in purple. Errors are taken from the standard error of the fit.

the signal-to-noise ratio is quite low but with high trioxane flow into the cell (8 sccm) some absorption features can be resolved. Figure 4.22 shows the background (no molecules) in blue and the direct absorption spectrum in purple. The most isolated and strongest transition on the graph is a $Q(16,15)$ (marked on Figure 4.22), which we use in our calculations. We prefer not to use the $Q(15,15)$ line because there is a neighbouring weak $Q(20,17)$ spectral feature preventing us from correctly fitting the $Q(15,15)$ line. Firstly, we need to determine the temperature of the molecules, which we do by fitting the spectral line with a Gaussian. The temperature obtained is about 20 K, which can be explained by a high trioxane flow. Using Equations 3.31 and 3.27 we can calculate the integrated line strength for the transition in question. For this transition we obtain $I = 8.2 \times 10^{-23} \text{ cm}^{-1} \text{ molecule cm}^2$.

Density determination

In our considerations a laser with an initial intensity $I_0(\tilde{\nu})$ and wavenumber $\tilde{\nu}$ interacts with a gaseous sample with concentration (or number density) n . For an interaction path of length L we can write the transmitted intensity $I_T(\tilde{\nu})$ according to a Beer-Lambert law

$$I_T(\tilde{\nu}) = I_0(\tilde{\nu}) \exp[-L n \epsilon(\tilde{\nu})]. \quad (4.20)$$

The $\epsilon(\tilde{\nu})$ is the Napierian absorption coefficient. We can assume the validity of the Beer-Lambert law in the case of our experiment because the transition researched is not saturated and the laser intensity is not enough to cause optical pumping, as calculated in Section 4.19. We can define the

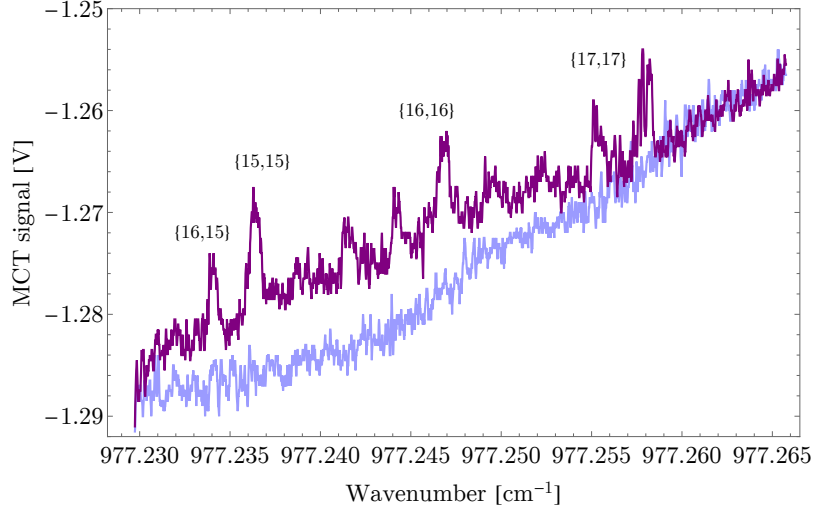


Figure 4.22: Direct absorption of trioxane in the Q-branch between 977.235 cm^{-1} and 977.255 cm^{-1} . Data are shown in purple and the background is in blue. Chosen spectral features were marked with labels of the form $\{J, K\}$.

transmittance τ as

$$\tau = \frac{I_T(\tilde{\nu})}{I_0(\tilde{\nu})}. \quad (4.21)$$

The definition of the integrated line strength is

$$I = \int \epsilon(\tilde{\nu}) d\tilde{\nu}. \quad (4.22)$$

Combining equations 4.20, 4.21, and 4.22 we can obtain the equation

$$I = -\frac{1}{L n} \int \ln \frac{I_T(\tilde{\nu})}{I_0(\tilde{\nu})} d\tilde{\nu}. \quad (4.23)$$

From this we can calculate the number density of molecules in the sample

$$n \approx -\frac{1}{L I} \int \ln \frac{I_T(\tilde{\nu})}{I_0(\tilde{\nu})} d\tilde{\nu}. \quad (4.24)$$

First, to use the experimental data for calculation we plot the measured $\ln \frac{I_T(\tilde{\nu})}{I_0(\tilde{\nu})}$ and fit it with a Gaussian function. The result is shown in Figure 4.23. Integrating the area under the Gaussian we obtain the experimental integrated line strength. Dividing it by the theoretical line strength for one molecule $I = 8.2 \times 10^{-23} \text{ cm}^{-1} \text{ molecule cm}^2$, and the interaction length $L = 5 \text{ cm}$, we estimate the number density of the molecules in the cell to be about $n = 5 \times 10^{21} \text{ m}^{-3}$. This is similar to the number density of the buffer gas in the cell, which confirms the validity of the number, as the trioxane flow was comparable to the flow of helium when taking these data.

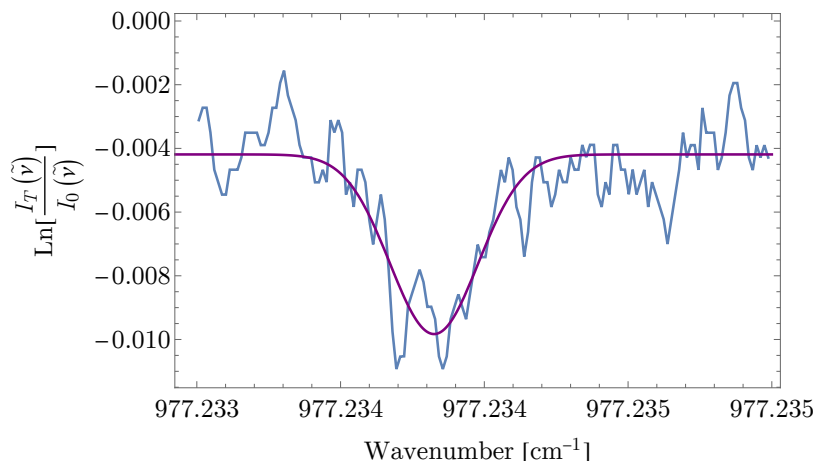


Figure 4.23: Natural logarithm of transmittance of the $Q(16, 15)$ spectral feature. Data are shown in blue and the Gaussian fit is in purple.

4.8 Sub-Doppler spectroscopy

One of the aims of the project is to observe sub-Doppler features of trioxane in the cold cell. Sub-Doppler spectroscopy probes features with widths much smaller than the Doppler broadening and limited mainly by collisional broadening. In sub-Doppler spectroscopy molecules interact with a pump beam and a counter-propagating probe beam. Due to the Doppler shift, only those molecules with zero velocity in the direction of the lasers can interact with the pump and probe simultaneously. The pump beam interacts with the molecules transferring the population from the ground to the upper state. The probe laser is absorbed less strongly when it interacts with these same molecules. That creates a sub-Doppler feature at the central transition frequency [122]. To understand the principle of sub-Doppler spectroscopy theoretically, the next section will first introduce the interaction of a singular two-level system with the laser light, continue to include the pump-probe interaction and then generalize to a sample of molecules with a Gaussian distribution of velocities.

Trioxane can be treated as a two level system to a good approximation because of its lack of internal vibrational relaxation, so the excited level can relax only to the ground level of the same vibrational mode. According to the selection rules, the rotational levels that an excited J level can relax to are ground J , $J - 1$, and $J + 1$ levels. The lifetime of these levels is about 1 s, which is much longer than the time the molecules interact with the laser beam. Calculating average helium velocity at 7 K to be 200 m/s we find transit time through the beam to be 0.02 ms. This means that the excited state won't have enough time for relaxation to any other J states allowing for a sub-Doppler measurement.

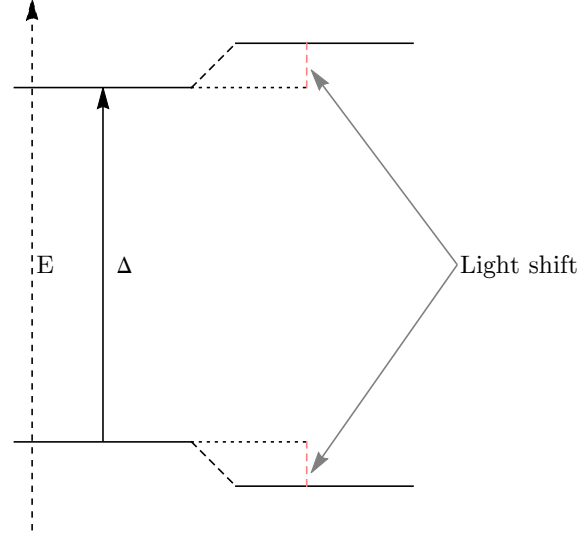


Figure 4.24: The energy level splitting caused by the interaction of the system with light.

4.8.1 Interaction of 2-level system with pump and probe fields

Dressed states In this section the simple two-level system interacting with light will be considered. It consists of excited and ground states denoted respectively by $|e\rangle$ and $|g\rangle$ [123]. We can write the state of the atom as

$$|\Phi\rangle = c_g |g\rangle + c_e |e\rangle, \quad (4.25)$$

where c_g and c_e describe the evolution of the state with time. We can write a rotating-frame Hamiltonian

$$H = H_A + H_{\text{In}} = -\hbar\Delta |e\rangle\langle e| + \frac{\hbar\Omega}{2}(|g\rangle\langle e| e^{i\omega t} + |e\rangle\langle g| e^{-i\omega t}), \quad (4.26)$$

where ω is the frequency of the light and Ω is the Rabi frequency. Δ signifies the detuning of the light field from the transition frequency ω_0 ,

$$\Delta = \omega - \omega_0. \quad (4.27)$$

After transforming to the rotating frame and expressing this equation in matrix form we have

$$\hbar \begin{bmatrix} -\Delta & \frac{\Omega}{2} \\ \frac{\Omega}{2} & 0 \end{bmatrix}. \quad (4.28)$$

The eigenvalues are

$$E_{\pm} = -\frac{\hbar\Delta}{2} \pm \frac{\hbar\tilde{\Omega}}{2}, \quad (4.29)$$

where $\tilde{\Omega}$ is defined as the generalised Rabi frequency:

$$\tilde{\Omega} = \sqrt{\Omega^2 + \Delta^2}.$$

When the system does not interact with an electromagnetic field ($\Omega = 0$) the states will be separated by $\hbar\Delta$. When the system is exactly on resonance ($\Delta = 0$) the dressed states will be degenerate at $\Omega = 0$, and the perturbation to energy levels coming from the interaction with light is $\pm\frac{\Omega}{2}$, as shown in Figure 4.24.

Steady state excitation and coherence, saturation parameter and intensity Substituting Eq. 4.25 and Eq. 4.26 into the Schrödinger equation and projecting respectively with $|e\rangle$ and $|g\rangle$ a pair of coupled equations can be obtained.

$$\partial_t c_g = -i\frac{\Omega}{2}c_e e^{i\omega t}, \quad (4.30)$$

$$\partial_t c_e = -i\Delta c_e - i\frac{\Omega}{2}c_g e^{-i\omega t}. \quad (4.31)$$

We can use the density matrix formalism, and rewrite the coupled equations as

$$\tilde{\rho}_{gg} = \rho_{gg} = c_g c_g^*, \quad (4.32)$$

$$\tilde{\rho}_{ee} = \rho_{ee} = c_e c_e^*, \quad (4.33)$$

$$\tilde{\rho}_{ge} = c_g c_e e^{-i\omega t} = \rho_{ge} e^{i\omega t}, \quad (4.34)$$

$$\tilde{\rho}_{eg} = c_e c_g e^{i\omega t} = \rho_{eg} e^{i\omega t}. \quad (4.35)$$

With this we arrive at the system of four equations

$$\partial_t \rho_{ee} = i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}), \quad (4.36)$$

$$\partial_t \rho_{gg} = -i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}), \quad (4.37)$$

$$\partial \tilde{\rho}_{ge} = -i\Delta \tilde{\rho}_{ge} - i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}), \quad (4.38)$$

$$\partial \tilde{\rho}_{eg} = i\Delta \tilde{\rho}_{eg} + i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}). \quad (4.39)$$

The first of these equations describes the excited-state population, the second the ground state population and the last two describe the coherences between the states. With those four equations we can progress to a more complex picture. We will include spontaneous emission with a rate Γ that will add to the population of the ground state but will deplete the population of the excited state. Additionally we will include dephasing effects from collisions γ_c . Both of them will be combined in the term $\gamma_{\perp} = \frac{\Gamma}{2} + \gamma_c$. Combining Equations 4.36 - 4.39 with relaxation and dephasing coefficients results in

$$\partial_t \rho_{ee} = i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) - \Gamma \rho_{ee}, \quad (4.40)$$

$$\partial_t \rho_{gg} = -i\frac{\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) + \Gamma \rho_{ee}, \quad (4.41)$$

$$\partial \tilde{\rho}_{ge} = -i\Delta \tilde{\rho}_{ge} - i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}) - \gamma_{\perp} \tilde{\rho}_{ge}, \quad (4.42)$$

$$\partial \tilde{\rho}_{eg} = i\Delta \tilde{\rho}_{eg} + i\frac{\Omega}{2}(\rho_{ee} - \rho_{gg}) - \gamma_{\perp} \tilde{\rho}_{eg}. \quad (4.43)$$

Solving the steady state equation we get the steady state excited level population

$$\rho_{ee}(t \rightarrow \infty) = \frac{\Omega^2}{2\gamma_{\perp}\Gamma} \frac{1}{1 + \frac{\Delta^2}{\gamma_{\perp}^2} + \frac{\Omega^2}{\gamma_{\perp}\Gamma}} = \frac{s/2}{1 + \frac{\Delta^2}{\gamma_{\perp}^2} + s}, \quad (4.44)$$

where we defined the saturation parameter

$$s = \frac{\Omega^2}{\gamma_{\perp}\Gamma}. \quad (4.45)$$

We also can calculate the steady state coherence

$$\tilde{\rho}_{eg}(t \rightarrow \infty) = -\frac{i\Omega}{2\gamma_{\perp}} \frac{1 + \frac{i\Delta}{\gamma_{\perp}}}{1 + \frac{\Delta^2}{\gamma_{\perp}^2} + \frac{\Omega^2}{\gamma_{\perp}\Gamma}} = \frac{\Gamma}{4\gamma_{\perp}} \frac{s(1 + \frac{\Delta^2}{\gamma_{\perp}^2})}{(1 + \frac{\Delta^2}{\gamma_{\perp}^2} + s)^2}. \quad (4.46)$$

Equation 4.44 is linear in s for small s . For $s \rightarrow \infty$ the excited state population reaches half of the full population. We can also define an equation for the saturation intensity. For the case of homogeneous broadening $\gamma_{\perp} = \frac{\Gamma}{2}$ and exact resonance $\Delta = 0$ we obtain:

$$\rho_{ee} - \rho_{gg} = -\frac{1}{1 + 2\frac{\Omega^2}{\Gamma^2}}. \quad (4.47)$$

Hence we can identify

$$\frac{I}{I_{\text{sat}}} = 2\frac{\Omega^2}{\Gamma^2}. \quad (4.48)$$

Line shape Recalling Equation 4.44 for steady-state population we can look at it in the weak ($\Omega \ll \Gamma, \gamma_{\perp}$) and strong driving limit ($\Omega \gg \Gamma, \gamma_{\perp}$). In the former case, and neglecting collisions, the excited state population is

$$\rho_{ee}(t \rightarrow \infty) = \frac{\Omega^2/4}{\Delta^2 + \Gamma^2/4}, \quad (4.49)$$

which is a Lorentzian with FWHM = Γ . In the latter case the equation is

$$\rho_{ee}(t \rightarrow \infty) = \frac{\Omega^2/4}{\Delta^2 + \Omega^2/2}, \quad (4.50)$$

which is a Lorentzian with FWHM of $\sqrt{2}\Omega$, much broader than in the weak driving limit. This phenomenon is referred to as power broadening.

4.8.2 Mollow treatment of interaction of two level system with a pump and probe fields

From the consideration of the interaction of a two-level system with an electromagnetic field we can progress to an explanation of an interaction of a two-level system with pump and probe

fields. In this model the probe field is much weaker than the pump. We are going to use $\Delta = \omega - \omega_0$ for the detuning of the pump beam from the transition frequency, and $\Delta_p = \omega_p - \omega$ for the detuning of the probe beam from the pump beam. For now we are considering only a singular atom so no velocity statistics are taken into account.

Following Mollow's treatment [124] we can obtain a solution for the absorption profile of the transition. In this treatment the coupling to the probe field is treated as the lowest order perturbation to the atomic density operator. From that the rate at which the energy is absorbed from a probe can be obtained. Assuming a stationary process the absorption spectrum is dependent on the correlation function between the raising and lowering operators. The Fourier transform of the correlation function will yield the final absorption profile

$$\begin{aligned}
 S_a(\omega_p) &= \\
 &= \frac{[\rho_{gg}(t \rightarrow \infty) - \rho_{ee}(t \rightarrow \infty)][(\Gamma - i\Delta_p)(\gamma_\perp + i(\Delta - \Delta_p) + \frac{i\Omega^2\Delta_p}{2(\gamma_\perp + i\Delta)})]}{(\Gamma - i\Delta_p)(\gamma_\perp + i(\Delta - \Delta_p)(\gamma_\perp - i(\Delta + \Delta_p) + \Omega^2(\gamma_\perp - i\Delta_p))} + c.c. \\
 &= (1 - \frac{\Omega_2/\gamma_\perp\Gamma}{1 + \Delta^2/\gamma_\perp + \Omega^2/\gamma_\perp\Gamma}) \\
 &\quad \frac{[(\Gamma - i\Delta_p)(\gamma_\perp + i(\Delta - \Delta_p) + \frac{i\Omega^2\Delta_p}{2(\gamma_\perp + i\Delta)})]}{(\Gamma - i\Delta_p)(\gamma_\perp + i(\Delta - \Delta_p)(\gamma_\perp - i(\Delta + \Delta_p) + \Omega^2(\gamma_\perp - i\Delta_p))} + c.c.
 \end{aligned} \tag{4.51}$$

The real part of Equation 4.51 corresponds to absorption in the system while the imaginary part describes the scattering. Figure 4.25 shows the real part of the equation for exact resonance $\Delta = 0$ assuming a low collisional relaxation. In Figure 4.25 we can observe three regimes:

1. $\Omega < \Gamma$ - dressed states are nearly degenerate, no additional transitions
2. $\Omega \simeq \Gamma$ - dressed states separated by Ω , additional spectral features appear
3. $\Omega > \Gamma$ - a photon from the pump beam is transferred to a probe beam resulting in a negative absorption

This section concerns only one two-level system interacting with the pump and probe beams. In the next section we will extend this to a sample of molecules, each treated as a two-level system, with a distribution of velocities.

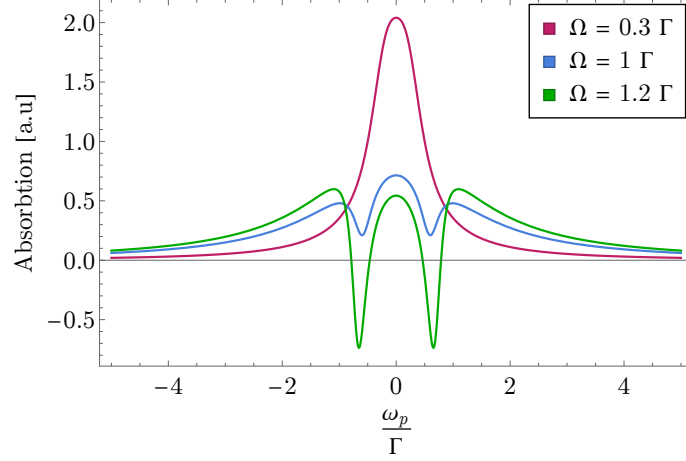


Figure 4.25: Spectrum for two-level system interacting with pump and probe fields for varying probe field detuning. The real part of the Equation 4.51 is plotted, assuming the exact resonance $\Delta = 0$ for varying strengths of the driving field Ω .

Line shape of a sample of molecules with distribution of velocities For the sample with a spread of velocities we know that the absorbing frequencies will be Doppler shifted [125]. If $\mathbf{k}$ is the wave-vector of the field and $\mathbf{v}$ is a velocity of the molecule we can re-write the equations for frequencies and detunings

$$\omega_v = \omega - \mathbf{k} \cdot \mathbf{v}, \quad (4.52)$$

$$\Delta \rightarrow \Delta - \mathbf{k} \cdot \mathbf{v}, \quad (4.53)$$

$$\Delta_p \rightarrow \Delta_p + 2\mathbf{k} \cdot \mathbf{v}, \quad (4.54)$$

where we are assuming that the wave-vectors for pump and probe are approximately the same and the pump and the probe propagate in the opposite directions. We can substitute into Equation 4.52 to get

$$\begin{aligned} S_a(\omega_p) &= \\ &= \left(1 - \frac{\Omega_2/\gamma_\perp \Gamma}{1 + (\Delta - \mathbf{k} \cdot \mathbf{v})^2/\gamma_\perp + \Omega^2/\gamma_\perp \Gamma}\right) \\ &\quad \frac{[(\Gamma - i(\Delta_p + 2\mathbf{k} \cdot \mathbf{v}))(\gamma_\perp + i(\Delta - \Delta_p - 3\mathbf{k} \cdot \mathbf{v}) + \frac{i\Omega^2(\Delta_p + 2\mathbf{k} \cdot \mathbf{v})}{2(\gamma_\perp + i(\Delta - \mathbf{k} \cdot \mathbf{v}))})]}{(\gamma_\perp - i(\Delta + \Delta_p + \mathbf{k} \cdot \mathbf{v}) + \Omega^2(\gamma_\perp - i(\Delta_p + 2\mathbf{k} \cdot \mathbf{v})))} \\ &\quad \frac{[(\Gamma - i(\Delta_p + 2\mathbf{k} \cdot \mathbf{v}))(\gamma_\perp + i(\Delta - \Delta_p - 3\mathbf{k} \cdot \mathbf{v}) + \frac{i\Omega^2(\Delta_p + 2\mathbf{k} \cdot \mathbf{v})}{2(\gamma_\perp + i(\Delta - \mathbf{k} \cdot \mathbf{v}))})]}{(\Gamma - i(\Delta_p + 2\mathbf{k} \cdot \mathbf{v}))(\gamma_\perp + i(\Delta - \Delta_p - 3\mathbf{k} \cdot \mathbf{v}))} + c.c. \end{aligned} \quad (4.55)$$

To perform the average with respect to velocities we assume that the laser propagates only in one direction (i.e. z) which gives $\mathbf{k} \cdot \mathbf{v} = kv_z = kv$. We assume that the speeds follow a Maxwell-

Boltzmann distribution

$$\sqrt{\frac{2m}{2\pi k_b T}} \exp\left[\frac{-mv^2}{2k_b T}\right]. \quad (4.56)$$

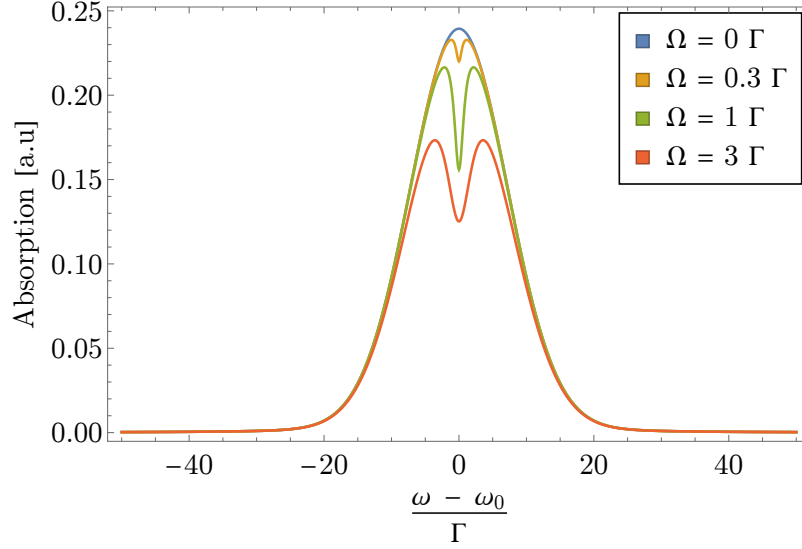


Figure 4.26: Spectrum of the velocity averaged two-level system interacting with pump and probe fields, for probe field at the same frequency as the pump. In Equation 4.56, the value of $\frac{m}{k_B T}$ was chosen to be 10.

Multiplying Equation 4.55 by this distribution and performing numerical integration from a chosen $-v$ to v will allow us to obtain a graph for the absorption spectrum for a sample of two-level systems interacting with the pump and probe light following a Maxwell-Boltzmann velocity distribution. This is shown in Figure 4.26, with values of Ω ranging from 0 to 3γ . We can see that the increase in Ω , which corresponds to the increase in the driving field, increases the “depth” and the width of the sub-Doppler feature. In a weak driving limit ($\Omega \ll \Gamma, \gamma_{\perp}$) the dips, also called Lamb dips or sub-Doppler features, have a width limited by the lifetime of the state. The equation for the line shape is given by

$$g(\omega) = \frac{\gamma/2\pi}{(\omega - \omega_0)^2 + (\frac{\gamma}{2})^2}. \quad (4.57)$$

For a vibrational transition lifetimes are of order 1 s hence if no other broadening mechanisms will be present the FWHM of the state will be of order 1 Hz [126]. There are several factors that will broaden the line: transit time, collisional, and power broadening, but overall it will be much narrower than the Doppler-broadened spectral features.

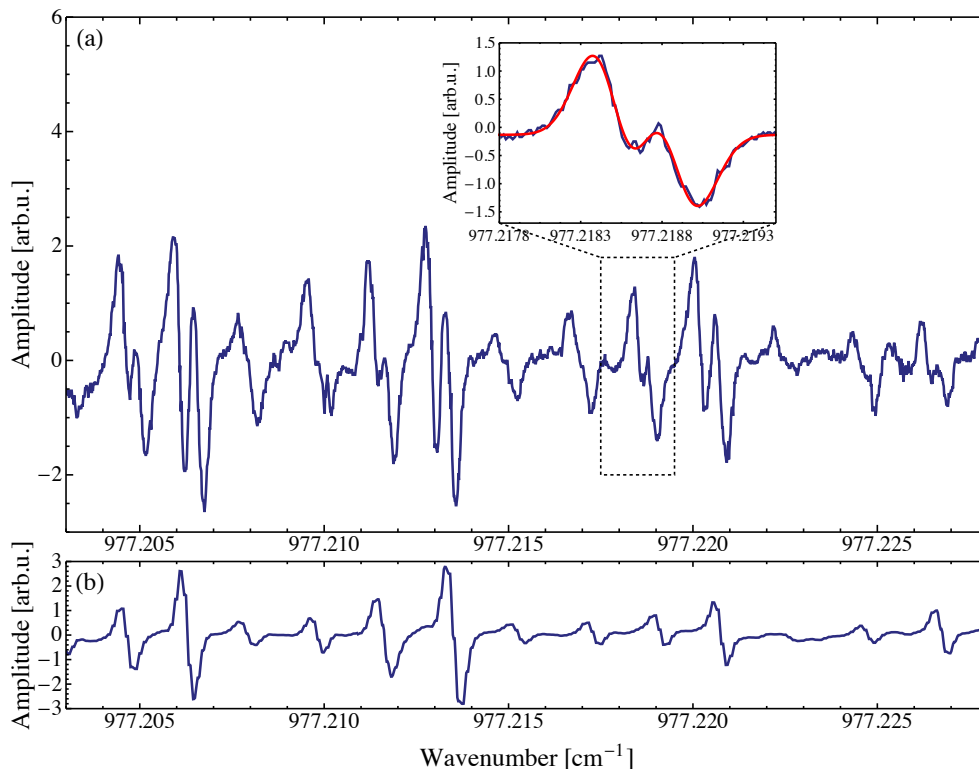


Figure 4.27: Plot a) shows the experimental spectrum of trioxane between 977.204 cm⁻¹ to 977.227 cm⁻¹, with the inset zoomed in on a singular spectral feature. The red fit in the inset is the sum of two separate Gaussian-derivative functions, one to represent the Doppler broadened part and another for the sub-Doppler part. We can notice additional structure in the middle of the transition which is due to the sub-Doppler feature. The plot b) shows Doppler-broadened experimental measurement of trioxane for the same span of wavenumber.

4.9 Sub-Doppler spectroscopy results

The spectrum in Figure 4.27 shows the WMS spectrum of trioxane in the Q-branch of the ν_5 vibrational mode between 977.204 cm⁻¹ to 977.227 cm⁻¹, covering the lines from $Q(12, 11)$ to $Q(15, 14)$. The spectrum was taken with 1 sccm of helium flow and 3.5 sccm of trioxane. In Figure 4.27b we see a Doppler-broadened spectrum of this region. Figure 4.27a shows the sub-Doppler experimental spectrum with the inset zoomed in on one spectral feature. The red fit in the inset is a sum of two Gaussian-derivative function, one to represent the Doppler broadened part and another for the sub-Doppler part that is fitted to the spectral feature. We can see that there is additional

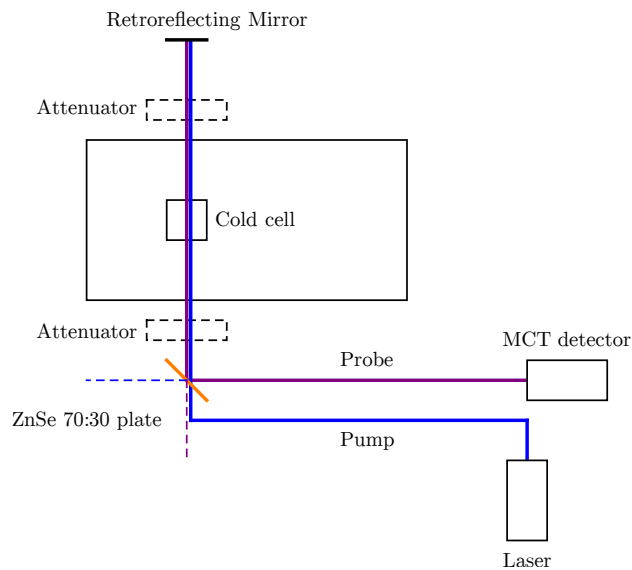
structure present in the middle of the Doppler broadened feature which comes from the presence of the sub-Doppler feature. The same type of feature can be noticed in the middle of almost all spectral features in Figure 4.27a. In this measurement we think that the pump beam was either an accidental retro-reflection from the surface of the MCT detector or a retro-reflection from a window in the cell or the source chamber. Recording a sub-Doppler dip in the spectral feature was a very exciting development because it can lead to measurement of even narrower lines. We cannot realistically measure sub-Doppler features limited only by the natural linewidth in this setup but we expect the linewidth to be limited by the collisional or transit-time broadening. The time between collisions for a trioxane molecule with flow of helium equal to 1 sccm is 4.66×10^{-6} s. This gives collisional broadening of about 0.2 MHz. Transit time broadening for these conditions and a beam which is 2mm in radius was calculated to be 96 Hz. We can hence expect that measuring the sub-Doppler feature will allow us to observe spectral features about an order of magnitude narrower than the Doppler broadened ones (6 MHz).

After investigation of the widths of the Doppler features sub-Doppler features are only a little narrower than the Doppler ones, probably because the parameters of the WMS spectroscopy were not optimised for sub-Doppler spectroscopy. For example, from the fit of the spectral feature shown on the inset in Figure 4.27 the observed width of the sub-Doppler feature is 10.3 MHz, while the width of the Doppler-broadened feature is 14.6 MHz. The amplitudes of the features are respectively 0.00048 V and 0.0008 V. The spectrum was recorded with high modulation amplitude, with both Doppler-broadened and sub-Doppler features artificially broadened. While trying to reproduce the results the modulation amplitude should be decreased to obtain a measurement of the sub-Doppler feature width.

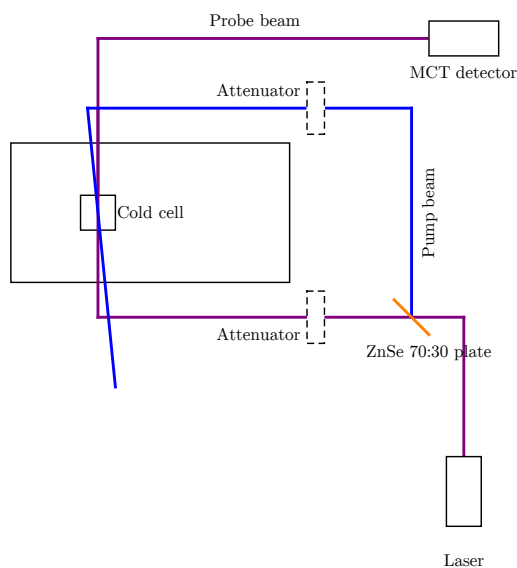
4.9.1 Reproducibility

The observation of the sub-Doppler features, shown in Figure 4.27 is an exciting development but in the current experiment we found it difficult to make the results stable and reproducible. We have tried a number of sub-Doppler setups and for most there was no observed sub-Doppler features at all. This section outlines the setups we attempted and suggests some possible reasons for the lack of reproducibility.

The first approach was to retro-reflect the laser beam (Figure 4.28a). The main beam acted as a pump and the retro-reflection was serving the role of a probe. This approach simplifies the alignment because it is easy to achieve a good overlap between the beams. The downside of this approach is less control over the pump and beam powers. The possible control is done by inserting attenuators in the beam path. Hence if one imagines the path the beam follows in Figure 4.28a, the beam has to go through some of the optical components twice, reducing power substantially. The second approach is



(a)



(b)

Figure 4.28: Two experimental approaches to measuring the sub-Doppler spectrum of trioxane in the cold cell. a) Setup with the pump beam created by retro-reflecting the probe beam after passing through the cold cell. b) Setup with the pump beam created by separating it from the probe beam with a 70:30 beam splitter.

using an independent pump and probe beam split by a zinc selenide (ZnSe) plate that acts as a 70:30 beam splitter (Figure 4.28b). This approach gives a precise control of the powers of both pump and probe beams. The downside of this method is that it involves much more difficult alignment- it is

hard to achieve good overlap. Neither of these approaches have led to observation of the sub-Doppler features, despite ensuring good overlap of the pump and probe beams. To do that the beams were traced with a visible Helium-Neon laser. The parameters varied to observe the spectral features were: ratio of the powers of pump and probe beams, WMS parameters (optimizing for the minimum noise, and good signal even from small sub-Doppler signals), and scan times over a spectral feature (to prevent the linewidth of the laser from obscuring the features). Different scan times over spectral features were researched. The smallest scan time when it was still possible to resolve the Doppler broadened signal from the noise was 100 ms, at which the linewidth of the laser is 2 ± 0.3 MHz. This should be enough to observe features as narrow as 2MHz, still substantially smaller than the Doppler-broadened features but no observation was made. There are two explanations for the initial observation of the sub-Doppler features. First is the lifetime of the laser: the linewidth of the laser may increase with time. Possibly the first observation was performed when the linewidth of the laser was small enough not to obscure sub-Doppler features. Another aspect is stability of the laser, which also worsens with time. Current and thermal fluctuations can create small shifts of laser frequency at short timescales. It could be possible that the laser was relatively stable at the time when the sub-Doppler features were observed, but less stable after that. The second explanation is that the experimental conditions are still incorrect. The first observation was made with the reflection from the front window of the MCT, which might have created a good combination of pump and probe powers for sub-Doppler observation. The conditions created in both outlined setups might have been insufficient for the observation of the sub-Doppler spectrum.

Chapter 5

Beam formation and detection

From the previous chapter, we know that we can successfully cool complex molecules inside the cold cell and investigate them with IR spectroscopy. Now we want to extend our method to the creation of a molecular beam propagating out of the cell. Our main incentives for creating a buffer gas beam is making an environment with reduced molecular collisions and a smaller spread of transverse velocities leading to smaller Doppler broadening. We additionally want to have a possibility of investigating the beam at longer distances than the length of the cell.

5.1 Theory of molecular beam creation

In this section, the equations that help to characterize the molecular beam will be provided. The cooling of molecules inside the cell was outlined in Section 4.1. Here, the extraction of the molecules through an aperture and properties of the formed beam will be discussed.

Gas flow regimes The properties of a buffer gas beam are determined by the Reynolds number Re that defines the ratio of inertial to viscous forces in a fluid flow. Following the definition given by Hutzler et al [120] we can define the Reynolds number as

$$Re = \frac{4r_{\text{aperture}}}{\lambda}, \quad (5.1)$$

where r_{aperture} is the radius of the exit aperture in the buffer gas cell and λ is the mean free path of a molecule in the cell. For a Reynolds number much lower than 1 the beam is in the effusive regime where the collisions between the molecules in the vicinity of the cell aperture are so infrequent they can be easily ignored and the beam creation can be attributed solely to the thermal properties of the species in the cell. If the Reynolds number is higher than 100 the gas is in the supersonic regime: it undergoes both cooling and boost while expanding into a vacuum. Between those two values the

flow is in the partially hydrodynamic regime. In this regime the properties of the beam are affected by collisions near the aperture but there is not much speed boost of molecules leaving the cell like in a case of the supersonic beam.

The extraction from the buffer gas cell To define the efficiency of the extraction of the species of interest from the cold cell we have to consider two phenomena. One of them is the diffusion of the molecules to the cell walls which will limit the amount extracted to the beam [127]. For the cell with side length l_{cell} the time of diffusion to the cell walls is given by:

$$\tau_{\text{diff}} = \frac{16}{9\pi} \frac{l_{\text{cell}}^2 n_B \sigma}{\bar{v}_B}, \quad (5.2)$$

where n_B is the number density of the buffer gas and $\bar{v}_B$ is the mean thermal velocity of the buffer gas. In this equation σ is a collisional cross-section between the species of interest and the buffer gas. To effectively transfer the molecules from the cell to the beam the “pump out” time has to be obtained, which will define how fast the molecules are extracted from the cell. The fluid conductance of the aperture gives the rate at which the sample is pumped out through an opening as

$$\dot{N} = -\frac{\frac{1}{4} N \bar{v}_B r_{\text{aperture}}^2 \pi}{l_{\text{cell}}^3}, \quad (5.3)$$

where N is the number of buffer gas atoms in the cell, and $\dot{N}$ is the rate of outflow of atoms from the cell. For the initial number of buffer gas atoms in the cell N_0 Equation 5.3 has the exponential solution

$$N = N_0 \exp\left(-\frac{t \bar{v}_B r_{\text{aperture}}^2 \pi}{4 l_{\text{cell}}^3}\right). \quad (5.4)$$

From this we can define the pump out time (time in which N falls to $1/e$ of its initial value) to be

$$\tau_{\text{pump}} = \frac{4 l_{\text{cell}}^3}{\bar{v}_B r_{\text{aperture}}^2 \pi}. \quad (5.5)$$

From that, we can define an extraction coefficient γ which is a ratio of the diffusion to pump-out time

$$\gamma = \frac{\tau_{\text{diff}}}{\tau_{\text{pump}}} = \frac{4}{9} \frac{n \sigma \pi r_{\text{aperture}}^2}{l_{\text{cell}}} \approx \frac{\sigma f}{l_{\text{cell}} \bar{v}_B}. \quad (5.6)$$

There are two limits on the value of γ . For $\gamma \ll 1$ the majority of the molecules are lost to the walls of the cell. For values above 1 the beam enters the regime of “hydrodynamic enhancement”, and the majority of molecules are extracted from the cell. The extraction coefficient, therefore, should not be treated as a simple fraction of molecules that make it out of the cell but gives a good estimate of how effectively molecules are extracted to the buffer gas beam [128].

Forward velocity and transverse velocity spread of the buffer gas beam Hutzler et al. have determined four different regimes for the forward velocity of the molecular beam, dependent on the Reynolds number (Equation 5.1) of the system [32]. Figure 5.1 illustrates what we mean by

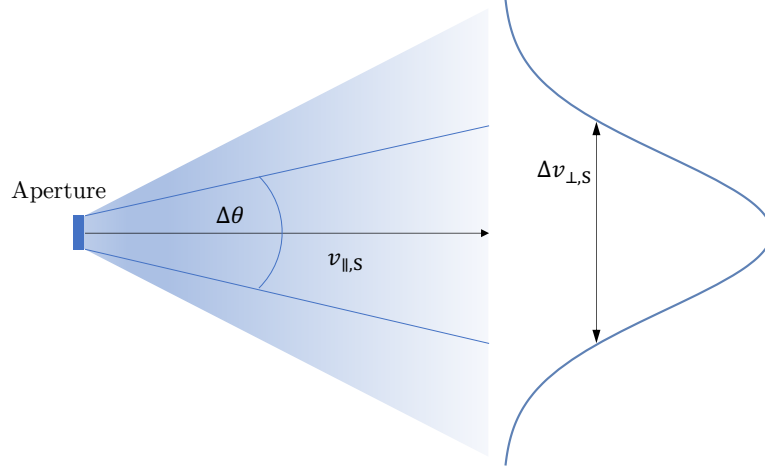


Figure 5.1: Forward velocity, transverse velocity spread and the beam divergence illustrated for the molecular beam.

the forward velocity, transverse velocity spread and the beam divergence for the molecular beam. For the mean thermal velocity of the species of interest $\bar{v}_S$ and mean thermal velocity of the buffer gas $\bar{v}_B$ we can calculate the species forward velocity $v_{||,S}$.

$$v_{||,S} \approx \frac{3\pi}{8} \bar{v}_S \quad Re \lesssim 1, \quad (5.7)$$

$$v_{||,S} \approx 1.2\bar{v}_S + 0.6\bar{v}_B Re \frac{m_B}{m_S} \quad 1 \lesssim Re \lesssim 10 \quad (5.8)$$

$$v_{||,S} \approx 1.4\bar{v}_B \sqrt{1 - 4Re^{-4/5}} \quad Re \gtrsim 10 \quad (5.9)$$

$$v_{||,S} \approx v_{||,B} \approx 1.4\bar{v}_B \quad Re \gtrsim 100 \quad (5.10)$$

For very high flows the forward velocity of the species is equal to that of the buffer gas $v_{||,B}$. That allows us to define transverse velocity spread of the species in the buffer gas beam $\Delta v_{\perp,S}$. It's important to note that for the transverse velocity spread the changes between regimes occur at different points than for the forward velocity. For small values of Re ($\lesssim 10$) the equation for transverse velocity spread is

$$\Delta v_{\perp,S} = 1.5\bar{v}_S. \quad (5.11)$$

For intermediate regime ($10 < Re < 100$) the transverse velocity spread is given by

$$\Delta v_{\perp,S} = 1.5\bar{v}_S + \frac{Re}{2} \bar{v}_B \frac{2r_{\text{aperture}}^2}{l_{\text{cell}}^2} \frac{m_B}{m_S}. \quad (5.12)$$

As the Reynolds number increases towards the supersonic regime the transverse velocity spread of the species will approach that of the buffer gas, which was observed experimentally [129].

Beam divergence The beam extracted from the cell will have some divergence θ , that can be described with equation

$$\Delta\theta = 2 \arctan\left(\frac{\Delta v_{\perp}/2}{v_{\parallel}}\right), \quad (5.13)$$

$\Delta v_{\perp,S}$ is a transverse velocity spread of the species seeded in the molecular beam and $v_{\parallel,S}$ is their forward velocity. For small values of Re , with the increase of Re the forward velocity increases but the transverse velocity spread remains constant. Therefore the beam divergence will decrease. When the molecules forward velocity approaches that of the buffer gas the minimum divergence can be approximated as

$$\Delta\theta = 2 \arctan\left(\frac{\Delta v_{\perp}/2}{v_{\parallel}}\right) \approx 2\sqrt{\frac{m_B}{m_S}}, \quad (5.14)$$

where m_b is the mass of the buffer gas atom and m_s is the mass of the species. With $Re > 10$ the transverse velocity spread increases with increase of Re but the simultaneous increase in the forward velocity means that divergence stays approximately constant.

5.1.1 Helium buffer gas beam properties

For the experiments described here, helium flows between 1 and 8 sccm can be used without resulting in a pressure that is too high to form a molecular beam. For those flows the Reynolds number is respectively 14 and 120, placing the beam in the intermediate regime. The extraction coefficient is 0.006 at a flow of 1 sccm, and 0.05 at 8 sccm.

The mean thermal velocity of trioxane at 7 K is about 40 m/s and the mean thermal velocity of helium at the same temperature is 192 m/s. Using the equations from the previous section, for 1 sccm of flow and $Re = 14$, we can calculate the forward velocity to be 193 m/s and transverse velocity spread to be 108 m/s. For 8 sccm of flow and $Re = 120$ we obtain the forward velocity of 269 m/s. With the value of $Re > 100$ we assume that the transverse velocity spread of the species is comparable with the buffer gas, which will give 192 m/s. With 1 mm radius beam exit aperture the maximum divergence of the trioxane buffer gas beam ($\Delta\theta$) is around 39 degrees, calculated for 8 sccm of helium. In the observation region located at 145 mm from the aperture the beam is therefore about 51 mm in radius and at the observation point at 235 mm the beam radius is around 83 mm. All of these values are summarised in Table 5.1.

5.1.2 Neon buffer gas beam properties

With flows of neon in the range from 1 to 20 sccm, the Reynolds number of the trioxane entrained in the neon buffer gas is between 10 and 207. It means that with the low flow of neon the beam is in the partially hydrodynamic regime, and for high flow, we enter the supersonic regime. For flow of 1 sccm the extraction coefficient is $\gamma = 0.01$ but for 20 sccm $\gamma = 0.2$. The maximum divergence of the trioxane beam is 45 degrees, for 1 mm radius beam exit aperture and neon flow of 1

Helium					
beam exit aperture radius	$r_{\text{aperture}}[\text{mm}]$	1		2	
buffer gas flow	f [sccm]	1	8	1	8
buffer gas number density	$n_{\text{B}} [\text{m}^{-3}]$	3×10^{21}	2.4×10^{22}	7×10^{20}	6×10^{21}
mean free path	λ [mm]	0.27	0.03	1.07	0.13
Reynolds number	Re	14	120	7	60
species forward velocity	$v_{ ,S} [\text{m/s}]$	193	269	84	248
species transverse velocity spread	$\Delta v_{\perp,S} [\text{m/s}]$	108	192	60	192
beam divergence	$\Delta\theta$	31	39	39	42
extraction coefficient	γ	0.007	0.05	0.006	0.05

Table 5.1: Summary of properties of buffer gas beam creation with helium for different aperture sizes and flows.

sccm. In two observation regions at 145 and 235 mm from the aperture, the radius of the molecular beam is respectively about 60 and 97 mm. At 17 K the mean thermal velocities of trioxane and neon are respectively about 63 m/s and 134 m/s. For 1 sccm of neon flow and $Re = 10$ the forward velocity is 113 m/s and the transverse velocity spread is 94 m/s. For 20 sccm of flow and $Re = 207$ the forward velocity is 187 m/s and the transverse spread is 134 m/s. All of these values are summarised in Table 5.2.

Bigger aperture To aid in the extraction of the molecules of interest, and prevent fast clogging of the aperture by trioxane, a bigger aperture was installed in the system $r_{\text{aperture}} = 2\text{mm}$. According to the equations outlined in Section 5.1 the only property that will be affected by the change is the flow regime of the beam. With the new aperture and 1 sccm of neon flow the new Reynolds number is 5, still in the partially hydrodynamic regime, and for 20 sccm of neon the Reynolds number is 103. With the new values of the Reynolds number for 1 sccm of neon and $Re = 5$ the forward velocity is 165 m/s and transverse velocity spread is 94 m/s. For the 20 sccm of neon flow and $Re = 103$ the forward velocity is 187 m/s and the transverse velocity spread is 134 m/s. According to the theoretical calculations the aperture size does not affect the extraction coefficient, however, in the buffer gas beam work at Harvard, it was observed that for neon buffer gas beams there is an increase in the number of molecules extracted to the beam with increasing aperture size [54, 130]. We should, therefore, be aware that the properties of buffer gas systems are dependent on the geometry of the system itself and the theoretical equations should be treated only as an estimate of the true values.

Neon					
beam exit aperture radius	$r_{\text{aperture}}[\text{mm}]$	1		2	
buffer gas flow	$f [\text{sccm}]$	1	20	1	20
buffer gas number density	$n_{\text{B}} [\text{m}^{-3}]$	4×10^{21}	8×10^{22}	1×10^{21}	2×10^{22}
mean free path	$\lambda [\text{mm}]$	0.4	0.02	1.5	0.08
Reynolds number	Re	10	207	5	103
species forward velocity	$v_{ ,S} [\text{m/s}]$	113	187	165	187
species transverse velocity spread	$\Delta v_{\perp,S} [\text{m/s}]$	94	134	94	134
beam divergence	$\Delta\theta$	45	39	32	39
extraction coefficient	γ	0.01	0.2	0.01	0.2

Table 5.2: Summary of properties of buffer gas beam creation with neon for different aperture sizes and flows.

5.1.3 Choice of buffer gas

The possibility of accessing higher flows and therefore higher extraction coefficient with neon has prompted us to try using it as a buffer gas. Additionally, data shown in [54] showed that while we have no hope of increasing the extraction of the molecules with the helium buffer gas by increasing the aperture size we possibly can extract more molecules to the beam using neon. Those two reasons, and easier pressure management, motivated us to change the buffer gas from helium to neon.

Because the changes to the system needed to implement neon buffer gas are easily reversible (thermal disconnection of the cold cell and different bobbin configuration) we are happy to characterise the molecular beam with both of the buffer gases for our system geometry and choose the best one for the observation of the molecular beam by WMS spectroscopy.

5.2 Characterising a trioxane beam with helium as buffer gas

So far the information about the molecules was obtained with the in-cell WMS spectroscopy. The width and amplitude of the spectral features, and temperature and number density of molecules in the cold cell can be measured with this method. However, because of the small values of the extraction coefficient calculated and the large divergence of the molecular beam, we expect the absorption signal in the beam to be much smaller than in the cell. Additional information is needed to optimize the creation of the molecular beam and to reach densities of molecules that can be optically observable. Hence a Halo Hiden Analytical quadrupole mass spectrometer that uses electron beam ionisation was installed in the system to collect information about the properties of

the molecular beam. We searched for trioxane at amu of 89, which indicates trioxane with one lost hydrogen. The measurements are taken with electron beam voltage of 70 V and current of 20 μ A. Optical data in the cell and mass spectrometer data in the beam were collected simultaneously. Data sets were taken for different flows of trioxane and helium into the cell and various positions of the end of the trioxane capillary with respect to the cell. These measurements allow us to correlate these parameters with the amount of trioxane in the beam and will also shine a light on the mutual dependence of the signals in the beam and in the cell. In the whole section the transition observed is $R(2, K)$ (Figure 5.2). Because three different K lines are present the spectrum is fitted with the sum of three derivatives of Gaussian functions. $K0$ line widths and amplitudes are reported. We infer the temperature of molecules from the Doppler broadening of the spectral lines. The inferred temperature is therefore proportional to the spectral line's width.

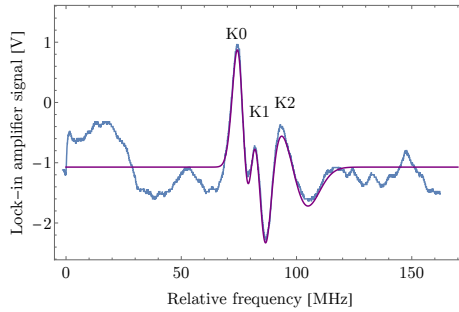


Figure 5.2: WMS spectrum of $Q(2, K)$ (blue) fitted with a sum of three derivatives of Gaussian functions (purple). Width and amplitude of the $K0$ line are reported.

5.2.1 Helium flow

Figures 5.3 and 5.4 show how the properties of trioxane in the cell and molecular beam depend on the He buffer gas flow. During the measurement, the flow of trioxane was set to 3.5 sccm, and the capillary was inserted 1mm into the cell.

The theory of buffer gas cooling suggests that higher number density of buffer gas in the cell results in the shorter time between collisions of the molecule and the buffer gas, which then decreases thermalisation time and length, as shown in Tables 4.1 and 4.2. However in the optical data taken in the cell there is no evidence that greater buffer gas density in the cell, either with helium as buffer gas presented here, or with neon (presented in Section 5.3.1), increases the cooling of the molecule, demonstrated in Figure 5.3a. Otherwise, there is a slight heating of the molecules as the buffer gas flow increases. This can be partially explained by the heat load that the buffer gas exerts on the cold cell. With no flow of helium the lowest cell temperature is about 6.5 K and with high flow of 7-8 sccm it can increase as much as 9 K. This translates to a higher temperature of the buffer gas beam

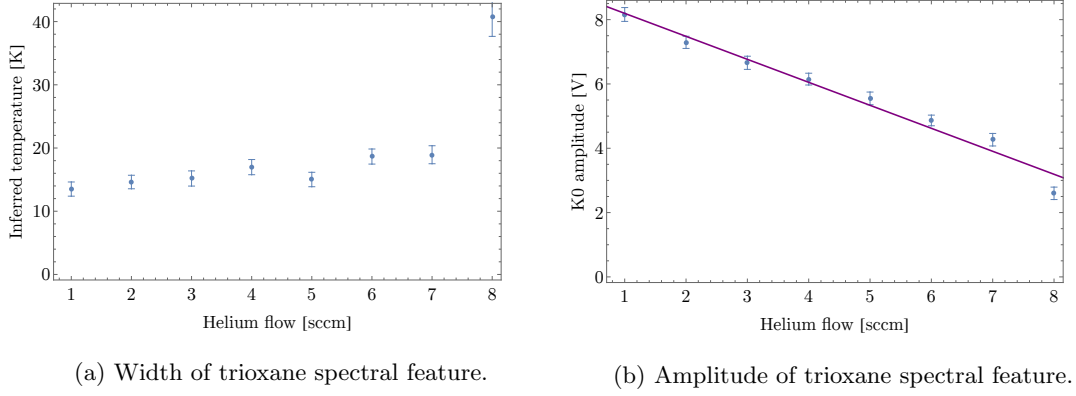


Figure 5.3: Dependence of the properties of the $K0$ line on the helium flow into the cell. The data (blue) is fitted with a linear function (purple). a) Width of the $K0$ line vs helium flow into the cell b) Amplitude of the $K0$ line vs helium flow into the cell. The error bars are obtained from the root mean square error of the fit.

and higher temperature that the trioxane molecules thermalise to. Even though the higher buffer gas density in the cell means that molecule movement regime can change from the direct expansion to the random one allowing for more collisions, we see that this feature is not enough to dominate the cooling. The data suggest that a flow of 1 sccm is already sufficient to bring the molecules close to thermal equilibrium with the buffer gas, which is also what our calculation suggest, at least in the case of the random walk model.

In Figure 5.3b the amplitude of trioxane spectral features decreases as the flow increases. That can be explained by the more efficient extraction of the molecules to the beam meaning a lower density available for optical observation. The extraction coefficient increases from 0.006 at 1 sccm to 0.05 at 8 sccm. In the same flow range the amplitudes fall by a factor of 2.

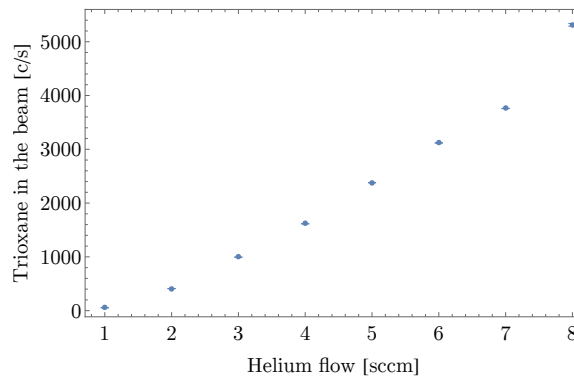


Figure 5.4: Amount of trioxane in the beam vs the helium flow. The data for each flow was recorded over a period of time (30 s) and the mean is taken as the data point. Standard deviation is taken as an error.

Figure 5.4 demonstrates that the number of trioxane molecules detected in the molecular beam increases rapidly above 1 sccm. The most He flow-dependent parameter for beam creation is the extraction coefficient. In the range of flows from 1-2.5 sccm the counts of trioxane increase by an order of magnitude while we can calculate that the extraction coefficient increases only by a factor of 2. This implies that an additional parameter impacts the brightness of the trioxane beam. The possible reason is that the divergence of the beam decreases in this range of flows, a phenomenon that was observed in other buffer gas systems, for example by Bulleid et al. [131].

5.2.2 Trioxane capillary position

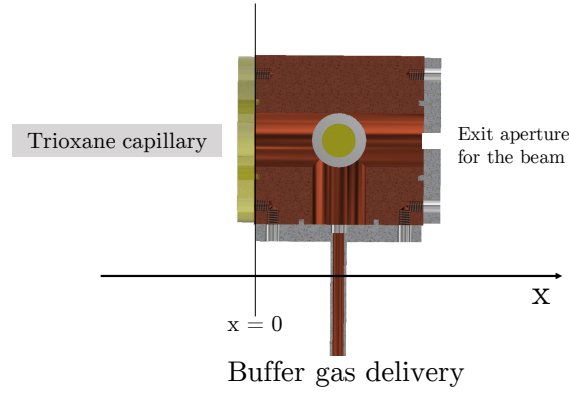


Figure 5.5: View of the cold cell with the movement of capillary shown. The end of the trioxane delivery line enters through an aperture in the PEI attachment and can move along the x -axis, with the cell wall being taken as $x=0$. The observation region is the yellow circle in the middle of the cell.

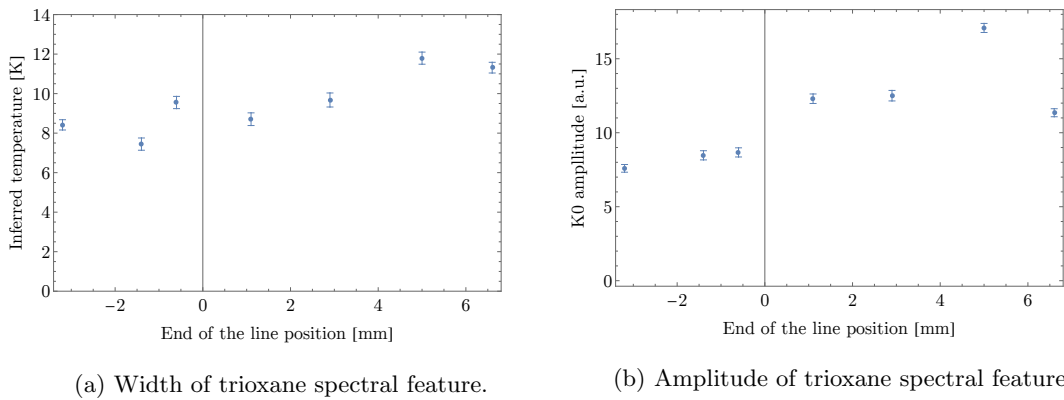


Figure 5.6: Dependence of the properties of the $K0$ line on the capillary position in the cell for the helium buffer gas. a) Width of the $K0$ line vs trioxane flow into the cell b) Amplitude of the $K0$ line vs trioxane flow into the cell. The error bars are taken as the root mean square error of the fit.

Figure 5.5 shows a half-projection of the cold cell with assigned x -axis. The yellow attachment on the left-hand side is the PEI attachment where the capillary is inserted. The right hand side has the aluminium flange with the beam exit aperture. The trioxane capillary can be moved in and out of the cell. We assume that it is moving along the x -axis, with the PEI attachment (cell wall) being taken as $x = 0$. Mass spectrometer and optical data were recorded for different positions of the capillary. The trioxane flow was kept at 3.5 sccm and helium flow was at 1 sccm.

In Section 4.1 we calculated that for 1 sccm of helium flow, ballistically-moving trioxane would not fully thermalize with the buffer gas. Figure 5.6a shows that the molecules are hotter when the capillary is closer to the observation region indicating that the molecules are not completely thermalized with the buffer gas, though the effect is quite small.

Figure 5.6b demonstrates that the closer the capillary is to the observation region, the higher are the amplitudes, directly proportional to the density of trioxane in the cell. Reducing the distance that molecules have to travel in the cell reduces the probability they will freeze to the wall and be lost from both the beam and the optical observations. We can conclude that moving the capillary even further in positive x -direction will increase the number of molecules available for investigation and therefore amplitudes of spectral lines. Analysis of widths however tells us that the molecules will have shorter distance to thermalise. That can be remedied with for example increasing the flow of helium, which by increasing the number density of molecules in the cell will decrease mean free path and thermalisation length (Equation 4.11)

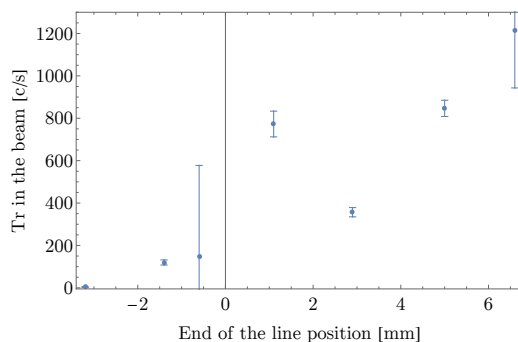


Figure 5.7: Dependence of the beam extraction on the capillary position inside the cell for the helium buffer gas. The data from the mass spectrometer for each capillary position is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data is then taken as an error. The large error registered at $x = -0.6$ mm is due to short (< 5 s) 20-times increase in trioxane c/s detected by the mass spectrometer, which we attribute to an explosion of trioxane.

Figure. 5.7 shows that moving the capillary closer to the beam aperture results in better extraction of the molecules. That is compatible with Equation 5.6, which shows that decreasing the effective

length of the cell will increase γ . However, the biggest change is seen between a capillary position just outside the cell where $x = -0.5$ mm and one just inside the cell, with $x = 1$ mm. The amount of trioxane extracted increases by a factor of 4, which we can attribute to molecules entering the cell more efficiently. With the capillary out of the cell we suspect that there is an “outflow” of helium through an opening in the PEI attachment that can prevent the molecules entering the cell. With the capillary in the cell the majority of the outflow is blocked and more molecules can make it in. The capillary can also be moved small distances in the y - and z -directions, but no impact on either the molecules in the cell or on the beam was observed.

5.2.3 Trioxane flow

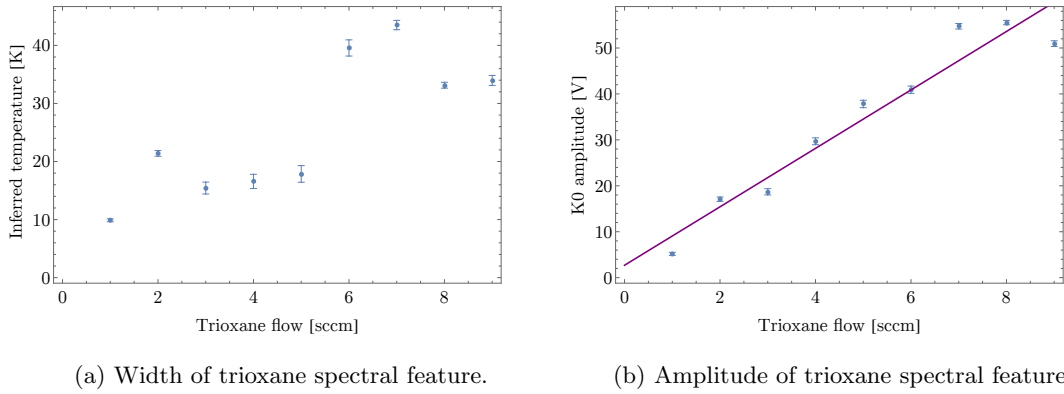


Figure 5.8: Dependence of the properties of the $K0$ line on the trioxane flow into the cell. The data (blue) is fitted with a linear function (purple). a) Width of the $K0$ line vs trioxane flow into the cell b) Amplitude of the $K0$ line vs trioxane flow into the cell. The error is taken as the root mean square error of the fit.

Figures 5.8a and 5.8b, show respectively the changes in amplitudes and widths of the spectral features with increasing trioxane flow. Figure 5.8a demonstrates that the temperature of the molecules increases. As the amount of trioxane increases already thermalised molecules warm up from the influx of “hot” molecules. As seen from the gradient of the best-fit-line in Figure 5.8b, $6.4 \pm 0.53\text{V/sccm}$, the amplitudes increase linearly with the increase in the trioxane flow.

Figure 5.9 shows the dependence of the amount of trioxane extracted to the beam on the trioxane flow to the cold cell. The helium flow is kept fixed at 2 sccm and capillary is inserted 1 mm into the cell. With the trioxane flow between 0-2 sccm, the signal at the mass spectrometer slowly increases and between 2-8 sccm the increase is fast and linear. Between 2 sccm and 8 sccm the amount of trioxane reaching the mass spectrometer increases by a factor of 12. Above the value of 8 sccm, the pressure in the beam increases above the allowed threshold value for the mass spectrometer hence these points are unreliable.

This provides an interesting experimental problem of optimizing the extraction while keeping the temperature of the molecules low. From Figures 5.8a and 5.9 flow of 5 sccm gives good extraction while keeping the molecules relatively cold. Between 2 and 5 sccm the amount of trioxane extracted from the cell increased by a factor of 8, and the temperature increased from 10 to 17 K.

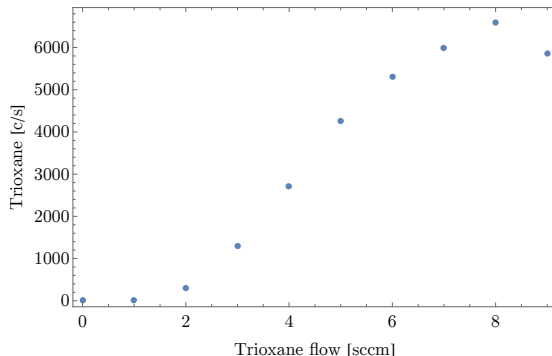


Figure 5.9: Dependence of the beam extraction on the trioxane flow into the cell. The data for each flow was recorded over a period of time (30 s) and the mean is taken as the data point. Standard deviation is taken as an error.

5.2.4 Different aperture sizes

With helium buffer gas the lifetime of the system is not restricted by the trioxane clogging the beam exit aperture, so there was no incentive to try measurements with bigger apertures. Nevertheless, two other aperture configurations were tried. In one configuration the radius was reduced from 1 mm to 0.5 mm, keeping the wall thickness the same at 2 mm. In the other configuration, the radius was increased to 2 mm and the wall thickness decreased to 0.5 mm. The first iteration yielded no molecules in the beam at all, and the second one produced similar results to the initial aperture. Decreasing the wall thickness provides less area for molecules to stick to inside apertures, so it can result in better extraction of trioxane to the molecular beam.

5.2.5 Optimised values and conclusions

The analysis of mass spectrometer and optical data presented in Sections 5.2.1, 5.2.2, and 5.2.3 provides us with a recipe for optimisation of the extraction of trioxane to the molecular beam. The helium flow should be set at the highest value possible: 8 sccm. While increasing trioxane flow to the highest possible value results in a high yield of trioxane in the beam it also increases the temperature of the molecules. The value of 3-4 sccm of trioxane flow is optimal, still ensuring efficient thermalisation and maximising the trioxane in the molecular beam. Data in section 5.2.2 shows that inserting the capillary even more into the cell will be beneficial for the amount of species

in the buffer gas beam however it will increase the molecules' temperature. With a low helium flow capillary position of 1 mm into the cell provides good extraction while still thermalizing the molecules to low temperature. With the 8 sccm of helium flow and 9.5 sccm trioxane flow we observe two orders of magnitude improvement of trioxane extraction to the molecular beam compared with a measurement with 1 sccm of helium and 3 sccm of trioxane.

5.3 Characterising a trioxane beam with neon as the buffer gas

To fully characterise the neon buffer gas beam optical data from the cell and mass spectrometer data were collected simultaneously. Several different parameters were varied and their influence on the widths and amplitudes of trioxane spectral features and the beam intensity were measured.

In the whole section the transition observed is $R(3, K)$ (Figure 5.1). Because there are four different K lines the spectrum is fitted with the sum of four derivatives of Gaussian functions and $K0$ linewidths and amplitudes are reported. We infer the temperature of molecules from the Doppler broadening of the spectral lines. The inferred temperature is therefore proportional to the spectral line's width.

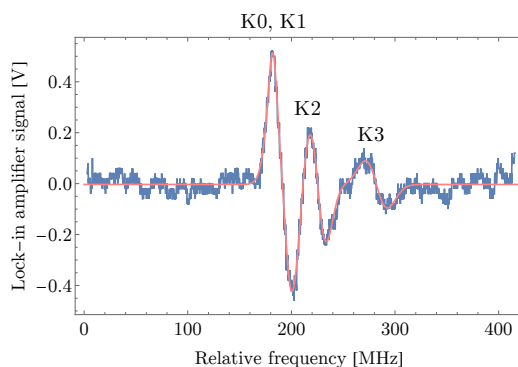


Figure 5.10: WMS spectrum of the $R(3, K)$ transition (blue) in trioxane, fitted with a sum of five derivatives of Gaussian functions (pink). $K0$ and $K1$ cannot be resolved in the spectrum. For all data sets the amplitude and the width of the $K2$ line is reported.

5.3.1 Neon flow

For neon buffer gas we have explored flows up to 16 sccm. Without the trioxane, the pressure within the system is suitable for the creation of a molecular beam up to 20 sccm of neon

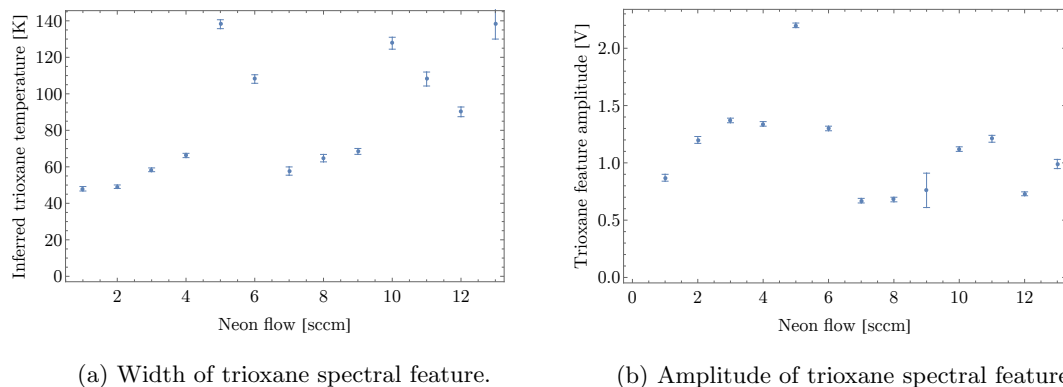


Figure 5.11: Dependence of the trioxane spectral feature properties on the neon flow into the cell. The data are shown in blue and the purple lines are linear fits. The error is taken as the root mean square error of the fit.

flow, but in the presence of trioxane the neon flow was limited to 16 sccm. For all measurements the trioxane flow was kept at 3.5 sccm.

Figure 5.11a shows the parameters of the trioxane feature with increasing neon flow. To prevent the neon freezing the cell was kept at 18 K, so the expected trioxane temperature is close to that. However, in this dataset the trioxane capillary is too close to the observation region to observe fully thermalised neon and from the data we established that trioxane undergoes about 10 collisions. With increasing neon flow we observe significant increase in the temperature. With increasing molecular flow molecules are extracted from the cell faster, so they arrive to the observation region less and less thermalised. Moving the trioxane capillary away from the observation region (in-cell distance closer to 0) would give molecules more time to thermalise even with decreased extraction time. A larger distance to travel, however, means that less molecules make it into the buffer gas beam, which is explored in Section 5.3.3. The heating of the cold cell with increasing buffer gas flow is significant but not enough to explain the heating of the molecules. With the highest flow of 16 sccm the temperature of the cell increases to 25 K.

Figure 5.11b shows how the amplitude of the spectral feature changes with the neon flow. Despite the initial increase after 4 sccm the amplitude of the features start decreasing. Between 4 and 16 sccm the spectral features decrease by roughly a factor of 2. For these flows the extraction coefficient increases from 0.04 for 4 sccm to 0.16 for 16 sccm. The increased extraction therefore can explain the decrease in the number density of molecules in the cell and therefore lower observed amplitudes of spectral features.

The final figure in this section, Figure 5.12, shows the amount of trioxane detected at the mass spectrometer versus the neon flow. The extraction increases up to about 7-8 sccm and then it starts decreasing. This observation is consistent through many data sets. We suspect that the geometry of

the cell affects the extraction at high flows. In this setup, the buffer gas inlet is placed in the middle of the cold cell and is at right angles to the trioxane flow. The hypothesis is that the high flow of buffer gas creates a barrier that prevents the trioxane molecules from entering the gas flow and therefore hinders the extraction of molecules to the molecular beam. In Section 5.3.3 we investigate this further by inserting the trioxane capillary very close to the region where the buffer gas enters the cell.

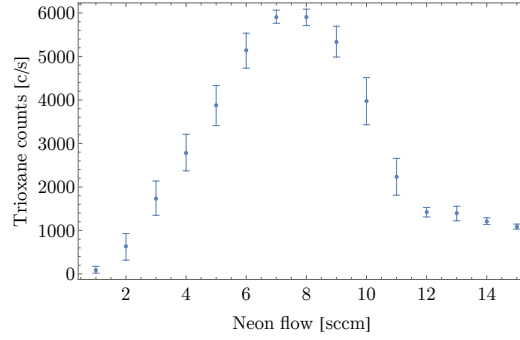
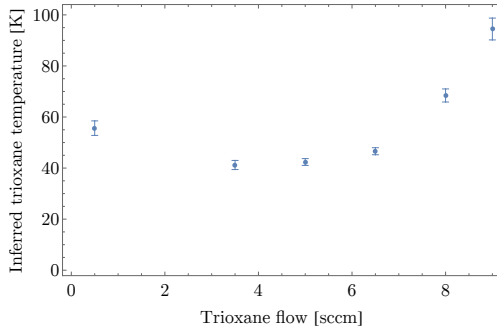
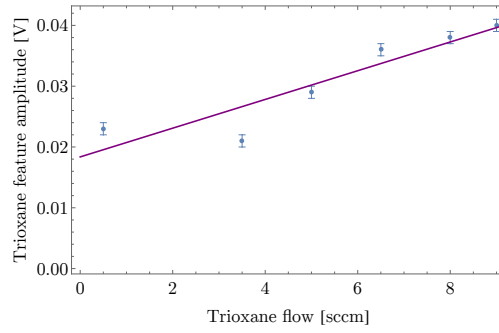


Figure 5.12: Amount of trioxane in the molecular beam versus the neon flow. The data from the mass spectrometer for each flow is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data is then taken as an error.

5.3.2 Trioxane flow



(a) Width of trioxane spectral feature..



(b) Amplitude of trioxane spectral feature.

Figure 5.13: Dependence of the trioxane spectral feature properties on the trioxane flow into the cell. The data are shown in blue and the purple line is a straight line fit. The error bars are the errors on the fit parameters.

Another parameter that we have studied is the trioxane flow into the cell. In all the measurements the flow of neon was kept constant at 8 sccm and the capillary was inserted 13 mm into the cell.

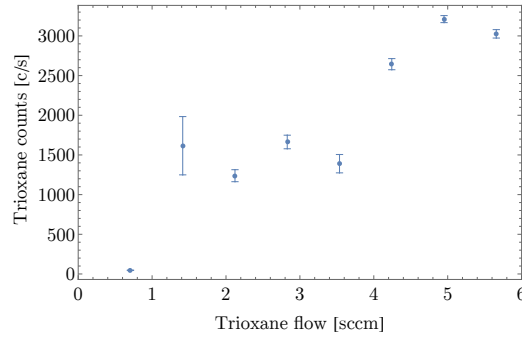


Figure 5.14: Amount of trioxane in the molecular beam versus the trioxane flow into the cell. The signal at the mass spectrometer for each trioxane flow is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data are then taken as an error.

Figure 5.13a shows the dependence of the trioxane feature on the trioxane flow. We can see that the temperature of the molecules increases as the trioxane flow increases. This is because the flow of hot trioxane is similar to the flow of cold neon, so the influx of trioxane places substantial heat load on the system. All the measurements show molecules at relatively high temperature, which is caused by the end of the capillary being too close to the observation region for these measurements (20 mm into the cell) so the molecules do not thermalise efficiently before reaching the observation region.

Figure 5.13b shows the dependence of the trioxane features' amplitude on the amount of trioxane delivered to the cold cell. The best fit line, with the slope of 0.002 ± 0.0005 V/sccm shows that the amplitude of the features increases with the increase of trioxane flow into the cell.

The amount of trioxane in the beam increases with trioxane flow as demonstrated in Figure 5.14. We can see that the increase could be interpreted as linear between points with flow of 0 sccm and 0 c/s and 5 sccm and 3200 c/s.

5.3.3 Trioxane capillary position

As in the helium case, the trioxane capillary can be moved in the x -direction inside the cell, with the cell wall (PEI attachment) being defined as $x=0$. The flow of neon was kept at 7 sccm and the flow of trioxane was set to 3.5 sccm. We have investigated how the position of the trioxane capillary affects the trioxane in the cell and in the molecular beam. Varying that particular value is very demanding because the seal around the capillary to create a vacuum is a rubber o-ring. Movements of the capillary can break the vacuum which causes gases to freeze in the system and requires cycling of the experiment.

Figure 5.15 demonstrates that the amplitude of the spectral features increases as the capillary is moved further into the cell. The main mechanism for the loss of trioxane is freezing to the walls,

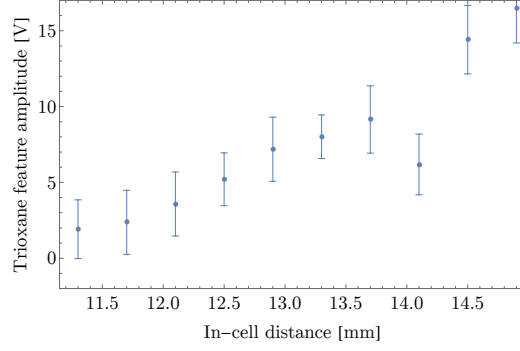


Figure 5.15: Dependence of the trioxane spectral feature amplitude on the capillary position in the cell. The x -axis signifies how far the capillary reaches into the cell (with $x=0$ being the cell wall). The error bars are the errors on the fit parameters.

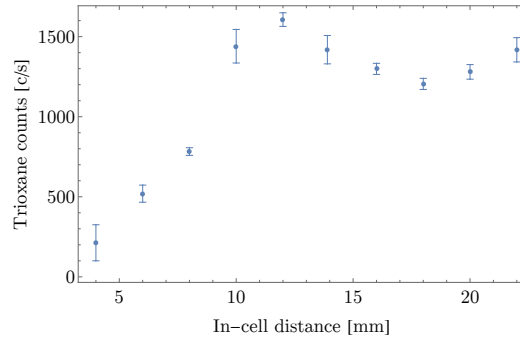


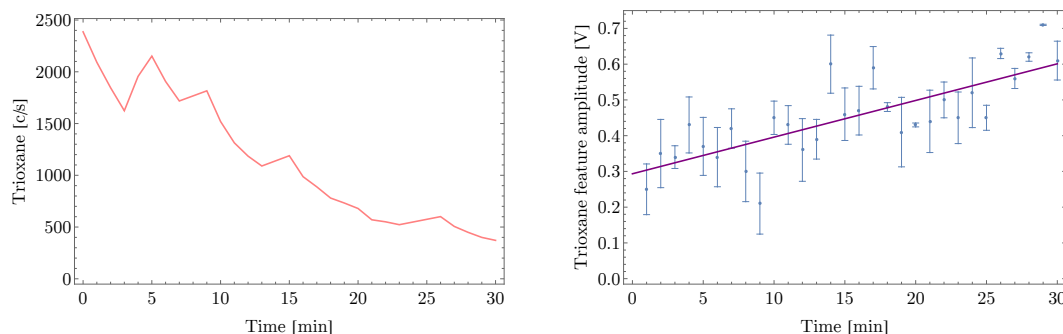
Figure 5.16: Amount of trioxane in the molecular beam versus the trioxane capillary position in the cold cell. The data from the mass spectrometer for each position is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data is then taken as an error.

and the further the capillary is from the beam aperture, the higher probability the trioxane has to get stuck to the wall and disappear from the pool of molecules available for investigation. Making that distance shorter results in more trioxane reaching the observation region and contributing to the amplitudes.

Our hypothesis, presented in Section 5.3.1, that the molecules encounter a buffer gas barrier which inhibits extraction to the molecular beam is not supported by the present data. The data shown in Figure 5.16 shows that even if the capillary is directly in the flow of the beam (22 mm in-cell) the extraction is not maximum. Instead, the optimum is achieved when the capillary is about 13 mm into the cell.

5.3.4 Time

A very significant problem present in this experiment is blocking of the beam aperture by the formation of trioxane crystals in the aperture, which prevents the formation of the molecular beam. Figure 5.17a presents the change of the amount of trioxane in the beam over the course of 30 minutes. The flow of neon was kept at 8 sccm and the flow of trioxane was set to 3.5 sccm. The capillary was inserted 13 mm into the cell. The amplitudes of the trioxane feature in time are presented in Figure 5.17b. The line of the best fit has a slope of 0.01 ± 0.002 V/min. The fact that the signal in the beam drops at the same time as the density of molecules in the cell increases indicates that the exit aperture is becoming blocked over this time period. The problem of blocking has to be solved before attempting the optical observations of the molecules in the molecular beam because it limits the time the data can be taken for. We expect that to detect the signal from the beam we need long averaging time which is impossible with the source blocking after an hour and needing at least a 24-hour warm-up and cooling cycle to be refreshed.



(a) Amount of trioxane molecules in the buffer gas beam with time. (b) Trioxane feature amplitude versus time (blue).

The error bars are the standard errors from the fit, and the data are fitted with a linear function (purple).

Figure 5.17: Change of amount of trioxane extracted to the molecular beam and trioxane spectral feature amplitude with time.

Aperture size/wall thickness The main hypothesis for the source of blocking is trioxane freezing/growing crystals in the beam aperture. This is not present while running with helium as a buffer gas. Trioxane is a solid even at room temperature, hence if during its propagation it reaches the cell wall it freezes, and when flowing out of the cell can easily create a deposit inside the aperture. In the first iteration of the buffer gas cell, the exit aperture had a wall thickness of 2 mm, which provided a lot of depth where the trioxane could freeze. We have therefore milled down the walls to 0.5 mm and again measured how the trioxane signal in the beam varies with time. The data comparing the

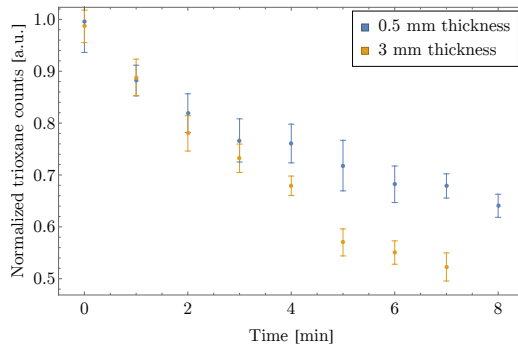


Figure 5.18: Extraction of trioxane molecules to the beam for different aperture wall thickness. The data for each flow was recorded over a minute and the mean is taken as the data point. Standard deviation is taken as an error.

trioxane extraction with those two wall thicknesses is shown in Figure 5.18. We can definitely see that decreasing the thickness of the walls decreases the rate of aperture blocking. The next step is to mill down the walls even further. Another idea is to install heating wire around the aperture to try and locally heat that area of the cell. This may slow down the crystal growth, and will remove the need to cycle the temperature of the entire apparatus when clogging does occur.

5.3.5 Optimised values and conclusions

After an analysis of mass spectrometer and optical data, we have established parameters that will optimise the neon buffer gas beam.

According to theoretical considerations increasing the neon flow will result in improved extraction, however, the data shows that the amount of trioxane detected in the beam is maximized when the helium flow is 8 sccm. Without changing the cell geometry it seems unlikely that this value can be improved. From the data, the optimum trioxane flow was established to be 3 sccm, and the optimum position of the trioxane capillary is 13 mm into the cell.

Decreasing the thickness of the trioxane walls increases the time that the experiment runs before the trioxane blocks the aperture, so decreasing the thickness up to a sharp edge can extend the lifetime of the source.

5.4 Cluster formation

Using the mass spectrometer we set out to observe possible cluster formation in this experiment. Table 5.3 contains masses of possible clusters. Figure 5.19 shows a scan over the whole mass range of the mass spectrometer. The start of the scan is taken as 40 so that the peaks due to helium or neon are not observed. The only peak we see attributable to trioxane is $\text{amu} = 89$ corresponding

to un-clustered trioxane. We know that small amounts of atmospheric gasses are present in the trioxane delivery line, and the peak at 43 amu can be attributed to the presence of CO_2 .

	number of units			mass [amu]
	trioxane	neon	helium	
trioxane-trioxane clusters	2	0	0	180
	3	0	0	270
	4	0	0	360
trioxane-neon clusters	1	1	0	110
	1	2	0	130
	1	3	0	150
trioxane-helium clusters	1	0	1	94
	1	0	2	98
	1	0	3	102

Table 5.3: Possible clustering configurations. For clustering with neon and helium only clusters involving relatively small numbers of atoms are included as those are deemed most likely to form and survive in the mass spectrometer.

The fact that no clusters are observed on the mass spectrometer does not unequivocally prove that there is no cluster formation in the system. Clusters can be forming on very short timescales such that they never reach the mass spectrometer. Additionally, mass spectrometer works by ionising incoming species, which means that surviving clusters can be destroyed during that step. Nevertheless, the absence of clusters at the mass spectrometer is a strong indicator of little clustering in buffer gas beam formation. This is consistent with similar observations at Harvard, where no clustering of buffer gas cooled trans-Stilbene with helium was observed [132].

5.5 Choice of buffer gas

With the mass spectrometer and in-cell data we can compare cooling and extraction to the beam with both neon and helium as buffer gas. Helium buffer gas is more demanding in terms of cryo-pumping that is needed to keep the pressure around the beam low enough not to destroy it. This, and heating of the system from the heat load deposited by the flow of the buffer gas are the biggest challenges of working with the helium buffer gas. We expect that more intense molecular beams could be created by improving the cryopumping so that a higher flow of helium could be used.

Neon is much easier technically, with less demand on the system's temperatures and cryo-

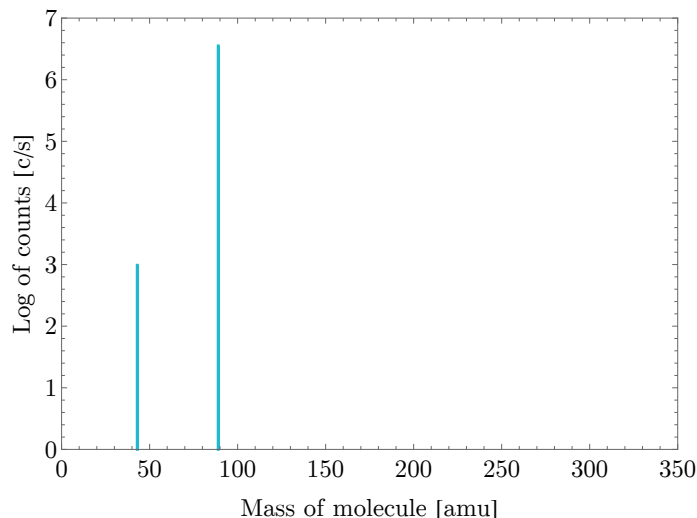


Figure 5.19: Mass spectrometer scan for masses from 40 to 350 amu. Lower masses were cut off to prevent overwhelming the mass spectrometer with neon. Peaks are present at 43 and 89 amu, corresponding respectively to CO_2 and trioxane. The y -axis is on a logarithmic scale. No clusters are observed.

umping setup. However, the main downside of working with neon was fast clogging of the beam exit aperture, which made the lifetime of the system really short. So far any possible ideas of unclogging the beam exit aperture are hard to implement technically, and this, combined with higher molecule temperatures and extraction peaking at 8 sccm makes neon buffer gas less suitable to our application than the helium buffer gas.

5.6 State-selective detection by absorption spectroscopy

5.6.1 Absorption spectroscopy in the beam

In Section 4.7 we calculated the number density of trioxane molecules in the cell to be $n = 5 \times 10^{21} \text{ m}^{-3}$. This number was obtained by direct absorption measurement of trioxane inside the cold cell. The measurement showed an absorption dip, the area of which is dependent on the strength of the probed transition and the number of species in the sample. The strength of the line was calculated theoretically and used to obtain the number density of molecules in the cell.

The next step is to calculate the number density of trioxane we expect to have in the beam. For that, we take the fraction of molecules extracted into the beam to be equal to the extraction coefficient introduced in Section 5.1. This is a good approximation when the extraction coefficient is small. With 1 sccm of helium flow, the extraction coefficient is 0.006, which gives the number density just after the beam exit aperture of $n_{\text{aperture}} = 3 \times 10^{19} \text{ m}^{-3}$. We assume that just after

leaving the cell the beam has a radius equal to the size of the beam exit aperture. The molecular beam diverges as it propagates, so that when it arrives at the far observation region, located 235 mm from the cold cell, the number density is lower. The ratio between the number density next to the aperture to that in the measurement region is inversely proportional to the ratio of the beam areas:

$$\frac{n_{\text{beam}}}{n_{\text{aperture}}} = \frac{r_{\text{aperture}}^2}{r_{\text{beam}}^2}. \quad (5.15)$$

From the above equation the density of atoms in the observation region is equal to $n_{\text{beam}} = 3.7 \times 10^{15} \text{ m}^{-3}$. To detect laser absorption in the beam, we use a probe beam with the same waist size and power as in the cell. We assume that the molecules will absorb the light the same way in the beam and in the cell so the absorption is proportional only to number density. In the cold cell the light is absorbed through the whole cell length $l_{\text{cell}} = 50 \text{ mm}$. The molecular beam will be probed by the laser through the whole diameter. We can take the ratio of the absorption in the cell to that in the beam.

$$\frac{\text{absorption}_{\text{beam}}}{\text{absorption}_{\text{cell}}} = \frac{n_{\text{beam}}}{n_{\text{cell}}} \frac{2r_{\text{beam}}}{l_{\text{cell}}} = 2.7 \times 10^{-6}. \quad (5.16)$$

Given the signal-to-noise ratio observed in the cell, the greatly reduced signal in the beam is undetectable unless we take some steps to increase the degree of absorption (the signal) or lower the noise.

5.6.2 Absorption and signal-to-noise enhancement in the beam

Based on the calculated difference between absorptions in the beam and the cold cell we do not expect to see the molecular features in the beam with the same system as the one used in the cold cell. After optimising WMS in the cell we have reached a signal-to-noise ratio of more than 100. With this, we can comfortably observe signals two orders of magnitude smaller. This means we have to improve absorption in the beam by at least three orders of magnitude to detect molecules in the beam. To perform WMS in the molecular beam we have identified and implemented several improvements which aim to increase the extraction to the beam and lower the signal-to-noise ratio. The changes include:

- comparing trioxane extraction and beam creation with two buffer gases: helium and neon
- optimisation of beam creation parameters with both helium and neon buffer gases, outlined in detail in Section 5.2
- installing a new observation region, closer to the cold cell, so the number density of molecules is increased
- increasing the interaction path of the laser with the molecular beam by using a multi-pass arrangement

- improving the laser and electronic setups to minimise the noise
- implementing a data taking procedure that allows for long averaging times

This section outlines details of these changes and how we predict each of these will affect the absorption in the beam.

New observation region

We installed a new observation region that is 90 mm closer to the cold cell compared to the initial one (respectively 145 and 235 mm from the beam exit aperture). The radius of the molecular beam at the observation region further from the cell is 1.6 times bigger than at the closer one. For helium buffer gas beam flowing at 1 sccm the number density in the new observation region increases from 3.7×10^{15} to $6 \times 10^{15} \text{ m}^{-3}$. The interaction length of the laser with the beam, however, will be shorter, and the ratio of absorption in the beam to the cell will be about 10^{-5} . Therefore we can expect about a factor of 2 increase from moving to the observation region 145 mm from the beam exit aperture.

Multipass

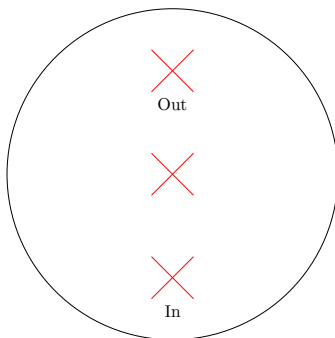


Figure 5.20: Multipass positions of the laser (red crosses) on the observation region window. The multipass is vertical, and the laser enters in the bottom of the window and leaves on the top. The multipass is installed in the observation region 145 mm from the cold cell, part 18 in Figure 2.1.

To increase the interaction length of the laser with the molecular beam, we pass the laser three times through the molecular beam. We call this the multipass. The multipass is constructed with two front-facing mirrors and the passes are along the vertical direction so no molecule passes through the laser more than once, with the laser position on the observation region window shown in Figure 5.20. From the discussion of trioxane as a two-level system in Section 4.8 we know that the excited state lifetime is very long. If the molecule passes through the beam and interacts with the light it will still be in the excited state for one second or about 200 m in case of trioxane entrained

in a helium buffer gas. A second or third pass horizontal multipass would interact with molecules in excited state, therefore not contributing to the signal. When the multipass is vertical, or each pass is above the subsequent one, the laser interacts with three different sections of molecules. ZnSe windows have 95% transmission at 10 μm , so the power of the laser decreases by about 23%. This does not mean a decrease in the quality of the signal: the power that the lock-in amplifier can work with is limited so we use an attenuator in front of the MCT, as shown in Figure 2.4. Change in attenuation brings the power received by the lock-in to the level before the installation of the multipass. With that, we expect that this will increase signal 3-fold.

Choice of buffer gas and optimised beam creation parameters

After optimising the beam creation parameters we recorded a substantial increase in molecules extracted to the molecular beam. For both helium and neon we have blocked the helium outflow from the opening around the trioxane capillary. We have also moved the capillary to the position that provides the optimised extraction: 13 mm into the cell. With helium running at 8 sccm, and 9.5 sccm of trioxane flow we recorded about 100 times of flux enhancement compared to the initial conditions of 1 sccm of helium and 2 sccm of trioxane.

For neon as a buffer gas at a flow of 1 sccm, the extraction coefficient is 0.01, which is about 2 times higher than the one for helium. In principle, about 20 sccm of neon can be run in the system which corresponds to an extraction coefficient of 0.2. This provides us with the hope that for the same parameters as with the helium buffer gas we will increase extraction of trioxane to the beam even more. However, Section 5.3.1 demonstrates that trioxane extraction to the beam peaks at around 8 sccm which corresponds to the extraction coefficient of 0.08. The data were taken for 8 sccm of neon flow, 9.5 sccm of trioxane flow and a position of the trioxane capillary of 13 mm into the cell. For these parameters, it was found that the flux of molecules in the beam is similar to that of helium. With neon, however, the experimental run time is limited by the blocking of the aperture. Since absorption signals from the beam are small, it is necessary to average for long periods, so we need the run time to be as long as possible. While it's easier to run the experiment with neon (smaller impact of heat loads on the pressure and better background pressure) we have chosen helium as a preferred buffer gas because with comparable extraction to the beam the run time is 3-4 times longer than with neon buffer gas.

Averaging

With helium as a buffer gas long averaging times are feasible. The signal-to-noise ratio scales as the inverse square root of the measurement time, so for example, averaging the scan for 1000 seconds would improve the signal-to-noise ratio by a factor of 32 compared to a 1 s scan, which is the

measurement time in the cold cell. Long averaging times were achieved by automating the data acquisition procedure.

Laser frequency drifts The main problem with long measurement times is the drift in the laser frequency. This results in drifts of the spectral features with respect to the beginning of the scan, or in other words that in different scans a slightly different region of the spectrum is recorded. If that happens, the signals from two different frequencies can be averaged together masking the presence of molecules. To counter this, we need a method that correctly overlaps multiple scans. We record both trioxane and ethylene signals at the same time, and make sure to record a trioxane line with an ethylene feature nearby for absolute frequency calibration. However, recording the ethylene signal at the same time means that two different laser paths are active. Depending on the precise alignment the presence of the second laser path can cause an etalon in the MCT signal. When etaloning is present we can remove it by a shutter implemented in the laser system. The shutter allows to alternate between recording the signal from both paths and only the trioxane path every 500 ms. This will ensure that we have a record of the ethylene spectrum for each trioxane scan and a signal scan without etaloning. Using the information from the ethylene we can overlap the scans negating any laser shifts. Then the signals can be averaged to form a trioxane spectrum.

Molecular shutter To effectively subtract the background from the molecular signal we have incorporated a shutter valve in the molecule delivery line that allows for subsequent recording of the beam signal with molecules on and off. The shutter valve is implemented after the needle valve and is controlled via a pattern generator produced by a National Instruments board. Using the valve the molecules can be shuttered on and off, which results in some scans with, and some without the molecular signal. Because the molecules disappear completely from both the cell and the beam only after about 2-3 seconds, the shutter operates at about 0.33 Hz. According to theory, when molecules are allowed into the cell they get extracted to the beam in few ms. This time is small compared to the length of the scan and can be ignored.

Data taking procedure When taking the data we cannot record the background and trioxane at the same time, so we strive to record them as close to each other as possible. From the mass spectrometer data, we observe that after the opening of the molecular shutter the signal in the beam decays after about 2 seconds. Additionally, we know it takes about 2-3 seconds for all molecules to completely disappear from the beam giving a clear background. With that knowledge, we have designed a data taking procedure that consists of six one-second scans with 2 seconds reset time, presented in Figure 5.21. We assume that the time between each of the scans is negligible. Two different channels are recorded simultaneously, the lock-in amplifier signal and the ethylene. If the presence of the ethylene path creates an etalon in the signal, each second is split into two halves, with

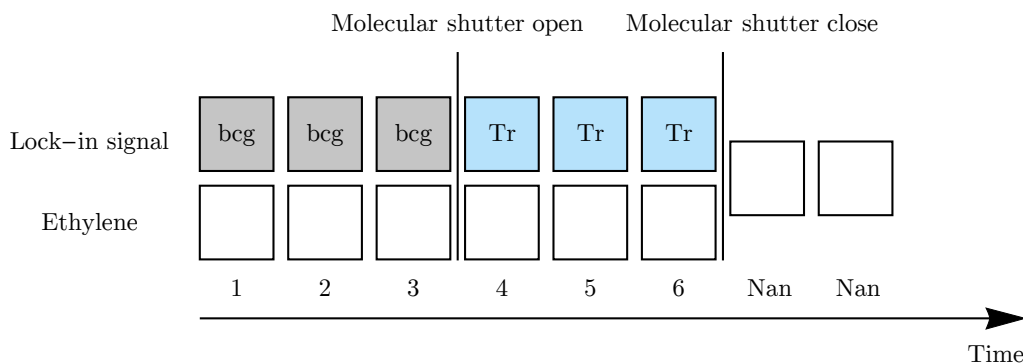


Figure 5.21: Overview of one data run. Each square signifies 1 second laser scan, with the lock-in amplifier and ethylene signal recorded simultaneously. Each data run consists of 6s in which data are taken and 2 seconds (signified as Nan) of the software reset time, after which a new data run starts. The molecular shutter opens letting the molecules (Tr) in after scan 3, and closes after scan 6 with the first 3 s being background (bcg).

both paths recorded for one half and only the lock-in amplifier signal for the other. In the majority of cases, including the experimental results shown in Section 5.6.3, the alignment doesn't produce any etaloning and shuttering of the paths is unnecessary. The molecular shutter opens letting the molecules in after the 3rd scan and closes after the 6th scan giving the molecules 5 seconds to be removed from the background. As a background we use scan 3, because it is completely free from molecules from the previous scan. The molecular signal is the highest in scans 4 and 5 and we can use either as the signal. A final result from one data run is obtained by subtracting a background scan from the signal scan.

To average the data we take about 1000 data runs, which takes about 2 hours to gather. As discussed previously each scan can be shifted in frequency, so we use the ethylene data from scan 3 from each data run to align all of the data in frequency.

Predicted absorption in the beam after optimisation

The methods outlined in the previous sections affect two aspects of detection of trioxane in the molecular beam: extraction of molecules to the beam and signal-to-noise-ratio. The combination of all the methods that improve the extraction increases the number of molecules in the beam by 2×10^2 . Another set of methods increases signal-to-noise ratio by either improving the signal (multipass, closer observation region) or decreasing the noise (averaging and high signal-to-noise ratio in the cold cell). These methods allow increasing the signal-to-noise ratio by 3 orders of magnitude. With these improvements, we should have enough sensitivity to take a WMS measurement of trioxane in the molecular beam.

5.6.3 Results

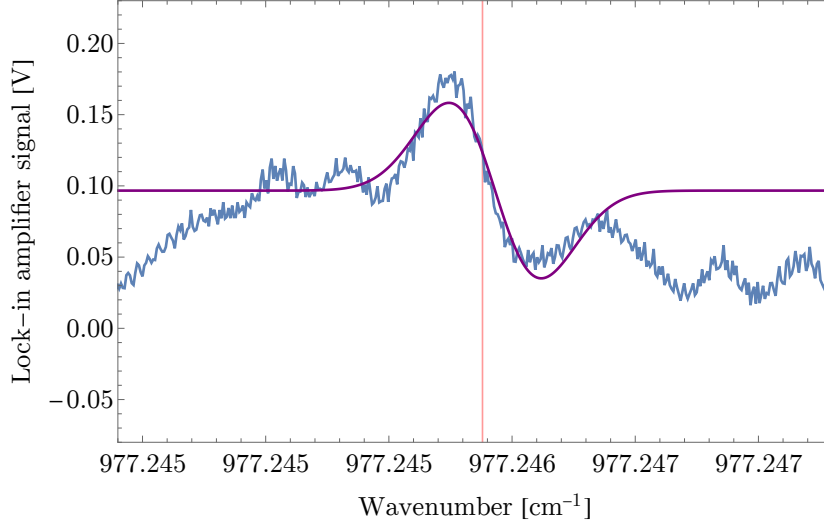
After implementing all the changes to the experimental setup, data acquisition, and data post-processing outlined in the previous section we have attempted observation of trioxane spectral features in the molecular beam with wavelength modulation spectroscopy.

Figure 5.22 presents data sets from two separate experimental runs, each consisting of an average of about 1000 data runs. Between each experimental run the system was warmed up to room temperature to refresh the charcoal cryosorbs and then cooled down. In both data sets we can see a feature dominating over a background at 977.2459 cm^{-1} , a place where we expect a $Q(16, 16)$, with data (blue) fitted with a first derivative of a Gaussian. For these data, we have used 7 sccm of helium flow and 6 sccm of trioxane flow. These values provide optimal extraction to the beam while ensuring that the heat load on the system is not too big and the temperatures are low enough for efficient cryopumping. The temperature of the cold cell while running was 8.9 K, with system pressure of 6×10^{-6} mbar.

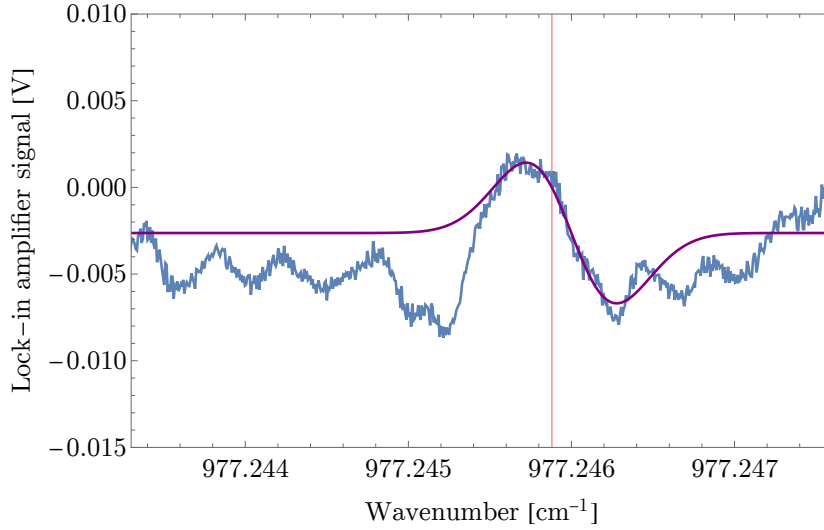
While we can see a similar feature in two separate experimental runs on two different days, with amplitude higher than the background, and at a wavenumber where we expect the transition to be, to be able to confirm with certainty that this constitutes observation of trioxane features in the molecular beam more measurements need to be conducted.

An observation of a different trioxane spectral line would confirm with certainty that we can observe trioxane features in a molecular beam. With the current setup, however, we have to use a trioxane transition that is close to an ethylene transition, for ensuring the frequency overlap. That severely limits the number of lines we can use for this type of measurement. With the experimental runs present in Figure 5.22 we were also limited by the strength of ethylene transitions. We were only able to record the strongest ethylene transition at 977.245 cm^{-1} at quite high J number. For the future iterations of the experiment this can be remedied by implementing a more robust setup for absolute frequency calibration, like a wavemeter or a different frequency reference. This will allow to probe more transitions, including lines closer to the start of the Q-branch, some an order of magnitude stronger than the $Q(16, 16)$ transition. A significant improvement would be to observe the trioxane lines without the need to average. The averaging procedure decreases the noise by about 30 times, but an increase in extraction, combined with observing a stronger trioxane transition, can produce a similar effect. Then the spectral features can be observed in a singular scan.

In Figure 5.22a data (blue) is fitted with a first derivative of a Gaussian, from which we can determine the width of the feature. The width of the observed feature corresponds to temperature of about 20 K. To increase amplitudes of spectral features and facilitate the observation, the data were taken with high modulation amplitude which contributes to artificial broadening of the spectral features. Therefore, this measurement should be taken as an upper limit to the temperature. A



(a) Data from experimental run on the 6th of January.



(b) Data from experimental run on the 8th of January.

Figure 5.22: Graphs showing results from two experimental runs of observing trioxane spectral features in a molecular beam with wavelength modulation spectroscopy. Each figure shows an average of 1000 data runs, with data in blue fitted with a first derivative of a Gaussian in purple. The first derivative is fitted to what we think is a $Q(16, 16)$ transition of trioxane, at 977.2459 cm^{-1} . The red line shows the expected position of the trioxane feature. The short period oscillations are attributed to the noise from lock-in and the electronic noise, the longer period oscillations are attributed to effects from etaloning and/or beam walking.

very significant step would be to observe the spectral feature with low modulation amplitude so the actual temperature of the molecules, and hence the transverse velocity spread, can be measured.

Chapter 6

Conclusions and outlook

6.1 Conclusions

This thesis reports the successful detection of buffer gas cooled trioxane molecules inside a cryogenically cooled cell, using mid-infrared wavelength modulation spectroscopy with a quantum cascade laser operating at 10 μm . The experimental system was based on a cryocooler with two cooling stages, one at 30 K, and one at 7 K. Cooling of molecules was done in the cold cell placed on the 7 K stage. On one of the faces of the cold cell we installed a beam exit aperture to allow molecules mixed with the buffer gas to leave the cell forming a molecular beam. In the cell the molecules were cooled via buffer gas cooling, in which a pre-cooled buffer gas mixes with hot molecules, to cool them via collisions. This method cools the molecules to a temperature close to that of the buffer gas. The molecules were delivered to the cell via a capillary thermally disconnected from the cell. We have measured spectra from the Q- and R-branches of the ν_5 vibrational mode of trioxane. Absolute frequency calibration was performed using the known spectral lines of ethylene, and the relative frequency scale between the ethylene lines was established using an etalon.

Two different buffer gases were used. First, we used helium buffer gas. This resulted in the successful production of cold molecules, with coldest measured temperature of 7.4 ± 0.3 K, which is consistent with the cold cell temperature of 7 K. The temperature of the cold cell is a few kelvin higher than in some other buffer gas cooling experiments, mainly because of the heat loads placed by the capillary and line-of-sight openings to the outside of the experiments.

Spectra of both Q- branch and part of the R-branch of the ν_5 vibrational mode were recorded inside the cold cell. The spectra were taken with enough resolution to resolve all the K lines for various transitions, apart from the $J < 7$ region of the Q-branch where the line density is very high. The width of the spectral features of the coldest molecules is about 6 MHz, which is so far the narrowest line observed in the buffer gas cell with a free-running laser. We have also recorded direct spectra of

trioxane inside of the cold cell and extracted the number density of the trioxane molecules inside the cell, equal to $n = 5 \times 10^{21} \text{ m}^{-3}$. These measurements show that complex molecules can be effectively cooled to low temperatures, which both allows for their precise spectroscopy and also might be a step towards direct laser cooling of polyatomic molecules, like demonstrated by the Harvard group on symmetric-top calcium monomethoxide, CaOCH_3 [133].

We recorded sub-Doppler features of a part of the trioxane Q-branch in the cold cell. The pump beam was formed by an accidental reflection of the laser from either the MCT detector window or one of the windows in the vacuum chamber or the cell. We attempted to repeat the measurement in a more controlled manner by arranging a pump-and-probe system. Performing sub-Doppler spectroscopy would allow to record the spectral features not limited by the Doppler broadening but by collisional broadening, which would result in the features with 0.2 MHz of full-width-half-maximum. We have not succeeded in repeating the measurement which can be attributed to the large laser's linewidth that effectively masks any feature that narrow. The laser's linewidth is worsening with time and it is possible that when the first scan was taken the laser was narrow enough and with little enough noise that such a measurement could be performed.

We extracted a trioxane beam from the buffer gas cell and detected this beam using a mass spectrometer placed about 280 mm downstream from the cell aperture. This detection method yielded a strong trioxane signal, and allowed us to optimize the molecular beam flux against the most critical parameters of the buffer gas source. We have observed that the extraction of trioxane to the beam is strongly influenced by the flow of buffer gas, with the extraction increasing with increase of the flow. The extraction also depends on the amount of trioxane delivered to the cold cell, and the higher the flow of trioxane the more molecules were observed in the beam. Finally we analysed how the extraction depends on the position of trioxane capillary in the cell. We have observed that the extraction peaks when the capillary is inserted about 13 mm into the cold cell, halfway between the PEI flange and the observation region. The size of the beam exit aperture seems to have no impact on the extraction of molecules of interest to the molecular beam. We also attempted state-selective detection of the trioxane beam by WMS absorption spectroscopy. Our first attempts to observe molecules in the beam by this method were not successful: we did not have enough trioxane number density in the beam for observable WMS signals. With helium we were limited by the system pressure, controlled by charcoal cryopumps. We were restricted in the size of the charcoal cryopumps and hence we could only use buffer gas flows up to 8 sccm.

To improve the conditions in the cell we used neon buffer gas. Neon has negligible vapour pressure below 15 K. This property of neon provides an essential advantage: any surface below 15 K acts as a cryopump. While using neon the temperature of the cold cell is kept at 17 K to prevent neon freezing inside the cell, whereas the cryosorbs are held at 7 K for efficient pumping. With more efficient neon cryopumping we can use flows up to 20 sccm. With the increase of the flow

more molecules of interest are entrained in the flow of buffer gas and the extraction of molecules increases. The increase of the flow should help with the extraction and observation of trioxane in the molecular beam. With neon buffer gas, the coldest molecules observed in the cell had a temperature of 21.3 ± 0.2 K. This is somewhat higher than the 17 K temperature of the cold stage, which we attribute to heating of the cell by the neon flow. The higher the flow, the more heat is deposited into the cell, and we have observed temperatures up to 30 K at high neon flows. Despite the good background pressure, even when running with 20 sccm of neon, the extraction to the beam consistently peaked at 8 sccm. Additionally, with neon, the lifetime of the system was very limited, with the beam exit aperture quickly clogging.

In Section 5.6.3 we have presented an attempt at WMS spectroscopy of the cold trioxane beam. We observe what is possibly a $Q(16,16)$ line in a Q-branch of trioxane at 977.2459 cm^{-1} . The buffer gas used for that measurement was helium, allowing for long averaging times. The measurement was done by averaging many scans which were post-processed to counteract any frequency shifts between scans. The signal from the molecular beam and the ethylene reference cell were recorded simultaneously. Measurement of the ethylene spectral feature established an absolute frequency reference and quantified the frequency shift between the scans. This limited the observation only to trioxane lines that are close to an ethylene feature (± 50 MHz from the centre). Because the trioxane number density in the beam was at least 10^5 smaller than in the cold cell several methods were used increase the signal-to-noise ratio in the beam, in addition to ensuring high extraction with optimised beam creation parameters. In the cold cell, the signal-to-noise ratio is about 100. We implemented a multi-pass arrangement to increase the interaction length of the laser with the beam, which provided a 3 times increase in the signal. Averaging resulted in 32 times decrease in the noise. Optimised extraction from the cold cell resulted in two orders of magnitude increase in the signal.

Similar features were observed on two different experimental runs, separated by warming the experiment up and cooling it down to refresh the cryosorbs. To confirm with certainty that this indeed constitutes a measurement of trioxane in the molecular beam we would need to observe another trioxane feature or to be able to observe this feature in a singular scan without averaging. While we don't think there is a possibility of more conclusive observation with the existing setup, the combination of successful WMS in the cell and possible observation of the beam means that the methods and reasoning presented in this thesis are suitable for cooling complex molecules. We also think that the molecular source, with the improvements outlined in the next section, can be used in the future experiment to detect parity violation in chiral molecules, presented in Section 1.6.

6.2 Outlook

This thesis presents a set of techniques that have proven useful for cooling complex molecules to low temperature, probing them by mid-infrared absorption spectroscopy, and forming a molecular beam. The work can be extended to other complex molecules, including to chiral molecules. Strong molecular signals were observed in the cold cell. Some possible trioxane features were observed in the molecular beam, and with an improvement to the cryogenic system temperature, and therefore pressure, there is a possibility of observing strong molecular signals in a molecular beam at a distance of 145 mm from the cold cell. With improvements to the laser system, especially laser linewidth, we could access much narrower spectral features and attempt to probe sub-MHz widths. These changes can also aid in reproducing the sub-Doppler measurements to explore the collisional environment both in the cell and in the beam.

6.2.1 Improvements to the setup

While we managed to optimize many parameters of the molecular beam creation, we can still identify several improvements that will contribute to increasing brightness of the molecular beam. The proposed changes will bring our setup in line with the buffer gas sources for atoms and small molecules. More still can be done to improve the signal-to-noise ratio and to improve resolution in the measurements. The changes proposed will lead to probing sub-MHz linewidths and will allow accessing weaker lines, both of which would be steps towards using this system to measure parity-violating effects in molecules.

Decreasing system temperatures

The biggest challenge with the experiment using helium buffer gas is the high background pressure of helium that limits the range of the flows used. Section 5.2.1 suggests that increasing the flow of helium can lead to increased extraction to the molecular beam. From that, it follows that reducing the pressure can lead to increased extraction. That can be done in two ways: either by increasing the size of charcoal cryosorbs present in the system or lowering the temperatures of existing ones such that the pumping is increased [134].

At present, the cryosorbs are at 7 K, which is close to their gas release temperature of 10 K. While running the experiment, the temperatures in the system are increased additionally by the heat load from the room temperature molecules and the flow of the buffer gas. Improving the base temperature will improve both cryopumping and extraction. This can be done by limiting the heat loads from the outside by decreasing the openings for the laser and capillary access, or by exchanging the cryocooler with a more powerful one.

The other way of improving cryopumping is to increase the surface area of the charcoal cryosorbs. The additional cryosorbs need to be close to the regions with a high concentration of helium. For example, when the outside of the present cryosorbs was covered with charcoal no improvement to the system pressure was observed. With limited space between the cold cell and the radiation shields, there are two possible improved cryosorbs setups. The first one is a tunnel surrounding the molecular beam from beam exit aperture to the observation region, covered in charcoal in the inside. The other idea is to have charcoal cryosorbs resembling hive frames in the Langstroth hive box [135]. In this design, plates covered with charcoal would be placed parallel to each other, with space in between to allow for distribution of the gas.

Solving clogging problems

One of the biggest challenges in working with neon as a buffer gas is clogging of the exit aperture. We believe clogging occurs because crystals of trioxane grow inside the exit aperture. This appears to happen more rapidly with neon. Flowing neon alone, without trioxane, does not cause clogging, and neither does flowing helium with trioxane, so either the neon itself or the elevated temperature needed for neon must help the trioxane crystals grow. When we first starting using neon buffer gas, the run time before clogging was limited to about 30 minutes. We improved this by first milling down the sides of the beam exit aperture to 0.5 mm and also by installing a bigger aperture. The first measure improved the lifetime of the source by a factor of 2, but more is still needed to run the system long enough for efficient averaging. The second measure, increasing the aperture size, leads to changes in buffer gas density inside a cell, so it involves a trade-off with the cooling length and time. There are two ideas for removing the molecular crystals that clog the aperture. The first one is purely mechanical and involves a little hammer that when activated would “crush” the trioxane crystals forming in the aperture. The other solution would be to construct the beam exit aperture from PEI to decrease thermal conductivity between the flange and the cell, and install a heating wire inside the aperture. The crystals’ bases would be melted off and trioxane removed.

These two methods should increase the lifetime of the system with neon as a buffer gas. If the problem of the trioxane extraction peaking at 8 sccm of neon flow will also be solved, for example by changing the cell geometry, then neon can be the preferred buffer gas for observation of complex molecules in the molecular beam.

Parallel buffer gas and trioxane inlets

The measurements of how different parameters increase extraction to the beam suggest that its efficiency is highly dependent on the entrainment of the species of interest in the buffer

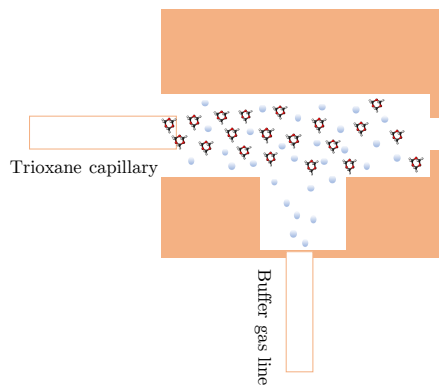
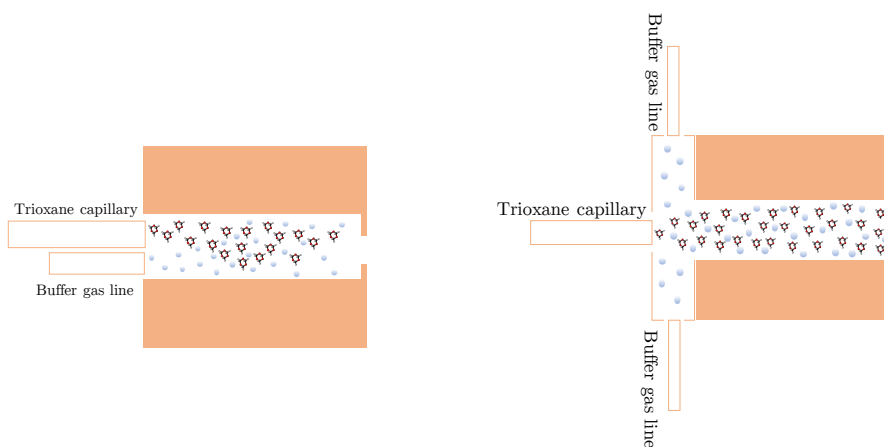


Figure 6.1: The current cold cell setup. The buffer gas inlet is positioned perpendicular to the trioxane capillary, 25 mm from the exit.

gas flow. The parameters that we have explored were the flow of the buffer gas and the position of the molecular capillary in the cell. We can expect that an additional parameter that affects the extraction to the buffer gas beam is the cell geometry. The impact of the cell geometry is hard to study theoretically as it involves modelling of gas flows, which is time consuming and computationally difficult. The usual approach to trying different cell geometries is trial and error of the cell in the cold system.



(a) Trioxane capillary and buffer gas inlet (b) A setup with an ante-room that creates a parallel to each other. buffer gas curtain.

Figure 6.2: Proposed cell setups that increase the number of molecules of interest entrained in the buffer gas beam.

So far the only cell geometry that we tried had the buffer gas and the molecular inlets at right angles to each other. The buffer gas inlet is in the middle of the cold cell, 25 mm from the trioxane capillary. In this scenario, the buffer gas first has to pick up molecules from close to the capillary

and subsequently change direction in order to exit the cell. This is illustrated in Figure 6.1. The measurements in Sections 5.2.2 and 5.3.1 show that when the capillary is closer to the buffer gas inlet the entrainment is easier and extraction to the buffer gas beam increases, therefore proving that molecules need to be “helped” to be efficiently removed from the cell. We can, however, facilitate the entrainment by installing the buffer gas beam inlet next to, or in a plane parallel to the trioxane capillary, as shown in Figure 6.2a. The molecules of interest will then be entrained almost automatically. To implement it in the existing buffer gas setup, we have to solve a few technical challenges. The trioxane capillary enters the cell through a PEI flange. The size of the opening in the flange matches the opening in the side of the cold cell. The opening in the PEI flange is slightly bigger than the capillary, and there is no space for a buffer gas pipe in this face of the cell. To be able to install a buffer gas inlet on this face of the cell the size of the hole can be increased or the trioxane capillary has to be made smaller. We have to make sure that the trioxane capillary, kept at 0°C, will not cause a heating of the buffer gas.

Another setup that can possibly increase the amount of trioxane entrained in the beam, is a buffer gas curtain next to the molecular capillary [136]. This is presented in Figure 6.2b. In the curtain setup, the cold cell has an ante-room area with two or more buffer gas beam inlets. The ante-room has an aperture much larger than the beam exit aperture but smaller than the side of the cell. The walls between the cold cell and the ante-room are used to direct the buffer gas beam flow towards the trioxane inlet. In this type of setup the buffer gas inlets can be perpendicular to the trioxane capillary but the walls in the ante-room direct the flow in such a way that it effectively mixes with trioxane very close to the trioxane capillary.

Laser locking

A substantial upgrade to the experiment would be locking the laser, which has the potential to solve two issues that limit the spectroscopic resolution of the system.

Firstly, the laser shifts in frequency in the duration of the scan. When scanning a single trioxane feature, we have observed that the scan start and therefore the laser frequency can shift by as much as 100 MHz. This is about 14 times the typical linewidth of a trioxane spectral feature. We are counteracting this with data post-processing but a locked laser with an adjustable lock-frequency would greatly simplify both data taking and analysis.

Secondly, the measurements of the laser linewidth have shown that the quantum cascade laser has quite a large linewidth at the timescales that are used to scan through the trioxane spectral feature. Additionally, the lack of observation of sub-Doppler spectral features, that we have calculated to be limited by collisional broadening and have a width of 0.2 MHz, suggests that to progress with measurement of narrow spectral features we have to decrease the laser’s linewidth. A few groups

have demonstrated laser locking of a QCL with several methods, some of which can be realised in our system. For example, QCLs have been phase-locked to a stabilised CO₂ laser [137] and to a tunable microcavity [138]. They have also been locked to an ultra-stable mid-infrared reference via a frequency comb and an optical link [108].

Another method that can be applied in our system is fixing the frequency of the laser to an ethylene reference. However, this would restrict us to observing parts of the spectrum that are close to an ethylene transition. Using Doppler limited absorption, the frequency of the laser could be fixed with a precision of about 1 MHz, but using sub-Doppler techniques much higher precision could be obtained.

The first step towards decreasing the linewidth of a QCL is to phase-lock it to a cavity. The group at the University of Bonn has reported the creation of a high-finesse cavity for mid-infrared radiation at 10.6 μm , with mirrors with $R \geq 99.5\%$. With a cavity of length 1.33 m they have reached a finesse of 600 and the full-width-half-maximum of a mode was reported to be 180 kHz [139]. By implementing a similar setup, the laser linewidth could be reduced by an order of magnitude.

6.2.2 Chiral molecules

We have proven that we can successfully cool and perform mid-infrared WMS spectroscopy of a relatively large molecule - one containing 12 atoms. There are very few other examples of cooling such large molecules, and no other examples of mid-infrared spectroscopy of buffer-gas cooled molecules, making this work quite unique. We have also presented molecular beam of these molecules, clearly detected using a mass spectrometer, and probably also by WMS spectroscopy. Now, to progress further in our aim to measure the effects of parity violation in chiral molecules we have to cool and create a beam of chiral molecules. There are several requirements that a molecule for the measurement of a parity-violating effect in a buffer gas beam must fulfil.

The creation of a chiral molecule, especially in an enantiopure form is not a simple process, and the molecule has to be produced before being used in the experiment. Because we have to know precisely what molecule is delivered to the cold cell, we have to use a method of capillary filling, already established in this system. The capillary filling requires molecules with a substantial vapour pressure of few millibars at room temperature. Let's assume that for successful observation of the molecular beam we are running the experiment with 4 sccm of trioxane for 1000 s. We can convert that to the number of molecules in grams we need to run the experiments. For trioxane this corresponds to 0.26 g per experimental run. We can repeat this calculation for an example of a synthesised chiral molecule that is a suitable candidate for a measurement of a PV effect [79]. In this we assume that the strength of the transitions in the new chiral molecule will be similar to that of trioxane. This candidate is a chiral oxorhenium complex bearing enantiopure 2- mercaptocyclohexan-

1-ol (mass of 332 amu), synthesized by the group at Institut des Sciences Chimiques de Rennes. The frequency shifts originating from the parity-violating effects for this molecule have been calculated to be a few hundred millihertz. The molecule has a few vibrational bands in the mid-infrared, for example, a characteristic Re=O stretching band at 1030 cm^{-1} , with a frequency shift from the PV violating effect of 0.478 Hz. The group have prepared 134 mg of both the right- and left-handed molecule. We have no information about its vapour pressure. For a successful detection of the beam of this chiral molecule, assuming running with 4 sccm of the chiral molecule flow, averaging for 1000 s, we would need about a gram of this substance.

Additionally we can consider a chiral molecule that can be laser cooled. Following the reasoning in a publication from the Harvard group of J.Doyle [49] we can see that in principle a chiral molecule of a form of MOR (alkaline earth monoalkoxide free radicals) can be created, with a radical part having the chiral centre. The combination of buffer gas cooling and direct laser cooling of these molecules would be a powerful way to make a cold, high-flux beam suitable for measuring the parity violating energy difference between chiral enantiomers.

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List of Figures

1.1	A view of the buffer gas cell with the molecule and buffer gas (green disks) inlets, demonstrating buffer gas cooling in the cold cell and molecules extracted to the buffer gas beam.	14
1.2	A cut-through of a buffer gas cell with different ways of introducing molecules into the cell demonstrated. a) ablation b) beam loading c) capillary filling. Reproduced with permissions from [51].	14
1.3	Image showing the direction of electrons observed in β -decay of the ^{60}Co nucleus, and its mirror reflection. The electrons are emitted preferentially in one direction, which violates parity symmetry.	17
1.4	JILA Cs experimental apparatus showing a molecular beam passing through interaction and detection regions. The spin polarisation of the molecules is defined in the interaction region where B is along the z -axis and E is along the x -axis. The handedness of the region is changed by flipping each of the field axes. Reproduced with permissions from [73].	18
1.5	Frequency comb schematics.	24
2.1	Components in the vacuum and cryogenic systems. The parts are named in Table 2.1.	28
2.2	Full view and a half projection of the cold cell.	31
2.3	Cold cell adjusted for the neon buffer gas. The cell is thermally disconnected from the 7 K plate with steel washers.	36
2.4	Schematic of the laser system in the experimental setup showing the components of the WMS system and the paths used for absolute and relative frequency reference. The outputs of the MCT, and two photodiodes are marked respectively with numbers 1,2 and 3, and their inputs are marked with the same number on the NI card and oscilloscope.	37

2.5	Laser output wavenumber as a function of supplied current and diode temperature. Graph reproduced from [114].	39
2.6	Laser output power as a function of supplied current and diode temperature. Graph reproduced from [114].	40
2.7	Ethylene spectrum in the range between 978 and 979 cm^{-1} . The vertical pink lines show central frequencies of three trioxane transitions $R(3, K)$ at 978.23 cm^{-1} , $R(4, K)$ at 978.58 cm^{-1} and $R(5, K)$ at 978.93 cm^{-1} . The notation used here will be explained in the next chapter. The ethylene lines are used for absolute frequency calibration of the trioxane spectra.	41
2.8	Scans of etalon in time and in frequency demonstrating relative frequency calibration using a Ge etalon with a free spectral range of 490 MHz.	42
2.9	Calibration of the drift of the laser using the gradient of the spectral feature. The laser frequency is set to the centre of the spectral feature where the lock-in amplifier signal is equal to zero. Any shift of the laser frequency will move it away from the central frequency of the spectral feature (i.e. the zero-crossing) causing non-zero reading. The linear fit shown in red can be used to convert recorded voltage to frequency shift of the laser.	43
2.10	Histogram of the laser frequency shifts within 1 s.	43
2.11	Average laser linewidths for different timescales. The x -axis is on a logarithmic scale. The errors are taken as the standard deviation of a number of measurements for a given time of acquisition.	44
3.1	Molecule of 1,3,5 Trioxane [116].	47
3.2	Trioxane energy levels between $J = 16$ and $J = 20$ for the ground vibrational state of the molecule. States with $K = 0$ are highlighted.	49
3.3	Energy level diagram of trioxane for J between 16 and 20 with $K = 16$ and 17. Transitions between levels with $K = 16$ and 17 are denoted respectively by green and red arrows. The labels “ground” and “excited” correspond to zero and one quantum of vibrational energy in this mode.	50
3.4	Spectrum of the ν_5 vibrational mode of trioxane at 7 K. The height of the lines is taken as the fraction of the population in the state.	55
3.5	Fraction of total population for various lines of Q-branch of ν_5 vibrational line at different temperatures.	55
4.1	Temperature of trioxane vs number of collisions with helium buffer gas. The molecules are cooled from room temperature 293 K by thermalising with the buffer gas at 7 K.	59

4.2	Temperature of trioxane vs number of collisions in neon buffer gas. The initial temperature of trioxane was 293 K and the temperature of the neon buffer gas is 17 K. .	61
4.3	Noise spectrum (blue curve) of an electronic device, showing the initial signal and the modulated signal moved to the higher frequency.	63
4.4	Internal block diagram of lock-in amplifier.	64
4.5	The lock-in response to change in the input signal. In the frequency domain the modulation amplitude determines the frequency range of the lock-in amplifier demodulation. The output signal is proportional to the slope of the input signal. . . .	65
4.6	Circuit diagram of a RC filter.	66
4.7	Example of a wavelength modulation spectroscopy spectrum.	67
4.8	Inferred temperature of the molecules with the increasing WMS modulation amplitude. The error in the data is taken as the standard error of the fit.	67
4.9	Amplitude and width of trioxane spectral features as a function of the WMS time constant. a) Width of the line versus the time constant b) Amplitude of the line vs time constant. The error is taken as the standard error of the fit to the data.	68
4.10	Changes in width and amplitude of trioxane spectral line measured in 1s scan with change in WMS modulation frequency. The error in the data is taken as the standard error of the fit.	68
4.11	Wavelength modulation spectroscopy signal and reference out of phase (orange) and in-phase (blue). The molecular signal is visible as the first derivative of the Gaussian function.	69
4.12	Q-branch WMS spectrum (blue) with an overlaid calculated spectra at 15 K (purple).	70
4.13	Q-branch WMS spectrum (blue) with assigned transition labels in the form of (J, K) . The red and green markers correspond to the arrows on Figure 3.3. The positions of the markers are calculated theoretically. The line $Q(20, 17)$ can barely be resolved.	71
4.14	Doppler-broadened Q-branch pGopher spectrum covering the same frequency range as Figure 4.13 with assigned transition labels in the form of (J, K) . The spectrum is produced for a temperature of 15 K. The red and green markers correspond to the arrows in Figure 3.3. The positions of the markers are calculated theoretically. . . .	71
4.15	Theoretical calculation of R-branch spectra with marked spectral features.	72
4.16	WMS spectrum of $R(0, K)$ transition (blue) fitted with the derivative of a Gaussian function (orange).	73
4.17	WMS spectrum of $R(1, K)$ transition (blue) fitted with a sum of two Gaussian-derivative functions (orange).	73

4.18	WMS spectrum of $R(2, K)$ transition (blue) fitted with a sum of three Gaussian-derivative functions (orange).	74
4.19	WMS spectrum of $R(3, K)$ transition (blue) fitted with a sum of four Gaussian-derivative functions (orange).	74
4.20	Amplitudes of the $R(3, 0)$ transition versus the laser power. The errors are root mean square errors of the fit. The data are fitted with Equation 4.19.	76
4.21	Width of the $Q(15, 15)$ transition versus power of the laser (blue), where 100% corresponds to 1.1 mW. The data are fitted with a linear fit, shown in purple. Errors are taken from the standard error of the fit.	77
4.22	Direct absorption of trioxane in the Q-branch between 977.235 cm^{-1} and 977.255 cm^{-1} . Data are shown in purple and the background is in blue. Chosen spectral features were marked with labels of the form $\{J, K\}$	78
4.23	Natural logarithm of transmittance of the $Q(16, 15)$ spectral feature. Data are shown in blue and the Gaussian fit is in purple.	79
4.24	The energy level splitting caused by the interaction of the system with light.	80
4.25	Spectrum for two-level system interacting with pump and probe fields for varying probe field detuning. The real part of the Equation 4.51 is plotted, assuming the exact resonance $\Delta = 0$ for varying strengths of the driving field Ω	84
4.26	Spectrum of the velocity averaged two-level system interacting with pump and probe fields, for probe field at the same frequency as the pump. In Equation 4.56, the value of $\frac{m}{k_B T}$ was chosen to be 10.	85
4.27	Plot a) shows the experimental spectrum of trioxane between 977.204 cm^{-1} to 977.227 cm^{-1} , with the inset zoomed in on a singular spectral feature. The red fit in the inset is the sum of two separate Gaussian-derivative functions, one to represent the Doppler broadened part and another for the sub-Doppler part. We can notice additional structure in the middle of the transition which is due to the sub-Doppler feature. The plot b) shows Doppler-broadened experimental measurement of trioxane for the same span of wavenumber.	86
4.28	Two experimental approaches to measuring the sub-Doppler spectrum of trioxane in the cold cell. a) Setup with the pump beam created by retro-reflecting the probe beam after passing through the cold cell. b) Setup with the pump beam created by separating it from the probe beam with a 70:30 beam splitter.	88
5.1	Forward velocity, transverse velocity spread and the beam divergence illustrated for the molecular beam.	92

5.2	WMS spectrum of $Q(2, K)$ (blue) fitted with a sum of three derivatives of Gaussian functions (purple). Width and amplitude of the $K0$ line are reported.	96
5.3	Dependence of the properties of the $K0$ line on the helium flow into the cell. The data (blue) is fitted with a linear function (purple). a) Width of the $K0$ line vs helium flow into the cell b) Amplitude of the $K0$ line vs helium flow into the cell. The error bars are obtained from the root mean square error of the fit.	97
5.4	Amount of trioxane in the beam vs the helium flow. The data for each flow was recorded over a period of time (30 s) and the mean is taken as the data point. Standard deviation is taken as an error.	97
5.5	View of the cold cell with the movement of capillary shown. The end of the trioxane delivery line enters through an aperture in the PEI attachment and can move along the x -axis, with the cell wall being taken as $x=0$. The observation region is the yellow circle in the middle of the cell.	98
5.6	Dependence of the properties of the $K0$ line on the capillary position in the cell for the helium buffer gas. a) Width of the $K0$ line vs trioxane flow into the cell b) Amplitude of the $K0$ line vs trioxane flow into the cell. The error bars are taken as the root mean square error of the fit.	98
5.7	Dependence of the beam extraction on the capillary position inside the cell for the helium buffer gas. The data from the mass spectrometer for each capillary position is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data is then taken as an error. The large error registered at $x = -0.6$ mm is due to short (< 5 s) 20-times increase in trioxane c/s detected by the mass spectrometer, which we attribute to an explosion of trioxane.	99
5.8	Dependence of the properties of the $K0$ line on the trioxane flow into the cell. The data (blue) is fitted with a linear function (purple). a) Width of the $K0$ line vs trioxane flow into the cell b) Amplitude of the $K0$ line vs trioxane flow into the cell. The error is taken as the root mean square error of the fit.	100
5.9	Dependence of the beam extraction on the trioxane flow into the cell. The data for each flow was recorded over a period of time (30 s) and the mean is taken as the data point. Standard deviation is taken as an error.	101
5.10	WMS spectrum of the $R(3, K)$ transition (blue) in trioxane, fitted with a sum of five derivatives of Gaussian functions (pink). $K0$ and $K1$ cannot be resolved in the spectrum. For all data sets the amplitude and the width of the $K2$ line is reported. .	102

5.11	Dependence of the trioxane spectral feature properties on the neon flow into the cell. The data are shown in blue and the purple lines are linear fits. The error is taken as the root mean square error of the fit.	103
5.12	Amount of trioxane in the molecular beam versus the neon flow. The data from the mass spectrometer for each flow is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data is then taken as an error.	104
5.13	Dependence of the trioxane spectral feature properties on the trioxane flow into the cell. The data are shown in blue and the purple line is a straight line fit. The error bars are the errors on the fit parameters.	104
5.14	Amount of trioxane in the molecular beam versus the trioxane flow into the cell. The signal at the mass spectrometer for each trioxane flow is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data are then taken as an error.	105
5.15	Dependence of the trioxane spectral feature amplitude on the capillary position in the cell. The x -axis signifies how far the capillary reaches into the cell (with $x=0$ being the cell wall). The error bars are the errors on the fit parameters.	106
5.16	Amount of trioxane in the molecular beam versus the trioxane capillary position in the cold cell. The data from the mass spectrometer for each position is recorded for a minute and the mean is taken as the trioxane counts in the beam. Standard deviation of the data is then taken as an error.	106
5.17	Change of amount of trioxane extracted to the molecular beam and trioxane spectral feature amplitude with time.	107
5.18	Extraction of trioxane molecules to the beam for different aperture wall thickness. The data for each flow was recorded over a minute and the mean is taken as the data point. Standard deviation is taken as an error.	108
5.19	Mass spectrometer scan for masses from 40 to 350 amu. Lower masses were cut off to prevent overwhelming the mass spectrometer with neon. Peaks are present at 43 and 89 amu, corresponding respectively to CO_2 and trioxane. The y -axis is on a logarithmic scale. No clusters are observed.	110
5.20	Multipass positions of the laser (red crosses) on the observation region window. The multipass is vertical, and the laser enters in the bottom of the window and leaves on the top. The multipass is installed in the observation region 145 mm from the cold cell, part 18 in Figure 2.1.	112

- 5.21 Overview of one data run. Each square signifies 1 second laser scan, with the lock-in amplifier and ethylene signal recorded simultaneously. Each data run consists of 6s in which data are taken and 2 seconds (signified as Nan) of the software reset time, after which a new data run starts. The molecular shutter opens letting the molecules (Tr) in after scan 3, and closes after scan 6 with the first 3 s being background (bcg). 115
- 5.22 Graphs showing results from two experimental runs of observing trioxane spectral features in a molecular beam with wavelength modulation spectroscopy. Each figure shows an average of 1000 data runs, with data in blue fitted with a first derivative of a Gaussian in purple. The first derivative is fitted to what we think is a $Q(16,16)$ transition of trioxane, at 977.2459 cm^{-1} . The red line shows the expected position of the trioxane feature. The short period oscillations are attributed to the noise from lock-in and the electronic noise, the longer period oscillations are attributed to effects from etaloning and/or beam walking. 117
- 6.1 The current cold cell setup. The buffer gas inlet is positioned perpendicular to the trioxane capillary, 25 mm from the exit. 123
- 6.2 Proposed cell setups that increase the number of molecules of interest entrained in the buffer gas beam. 123

List of Tables

2.1	Components of the vacuum and the cold system, as shown in Figure 2.1.	29
4.1	Summary of properties of buffer gas cooling with helium for different aperture sizes and flows.	60
4.2	Summary of properties of buffer gas cooling with neon for different aperture sizes and flows.	62
5.1	Summary of properties of buffer gas beam creation with helium for different aperture sizes and flows.	94
5.2	Summary of properties of buffer gas beam creation with neon for different aperture sizes and flows.	95
5.3	Possible clustering configurations. For clustering with neon and helium only clusters involving relatively small numbers of atoms are included as those are deemed most likely to form and survive in the mass spectrometer.	109