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Progress towards laser cooling of BH molecules

by
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Declaration of Authorship

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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The body of work which this thesis describes was undertaken at the Centre for Cold Matter at Imperial College London under the supervision of Drs Michael Tarbutt and Ben Sauer. The experimental work was carried out with two postdoctoral research associates, Drs Stefan Truppe and Richard Hendricks. The work in the second chapter was undertaken with the assistance of Stefan in building the experimental apparatus and taking data. Richard managed the quantitative analysis of the data. The work in the fourth chapter was also accomplished with the assistance of Richard in setting up the experimental apparatus.

Abstract

This thesis investigates the suitability of BH molecules for laser cooling and describes progress towards the laser cooling of this molecule. We produce a molecular beam of BH and measure the branching ratios for the excited electronic state, $A^1\Pi(v'=0)$, to decay to the various vibrational states of the ground electronic state, $X^1\Sigma$. We verify that the branching ratio for the spin-forbidden transition to an intermediate triplet state is inconsequentialy small. We measure the frequency of the lowest rotational transition of the X state, and the hyperfine structure in the relevant levels of both the X and A states, and determine the nuclear electric quadrupole and magnetic dipole coupling constants. We use a semiclassical model of the molecule-light interaction to investigate the expected cycling behaviour on the main cooling transition using light with modulated polarisation. The results of the model are compared with the effect of modulating the polarisation experimentally using an electro-optic modulator. In order to repump the population that leaks into the first vibrationally excited state, we have designed, built and tested a suitable repump laser and have demonstrated that we can drive the repump transition. We have also designed a Zeeman slower for slowing molecules to low velocity so that they can be trapped. Our results show that a relatively simple laser cooling scheme can be used to cool, slow and trap BH molecules.

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Chapter 1

Introduction

1.1 Introduction

In this thesis I have described our efforts to engineer an apparatus which produces diatomic BH molecules in their ground quantum mechanical state at velocities suitable for trapping. This work constitutes original research but relies on a number of innovations produced by the effort of others in the scientific community. In this first chapter I would like to discuss the recent interest in producing cold dipolar molecules and introduce the techniques upon which the field relies.

The motivation for studies of ultracold molecular vapours can be divided into those which aim: (i) to develop tools for precise measurement of fundamental physical constants, (ii) to simulate the dynamics of systems in which interactions are dominated by quantum mechanical interference effects and (iii) to process information with an architecture which exploits phenomena driven by the same effects. This division highlights that some experiments are motivated primarily by testing the standard model of particle physics (i), while others focus on developing new tools for problem solving (ii & iii).

The measurement of the fundamental physical constants, such as the fine-structure constant, α , can be achieved directly by probing atomic transitions in the lab. In an ultracold gas there is a high degree of control over the quantum state of the

population. Measurements on atomic or molecular species in this form benefit from the increased population which can be interrogated as each molecule improves the statistics of the outcome. Atomic and molecular species are chosen for a particular measurement based on the available transitions and the ability to reduce the impact of systematic effects.

The detailed description of certain systems of interacting particles in the solid state requires the inclusion of interference effects between their wavefunctions, when the wavefunction of the system is no longer separable into a product of the wavefunctions of the individual particles. This is the case in systems described by the Ising model. Dipolar molecules can be used to model such systems by engineering an isomorphic system than can be studied in a controllable way. An example of this is the use of an array of interacting dipolar molecules with non-zero spin angular momentum to simulate a spin-lattice model [1].

Further developing the idea of simulation, processing information using a system which exploits quantum dynamics promises the opportunity to change the class of problems which are efficiently computable. DeMille et al. [2] have suggested a design which would allow information processing in an array of trapped molecules occupying a well defined state. The information can be stored in a qubit specified by the state of the molecular dipole in an external electric field. The applied electric field varies in strength to allow the single-state addressing of qubits by a microwave field. The dipole-dipole interaction between adjacent molecules is used to engineer a two qubit controlled logical operation which, together with single qubit unitary operations, is required for information processing.

These motivations have driven a number of different approaches to molecule cooling, each of which has its own benefits and challenges.

1.2 Methods for producing ultracold molecules

The methods used to produce, trap and detect ultracold molecular vapours have been developed from those which have found success in studies with atoms. The first ultracold atomic vapours were isolated in the early 1980s and have been used since

then as an experimental tool in studies which have various aims. Trapped ultracold atoms have been used to improve the precision of atomic clocks and to study the dynamics of systems which would be otherwise impossible to model. In some of these studies, particularly those which make a precise measurement using the interaction between the atomic system and an optical field, the macroscopic state of the vapour is unimportant. In these cases, each atom is assumed to interact with the controlling fields independently of the others, and the precision of the measurement is aided by the large number of experiments which are being run in parallel. In other studies, the interaction between atoms is important and the experiment would be impossible without an extremely well-defined state for the ensemble. However, all of the studies of ultracold atoms rely on the ability to precisely determine the state of each atom across the ensemble. This is facilitated by laser-generated optical fields with good spatial and temporal coherence. For a nice overview of the history of ultracold atom experiments, see Phillips's Nobel lecture [3]. The rest of this section will assume some familiarity with methods used with ultracold atoms.

From the successes in the field of ultracold atoms, an interest in producing molecular vapours developed fairly naturally. Some of the first studies which looked at the production of ultracold molecules were interested in molecule formation as a loss mechanism in atom traps. These early studies focussed on the production of molecules from atoms which have already been cooled and are usually referred to as indirect production methods. They have been successful in producing samples of cold, trapped, ground-state molecules where the molecules' constituent atoms have already been cooled. This requirement that the atoms be already cooled places a restriction on the molecular species that can be produced. Here we encounter one of the difficulties with cooling molecules: to facilitate a number of experiments of different types, we would like to have access to a variety of different molecules, but to control a molecule well requires an approach which is targeted to the properties of that molecule. The result is that we have a number of different methods which have been tried, although the most successful have tended to be the most inflexible. In the following sections we will look at some of the most prominent studies in the field, divided between the indirect methods, which use cooled atoms to form cooled molecules, and the direct methods, which cool molecular species directly.

Before we begin we should make a note of the important characteristics of any cooling experiment. Many studies report the number, or number density of molecules, and their temperature. We should be careful to specify exactly what is meant by the temperature, as a gas of non-interacting molecules cannot be assumed to be in thermal equilibrium. In most cases, the temperature measurement is performed by allowing a trapped cloud of molecules to expand, without trapping fields, and then a measurement is made of their spatial distribution. This measurement reveals the distribution of velocities (usually in one dimension) and can be equated to the temperature of an ideal gas in thermodynamic equilibrium through the Maxwell-Boltzmann distribution. The number of molecules is rather harder to measure accurately, and normally relies on a measurement of the molecules' fluorescence or absorption following illumination with a laser beam tuned to a molecular transition. In the case of fluorescence measurement, the absolute efficiency of the detection can be difficult to calibrate, leading to large uncertainty in the determination of the molecule number.

The following sections review some of the literature in the field. An editorial article in the European Physical Journal D, [4], has some more information and a more detailed review was carried out in 2009 by Carr, DeMille, Krems and Ye [5]. Although Stark deceleration [6] can be used to reduce the velocity of a molecule, and has been very successful in a number of applications, it does not have the effect of reducing velocity distribution which characterises cooling. If we were to start from a cold source of molecules and use a Stark decelerator, we would still need to include an extra step in order to reduce the entropy of the ensemble to ultracold temperatures. For a more complete description of Stark deceleration it is better to consult [7].

1.2.1 Photoassociation

Photoassociation is the name given to the formation of a bound molecular state from two atoms, initially in low-lying states, in the presence of an optical field, or photoassociation laser. The frequency of the photoassociation laser is tuned so that it matches the excitation between the initial state of the system, corresponding to

two free atoms, and the bound molecular state. The resulting molecule is usually in a highly excited vibrational state, where the expected separation of the nuclei corresponds to the separation of the free atoms that formed it. The molecules can then be transferred to a lower-lying vibrational state through spontaneous or stimulated emission.

The study of photoassociation began with interest in its behaviour as a loss mechanism in magneto-optical traps for cold atoms and as a tool for the spectroscopy of excited states of bound molecules. In an early study, [8], 10 mK Na atoms were transferred to a bound molecular state with a single laser frequency, then decaying from the excited state by spontaneous emission. Other early studies, e.g. [9] with Rb, focus on the spectrum obtained by scanning the frequency of the photoassociation laser and observing the variation in fluorescence from the trap. When atomic population is transferred to the molecular state there is a decrease in the fluorescence from the trapped atoms. Later studies, [10] consider the possibility of using the photoassociation process as the starting point for generating cold molecules. In [10] they discuss trapping the molecules using the optical dipole force which results when an optical field is detuned from a molecular transition.

The development of the photoassociative method of molecule production continued with interest in schemes which could be applied to the alkali metals. A description of a scheme for the production of Cs_2 [11] was followed by two realisations [12, 13], and trapping of molecular caesium with the parent atomic Cs, [14]. Further work led to trapping of K_2 molecules, [15], and Rb_2 , [16]. Eventually, the work has moved on from homonuclear combinations of alkali atoms to heteronuclear, with KRb [17], RbCs [18–20], LiCs [21] and others.

Molecules, once produced, can be transferred to the lowest-lying state through stimulated Raman adiabatic passage (STIRAP) [22]. In this process the molecular state is coupled through an intermediate state and two optical fields. The intensities of the optical fields are varied such that the molecular population can be coupled to the final state without significant population ever entering the intermediate state. The process is coherent and highly efficient, and it has been used with great success

to produce ultracold ground-state molecules. The difficulties with the photoassociative technique are that the rate at which molecules are produced can be relatively low and that the molecules tend to couple to high-lying vibrational states which may then dissociate.

1.2.2 Magnetoassociation

In addition to methods which associate molecules from atoms with a transition stimulated by an optical field alone, there have been many examples of schemes which use a time-varying magnetic field to couple unbound atoms to bound molecular states. These techniques have found great success in coherently transferring laser-cooled atomic species to molecules resulting in excellent samples of high density and low temperature.

The interaction of ultracold atoms in collision is described by quantum mechanical scattering theory, in which the contribution to the scattering wavefunction due to the total angular momentum of the system is often separated into components of differing angular momenta. This results in components we call ‘s-wave’, ‘p-wave’ etc. scattering. At low temperatures, where the atoms are moving very slowly, most scattering processes can be approximated as being wholly due to the s-wave-component. The scattering process reduces wholly to s-wave scattering because there is a centrifugal barrier to all other partial waves and there is not enough energy to overcome the barrier at ultracold temperatures. As a result, the scattering wavefunction can feature resonances in which the value of the s-wave scattering length becomes very large. At these resonant conditions the atomic population is coupled to a bound molecular state.

The scattering conditions can be altered by the introduction of a magnetic field, which allows molecules to be produced from atoms in a coherent process. This is the basic technique used in magnetoassociation. The molecules can then be transferred to the ground state through STIRAP. If this process is used on an already cooled atomic vapour, then the resulting molecules will have an extremely high phase-space density as the steps all transfer the population coherently.

There have been many demonstrations of ultracold molecule production by Feshbach resonance using laser-cooled alkali atoms, including: rubidium-85 condensates [23], sodium [24], lithium-6 [25] and potassium-40 [26, 27]. In these studies the molecules are produced by a swept magnetic field, in the case of [25] and [26] the association is also dissociated by reversing the sweep. The studies measure the number of molecules produced using several different techniques, [23] observes loss of atoms from the initial condensate, while [26] directly detects the molecules by measuring the radiofrequency photodissociation spectra. The procedure can be far more efficient than a photoassociative scheme. In [25] the conversion efficiency from atoms to molecules is 50%, and can result in around 10^5 molecules being produced at temperatures around 600 nK. Further studies have demonstrated the ability to transfer molecules to the lowest lying state through STIRAP [28, 29]. These experiments also demonstrated trapping of the molecules using optical lattices.

Experiments have progressed from homonuclear molecules to the formation of heteronuclear species from co-trapped atoms, which offer further potential due to their larger electric dipole moments. RbCs [30, 31] has been produced with up to 90% conversion efficiency and transferred to the ground-state through STIRAP. KRb has been produced and trapped in an optical lattice [32]. All of these developments make magnetoassociation a powerful tool in the field of ultracold molecules.

1.2.3 Buffer-gas cooling

The most general method of cooling which has been proposed to date is probably buffer-gas cooling [33], in which a cell is filled with helium gas at pressures of around 10^{-2} mbar and cooled to a cryogenic temperature. The molecules to be cooled are introduced into the cell, by laser ablation of a precursor target or through a warm capillary. The collisions between the cryogenic buffer gas and the molecules reduce their temperature. The cooled molecules can then be extracted from the cell through an aperture in order to produce an intense, slow-moving beam of molecules. Alternatively, the cell is placed in a strong magnetic trap and the buffer gas is pumped out following cooling to prevent inelastic collisions.

Buffer-gas cooling can be applied to many different molecular species, including those which are chemically reactive, but its generality is offset by the limited degree of control of the state of the molecules output. If the source brightness becomes sufficiently high then selectively trapping the molecules which are in the ground state is a viable option. The first successes trapping CaH molecules from a buffer gas source were reported in [34]. Further studies have been concerned with characterising the dynamics of the molecular beam, [35], and guiding the molecules once they have left the cell [36]. In [37] a buffer-gas has been used to cool CrH and MnH, which were then magnetically trapped for up to 180 ms. CaH is cooled in a two-stage buffer-gas cell in [38], where the beam dynamics, thermalisation and slowing are studied. The resulting beams can be very bright, in [39] 10^{11} ThO molecules are produced in a single electronic, vibrational and rotational quantum state, with a narrow distribution of velocities, while in [40] 1.2×10^{12} SrF molecules per steradian per pulse are produced in the electronic ground state.

1.2.4 Laser cooling experiments

The difficulty of applying laser cooling methods to molecules stems from the many degrees of freedom that need to be cooled. The first suggestion is for a sequential cooling scheme, in which the translational, rotational, vibrational and electronic degrees of freedom are cooled by subsequent optical cycling processes. In this scenario a very large number of laser frequencies has to be generated, which poses a technical challenge [41].

Rather than use a complicated laser system, it proves useful to think about molecules whose structure might be amenable to cooling with just a few laser frequencies. A few possible candidates were pointed out by di Rosa in 2004 [42]. Since laser cooling has proven to be such a powerful method for cooling atoms to very low temperatures, there is a strong motivation for applying it to molecules, despite the additional complexity involved. The laser light can be used to both cool the molecules and decelerate a molecular beam. In the case of deceleration it is necessary to follow the changing Doppler shift as the molecules slow down to ensure that the molecules remain in resonance with the light. This can be done by chirping the

laser frequency, broadening the laser linewidth or Zeeman shifting the transition frequency using a Zeeman slower.

The application of basic laser cooling techniques to molecules was taken up with work from the DeMille group on SrF: a demonstration of the radiative force from optical cycling in 2009 [43] and the results of the first cooling experiments in 2010 [44]. The excitement surrounding the results is also associated with the possibility of trapping a species with a different chemical composition to the alkali molecules produced using Feshbach resonance.

Most recently, a beam of SrF was decelerated to below 50 m s^{-1} using the radiation pressure of counter-propagating light [45], and the molecules have been trapped in a magneto-optical trap [46]. Direct laser cooling has also been demonstrated with CaF at our group at Imperial in the work of Zhelyazkova [47], and laser cooling has been applied to YO molecules in the work of Hummon et al. [48]. Most recently there have been more advanced achievements with optoelectrical Sisyphus cooling [49]. The movement towards direct laser cooling of particular species of interest nicely sets the stage for the BH experiment, which began in 2012.

1.3 The mechanics of laser cooling

The achievements in producing and trapping ultracold atomic gases have rested on the development of a set of techniques for manipulating their internal and external states through the interaction with laser fields. The principles of laser cooling and trapping techniques for atoms are the subject of several textbooks, including Metcalf and van der Straaten [7] and Foot [50].

The limits to our ability to manipulate the state of an ensemble depend experimentally on the rigour with which we can produce a well-defined electromagnetic field, and fundamentally on the physical processes which we exploit. When we rely on spontaneous emission we have to accept a degree of random behaviour on the order of the momentum of a single photon. Over many cycles of absorption and emission this effect can become the limiting factor (the Doppler limit) in cooling

experiments. In certain, well-designed experiments using polarisation-gradient cooling it has been possible to surpass this limitation by exploiting stimulated emission. The limiting value is then due to the recoil momentum of a single photon.

Before discussing the work undertaken in this thesis I will give a brief overview of the laser cooling method. The separate chapters of this thesis describe work towards cooling and slowing a sample of BH molecules to a point at which they can be captured in a trap. We could envisage building something like the magneto-optical trap used for atomic species with a few alterations [46]. Here I discuss the background of laser cooling and its mechanism of action.

1.3.1 Supersonic expansion

The expansion of a molecular gas into a low-pressure region is key to the cooling process. The first stage is the acceleration of the gas to speeds greater than the local speed of sound. This is achieved through the use of a converging nozzle. As with a converging-diverging rocket nozzle the conservation of mass requires that as the flow's cross-sectional area is restricted its speed increases. At a critical cross-sectional area, called the throat, the flow becomes sonic (equal to the local speed of sound).

The properties of the supersonic flow are best understood by considering its thermodynamic properties. We follow Scoles, [51], and assume continuum flow in the region within the valve and immediately upon exiting to the vacuum chamber. This means that the fluid mechanics can be analysed using only macroscopic properties of the flow, rather than using an approach from statistical mechanics and stems from the fact that the molecules making up the gas collide frequently. The number of collisions between the molecules naturally decreases as the gas expands into the source chamber and the mean free path of the molecules eventually increases beyond the validity of this approximation but this treatment gives an idea of the variation in the properties of the flow as it begins to expand. We write Bernoulli's equation as follows:

$$h + \frac{v^2}{2} = h_0, \quad (1.1)$$

where h is the enthalpy, v is the flow velocity and h_0 is a constant for a given streamline. As all streamlines begin in the valve their constants will be the same. The equation can be rewritten using the definition of the heat capacity at constant pressure, $C_p = \frac{dh}{dT}$, where T is temperature. C_p can also be written in terms of Boltzmann's constant, k_B and the molecular mass, m :

$$dh = C_p dT, \quad (1.2)$$

$$C_p = \frac{k_B}{m} \frac{\gamma}{\gamma - 1}, \quad (1.3)$$

where we have $\gamma = \frac{5}{3}$ for a monatomic gas (the argon carrier gas). Using these expressions we obtain:

$$dh + d\left(\frac{v^2}{2}\right) = C_p dT + d\left(\frac{v^2}{2}\right) = \frac{k_B}{m} \frac{\gamma}{\gamma - 1} dT + d\left(\frac{v^2}{2}\right) = 0. \quad (1.4)$$

Integrating this expression from T_0 to T , and assuming that the specific heat capacities, C_P and C_V , (and so also γ) are constant over the integration, gives:

$$\frac{k_B}{m} \frac{\gamma}{\gamma - 1} (T - T_0) + \frac{v^2}{2} - \frac{v_0^2}{2} = 0, \quad (1.5)$$

but we have that the flow velocity inside the valve, $v_0 = 0$, so we can find the velocity further downstream as long as we know the corresponding temperatures:

$$\frac{k_B}{m} \frac{\gamma}{\gamma - 1} (T - T_0) + \frac{v^2}{2} = 0. \quad (1.6)$$

If we assume that $T \ll T_0$ then then we have that the terminal flow velocity is given by:

$$v_\infty = \sqrt{\frac{2k_B T_0}{m} \frac{\gamma}{\gamma - 1}}. \quad (1.7)$$

For a mixture of gases we will use the average molecular mass here instead of m , which tells us that we can reduce the terminal velocity of the flow by introducing molecules of a heavier species. In the experimental set-up we seed the molecule of interest in an argon carrier gas, which results in a slower terminal velocity. This will be beneficial when we begin to decelerate the molecules.

With the introduction of the speed of sound in an ideal gas, given by $a = \sqrt{\gamma k_B T / m}$, and the Mach number, which is defined as the ratio of the flow velocity to the local speed of sound, $M = v/a$; we can rewrite (1.6) in terms of the Mach number:

$$\frac{k_B}{m} \frac{\gamma}{\gamma - 1} (T - T_0) + \frac{v^2}{2} = \left(\frac{\gamma k_B T}{m} \right) \frac{1 - \frac{T_0}{T}}{\gamma - 1} + \frac{v^2}{2} \quad (1.8)$$

$$= a^2 \frac{1 - \frac{T_0}{T}}{\gamma - 1} + \frac{v^2}{2} = 0 \quad (1.9)$$

$$\Rightarrow \frac{v^2}{2a^2} = \frac{M^2}{2} = \frac{\frac{T_0}{T} - 1}{\gamma - 1} \quad (1.10)$$

$$\Rightarrow \frac{T}{T_0} = \frac{1}{1 + \frac{M^2(\gamma - 1)}{2}} \quad (1.11)$$

This shows us that the temperature of an isentropic flow of ideal gas which has reached sonic ($M = 1$) speeds and continues to accelerate will decrease. We can further obtain the relation governing the dependence of the pressure and the density of the gas on the Mach number as shown in [51] to determine that they will also decrease with increasing Mach number. It is this cooling property of the expansion which we wish to exploit. However, as the flow continues to expand into the source chamber and its density decreases, the number of collisions between the molecules will drop below the point at which we can assume continuum flow.

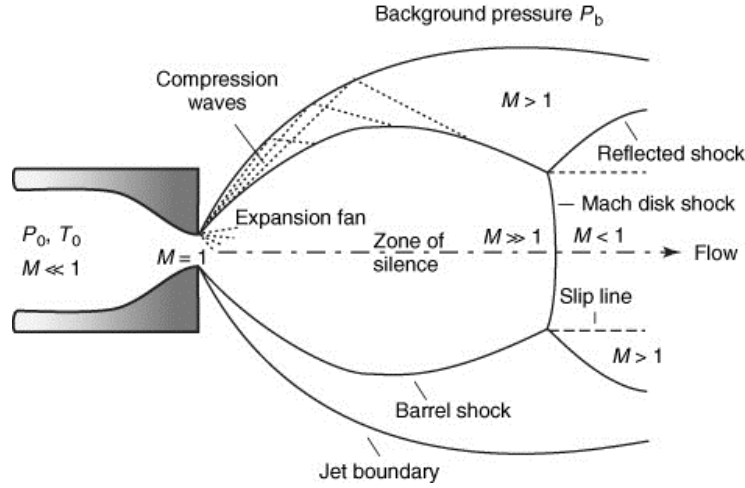


FIGURE 1.1: The supersonic expansion in from a nozzle: M is the Mach number, P_0 is the base pressure and T_0 is the temperature inside the valve.

As the gas moves from continuum flow to free molecular flow and the cooling ceases to be a prominent factor, the translational, rotational and vibrational temperatures are ‘frozen in’ and cease to vary significantly. In this free molecular flow we can speak of a temperature associated with each degree of freedom although the relationship between the temperature and the distribution of energies may not be identical to that at equilibrium. By extracting a molecular beam downstream from the freezing surface we can ensure that the lowest possible temperatures have been reached.

As long as the expansion is supersonic the flow cannot adapt to its surroundings gradually, since information about the surroundings travels at the local speed of sound. A high background pressure in the source chamber causes a shock wave structure which forces the flow to meet the boundary conditions 1.1. The shock waves are regions of high density, pressure and temperature gradients and it is necessary to extract the beam from within the zone of silence in order to obtain a cool, collimated beam. The distance from the nozzle to the Mach disk shock, x_M , is determined by the ratio of the initial pressure of the gas inside the valve (the backing pressure), P_0 , to the background pressure in the chamber, P_b , in the following formula [51]:

$$\frac{x_M}{d} = 0.67 \sqrt{\frac{P_0}{P_b}}, \quad (1.12)$$

with d the nozzle diameter. As we work at a backing pressure of around 1 bar in a vacuum chamber at 10^{-7} mbar the Mach disk should be located $67,000d$ from the nozzle, which would be located outside of the chamber (typical nozzle diameters being of the order 0.1–1 mm). This shows that the background pressure in the chamber is low enough that the skimmer will always be extracting from the supersonic flow region.

1.3.2 Laser cooling the two-level atom

In order to produce a cooling effect which narrows the velocity distribution we need to have a dissipative mechanism which causes the motion of the molecules to tend towards a particular value. This mechanism will cause the cooling effect in the system. We also need to reduce the mean velocity of the gas. We can achieve both of these things using the interaction of the molecular system with light. We look first at a two-level system to introduce the useful concepts when considering the interaction of an atomic or molecular system with an oscillating electromagnetic field.

We only consider electric dipole (E1) transitions as the strength of the interaction with the magnetic field of the wave is α^2 times smaller, where α is the fine-structure constant. A strong, oscillating electric field resonant with the transition between the two states of the system mixes the electronic states. The system can be treated semiclassically, with quantised atomic states and a classical field. This treatment is possible because the atomic system is coupled to an infinite number of free space modes, and because the laser field is very intense. In this case there is no reason to expect the emission of light by the atom to substantially alter the strong field which excites the atom. The semiclassical description of the radiative force on a two-level atom can be found in [50].

The force on the atom is related to the rate of scatter, $R_{\text{scatt}} = \Gamma \rho_{22}$, where Γ is the spontaneous emission rate for the system, and ρ_{22} is the density matrix

element for the excited state. The optical Bloch equations (see [50] or [52]) give us a relationship for ρ_{22} , and we can write down the rate of scatter as follows:

$$R_{\text{scatt}} = \frac{\Gamma}{2} \frac{\Omega^2/2}{\delta^2 + \Omega^2/2 + \Gamma^2/4}, \quad (1.13)$$

where Ω is the Rabi rate for the transition and δ is the detuning of the optical frequency from resonance with the transition between the two states in the system. The force due to the scattered light is then simply the momentum carried by a single photon multiplied by this rate of scatter. It is important to note that the detuning, δ , depends not only on the optical frequency but also on the speed of the atoms through the Doppler effect. As the atoms start to scatter light and their momentum is reduced the detuning will change. In order to counteract this effect it is necessary either to chirp the frequency of the laser so that it contains different frequencies, or to apply a magnetic field and shift the transition back onto resonance. Equation 1.13 shows that when resonant with the optical field ($\delta = 0$) the maximum rate of scatter becomes $\Gamma/2$. The maximum deceleration achievable will then set the length of the slowing experiment. The limits to cooling in simple experiments using the scattering force is usually the Doppler limit.

1.3.3 Laser cooling the molecule

The two-level system is complicated by the addition of further electronic states, which even a simple atom has, but with a molecule there are also vibrational and rotational degrees of freedom that increase the number of levels that are coupled by the optical field. The effect is always to reduce the scattering rate given in 1.13 so that the deceleration of the molecules is reduced. Additionally, it can be difficult to cause continuous optical cycling in a multi-level system where there are states which the optical field cannot address.

For BH the scattering rate is 1.2 MHz [53] and the single-photon recoil velocity is 0.078 m s^{-1} .

1.4 The thesis

BH has been suggested by di Rosa [42] as a possible candidate for laser cooling. In the second chapter I present the results of our spectroscopy experiments to determine the vibrational branching ratios and hyperfine parameters of BH. These are the crucial parameters for assessing the suitability of the molecule for laser cooling and for designing the best laser cooling scheme. In the third chapter I present the results of a numerical model of the molecular system and experiment to understand the dynamics of the molecule driven by a continuous resonant laser field. Here I show the first evidence for optical cycling (i.e. scattering multiple photons) in the BH molecule. The fourth chapter covers the building of a repump laser and the demonstration of its effect on the molecules. The final chapter summarises the results and presents a design for a Zeeman slower suitable for bringing a beam of BH to rest.

Chapter 2

Spectroscopy of BH

2.1 Introduction

This chapter describes work undertaken to make precise measurements of the properties of BH relevant to a laser cooling experiment. I begin by reviewing quantum mechanics applied to molecular systems and then introduce the structure of BH. The remainder of the chapter is devoted to a description of the experimental methods which have been used to probe this structure, and the results of those experiments.

Prior to this work a number of studies of BH had already been carried out; these were either *ab initio* calculations of the molecular constants and Franck-Condon factors, or the results of spectroscopy experiments to determine these constants. These studies have served as a starting point for us to begin thinking about the design of a cooling experiment for BH, and some of their results have been useful for comparison with our own. I will mention them in more detail as they become relevant.

The results of this chapter were published in Hendricks et al. 2014, [\[54\]](#).

2.2 Theory

In this section I give an introduction to the description of a diatomic molecule, based on Herzberg's *Spectra of Diatomic Molecules* [55], and Brown and Carrington's *Rotational Spectroscopy of Diatomic Molecules*, [56]. I will discuss the following subjects: the aims of molecular theory, the Born-Oppenheimer approximation, the electronic state and angular momentum, the vibrational and rotational state of the molecule, the doubling of levels due to Lambda-doubling, the symmetry properties of the wavefunction, and the hyperfine interaction. Although this may seem like a daunting number of topics to present, their discussion will allow us to understand the more concise expression of the molecular state in the level diagram in the subsequent section.

2.2.1 Quantum mechanics applied to molecules

The theory of diatomic molecules aims to produce a description of a molecular state which is both useful and accurate. Although this would seem to be an obvious aim, its accomplishment is made difficult by the complexity of the system under study. A diatomic molecule is only a bound state of a system of charged particles interacting via the electromagnetic interaction, exactly as in an atom. However, in an atom we are concerned only with the motion of the electrons around a stationary nucleus. A diatomic molecule has two additional modes of motion associated with its nuclei; the oscillatory motion along the line connecting the nuclei, and the motion associated with rotation of the nuclei about an axis perpendicular to the line connecting them. Faced with these additional degrees of freedom we have to make a different approximation, by separating the different motions according to their characteristic periods, and by computing the state of each degree of freedom with the others held fixed. In the end we hope to be able to reduce our problem to a set of parameters, each representing an independent motion of the system, which will allow us to calculate the energies of the molecular states. We have some freedom about how we choose our parameters so we let them correspond to the conserved quantities of the system. In this way we sacrifice some accuracy in our description

of the system but as a result we gain a more self-explanatory set of labels for the molecular state.

We write a wavefunction, $|\Psi\rangle$, for the molecule, which contains all of our knowledge of the molecular system. The next step is to separate this wavefunction into factors depending on parameters associated with different energy scales of the system. In a diatomic molecule we can distinguish between the motion of electrons, which are relatively light, and the motion of the nuclei, which are much heavier. We can separate the nuclear motion further into motion along the line connecting the nuclei, the internuclear axis, or rotation about a line perpendicular to this axis which passes through the geometric centre of the molecule. These motions have different characteristic timescales, the electronic motion being the fastest and the end-over-end rotation of the nuclei being the slowest. The difference in timescales means that the motion of the electrons easily adapts to the slowly-changing positions of the nuclei. This principle underlies the Born-Oppenheimer approximation, in which the molecular wavefunction separates completely into three independent factors, each dependent on only one type of motion. This approximation provides an accurate description of the system when the molecule is in a well-bound state that is well-isolated from all other electronic states. In more energetic states the vibrational motion of the nuclei along the internuclear axis, for example, will begin to affect the electronic motion, and the approximation becomes invalid.

We separate the molecular wavefunction into three parts

$$|\Psi\rangle = |\Psi_e\rangle |\Psi_v\rangle |\Psi_r\rangle, \quad (2.1)$$

where e , v , and r represent the electronic, vibrational and rotational degrees of freedom respectively. We separate the Hamiltonian similarly into terms which depend on the electrostatic interaction of the electrons and the fixed nuclei, $\mathbf{H}_e$, the vibration of the nuclei, $\mathbf{H}_v$, and the rotation, $\mathbf{H}_r$. To accurately calculate the eigenvalues it becomes necessary to include corrections which account for the effect of the rotational motion of the nuclei on the vibrational and vice-versa. This can be achieved by using the Dunham correction, see Herzberg [55]. However, for the purposes of

explanation we will ignore these corrections and only consider the salient points relating to each part of the wavefunction.

In an atom the electronic state can be completely specified by four quantum numbers for each electron: n , the principal quantum number, j , the total angular momentum, l , the orbital angular momentum, and s , the spin angular momentum. The electronic state of a molecule can be specified similarly. However, the electric field between the nuclei removes the spherical symmetry which characterises the atomic system. The electronic angular momenta are no longer completely conserved, but the component of the angular momentum vector along the internuclear axis is. States of a diatomic molecule are labelled by the quantum numbers Ω , Λ and Σ which are, respectively, the projections of the total electronic angular momentum, the orbital angular momentum, and the electronic spin onto the internuclear axis. They are related through $\Omega = \Lambda + \Sigma$. The electronic spin is usually a conserved quantity too, and so it is also used to label the state. We write a term symbol $^{2S+1}\Lambda_{\Omega}$ which contains this information. To make matters a little more confusing, the term symbol is written with numerical values for the spin and total angular momentum, but with another Greek letter to represent the numerical value of Λ . A state with $\Lambda = 0$ becomes a Σ -state and one with $\Lambda = 1$ becomes a Π -state. Thankfully, that is all we will need to understand BH. We then label the electronic state by a Latin letter (X is reserved for the ground state) followed by this term symbol.

We have already included a rather large number of degrees of freedom into our description of the molecule. To write a description of the molecule which is relatively simple we have to obscure some of the detail of the situation. We write an effective Hamiltonian, which is useful within a single vibrational and electronic state, and reproduces the correct eigenvalues for the system. Information about couplings between different vibronic states are introduced into the Hamiltonian perturbatively, so the choice of Hamiltonian has to be made carefully, to approximate the system well. In our spectroscopy we use different effective Hamiltonians to describe the different states in BH.

The vibration of the nuclei is considered having fixed the electronic state. The attraction between the nuclei and this fixed charge distribution, considered together with the repulsion of the nuclei, results in a potential curve describing the nuclear coordinate which has a minimum at some preferred separation of the nuclei. The potential is harmonic near this equilibrium separation, but anharmonic when the nuclear separation is small and when it is large. The vibrational wavefunctions of the low-lying states are then much like harmonic oscillator states, with a few correction terms to allow for the anharmonicity of the potential. The state can be entirely specified by a single quantum number, which we label v . The energy difference between states with different values of v is far smaller than that of the electronic states. The vibrational states form a ladder, $v = 0, 1, 2, \dots$ within each electronic state. There is no selection rule governing transition between states with different values of v when the electronic state also changes.

The rotational states of the molecule are also each specified by a single quantum number, and they form a ladder within each vibrational level of an electronic state. However, the angular momentum due to the rotation has to be coupled to the other angular momenta present in order to determine whether or not there can be a transition between two states. The resultant of the coupling between the electronic angular momenta and the molecular rotation we label J . The selection rules on the change in total angular momentum have to be considered in order to find a rotationally closed transition for laser cooling. At this stage we have discussed most of the quantum numbers relevant to the description of the molecular state. We now have a few additional considerations due to the symmetry of the system.

Our first issue is the lambda-doubling of states with $\Lambda > 0$, e.g. a Π state. Each level of the rotational ladder in a state with $\Lambda > 0$ is doubly degenerate because the energy of the system is not changed when we reverse the direction of motion of all the electrons in the system at the same time. In this reversal the magnitude of the orbital angular momentum remains the same but its projection onto the internuclear axis is reversed. This doubling of levels is only degenerate when there is no mixing of the electronic states. Typically, a Π state is slightly mixed with a Σ state of the molecule, and this leads to a lifting of the degeneracy. Then, the degenerate state splits into two states of opposite parity. There is one further point to make

about the symmetry of the Σ state. Since this state has spherical symmetry, the electronic wavefunction will either be symmetric or antisymmetric under reflection of the molecular coordinates through a plane including the internuclear axis. This symmetry is indicated by a $+$ or a $-$ symbol, e.g. Σ^+ . Eventually this affects the parity of the full molecular wavefunction, which is important because we can only connect states of opposite parity in electric dipole transitions.

We must also concern ourselves with the interaction between the magnetic dipole moments due to electronic angular momentum and those due to nuclear spin. As the nuclei are more massive than the electrons, the magnetic dipole moments due to them are correspondingly smaller, and this interaction leads to a splitting of levels which is of a much smaller scale than the effects already discussed. Nevertheless, the total angular momentum of a state is determined by coupling the electronic and nuclear angular momenta to that of the molecular rotation. In BH, there are two nuclei and both have spin angular momentum: the hydrogen nucleus, $I_H = 1/2$, and the boron-11 nucleus, $I_B = 3/2$. The resultant of coupling J to the boron nuclear spin we call F_1 , and the final angular momentum which results when we include the hydrogen nuclear spin is labelled F .

2.2.2 BH level structure

In figure 2.1 we see a level diagram for the BH molecule which contains the elements we have discussed in the previous section. The vibrational structure has been removed, so that we only consider the lowest vibrational level in each electronic state. The figure shows the first three electronic states of the molecule, which are labelled $X^1\Sigma$, $a^3\Pi$, and $A^1\Pi$. We note here that neither the $^1\Sigma$ or the $^1\Pi$ state has an unpaired spin. The rotational states of the molecule are shown, together with the overall parity of the wavefunction, labelled either $+$ or $-$. In the ground state, $X^1\Sigma^+(v=0)$, the three lowest rotational states, labelled $J=0, 1, 2$ are relevant to the work described here. Of these, the most important is the $J=1$ level, since it is the lower level of the transition we plan to use for laser cooling. This allows a Q(1) transition in which the rotational quantum number does not change and avoids leaks to other rotational states. This level lies 708 GHz above the ground state.

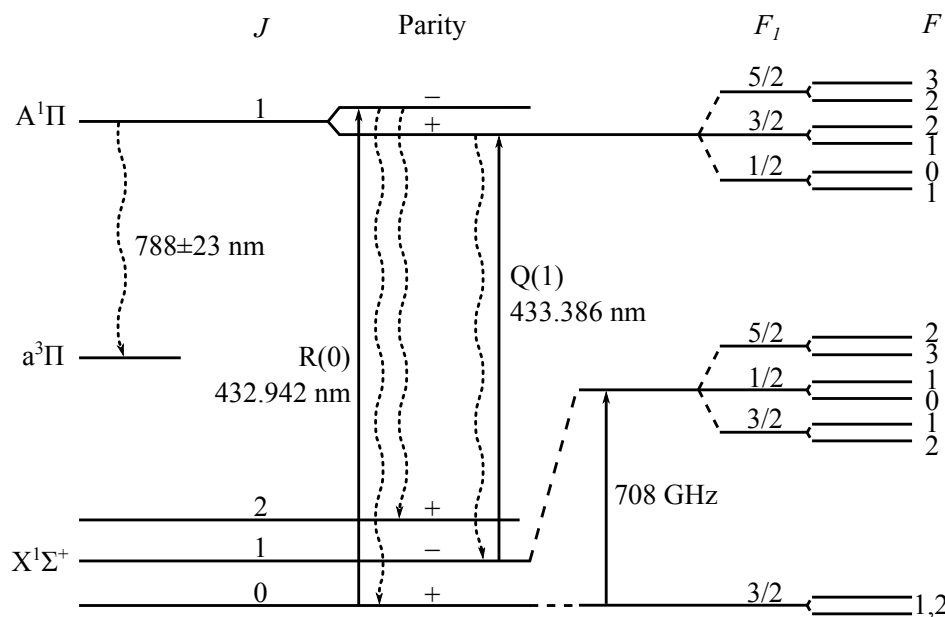


FIGURE 2.1: The three lowest-lying electronic states of BH. The state labels are described in the text. The labelled transitions are to be understood in the context of the spectroscopy experiment. The vertical axis is represents energy.

Our method of producing BH makes molecules almost exclusively in the ground rotational state, and so we have to drive this 708 GHz rotational transition in order to populate $J = 1$. The hyperfine structure of the $J = 1$ level is also relevant, and is shown in the figure. The largest splitting is due to the spin of the boron nucleus and splits the level into three components labelled by $F_1 = 1/2, 3/2, 5/2$. These are each further split into two due to the interaction with the hydrogen nuclear spin, giving 6 hyperfine levels in total. The upper level of the laser cooling transition is the lowest energy level of positive parity in the the $A^1\Pi(v = 0)$ state, which has $J = 1$. This level is also split into 6 components by the hyperfine structure, which is very much larger in the excited state than in the ground state (around 270 MHz as compared to 2.7 MHz). The other relevant state in this work is the intermediate $a^3\Pi$ state. It represents a potential leak out of the cooling cycle through a spin-forbidden (but weakly allowed) transition.

In figure 2.2 we see some of the vibrational structure that was not shown in figure 2.1. The figure shows the three lowest-lying vibrational states in the ground

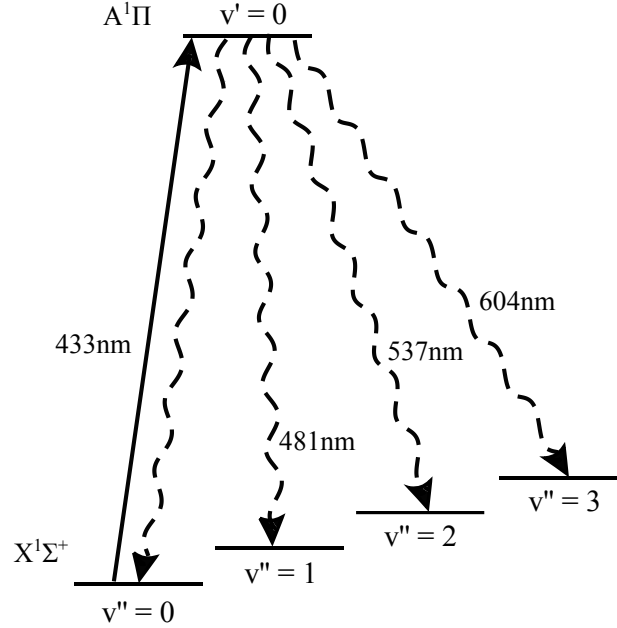


FIGURE 2.2: The three lowest-lying vibrational states of BH.

electronic state and the transition wavelengths to those states are labelled. The wavelengths are calculated using the molecular constants reported in [58]. The modelled potential energy curves can be seen in figure 2.3. These vibrational levels are relevant because the excited state in the laser cooling transition may decay to these levels, taking population out of the laser cooling cycle. In order to know how many of these transitions need to be addressed for successful laser cooling, we need to know the branching ratios to each of them. That is the one of the aims of the work described in this chapter.

Now that we have some understanding of the molecular states involved in the interaction, we can move on to consider the spectroscopy experiments. We will refer to figure 2.1 in the description of the experimental procedure.

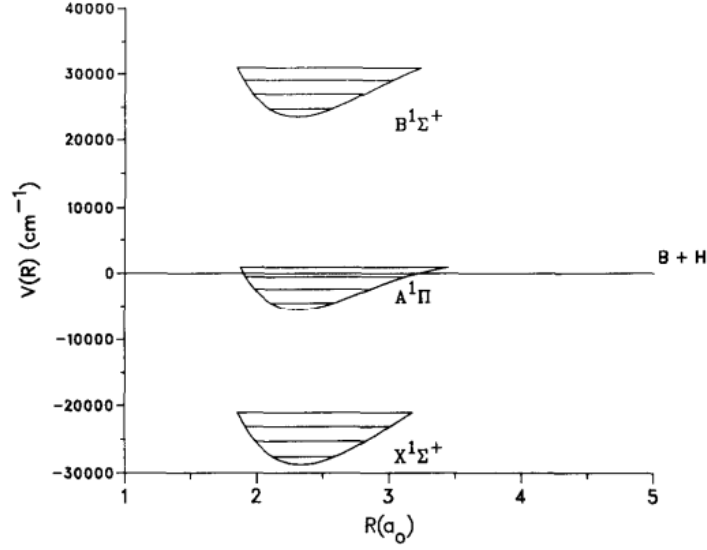


FIGURE 2.3: The RKR potential curves for the three lowest electronic states of BH, plotted with vibrational states, from [57]. R is internuclear separation and V the potential energy.

2.3 Methods

The aims of the work described in this section are: (i) to measure the vibrational branching ratios $A^1\Pi(v' = 0) \rightarrow X^1\Sigma^+(v'')$; (ii) to measure the frequency of the lowest rotational transition in the X state; and (iii) to measure the hyperfine structure of both the X and A states. All are important for a laser cooling experiment. The experimental set-up described here is relevant to these measurements and to later chapters.

2.3.1 Molecular source

We produce BH in a collimated molecular beam which has a velocity of around 600 m s^{-1} in its direction of travel. We require that the molecules have a narrow distribution of velocities, so that we can expect all of the molecules to respond

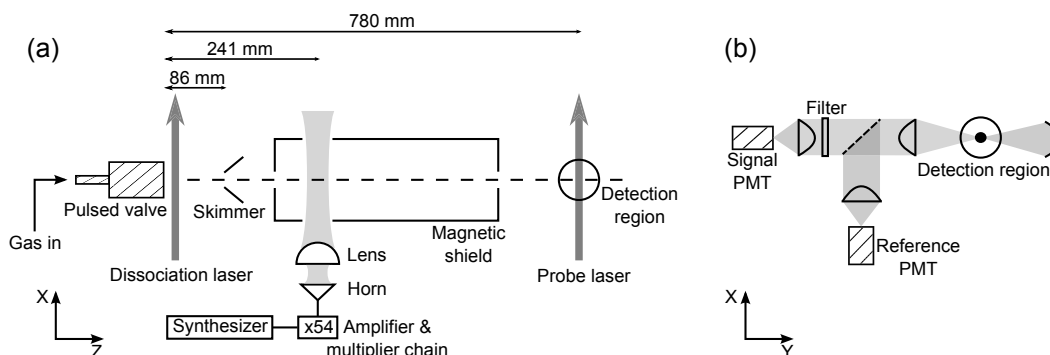


FIGURE 2.4: (a) Apparatus for producing and detecting a supersonic beam of BH molecules and for driving transitions between rotational states. (b) Laser-induced fluorescence detection set-up. Using a set of interference filters placed in the arm containing the signal PMT, the branching ratios to various vibrational states is determined. The reference PMT is used to account for fluctuations in molecular flux.

in approximately the same way when we address the beam with a narrowband electromagnetic field. Where there is a broad distribution of velocities, the Doppler shift causes different molecules to experience different frequencies, making it more difficult to control the molecules. We also require the molecules to be initially in the same quantum mechanical state; again, this is so that the field which addresses them affects them all in the same way. The well-established molecular beam method makes this high degree of control possible.

Figure 2.4 shows a schematic of our molecular beam machine. There are three processes which allow us to generate a well collimated beam of BH molecules with a significant fraction of the molecules occupying the lowest lying electronic, vibrational, and rotational state. These are: the photodissociation of a B_2H_6 (diborane) precursor, the subsequent free expansion of the gaseous BH molecules, and the collimation of the molecular beam produced. I will now discuss each of these in turn.

To produce BH molecules we follow the method used in [59]. A solenoid valve (General Valve Series 99) is filled to a pressure of 3 bar with a mixture of 1% diborane (B_2H_6) in argon. The valve is opened for about 140 μs by applying a short, 300 V pulse to the solenoid. A pulsed ArF excimer laser (MPB ASX-750) produces a 19 ns pulse of light at 193 nm which crosses the molecular beam about 1 mm from

the valve face, causing the B_2H_6 molecules to photodissociate to BH. We measure the power of each pulse to be 100 mJ. The photodissociation of diborane to BH has been studied in [60] and can occur by two routes, both of which are two-photon processes, which makes the molecular yield particularly sensitive to the alignment of the excimer beam and its power.

The BH molecules, carried in the argon beam, undergo a rapid free expansion into the vacuum chamber which redistributes their internal energy through collisions. The solenoid valve provides short pulses to prevent the background pressure in the chamber from rising high enough to halt the free expansion of the molecules. The chamber into which the molecules expand is evacuated by a turbomolecular pump (Leybold MAG 1300C) with a pumping speed of 1100 l s^{-1} , backed by a rotary-vane pump (Leybold TRIVAC D16B). During the free expansion, collisions between the molecules and the monoatomic carrier gas cause the molecular ensemble to thermalise. The rapid expansion results in the molecules having a high forward velocity with a mean of around 600 m s^{-1} , and a narrow distribution around this mean, which can be modelled as a gaussian with a full-width-at-half-maximum of about 60 m s^{-1} . The internal state of the molecule is also affected by the expansion, with the resulting molecular pulse having a high ground state occupancy and a narrow distribution of states, due to the cooling effect of the expansion. The thermodynamics of the free expansion is described in Scoles [51].

A conical skimmer 86 mm downstream from the valve selectively passes the central section of the molecular pulse into the subsequent part of the apparatus. By selecting the centre of the pulse, we exclude those molecules which are rapidly diverging from the beam axis. The velocities of the molecular ensemble, perpendicular to the beam axis, are then narrowly distributed about zero.

Figure 2.5 shows the fluorescence collected when the molecules pass through the detection region, which is 780 mm downstream of the position where the BH molecules are produced. The detection process will be explained in a later section. We fit a Gaussian to the time-of-flight profile and from this we extract the mean velocity and the full-width-at-half-maximum. Using the distance which the molecules

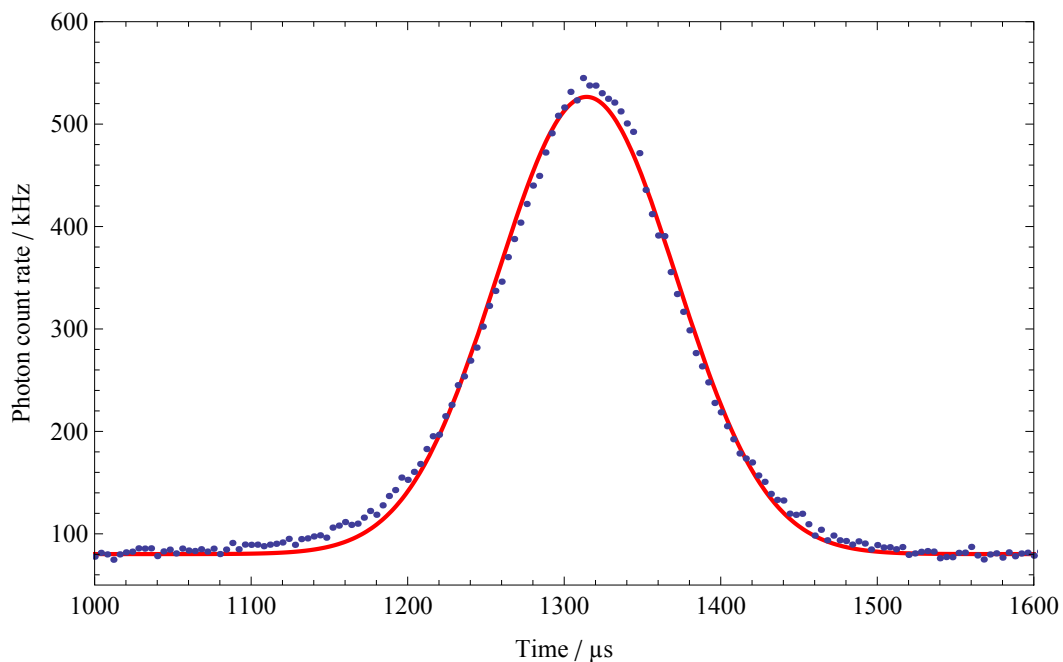


FIGURE 2.5: The time-of-flight profile, recorded 780 mm from the source, for molecules which have undergone supersonic expansion. The red line is a Gaussian fit to the data. Time-bin is $3\text{ }\mu\text{s}$.

traverse in this time, we estimate their mean velocity to be 593 m s^{-1} , with a full-width-at-half-maximum of 61 m s^{-1} . To extract an absolute temperature from these data, we model the velocities as being distributed according to the Boltzmann distribution centred on the mean velocity, as they would be in an ideal gas. Then we obtain a temperature for the translational degree of freedom of 0.96 K . Since the molecular vapour is not in thermodynamic equilibrium, this treatment can only be used to provide a number for comparison with other experiments. An ideal gas with a temperature of 0.96 K would have a mean velocity far lower than 593 m s^{-1} .

After the skimmer, we are able to change the internal state of the molecules with a high degree of finesse. Here I use finesse to mean that the majority of the molecules in the ensemble can be considered to behave identically under the influence of the driving electromagnetic field. The generation of the driving fields, and their properties, are discussed in the following two sections.

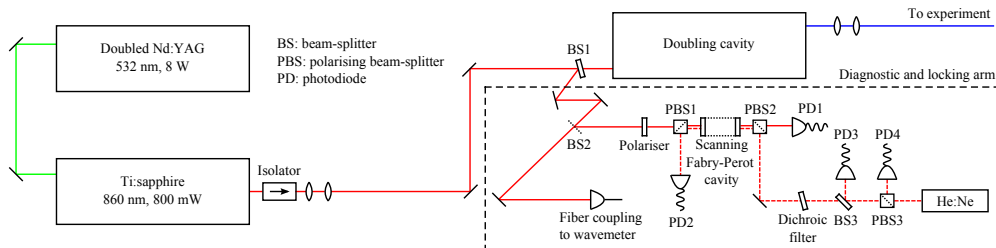


FIGURE 2.6: The system used to produce an intense, stable field at the optical frequency corresponding to the $A^1\Pi(v' = 0, J' = 1) \leftrightarrow X^1\Sigma(v'' = 0, J'' = 1)$ transition in BH.

2.3.2 Exciting the rotational transition

Our laser cooling scheme uses a transition from the first excited rotational state of BH. Following the free expansion approximately $\sim 90\%$ of the molecular population is in the ground rotational state. The rotational states have lifetimes that are much longer than the lifetime of the experiment. We excite the rotational transition with an electromagnetic field resonant with the transition between the ground and first excited rotational states.

We produce the electromagnetic field to excite the rotational transition at 708 GHz using a microwave synthesiser and a harmonic multiplying circuit. A synthesised signal generator (Gigatronics 7100) generates an oscillating electrical signal at 13 116.853 73 MHz, which drives an amplifier-multiplier chain unit (VDI WR1.5) with 10 dBm of power. The amplifier-multiplier chain unit multiplies the frequency of the oscillation by a factor 54, to 708 GHz, and couples it to a gaussian beam in free space by a diagonal microwave horn. The beam is collimated by a PTFE lens before entering the vacuum chamber through a PTFE window.

2.3.3 Exciting the optical transition

To detect the molecules in the molecular beam we use the Q(1) transition shown in the level scheme 2.1. This corresponds to the $A^1\Pi(v' = 0, J' = 1) \leftrightarrow X^1\Sigma^+(v'' = 0, J'' = 1)$ cycling system. This transition was measured by [53] to be at 433.2 nm.

We can produce light at this wavelength using a tunable $\text{Ti:Al}_2\text{O}_3$ laser, whose output is doubled in frequency by a nonlinear optical crystal. The laser beam then passes into the vacuum chamber and intersects the molecular beam at right angles. Here I discuss each of the laser systems and their locking mechanisms in more detail. A schematic of the laser system is shown in figure 2.6.

The $\text{Ti:Al}_2\text{O}_3$ (Coherent MBR-110) is pumped by a solid state Nd:YVO_4 laser (Coherent Verdi-V8), which delivers 8 W of power at 532 nm. The lasing action is due to a titanium-doped, sapphire rod, located in an optical build-up cavity in a bow-tie configuration. The cavity ensures single-mode operation of the laser. The frequency stability is achieved by different mechanisms which correct for short- and long-term drift. The infra-red (IR) output of the lasing cavity is fed into a scanning reference cavity which is used to detect changes in the laser frequency. The error signal generated by the reference cavity controls adjustments of the length of the lasing cavity by a piezo-mounted mirror, which forms part of the cavity, to correct for high-frequency noise. Small rotations of two glass plates inside the laser cavity, that intersect the light at Brewster's angle, are used to adjust the length of the cavity to maintain a stable frequency on a longer timescale.

Once the beam leaves the MBR-110 unit it is split, so that a small amount of light can be sent to a wavemeter for an approximate measurement of the wavelength, and to another scanning reference cavity. This cavity is external to the MBR-110 and is used to compare the frequency to that of a temperature-stabilised He:Ne gas laser. The He:Ne laser can be made to be stable over much longer timescales and acts as a stable reference frequency. The He:Ne and IR beams pass through the scanning reference cavity in opposite directions, and the transmitted beams are detected by photodiodes. As the cavity is scanned, cavity transmission peaks are observed on each of these photodiodes. A control program sends a feedback signal to the IR laser in order to keep fixed the spacing between the He:Ne transmission peak and the IR transmission peak. This transfers the stability of the He:Ne to the IR laser. The frequency stability of the laser when locked to the He:Ne reference is limited by the uncertainty in the He:Ne frequency and is about 2 MHz over several hours.

Most of the power in the IR beam goes on to the frequency-doubling unit (Coherent MBD-200). It contains a LBO crystal in a build-up cavity in a bow-tie configuration. The perturbation of the intense laser field in the nonlinear medium of the crystal results in some light being coherently produced at double the frequency of the fundamental oscillation. The doubling process is nonlinear and the intensity of the light generated at the second harmonic frequency varies as the square of the intensity of the fundamental. The build-up cavity increases the intracavity intensity in order to increase the output power of the frequency-doubled light. The length of the cavity is stabilised using the Hänsch-Couillaud method, where the intensity of orthogonally polarised modes reflected from the cavity are used to generate an error signal to feed back to the cavity.

The frequency doubled light is our probe beam. It is collimated and passes into the vacuum chamber. We align the beam with the centre of the chamber and allow it to pass out the other side to limit the amount of light which is scattered inside the detection region. The detection optics lie at the intersection of the molecular beam and the probe beam. As molecules pass through the probe beam they are excited to the $A^1\Pi$ -state and fluoresce, emitting radiation uniformly in all directions. The lifetime of the excited state is 127 ns [53].

2.3.4 Detection

The fluorescence emitted by the molecules as they pass through the probe beam is the main source of information about the molecules. Figure 2.4 shows the detection set-up. An aspheric condenser lens collects and collimates part of the fluorescence, and a second lens images the fluorescence onto a photomultiplier tube (PMT). Fluorescence emitted in the opposite direction is re-directed into the detection optics by a parabolic mirror, roughly doubling the signal. The photocurrent from the PMT passes through a discriminator which removes signals below a certain voltage, due to electrical noise such as dark current from the PMT. We operate in ‘photon-counting’ mode, where the count rate is low enough that there is no pile-up and individual photons can be counted. Once the signal has been cleaned of noise, it is

amplified by an analogue circuit after the discriminator and passed to an analogue-to-digital converter, for storage on a PC. In this way, we record the time-of-flight profile (TOF) of each pulse of molecules as a series of photon counts with associated timings. An example was shown in figure 2.5. Filters can be placed in the collimated part of the light in order to distinguish between the various wavelengths present in the fluorescence.

The efficiency of the PMT is around 20% at the wavelength of interest. The collection optics gather about a tenth of the total fluorescence emitted by the molecules although a more exact calibration would need to be performed in order to give a reliable estimate of the number of BH molecules present in the molecular pulse.

The experiments carried out in this chapter use two PMTs, one to record the fluorescence filtered according to wavelength, and the other to record total signal. Both are shown in figure 2.4. The collected light is split by a non-polarising beamsplitter cube into two branches. On one branch a filter sits in the path of the beam and in the other there is no filter. The normalisation branch, with no filter, continuously records the total fluorescence intensity so that fluctuations in the molecular beam flux and probe beam intensity can be accounted for when we analyse the data.

2.3.5 Experiment control

Control of the experiment is achieved through the use of two NI-DAQ cards, run by a suite of software written in C# by various people in the *Centre for Cold Matter*.

To scan the optical frequency we send a voltage to the MBR-110 control box that changes the length of the lasing cavity by varying the length of the piezostack on which one of the cavity mirrors is glued. We scan the mm-wave frequency using GPIB commands sent to the microwave synthesiser.

In a typical scan, a single parameter (e.g. probe laser frequency) is varied. The time-of-flight (TOF) profile is recorded at each point in the scan. If the signal-to-noise ratio is poor, several TOF profiles can be recorded at each point in the scan and then averaged together.

The experiment is controlled through three NI-DAQ cards. One, the pattern generator, triggers the valve, the excimer laser, and the data acquisition. The second, a general purpose DAQ board, acquires the data from the detector and sends the control voltage to scan the laser. The third is a GPIB board that controls the microwave synthesiser.

2.4 Results I - vibrational branching ratios

2.4.1 Definition of Franck-Condon factor

The vibrational branching ratios are of interest to us because they tell us how many photons each molecule will scatter, on average, before being optically pumped into a state which is not resonant with the laser field. The Franck-Condon factors, $Z_{v',v''}$ are defined as the square of the overlap integrals between the vibrational wavefunctions in the upper and lower states (marked by single and double primes respectively):

$$Z_{v',v''} = | \langle \psi_{v'} | \psi_{v''} \rangle |^2. \quad (2.2)$$

The branching ratio to a given vibrational state is simply the fraction of the population that will decay to that state. It can be written

$$a_{v',v''} = \frac{A_{v',v''}}{\sum_{v'''}^{\infty} A_{v',v'''}} \quad (2.3)$$

where $A_{v',v''}$ is the Einstein coefficient for spontaneous decay from a vibrational level in the excited electronic state, v' , to one in the ground electronic state, v'' . The Einstein A coefficient is

$$A_{v',v''} = \frac{\omega_0^3 d^2}{3\pi\epsilon_0\hbar c^3}, \quad (2.4)$$

$$d = e \langle \text{excited} | \mathbf{r} | \text{ground} \rangle. \quad (2.5)$$

Here, ω_0 is the natural frequency of the transition and d is the transition dipole moment, defined with the position operator $\mathbf{r}$. In the Born-Oppenheimer approximation the wavefunctions are products of the electronic, vibrational, and rotational parts. In the transition dipole moment d , the electronic and rotational parts are common to all vibrational states v' and v'' and so they drop out of the ratio in equation 2.3. To a good approximation, the vibrational part of d is the overlap integral between the vibrational wavefunctions, and so d^2 is proportional to the Franck-Condon factor.

Experimentally, we use filters to isolate the fluorescence emitted in the transition to each of the vibrational states; then by comparing the intensity of the fluorescence collected on different transitions we determine the branching ratios. In order to calculate the quantity $a_{v',v''}$, we need to know the decay to every vibrational level in the ground electronic state. In our calculation, we make the assumption that there is no decay to the vibrational levels with $v'' > 3$, effectively truncating the sum in the denominator of 2.3. We also measure directly the amount of fluorescence emitted in transitions to all states with $v'' > 3$ using a long-pass filter.

2.4.2 Measurement procedure

To measure the vibrational branching ratios we record a series of time-of-flight profiles with a filter isolating each transition of interest. Figure 2.7 shows some typical data. The signal is the integral of the TOF profile between the two “signal gates” shown in the figure. The background is the integral between the two “background gates” multiplied by the ratio of the signal gate duration to the background gate duration. We subtract the background from the signal. We also record time-of-flight profiles with the probe beam blocked so that we can monitor the light that is not

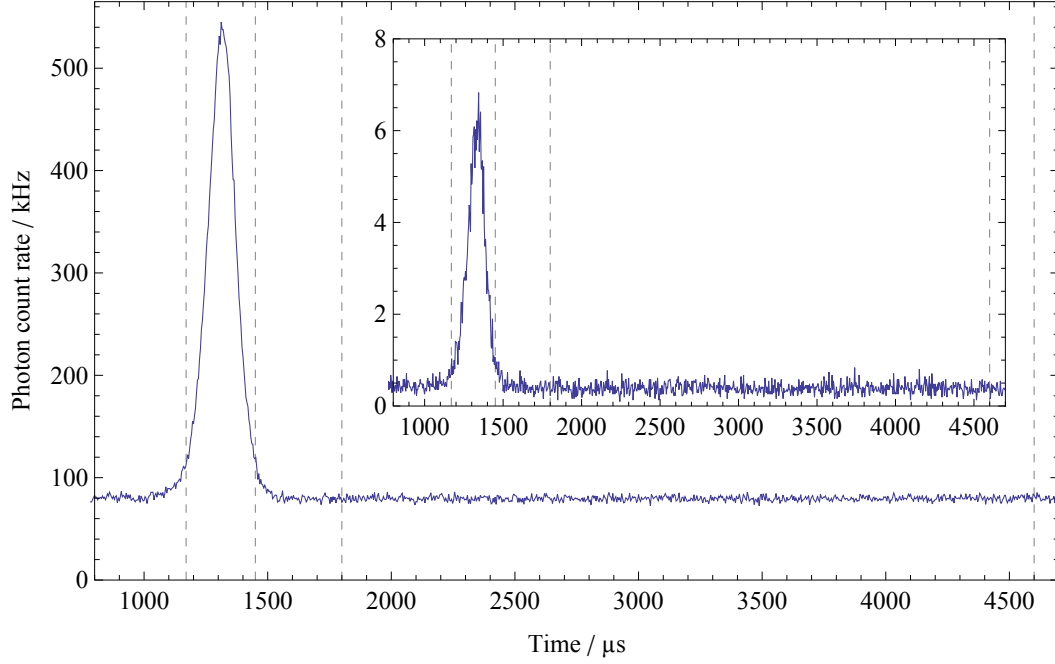


FIGURE 2.7: The time-of-flight profile we record on the signal PMT with a filter isolating the $A^1\Pi(v' = 0, J' = 1) \leftrightarrow X^1\Sigma^+(v'' = 0, J'' = 1)$ transition. Each time-of-flight profile is an average of 200 measurements. Inset: the time-of-flight profile for the $A^1\Pi(v' = 0, J' = 1) \leftrightarrow X^1\Sigma^+(v'' = 1, J'' = 1)$ transition (axes in the same units as the main plot). The dashed lines show the signal ($t = 1150, 1450$) and background ($t = 1800, 4600$) gates which we use in processing the data. The method of processing the data is described in detail in the text.

due to laser-induced fluorescence, since there may be some fluorescing by-product of the photodissociation process.

2.4.3 Characterisation of detection optics

As the amount of fluorescence we detect in transitions to higher lying vibrational states is expected to be very small, the calculation of the branching ratios becomes sensitive to the amount of light transmitted by each filter at the wavelength of the probe beam.

We have measured the transmissions of all of the filters and the non-polarising beam cube at the wavelengths of interest using a Fourier-transform spectrometer. We measured the transmission at the wavelength of the probe beam by sending

	430 nm filter	480 nm filter	540 nm filter	Longpass filter	Beamcube
433 nm	0.455(8)	$6(4) \times 10^{-7}$	$4.4(4) \times 10^{-6}$	$1(4) \times 10^{-7}$	0.51(4)
481 nm	1×10^{-5}	0.605(6)	5×10^{-7}	2×10^{-5}	0.52(4)
536 nm	1×10^{-5}	1×10^{-6}	0.568(8)	4×10^{-6}	0.51(4)
580 nm	3×10^{-6}	5×10^{-7}	5×10^{-7}	0.33(5)	0.47(4)

TABLE 2.1: The transmissions of the optical elements used in the detection set-up, at four different wavelengths. The standard error in the final digit is quoted in parentheses. Where there is no parenthesis, the measurement is limited by the statistical uncertainty, and the standard error is the same as the quoted transmission.

The longpass filter passes light with a wavelength greater than 570 nm.

	Efficiency
433 nm	0.20(2)
480 nm	0.17(2)
536 nm	0.13(2)
580 nm	0.09(2)

TABLE 2.2: PMT efficiencies at the wavelengths of interest. The 1σ uncertainty in the the final digit is shown in parentheses.

the probe beam through and measuring the transmittance on a photodiode. The measured transmissions of these optical elements are shown with their associated uncertainties in table 2.1.

We also measured the efficiency of the PMT response by shining light from a monochromator onto the PMT and recording the PMT current as a function of the wavelength of the light. The intensity of the light was determined using a calibrated photodiode. The efficiencies we measure are shown in table 2.2.

2.4.4 The results

In this section I present the measured count rates, and the procedure to convert these into a branching ratio. The data shown in tables 2.3 shows the average number of photons recorded by the signal PMT, which has a filter isolating the transition of interest, on a single run of the experiment. The counts shown in the table are from the “signal gate”, when the molecules pass through the detection region, with the count from the “background gate” subtracted, after multiplying by the ratio of the

	On shots	Off shots	Difference
$v'' = 0$	41.00(3)	0.017(2)	40.99(3)
$v'' = 1$	0.675(6)	0.003(2)	0.673(6)
$v'' = 2$	0.046(2)	0.004(1)	0.042(2)
$v'' = 3$	0.0007(6)	0.0018(6)	-0.0011(9)

TABLE 2.3: Photons per shot recorded on signal PMT. The vibrational state labelling refers to the transition isolated by the filter being used. All values represent a number of photons counted in the signal gate with the count from the background gate, multiplied by the ratio of signal gate duration to background gate duration, subtracted. On shots are taken with the probe beam illuminating the molecular pulse, off shots without. The difference shown is the number of laser-induced fluorescence photons that we report.

	On shots	Off shots	Difference
$v'' = 0$	116.73(6)	0.067(3)	116.66(6)
$v'' = 1$	127.74(9)	0.071(5)	127.66(9)
$v'' = 2$	146.97(7)	0.062(4)	146.91(7)
$v'' = 3$	120.58(3)	0.046(2)	120.53(3)

TABLE 2.4: Photons per shot recorded on normalisation PMT. The vibrational state labelling refers to the transition isolated by the filter being used. All values represent a number of photons counted in the signal gate with the count from the background, multiplied by the ratio of signal gate duration to background gate duration, subtracted. On shots are taken with the probe beam illuminating the molecular pulse, off shots without. The difference shown is the number of laser-induced fluorescence photons that we report.

the two gate durations. We alternate runs of the experiment with and without the probe beam, to remove any fluorescence not induced by the laser. These “on” and “off” shots are then subtracted to give the average number of photons recorded in a single shot. In table 2.4, the same data is shown for the normalisation PMT, which has no filter and continuously monitors the fluorescence to account for fluctuations of the molecular beam flux and probe beam intensity from shot to shot.

After subtracting these backgrounds, the ratios of the counts on the signal and normalisation arms of the detection set-up are shown in table 2.5. From these ratios we calculate the branching ratios between levels m and n , $Z_{m,n}$. The ratio is the sum of the amount of light emitted on each transition, scaled by the efficiency of the detection optics and a constant factor which accounts for the normalisation, k . Equation 2.6 gives the relationship for the ratio obtained when the 430 nm band-pass

Signal-normalisation ratio	
$v'' = 0$	0.3513(3)
$v'' = 1$	0.00527(5)
$v'' = 2$	0.00029(2)
$v'' = 3$	-0.0000009(8)

TABLE 2.5: The ratios of the photon count between the signal and normalisation PMTs for each transition.

filter is used. For the contribution of the detection optics we have the transmissions of the filter, $T_{F,\lambda}$, and the beamcube, $T_{B,\lambda}$, at wavelength λ ; and the efficiency of the PMT at that wavelength, ϵ_λ . There are three terms which account for light due to the transitions to the three lowest-lying states, and a fourth term which includes the contributions from transitions to all higher-lying vibrational states, $n > 2$.

$$R_{430} = \frac{1}{k}(\epsilon_{433}T_{B,433}T_{F430,433}Z_{0,0} + \epsilon_{481}T_{B,481}T_{F430,481}Z_{0,1} + \epsilon_{536}T_{B,536}T_{F430,536}Z_{0,2} + \epsilon_{\lambda>570}T_{B,\lambda>570}T_{F430,\lambda>570}Z_{0,n>2}). \quad (2.6)$$

In addition to equation 2.6, there are similar equations for the ratios obtained using the other filters. The scaling factor, k , and the branching ratios, $Z_{0,n}$, are common to all of the equations. These equations, taken together with the constraint $Z_{0,0} + Z_{0,1} + Z_{0,2} + Z_{0,n>2} = 1$, form a set of equations which can be solved for the branching ratios.

Table 2.6 shows the transition probabilities which we compute. The effect of the rotational state on the transition probabilities is expected to be negligible; within the Born-Oppenheimer approximation the rotational state has no effect on the vibrational degree of freedom. The measurement was repeated exciting the R(0) transition and the values were found to be identical within the uncertainty of the measurement.

A previous measurement found $A_{01}/A_{00} = 0.0051(7)$ [53], which differs from our result by 4 standard deviations. None of the other branching ratios had previously been measured. There have been calculations of the branching ratios by Luh and

	Experimental	Theoretical
$v'' = 0$	0.9863 (19)	0.99054
$v'' = 1$	0.0128 (18)	0.00888
$v'' = 2$	0.00093 (15)	0.00057
$v'' = 3$	< 0.00007	9.46×10^{-6}

TABLE 2.6: Probabilities for decay from $A^1\Pi(v' = 0)$ to $X^1\Sigma^+(v'')$. The numbers in parentheses are the 1σ uncertainties in the final digits. For $v'' = 3$ we give the 90% confidence upper limit. Theoretical values are derived from [57].

Stwalley [57], which agree with our results to an absolute accuracy of 0.004, and to within 2.5 standard deviations.

The experimental results are normalised so that their sum is unity, assuming that the branching ratios to all $v'' > 3$ are much smaller than those measured. From Luh and Stwalley [57] we find the branching ratios to $v'' > 3$ to be 10^{-7} or less, justifying this assumption. For $v'' = 0, 1$ and 2 the uncertainty is dominated by the uncertainties in the relative transmission of the detection optics and sensitivity of the PMT at different wavelengths. Our $v'' = 3$ upper limit is limited by the statistical uncertainty in the measured difference between probe on and off. The measured decay probabilities allow for an average of 78 scattering events before loss to $v'' = 1$ or, if this state is included in the cooling scheme, 1075 scattering events before loss to $v'' = 2$. In this case a molecule could be decelerated by about 83 m s^{-1} .

2.4.5 Transition to triplet state

The $a^3\Pi$ state, shown in figure 2.1, is lower in energy than the $A^1\Pi$ -state. The energy separation of the X and a states has been measured to within a few percent from the difference in their dissociation energies [61, 62], and this is in agreement with values obtained theoretically [63, 64]. From these, we expect the wavelength of the $A^1\Pi \rightarrow a^3\Pi$ transition to be at 788(23) nm. We expect the branching ratio for this transition to be strongly suppressed as an electric dipole transition cannot change spin. The transition can occur as a magnetic dipole transition, or through a mixing of the electronic states, although the rate would be much slower. Using

a broadband interference filter, we isolate the light in this wavelength range and search for fluorescence from this transition. We see none, and thus determine a 90% confidence upper limit to the branching ratio for this decay route to be 3.4×10^{-4} , limited by the statistical uncertainty.

2.5 Results II - hyperfine structure of the $A^1\Pi(J = 1)$ state

To design the laser cooling experiment we need to understand the hyperfine structure of the excited state involved in the laser cooling transition. This will allow us to select which hyperfine component is used in the cooling scheme. Here, we measure this hyperfine structure and determine the associated molecular constants.

2.5.1 Hamiltonian used to model system

The hyperfine structure of the excited state is modelled using the Hamiltonian [56]

$$H = a_B(\mathbf{I}_B \cdot \mathbf{L}) + a_H(\mathbf{I}_H \cdot \mathbf{L}) - eT^2(\nabla\mathbf{E}) \cdot T^2(Q), \quad (2.7)$$

where $\mathbf{L}$ is the electronic orbital angular momentum, and $\mathbf{I}_B$ and $\mathbf{I}_H$ are the spins of the boron and hydrogen nuclei. The hyperfine parameters a_B and a_H determine the strength of the interaction between the nuclear magnetic moments and the magnetic field at the nuclei due to the electronic motion. The final term in 2.7 describes the interaction of the electric quadrupole moment of the boron nucleus, Q , with the electric field gradient, $\mathbf{E}$, at the nucleus and is represented as the scalar product of two second-rank tensors. The matrix elements of this electric quadrupole interaction are given by equation (8.382) of reference [56]. Two coefficients appear in these matrix elements, eq_0Q and eq_2Q , where q_0 represents the electric field gradient in the direction of the internuclear axis, and q_2 the field gradient in the perpendicular direction. The matrix elements of the electric quadrupole interaction are proportional to $eq_0Q - eq_2Q$ for the positive parity component, and to $eq_0Q +$

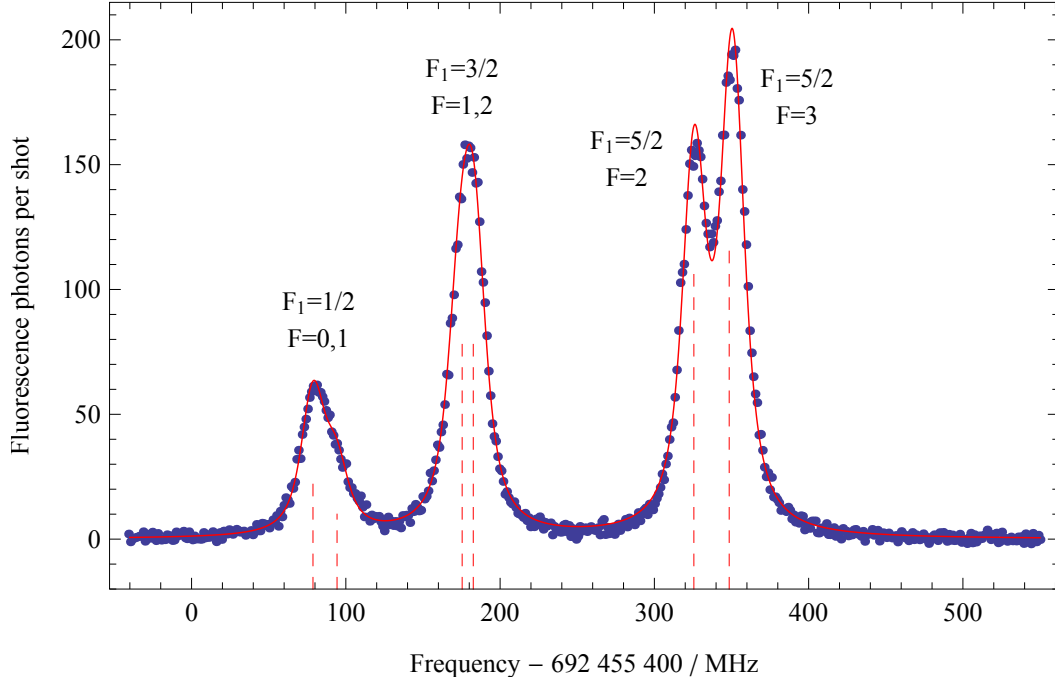


FIGURE 2.8: The optical spectrum obtained by scanning the frequency of the probe laser over the R(0) component. The fitted line is a sum of six Voigt functions. The hyperfine components of the upper state to which the peaks correspond have been labelled. The line centres and their associated errors obtained from the fitting process are tabulated in 2.7.

eq_2Q for the negative parity component of the A state, and so these two components can be separated by measuring both the R(0) and Q(1) optical spectra, which connect to the negative and positive parity components respectively, as shown in figure 2.1.

2.5.2 Results

Figure 2.8 shows the laser-induced fluorescence spectrum of the R(0) component of the $A^1\Pi(v' = 0) \leftrightarrow X^1\Sigma^+(v'' = 0)$ transition, which results from scanning the laser frequency. Each point on the plot is the total signal observed in a 250 μ s time window, centred around the peak of the TOF profile. The signal from both PMTs is summed in this measurement and there is no filter in front of either. A similar spectrum is recorded on the Q(1) line.

Line centre / MHz	78.7	93.7	173.8	183	325.8	350.68
Error / MHz	0.3	0.6	0.4	0.3	0.08	0.06

TABLE 2.7: Line centres and errors from Voigt profiles fitted to the data in figure 2.8.

The transition shows broad splitting into three components due to the hyperfine interaction in the upper state, where there is non-zero electronic orbital angular momentum. The hyperfine structure of the ground state is far smaller and can be neglected here. The three main lines in the spectrum 2.8 correspond to the three F_1 components arising from the boron nuclear spin. The smaller splitting due to the hydrogen nuclear spin is resolved in the $F_1 = 5/2$ component, results in a shoulder in the $F_1 = 1/2$ component, and is unresolved in $F_1 = 3/2$. The data in the spectrum is fitted with a sum of six Voigt functions, with Lorentzian and Gaussian widths common to each component. For the Gaussian component, due to Doppler broadening, we find the full width at half maximum to be 11 MHz, while for the Lorentzian component, due to power broadening, it is 14 MHz. From these fits we obtain the hyperfine intervals with an accuracy limited by the frequency calibration of the laser scan. We analyse the Q(1) data in a similar way. We fit measured hyperfine intervals to the eigenvalues of Hamiltonian 2.7 to determine the hyperfine constants given in table 2.8. With these best fit values, the experimental hyperfine intervals, and those determined from the Hamiltonian 2.7, all agree within one standard deviation, showing that the Hamiltonian is adequate to describe the data.

2.6 Results III - hyperfine structure of the $X^1\Sigma^+(v = 0, J = 0)$ state

The magnitude of the hyperfine interaction in the ground state had not previously been measured. The splitting of the lower state is of particular importance to the design of the cooling scheme because, if the levels are well separated, then the laser linewidth may have to be broadened in order to address all of the levels. We use the Hamiltonian given in Rothstein [67] to describe the ground-state hyperfine

		Experimental	Theoretical
$X^1\Sigma^+(v=0)$	f_{01}	708309.211 (9)	-
	eq_0Q	-6.43(5)	-6.5951
	c_B	0.410(5) (15)	0.45374
	c_H	$ c_H < 0.04$	-0.01370
	c_3	$c_3 < 0.03$	-0.02020
	c_4	$c_4 < 0.03$	-
$A^1\Pi(v=0)$	a_B	108(11)	-
	a_H	36(5)	-
	eq_0Q	30(6)	-
	eq_2Q	-27(6)	-

TABLE 2.8: Lowest rotational transition frequency, and hyperfine constants for ^{11}BH . All values are in MHz. The theoretical values are derived from Vojtík et al. [65] and Sauer and Paidarová [66].

structure. The hyperfine structure in $J = 1$ is dominated by the interaction of the electric quadrupole moment of the boron nucleus with the local electric field gradient (coefficient $-eq_0Q$), and the interaction of the magnetic dipole moment of the boron nucleus with the magnetic field arising from the rotation of the molecule (coefficient c_B). Together, these give rise to a splitting into three main components with intermediate quantum number $F_1 = 1/2, 3/2, 5/2$. When the hydrogen nuclear spin is included, each of these is further split, resulting in six levels with total angular momentum $F = 0, 1, 1, 2, 2, 3$ as shown in 2.1. This splitting is very small and is due to the interaction of the hydrogen magnetic dipole moment with the magnetic field of the rotating molecule (coefficient c_H), along with the direct and electron-mediated interaction between the two nuclear spins (c_3 and c_4). For $J = 0$, only the c_4 term is present and the hyperfine structure is exceedingly small.

We measure the ground state $J = 1$ hyperfine structure by driving the millimetre-wave transition between $J = 0$ and $J = 1$. Figure 2.9 shows typical millimetre-wave spectra obtained by measuring the fluorescence on either R(0) or Q(1) as a function of the millimetre-wave frequency, which is stepped between shots of the experiment in a random order. In the lower trace the probe is resonant with the $J = 0$ sublevels, and we see a drop in the fluorescence rate as molecules are driven into the $J = 1$ sublevels by the millimetre-wave radiation. With the laser locked instead to the Q(1) transition, we see a corresponding resonant increase in the fluorescence rate,

Line centre / MHz	-2.4674	-0.187	0.1677
Error / MHz	0.0005	0.001	0.0004

TABLE 2.9: Line centres and errors from Gaussian profiles fitted to the data in figure 2.9.

as shown in the upper graph. After accounting for the molecular population already in the $J = 1$ state, we estimate a peak transfer efficiency of about 40%, limited by the available millimetre-wave power. In these spectra we observe splitting into the three F_1 components arising from the boron nuclear spin. The smaller splitting due to the hydrogen nuclear spin is not resolved. We fit the spectra to a sum of three Gaussians to obtain the centre frequencies of the three components. The centroids and errors associated with the fits are tabulated in 2.9. Assignment of the lines is aided by the observation that the number of components in the spectrum depends on which of the excited state hyperfine components of the Q(1) transition is used for detection (see figure 2.8). When the laser is tuned to excite the $F_1 = 3/2$ component of the A state, all three hyperfine components of the rotational transition are observed, as shown in figure 2.9. However, if the $F_1 = 5/2(1/2)$ component of the A state is used for detection, the $F_1 = 1/2(5/2)$ component of the rotational transition disappears.

Inevitably, the rotational spectrum is Doppler-shifted because the millimetre-wave beam is not perfectly perpendicular to the molecular beam. We measure this shift by changing the speed of the molecules. This is done by mixing the diborane and argon gas with helium in various ratios. The reduction in the average mass of the carrier gas increases the speed of the molecular beam. The fitted line centres shift linearly with the speed, with a gradient of 30 Hz/(m/s). The shift of one of the peaks is shown in figure 2.10. We extrapolate to zero speed to obtain the Doppler-free centre frequencies. These frequencies are fitted to the model $f_{01} + \langle \mathbf{H}_{\text{hfs}} \rangle$, where f_{01} is the hyperfine-free rotational transition frequency, and $\langle \mathbf{H}_{\text{hfs}} \rangle$ are the eigenvalues of the hyperfine Hamiltonian in Rothstein [67], with c_{H} , c_3 and c_4 all set to zero. The values of f_{01} , eq_0Q and c_{B} determined in this way are given in table 2.8. Their uncertainties are dominated by the unresolved substructure due to the hydrogen nuclear spin, which limits the precision to roughly the linewidth. The two hyperfine constants agree with the theoretical predictions [65, 66] to within 2.5%

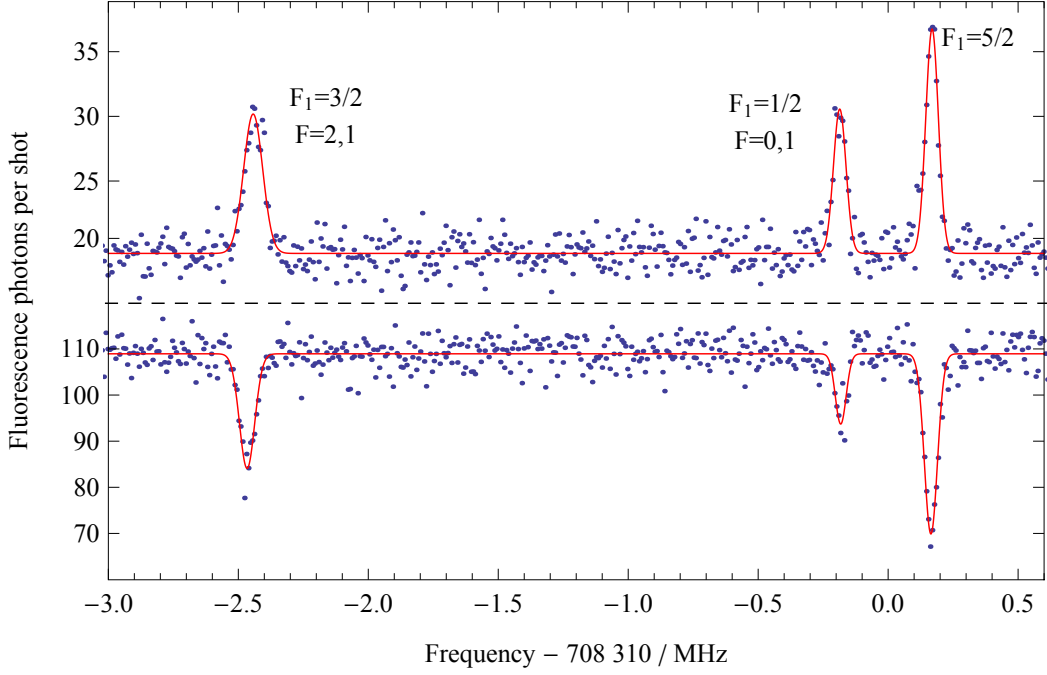


FIGURE 2.9: Spectra observed scanning the THz frequency with the laser locked to the Q(1) transition. The upper part of the figure shows the fluorescence when we look at the $A^1\Pi(v' = 0, J' = 1, F' = 3/2) \leftrightarrow X^1\Sigma^+(v'' = 0, J'' = 1)$ transition. The lower part of the figure shows the fluorescence when we look at the $A^1\Pi(v' = 0, J' = 1, F' = 3/2) \leftrightarrow X^1\Sigma^+(v'' = 0, J'' = 0)$ transition. The red line is a fit to the data of a sum of three Gaussians. The Gaussian centroids and associated errors are tabulated in 2.9.

and 10% respectively. Using the measured linewidths, and the fact that all three widths are equal within their uncertainties, we obtain the upper limits to c_H , c_3 and c_4 given in table 2.8. These are also consistent with the theoretical predictions. The microwave transition lies in the THz region of the spectrum. We measure the transition frequency to a precision of 10 parts-per-billion, making this a very precise measurement. It is important to know this frequency, since in later experiments we fix this frequency in order to populate the $J = 1$ state that we need to use for the laser cooling work.

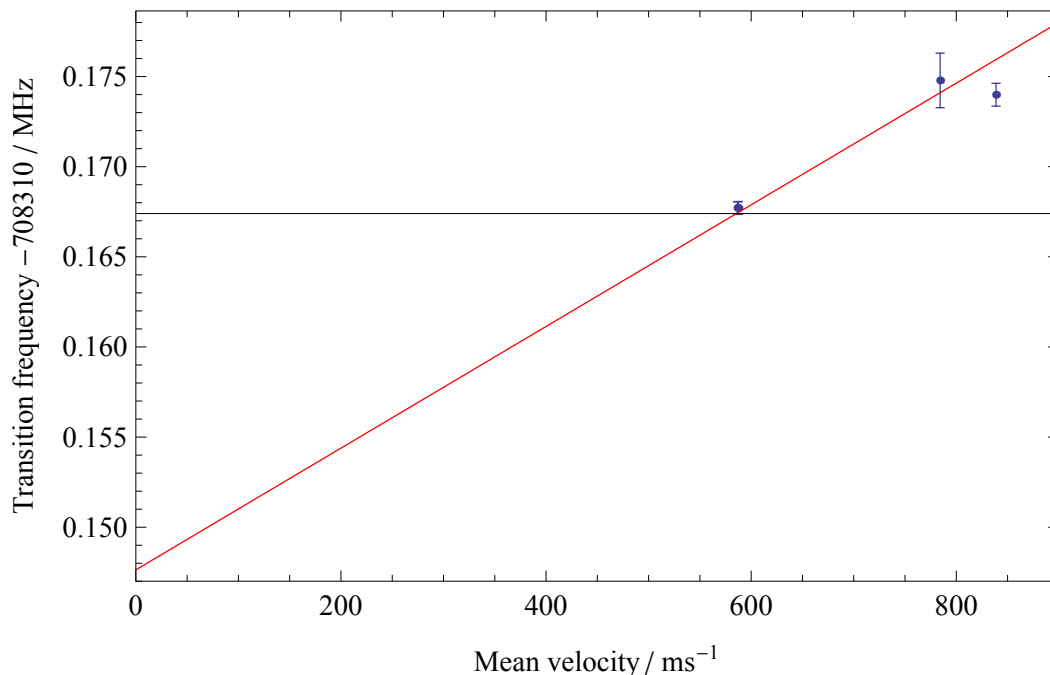


FIGURE 2.10: The shift of one of the peaks in figure 2.9 as the mean velocity of the molecular pulse is changed by varying the carrier gas. We fit a straight line to the data points to extrapolate to the Doppler-free transition frequency. The same fitting procedure is used for the other two peaks in figure 2.9.

2.7 Discussion

The results obtained in this chapter indicate that BH is a good choice of molecule for laser cooling on the $A(v' = 0) \leftrightarrow X(v'' = 0)$ Q(1) transition. Two laser frequencies, one addressing the $v'' = 0$ branch at 433 nm and the other repumping the $v'' = 1$ branch at 481 nm, are sufficient to allow each molecule to scatter an average of 1000 photons before being optically pumped to a higher vibrational state. This corresponds to a change in velocity of 77 ms^{-1} , sufficient to capture a large fraction of the velocity distribution emitted by a cryogenic buffer gas source [38].

The ground state hyperfine structure spans 2.7 MHz, about twice the natural linewidth of the transition. The next chapter considers the issue of addressing all of the hyperfine components in the ground state.

Chapter 3

Optical cycling experiments

3.1 Introduction

Having established that the vibrational structure of BH is amenable to laser cooling, the next steps are to determine the best way of addressing the ground-state hyperfine components and to choose the excited-state hyperfine level we should use. At first sight it may appear that the choice of upper state is irrelevant; whichever state we excite to, the population will spontaneously decay, and the decay will return most of the population to the initial state. However, the excited states differ in the value of the total angular momentum quantum number, F , which restricts the ground states which will couple to them. So we have to consider which system of states coupled by laser radiation can give the greatest scattering rate and thus, rate of momentum transfer. The rate of scatter is proportional to the excited state population, so that we have to consider the conditions which give the greatest excited state population.

In addition to choosing the upper state in the excited system, we have also to consider the possibility that the coupled light-molecule system will develop eigenstates which do not cause further scattering of light. In the basis of the unperturbed molecular states, these dark states can be seen as coherent superpositions of the ground state sublevels, for which the transition dipole matrix element with any of the excited states vanishes.

Initially, we consider the interaction of radiation which has a linear polarisation fixed in space, with a molecule in field-free space. In an electric dipole transition, the total angular momentum of the molecular state can change by at most one unit. The combinations of excited- and ground-state angular momentum which give rise to dark states are listed in Berkeland [68]. For half-integer systems, including the $A^1\Pi(v' = 0; J' = 1; F' = 1/2, 3/2, 5/2) \leftrightarrow X^1\Sigma^+(v'' = 0; J'' = 1; F'' = 1/2, 3/2, 5/2)$ systems of BH, coupled by a linearly polarised exciting field, we expect there to be a dark state when F' is smaller than F'' . This means there will be a dark state for the $A^1\Pi(v' = 0; J' = 1; F' = 3/2) \leftrightarrow X^1\Sigma^+(v'' = 0; J'' = 1; F'' = 5/2)$ system. Exciting to $F' = 5/2$, on the other hand, there is no dark state for linear polarisation (although there is for circularly polarised light). Upon first inspection, it appears to be better to excite to the $F' = 5/2$ excited state, although this will mean that population in the $F'' = 1/2$ ground state cannot be excited, due to the angular momentum selection rules associated with the transition. Which system to excite is one of the questions that this chapter seeks to answer.

Ultimately, we would like to be able to independently vary several parameters, including the laser intensity in order to determine the optimal situation for optical cycling. We have two further considerations which are: first, how to address all of the hyperfine components in the ground state simultaneously, and second, how to destabilise dark states. The solution to both of these questions turns out to be the same, because in both cases we have to perturb the sublevels of the ground electronic state. This can be achieved in a number of ways, some of which are listed in Berkeland [68]. Typically, we would either apply a magnetic field at some angle to the axis in which the exciting field is polarised, or alternatively, continuously vary the polarisation of the exciting field. These methods both exploit the fact that a dark state is one which is invariant under the application of the oscillating electric field. We destabilise any such invariant state by changing the axis in which the field is polarised, or by applying a magnetic field at some angle to the polarisation, so that the states in the basis of the field experience a perturbation which constantly remixes the population.

The approach taken in this chapter roughly follows the order in which the work has been done and is laid out as follows: first, I model the interacting light-molecule

system semiclassically to understand how best to ensure a high scattering rate; following this I will describe the experimental work, which was informed by the results of the model, and demonstrates our ability to continuously cycle photons.

3.2 Modelling the light-molecule interaction

3.2.1 Treatment

We would like to write down an accurate description of the system of interacting states of the bound molecule and perturbing radiation field. We have already considered the description of the bound states of the molecule in chapter 2, and found that we are able to find a set of quantum numbers which adequately describe the molecular state at low excitation numbers. To include the quantum mechanical state of the radiation field in our description, we have to follow another approximation, as the number of possible states of the field which can interact with the molecule is infinite for a field in free space. In particular, we need to obtain information about the rate at which vacuum fluctuations of the field cause the excited molecular state to decay to the ground state. We also need to be able to model the perturbing laser field, which causes the initial excitation. These two couplings have very different properties, so they are treated separately.

The vacuum fluctuations of the field in free space constitute an infinite set of states which cannot be explicitly included in a calculation. They are dealt with using the formalism of the Markovian master equation, which allows us to sacrifice information about the state of the field, and keep information about the rate at which the perturbation causes decay. On the other hand, the laser field is in a coherent state, and can be treated as a classical field. Since the molecule only emits a small amount of light, and the laser field is very intense, it does not significantly perturb the state of the laser field. Including these two components in the description, together with the free evolution of the molecular state, allows us to calculate the elements of the density matrix. The resulting Liouville equations for the time-evolution of the elements of the molecular density matrix are the generalisation of the optical Bloch equations for a two-level system.

We now discuss the optical Bloch equations for the two-level system. The full list of equations for our system has been included in appendix A for reference. We can write down a reduced density matrix for the two-level system, σ , which does not contain any information about the state of the radiation field

$$\sigma = \begin{pmatrix} \sigma_{aa} & \sigma_{ab} \\ \sigma_{ba} & \sigma_{bb} \end{pmatrix}. \quad (3.1)$$

In our system, a labels the ground state, and b , the excited state. The time-dependence of the elements of the reduced density matrix, neglecting the interaction of the system with the vacuum field, is given by the Schrödinger equation,

$$i\hbar\dot{\sigma} = [H_A - d \cdot \mathbf{E}_0 \cos \omega_L t, \sigma]. \quad (3.2)$$

Here H_A is the Hamiltonian of the isolated two-level system, $\mathbf{d} = \langle \psi | e \mathbf{r} | \psi' \rangle$ is the transition dipole moment between the two states of the system, and $\mathbf{E}_0$ is the amplitude of the incident, monochromatic field of frequency ω_L .

The elements of the density matrix can then be shown to be given by the optical Bloch equations, which also include a damping term, Γ . See Cohen-Tannoudji [52] for more details of the derivation.

$$\dot{\sigma}_{bb} = i\Omega_R \cos \omega_L t (\sigma_{ba} - \sigma_{ab}) - \Gamma \sigma_{bb}, \quad (3.3)$$

$$\dot{\sigma}_{aa} = -i\Omega_R \cos \omega_L t (\sigma_{ba} - \sigma_{ab}) + \Gamma \sigma_{bb}, \quad (3.4)$$

$$\dot{\sigma}_{ab} = i\omega_0 \sigma_{ab} - i\Omega_R \cos \omega_L t (\sigma_{bb} - \sigma_{aa}) - \frac{\Gamma}{2} \sigma_{ab}, \quad (3.5)$$

$$\dot{\sigma}_{ba} = -i\omega_0 \sigma_{ba} + i\Omega_R \cos \omega_L t (\sigma_{bb} - \sigma_{aa}) - \frac{\Gamma}{2} \sigma_{ba}. \quad (3.6)$$

The intensity of the perturbing laser field is contained within Ω_R , the Rabi rate; defined as

$$\hbar\Omega_R = -\mathbf{d} \cdot \mathbf{E}_0. \quad (3.7)$$

The equations, 3.3-3.6, can be used to compute the population occupancies (σ_{aa} and σ_{bb}) and the coherences (σ_{ab} and σ_{ba}) as a function of time. The rate at which light is scattered from the molecules depends on the excited state population as $\Gamma\sigma_{aa}$. The first consideration is whether population will be driven into a dark state which cannot be excited by the laser. The next is to find the intensity of radiation that will optimise the excited state population. In the case where the polarization is being continuously modulated, there is no steady state, but we can identify a quasi-steady state by averaging over a few times the modulation period. We compute the population in the quasi-steady-state to see how much momentum can be transferred to a molecule.

We can add a magnetic field to this picture by modifying the molecular Hamiltonian to include a term for the Zeeman shift of the levels, $-\mu B$; with μ , the mean value of the component of the magnetic moment in the field direction, and B , the magnetic field strength. The magnetic moment has contributions due to the electronic and nuclear angular momenta. The electronic motion leads to a contribution on the order of the Bohr magneton, μ_e , while the nuclear motion has a contribution on the order of the nuclear magneton, $\mu_N \sim 1/1850\mu_e$. In the $A^1\Pi$ state, the electronic motion has the greatest contribution, while in the lower state the magnetic moment is mostly due to the rotation of the molecule. The sublevels of the $X^1\Sigma^+$ state are, therefore, only weakly perturbed by a magnetic field. By modelling the system, we determine the magnetic field that would be required to maintain a significant excited state population.

We solve the problem in the basis of the eigenstates of the molecule in the presence of the magnetic field. The polarisation of the electric field is defined relative to the magnetic field axis. We can make the angle at which the electric field is polarised time-dependent following Berkeland [68], by writing the electric field in terms of its spherical components (E_{-1}, E_0, E_{+1})

$$\begin{pmatrix} E_{-1} \\ E_0 \\ E_{+1} \end{pmatrix} = \frac{E_0}{\sqrt{2}} \begin{pmatrix} 1 + ie^{-i\phi(t)} \\ 0 \\ 1 - ie^{-i\phi(t)} \end{pmatrix}, \quad (3.8)$$

$$\phi = \frac{1}{2}\Phi(1 - \cos(\delta_{\text{EOM}}t)). \quad (3.9)$$

This represents the electric field modulated by an electro-optic modulator (EOM) with retardation ϕ ; with δ_{EOM} , the EOM drive frequency, and Φ , the phase-modulation amplitude. We investigate the effect of changing the modulation frequency and determine the excited state population that can be achieved for different laser intensities.

The following section gives the results of the model. The set of equations given in appendix A are solved using *Mathematica* 7.0. The data for figure 3.2 was produced using the *Atomic Density Matrix* package (Rochester Scientific LLC).

3.2.2 Results

We first confirm that if a magnetic field alone is used to destabilize the dark states it would have to be extremely intense to ensure a good scattering rate in the BH molecule. We then consider the effect of modulating the polarisation on the excited state population in both systems (i.e. driving to either $F' = 5/2$ or $F' = 3/2$), for different beam intensities. The two schemes are illustrated in figure 3.1.

The dependence of the excited-state population on the magnetic field is shown in figure 3.2, for a field aligned at $\theta = 45^\circ$ to the polarisation of the exciting laser field. The laser excites the transition to the $F_1 = 5/2$ excited state. The data is calculated by solving the Liouville equations in the steady state using the *Atomic Density Matrix* package. The figure shows that applying a strong magnetic field at $\theta = 45^\circ$ (or at any angle other than $\theta = 0^\circ$) destabilises the dark state to some degree. The Zeeman effect in the ground state is assumed to be approximately $3\mu_N B$, as the nuclear magnetic moments of the boron and hydrogen nuclei are 2.7 and $2.8\mu_N$, respectively [58].

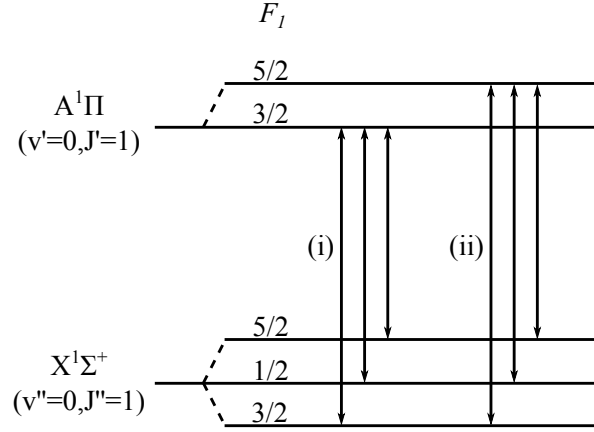


FIGURE 3.1: The two schemes we investigate for optical cycling: (i) the $A^1\Pi(F' = 3/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system and (ii) the $A^1\Pi(F' = 5/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system.

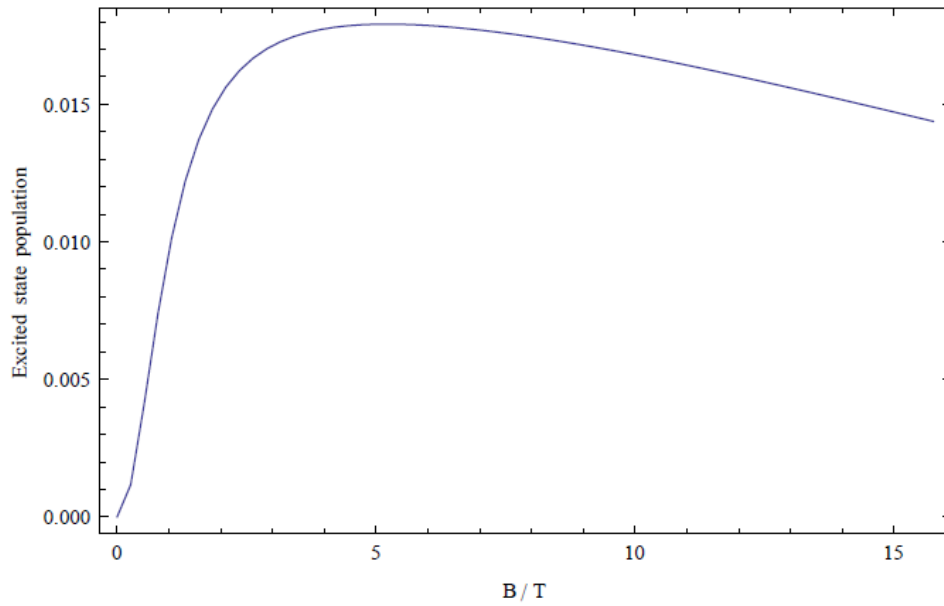


FIGURE 3.2: Excited state occupancy as a function of magnetic field, with a field applied at 45° to the polarisation of the laser field. Here, the laser drives to the $F_1 = 5/2$ excited state. The applied laser field produces a Rabi rate equal to the rate of spontaneous emission ($\Omega_R = \Gamma$).

The figure shows clearly that there is an optimal magnetic field strength which produces the highest occupancy of the excited state. At low field strength, the laser field drives the population into a dark state, and there is no excited-state population in the steady state. As the magnetic field strength increases, the dark state is destabilised and so the excited-state population increases. At higher field strengths, the levels are Zeeman-shifted off resonance, and so the excited-state population decreases again. Further investigation shows that the excited-state population can be increased by increasing the laser intensity, which power-broadens the transition. A very large field is required due to the small magnetic moment in the ground state.

Figures 3.3 and 3.4, show the time-evolution of different states in the $A^1\Pi(F' = 3/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system, obtained by solving the Liouville equations. Figure 3.3 shows the evolution of the states with a laser field that has a fixed polarisation, while figure 3.4 shows the time-evolution with modulated polarisation. In this system, a superposition of states from the $X^1\Sigma^+(F'' = 5/2)$ form a dark state in which population accumulates, when there is a fixed polarisation. We see that modulating the polarisation allows there to be some excited state population in the steady-state, although it is not very large.

Figure 3.5, shows how the excited-state population depends upon both the Rabi rate and the modulation frequency. To approximate the steady-state population, I calculate the excited-state population for a given set of parameters using the Liouville equations, and then compute the mean population over ten natural lifetimes (10τ) in the region $35\tau < t < 45\tau$. In this figure, we can see that there is an optimal combination of Rabi rate and modulation frequency; as in the case of the magnetic field, an excessively high modulation rate does not give ever increasing returns, in this case because modulating the polarization also adds frequency sidebands to the laser and too much of the intensity goes into these sidebands when the modulation rate is high. We see here that increasing the Rabi rate to many times the spontaneous emission rate produces a higher occupancy in the excited state. The excited state population reaches about 20% when the Rabi frequency is about 12Γ and the polarisation modulation rate is about 3Γ . The best Rabi frequency is always about four times the polarisation modulation rate.

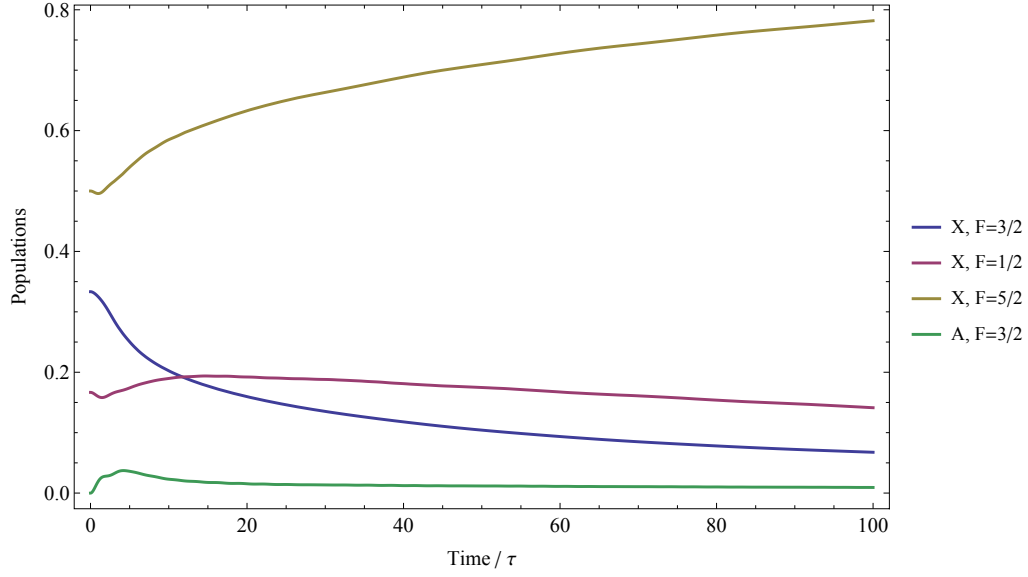


FIGURE 3.3: State occupancies for all states in the $A^1\Pi(F' = 3/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system with time, in units of the natural lifetime. The applied laser field is plane-polarised ($\theta = 0^\circ$), and has a Rabi rate equal to the rate of spontaneous emission ($\Omega_R = \Gamma, \delta_{\text{EOM}} = 0$).

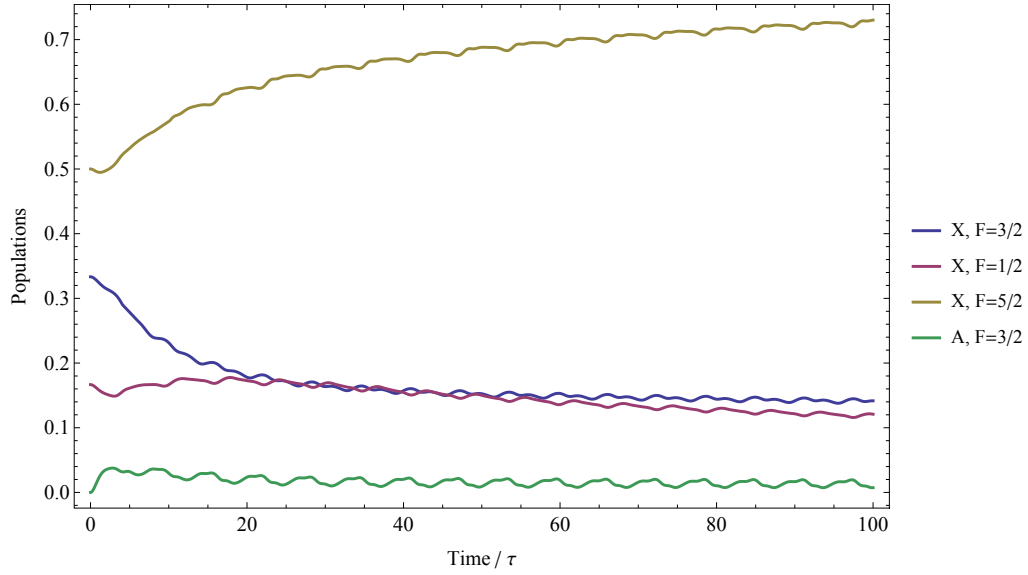


FIGURE 3.4: State occupancies for all states in the $A^1\Pi(F' = 3/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system with time, in units of the natural lifetime. The applied laser field produces a Rabi rate equal to the rate of spontaneous emission, and has its polarisation modulated at the same rate ($\Omega_R = \delta_{\text{EOM}} = \Gamma, \Phi = \pi$).

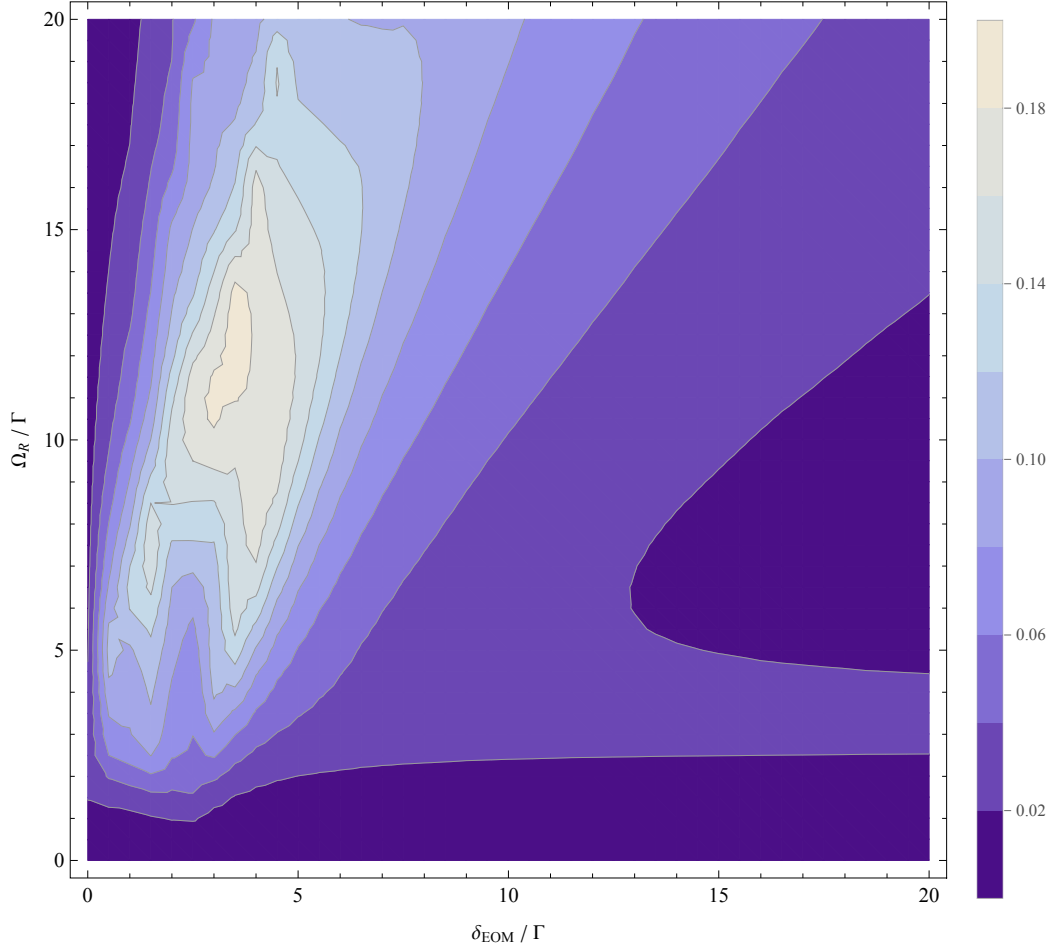


FIGURE 3.5: $A^1\Pi(F' = 3/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ excited-state occupancy in the steady state, for various combinations of Rabi rate and modulation frequency.

Figures 3.6, 3.8, and 3.9, show the same situations but for the $A^1\Pi(F' = 5/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system. The excited-state population is still dependent on the modulation frequency, but there is no dark state for plane-polarised light, and figure 3.9 shows that there is no region of optimal laser intensity. Figure 3.7 shows the case for plane polarised light at a higher intensity. Here the excited state population is more clearly visible, showing that there is no dark state. The modulation is still useful, because it shifts some of the laser power into additional frequency sidebands, which are better able to address the ground-state sublevels.

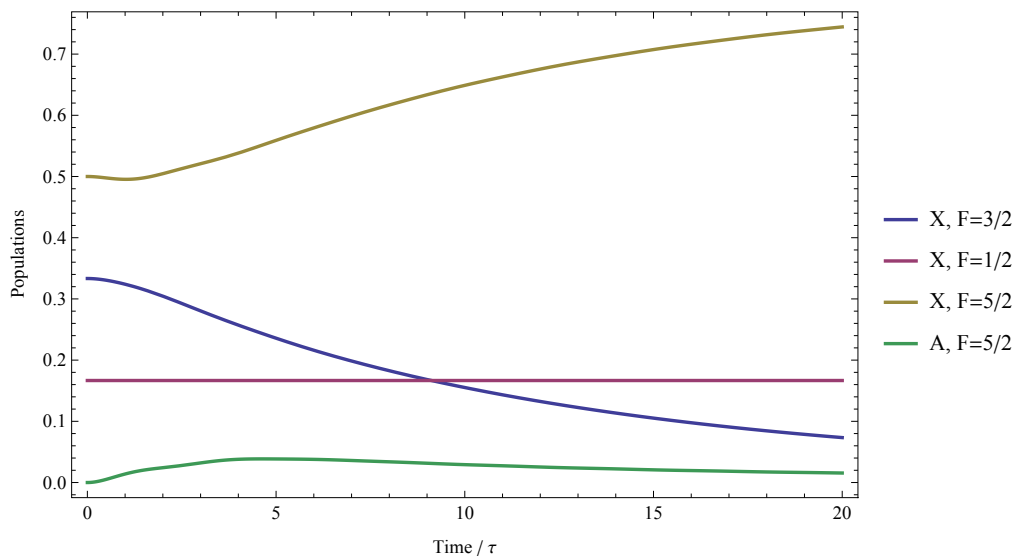


FIGURE 3.6: State occupancies for all states in the $A^1\Pi(F' = 5/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system with time, in units of the natural lifetime. The applied laser field is plane-polarised ($\theta = 0^\circ$), and has a Rabi rate equal to the rate of spontaneous emission ($\Omega_R = \Gamma, \delta_{\text{EOM}} = 0$). The $A^1\Pi(F' = 5/2)$ -state contains a very small, but non-zero, fraction of the population (around 0.4% at $t = 200$).

Compare with figure 3.7.

We can also see that population in the $X^1\Sigma^+(F'' = 1/2)$ state is not coupled to the system, due to the angular momentum selection rules.

An important feature of figure 3.9 is the small region at ($\delta_{\text{EOM}} = 0, \Omega_R = 6\Gamma$), where the excited-state occupancy reaches 0.2 without any modulation. This suggests that a sufficient increase of power broadens the transition to a point which allows us to ignore the splitting of the ground-state sublevels.

3.2.3 Discussion

The results of modelling the molecule-light interaction using the Liouville equations tell us that a magnetic field would need to be around 5 T in order to produce a useful effect in destabilizing dark states. This is too high to be feasible. We also find that we can do better if we excite population to the $F' = 5/2$ level, reaching excited state occupancies of around 0.25 rather than 0.18 for $F' = 3/2$. We see, however, that to

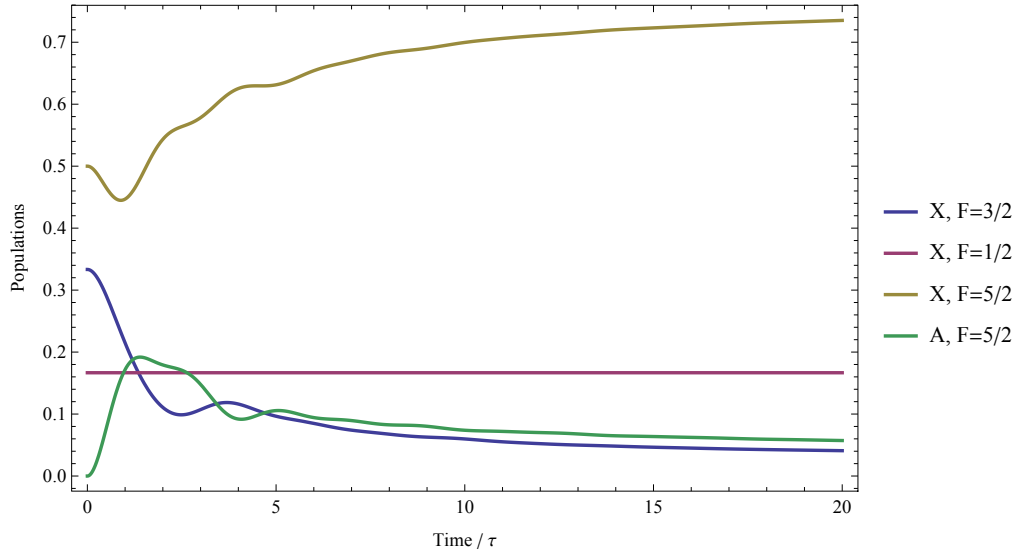


FIGURE 3.7: State occupancies for all states in the $A^1\Pi(F' = 5/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system with time, in units of the natural lifetime. The applied laser field is plane-polarised ($\theta = 0^\circ$), and has a Rabi rate equal to four times the rate of spontaneous emission ($\Omega_R = 4\Gamma, \delta_{\text{EOM}} = 0$). Compare with figure 3.6 which is the same but with a less intense laser field.

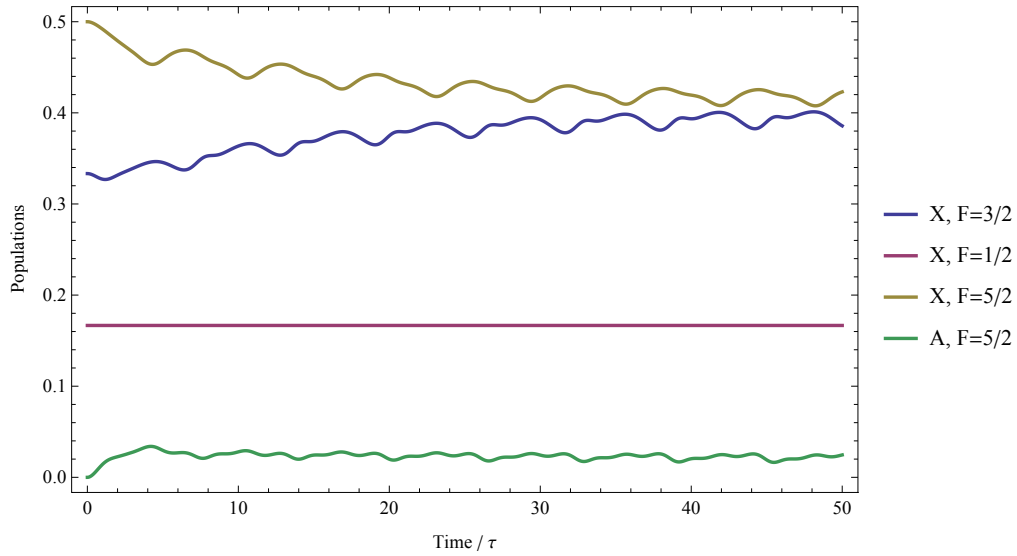


FIGURE 3.8: State occupancies for all states in the $A^1\Pi(F' = 5/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ system with time, in units of the natural lifetime. The applied laser field produces a Rabi rate equal to the rate of spontaneous emission, and has its polarisation modulated at the same rate ($\Omega_R = \delta_{\text{EOM}} = \Gamma, \Phi = \pi$).

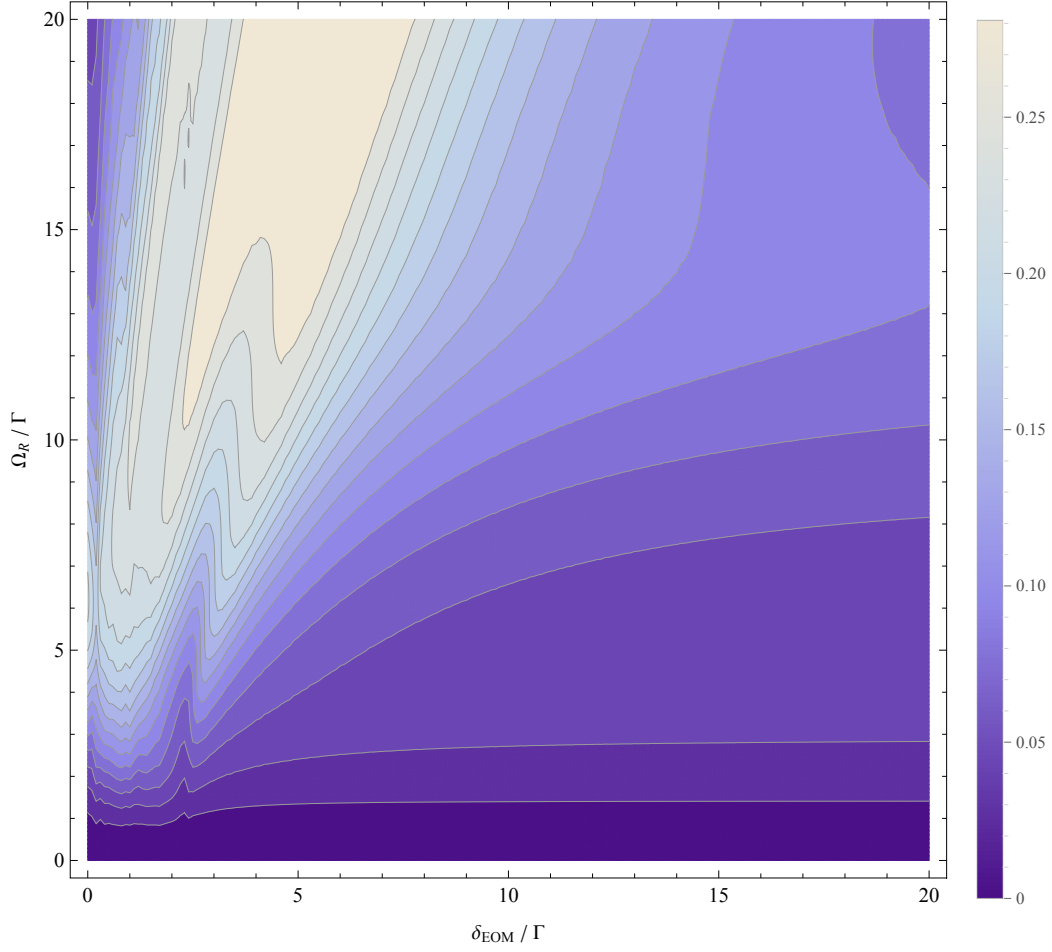


FIGURE 3.9: $A^1\Pi(F' = 5/2) \leftrightarrow X^1\Sigma^+(F'' = 1/2, 3/2, 5/2)$ excited-state occupancy in the steady state, for various combinations of Rabi rate and modulation frequency.

reach these high occupancies we need to produce a laser field which has a Rabi rate around ten times the rate of spontaneous emission, with the polarisation modulated at a frequency around four or five times Γ . The large Rabi rate power-broadens the transition, and this is effective in our system because the splitting between the ground-state sublevels is only a few times the natural linewidth of the transition.

With a Rabi rate ten times the rate of spontaneous emission, we can hope to have around a fifth of the total population in the excited state at any given time. We then have a scattering rate of 240 s^{-1} , which produces an acceleration of $18\,000 \text{ m s}^{-2}$. At

this rate of deceleration, we can envisage slowing molecules from an initial velocity of 400 m s^{-1} to rest in about 4 m, if we can maintain the resonance condition during the deceleration. If the starting speed is reduced to 200 m s^{-1} , for example by using a cryogenic source of molecules, the decelerator length is reduced to 1 m. Our results show that modulating the polarisation has the greatest effect when we already have a very intense laser field.

There is a further note which has to be made regarding the validity of the modelled results. In everything that has been considered in this section, we have used the intermediate quantum numbers which result from coupling the electronic angular momenta to the boron nuclear spin. The true state also requires the hydrogen nuclear spin to be coupled, and this will not only change the quantum numbers, but will also result in a system of integer angular momenta which have different selection rules. The perturbation by the hydrogen nuclear spin is, however, a small correction. The description provided by our model is sufficient to gain a fair understanding of the system.

3.3 Modulating the polarisation

3.3.1 Apparatus

The experimental apparatus remains mostly unchanged from that described in chapter 2, but with the addition of an electro-optic modulator (EOM) (Thorlabs EO-AM-NR-C4) to apply the modulation to the laser field, and some additional elements which allow us to determine the effect of the modulation. The additional apparatus is shown schematically in figure 3.10.

The 433 nm light leaving the doubler is focussed at the centre of the EOM, and then collimated by the cylindrical lenses on the way to the experiment. The beam is expanded horizontally by a telescope formed of two cylindrical lenses in order to increase the size of the interaction region between the light and the molecules. One of the mirrors directing the beam is on a flip-mount, and can be removed from the beam path to pass the light on to the diagnostic arm. The diagnostic arm

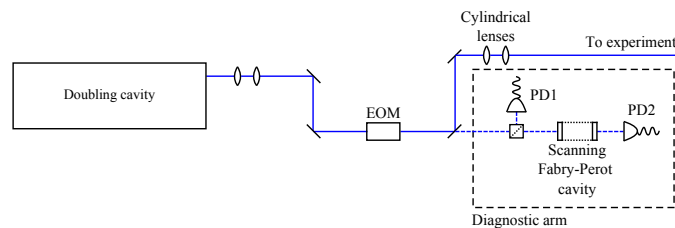


FIGURE 3.10: The EOM and diagnostic set-up, which allow us to analyse the modulation we apply to the polarisation, and to the frequency.

consists of a polarising beam splitter, which reflects light of one polarisation onto a photodiode, and a 15 cm-long scanning Fabry-Perot cavity with a photodiode at the far end. The polarising beam splitter is also mounted on a flip-mount, to allow both polarisation components to pass to the cavity. We can determine the effect that the modulation is having on the polarisation, by looking at the variation in the intensity of the light reflected by the polarising beam splitter onto the first photodiode. The scanning cavity allows us to see the effect of the modulation on the frequency of the light.

The EOM consists of an electro-optic crystal sandwiched between two electrodes. Applying an electric field along the crystal axis changes the birefringence of the material, making the EOM equivalent to a waveplate of variable retardance. Continuously varying the potential difference allows us to modulate the polarisation of the transmitted wave. Since the modulation affects the phase of the wavefront, it also modulates the frequency of the carrier, producing frequency sidebands differing from the fundamental by multiples of the modulation frequency. In this sense, the EOM is the answer to both of the problems we expected to have with BH: it can modulate the polarisation of the wave, destabilising dark states; but the same modulation can also be seen as giving additional frequency components to the wave, which help to address the ground-state sublevels.

To drive the EOM, we made an LC tank circuit driven by a synthesised signal generator (Agilent). The circuit is resonant at around 1 MHz. Since the depth of the modulation, the degree to which the polarisation rotates on passing through the

crystal, varies depending on the applied voltage, we have to be careful to ensure that the voltage applied to the crystal is the same at all frequencies. The correct voltage has to be determined by changing the input frequency and the applied voltage together and examining the effect with the polarisation analyser.

We constructed the Fabry-Perot cavity from two high reflectivity (390 nm–440 nm, $R > 99.9\%$) mirrors with 150 mm radius of curvature. The mirrors are housed in stainless steel mounts separated by a quartz tube. The quartz tube has a very low coefficient of the thermal expansion that reduces the dependence of the cavity length on the ambient temperature. The cavity length is scanned by a piezo stack which supports one of the mirrors. The details of the design can be found in the thesis of John Barry [69]. We measure the cavity finesse to be around 400 and the free spectral range is 500 MHz.

This apparatus allows us to characterise the properties of the light we produce and apply it to molecules produced in the same way as in the preceding chapter.

3.3.2 Results

The results in this section show the effect of modulating the polarisation on the laser-induced fluorescence signal that we observe. In two separate experiments we drive the molecules to each of the two possible excited states and observe how the laser-induced fluorescence signal increases with increasing laser power, both with and without modulation. We also look at the effect of changing the modulation depth and frequency. Figure 3.12 shows the saturation of the laser-induced fluorescence signal as we increase the probe beam intensity, without modulating the polarisation. We have corrected for the saturation of the PMT by light at the wavelength of the probe beam using a standard model for detector response, in which we account for the possibility that two photons may arrive separated by too small a time to be distinguishable. Equation 3.10 relates the observed count rate, N , to the actual count rate, M , in terms of the PMT dead time (pulse pair resolution), τ_d .

$$N = \frac{M}{1 - M\tau_d} \quad (3.10)$$

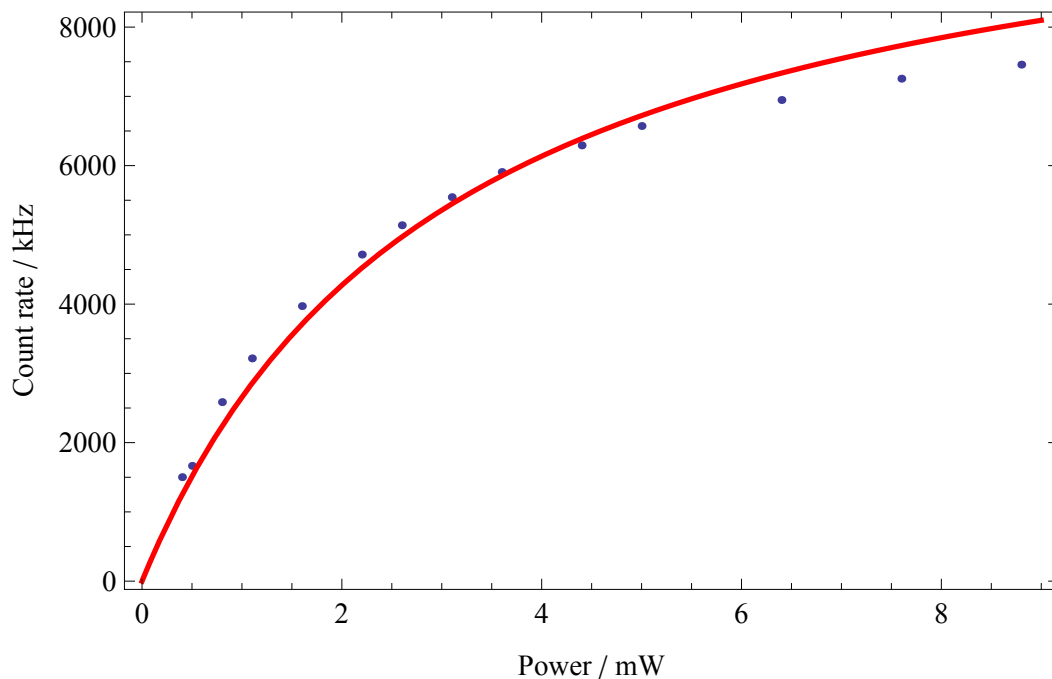


FIGURE 3.11: The response of the PMT count rate to light scattered from the probe beam at various powers. Only a small fraction of the measured power is scattered onto PMT photocathode. The red line is a fit of equation 3.10 to the data.

The model assumes that each counting event can be either: a correctly identified single-photon event, or an incorrectly identified two-photon event. The model provides a poor estimate of the true rate of fluorescence if the radiation is too intense, so that there is a large number of events in which three or more photons are incident on the detector, within the smallest period which can be resolved, τ_d . In order to determine τ_d , we slightly misalign the probe beam through the chamber without running the molecular beam. A small amount of the laser light is scattered into the PMT by reflective surfaces in the apparatus. We record the power of the probe beam outside of the vacuum chamber with a power meter and the PMT count rate. The results are shown in figure 3.11. We fit our model for the PMT response to the data to determine τ_d and we can then use our model to correct our observed fluorescence for PMT saturation. We can see that the model begins to deviate from the data at high powers, where there are more two-photon events.

The fluorescence rate we observe should depend on four factors: the number of

molecules we have, the efficiency of the detection system, the intensity of probe light related to the saturation intensity, and the amount of time each molecule spends in the detection region. In order to understand the response of the laser-induced fluorescence to the probe-beam intensity we have to model the scattering rate in our system. To interpret our data we use a model based on the scattering rate for a two-level system,

$$R = R_{\max} \frac{2a\Omega_R^2/\Gamma^2}{1 + 2a\Omega_R^2/\Gamma^2}. \quad (3.11)$$

Our model has two free parameters, $R_{\max}$ and a . $R_{\max}$, the maximum scattering rate, accounts for the number of molecules, the efficiency of the detection system, and the amount of time each molecule spends in the detection region. Our a parameter is used to quantify the difference between the two-level model and the many-level system. It multiplies the intensity needed to saturate the transition by the factor $1/a$. We note that, in this situation, the effective saturation intensity is very different to the usual saturation intensity for a two-level atom. The count rate will saturate once the intensity is sufficient to optically pump the molecule into the dark state during the time taken for the molecule to pass through the laser beam. This is typically a far smaller intensity than the usual two-level saturation intensity which requires the scattering rate to approach the spontaneous emission rate.

In figures 3.12–3.15, the mean Rabi rate is obtained by calculating the mean intensity of the probe beam over a circular region having a radius equal to the beam waist size, and then converting the intensity into a Rabi rate using 3.7.

Figures 3.12 and 3.13 show the saturation curves, with and without a modulation applied, respectively. The modulation applied to the EOM has a frequency of 1.2 MHz and is applied so as to achieve full modulation depth ($\Phi = \pi$ in equation 3.9). The results of fitting the model for the two-level system are shown in table 3.1. We see that when we apply the modulation the Rabi rate we need to saturate the sample increases by a factor of 4 and the total fluorescence signal we observe increases by a factor of 2. We can explain both observations if we remember that there is a dark state for fixed polarisation in this case; applying the modulation

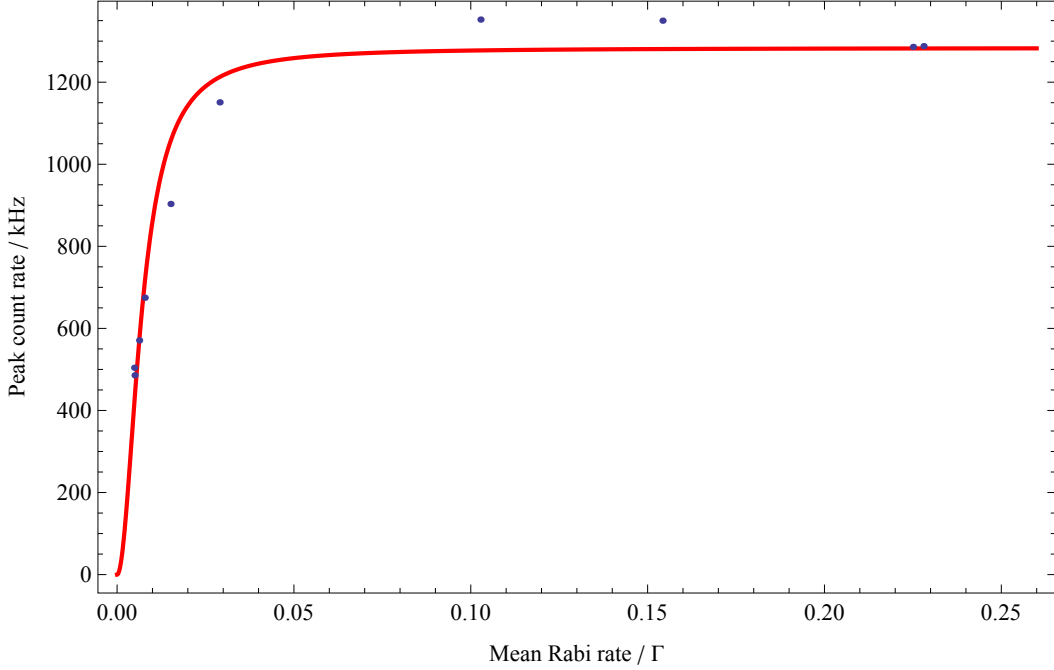


FIGURE 3.12: Saturation curve driving to $F' = 3/2$ without polarisation modulation. The red line shows a fit to the data of the model in equation 3.11.

	$R_{\max} / \text{kHz}$	a
Modulation on	2474(149)	2548(916)
Modulation off	1283(36)	10173(1441)

TABLE 3.1: The parameters which result from fitting 3.11 to the saturation data driving to driving to $F' = 3/2$, as shown in figures 3.12 and 3.13. Numbers in parentheses are the standard errors obtained from the fitting algorithm.

destabilises the dark state, increasing the maximum fluorescence and also increasing the probe intensity needed to reach that maximum.

Figures 3.14 and 3.15 show saturation curves for the transition to $F' = 5/2$. We see the same result as before: an increase in both the total fluorescence rate, and in the intensity required to saturate the sample.

Figure 3.16 shows the effect of increasing the voltage applied to the EOM. Driving the EOM past the half-wave voltage, V_π , at which the polarisation is fully modulated ($\Phi = \pi$ in 3.9), puts additional power into the sidebands. At low Rabi rates the count rate shows hardly any dependence on the depth of modulation. This indicates

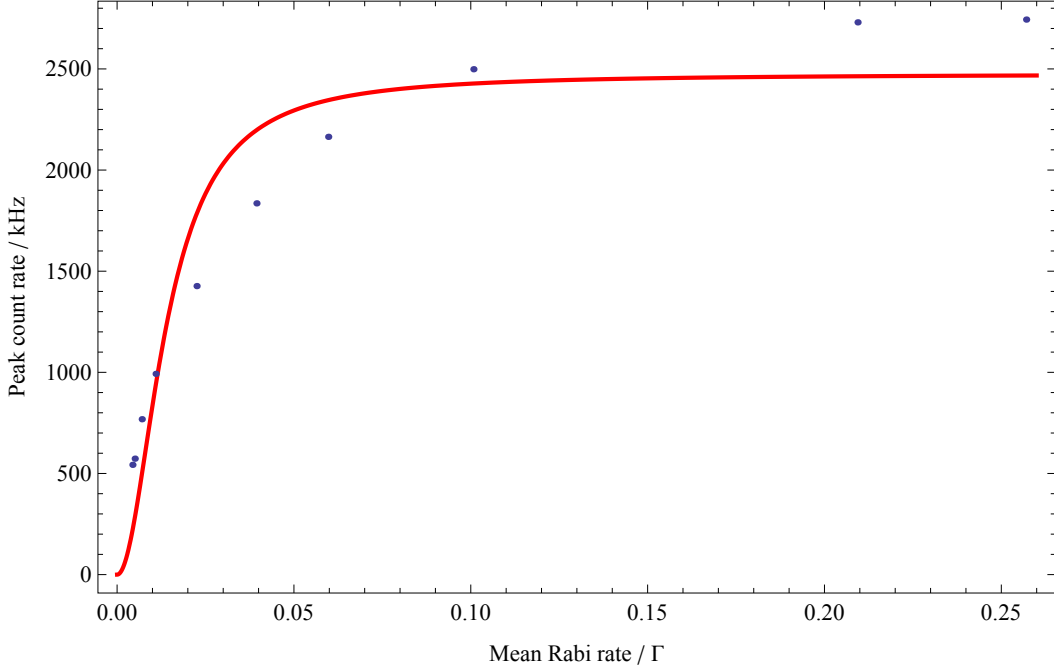


FIGURE 3.13: Saturation curve driving to $F' = 3/2$ with the polarisation modulated at the damping rate ($\delta_{\text{EOM}} = \Gamma$). The red line shows a fit to the data of the model in equation 3.11.

	R_{max}	a
Modulation on	2365(163)	3109(1155)
Modulation off	1280(53)	10241(1792)

TABLE 3.2: The parameters which result from fitting 3.11 the saturation data driving to driving to $F' = 5/2$, as shown in figures 3.14 and 3.15. Numbers in parentheses are the standard errors obtained from the fitting algorithm.

that these low Rabi rates are insufficient to optically pump into the dark state during the time the molecule traverses the laser beam. At higher intensities the count rate increases with modulation depth, and continues to increase well beyond the amplitude needed to produce a π phase shift. Since we rely on the sidebands to drive the different components of the ground state, we see that putting more of the beam power into those sidebands increases the fluorescence signal.

Figures 3.17 and 3.18 show the effect of varying modulation frequency on the fluorescence signal, driving to $F' = 3/2$ and $F' = 5/2$, respectively. Consider first the $F'=3/2$ data. We see that at low Rabi rates the count rate is independent

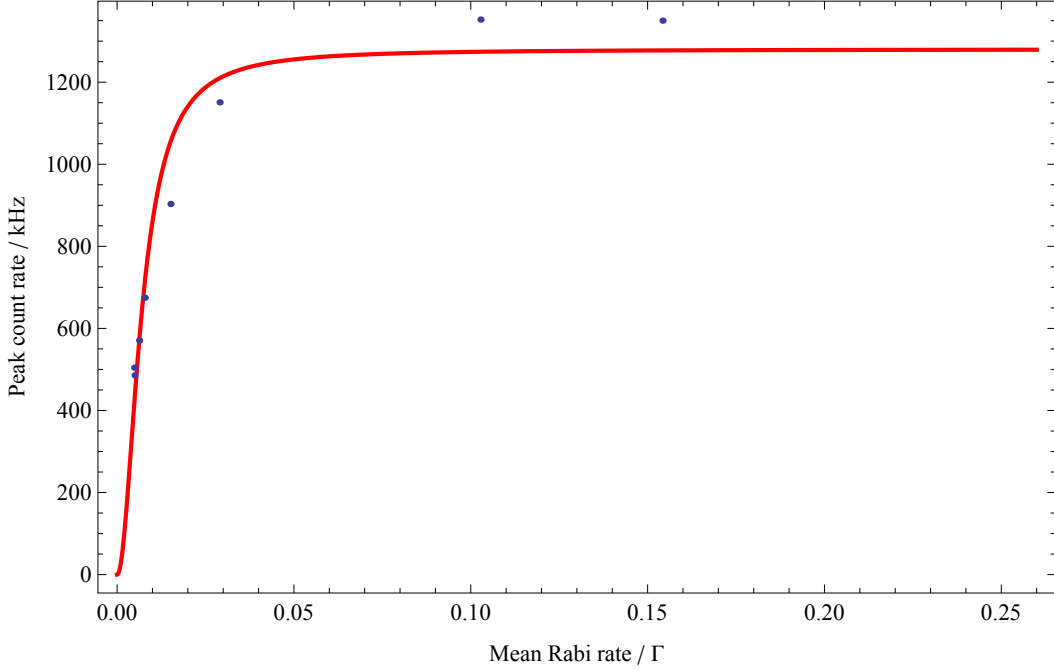


FIGURE 3.14: Saturation curve driving to $F' = 5/2$ without polarisation modulation. The red line shows a fit to the data of the model in equation 3.11.

of the modulation frequency. Once again, this is because the molecules are not optically pumped to the dark state during their passage through the laser beam when the intensity is low. At higher Rabi rates, we see a strong dependence of the count rate on the modulation frequency. The count rate peaks when the modulation frequency is between 1 and 1.5Γ , and the count rate at the peak is about twice the value without modulation. We note that the modulation frequency that maximizes the count rate is similar to the size of the ground-state hyperfine splitting; this suggests that the main effect of the modulation may be to add frequency sidebands that address the various hyperfine components of the transition. Turning now to the $F' = 5/2$ data shown in figure 3.18, we see that the polarization modulation increases the count rate, but that at modulation frequencies above 0.5 MHz there is little dependence on the modulation frequency for all the Rabi rates explored.

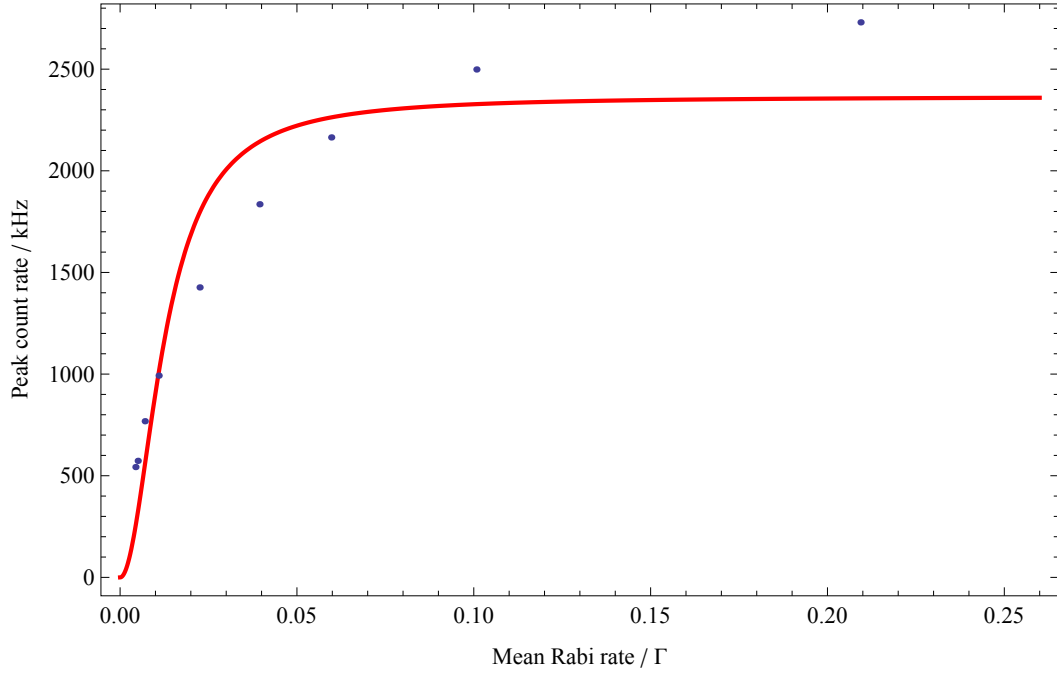


FIGURE 3.15: Saturation curve driving to $F' = 5/2$ with the polarisation modulated at the damping rate ($\delta_{\text{EOM}} = \Gamma$). The red line shows a fit to the data of the model in equation 3.11.

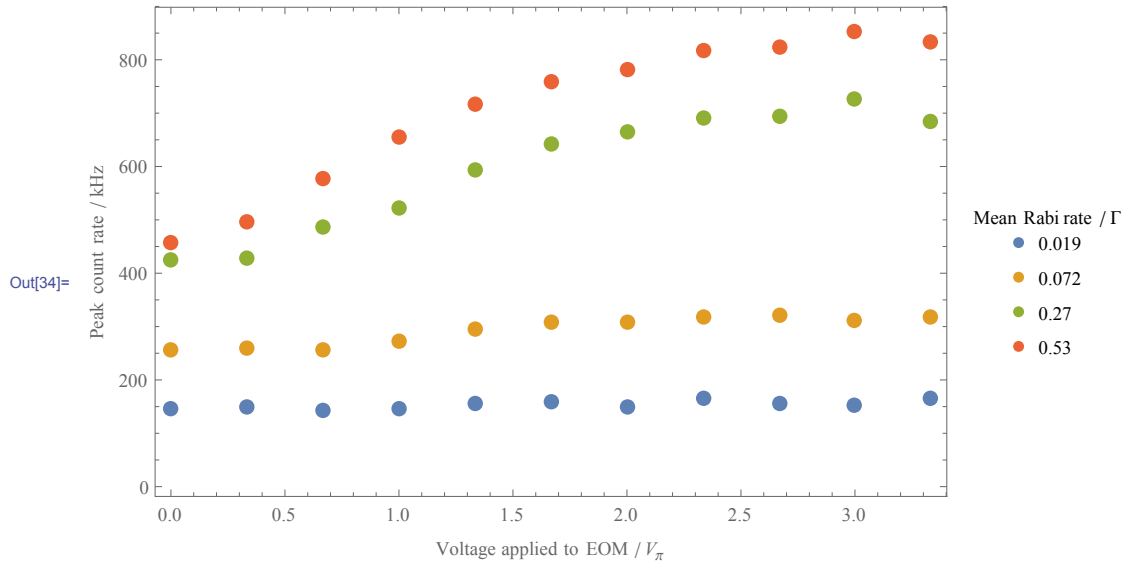


FIGURE 3.16: Effect of modulation depth with signal for different probe intensities driving to $F' = 3/2$. The half-wave voltage V_π is the voltage which causes the modulation to be full (i.e. $\Phi = \pi$ in 3.9). The modulation is applied at the same rate as the damping ($\delta_{\text{EOM}} = \Gamma$).

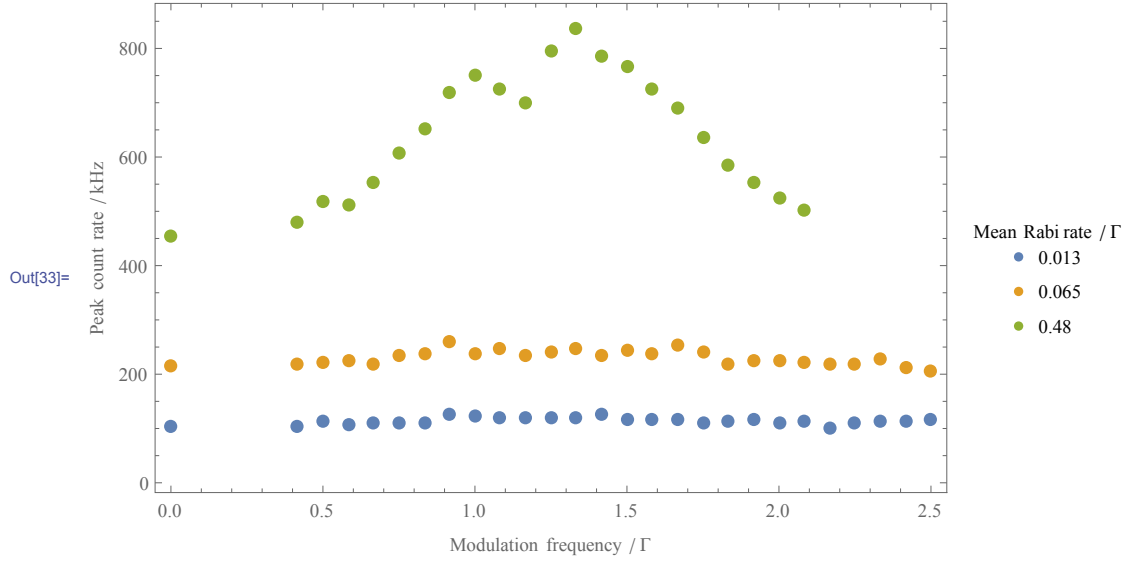


FIGURE 3.17: Effect of modulation frequency driving to $F' = 3/2$ for different probe intensities. The modulation is at the half-wave voltage.

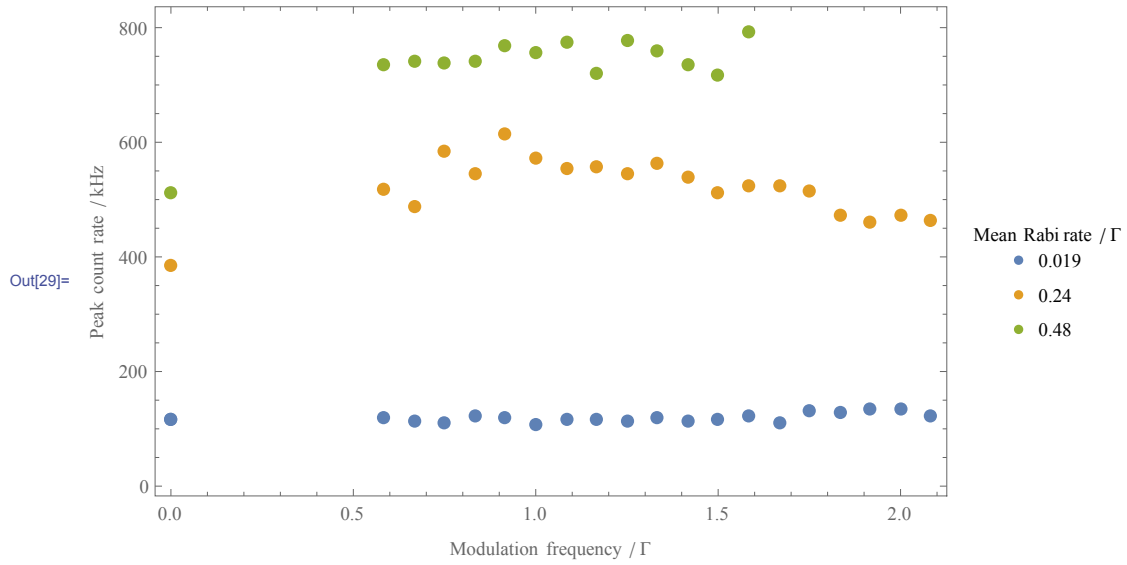


FIGURE 3.18: Effect of modulation frequency driving to $F' = 5/2$ for different probe intensities. The modulation is at the half-wave voltage.

3.4 Conclusion

In conclusion, we find the highest scattering rate when we choose to excite the molecule to $F' = 5/2$. We can achieve a good excited-state occupancy, either by increasing the beam intensity, or by increasing both beam intensity and modulation frequency. Our results from the lab show that the system is particularly sensitive to modulation frequency when we drive to the $F' = 3/2$ state.

The effect of modulating the polarisation differs in the two cycling systems. In one, there is no dark state but the modulation acts to broaden the linewidth of the laser light which improves the scattering rate (or ability to address the ground-state sublevels), in the other there is a dark state which can be destabilised through modulating the polarisation but the intensity still needs to be quite high.

The reliability of the model depends on the assumption that no light which is spontaneously emitted from one molecule is absorbed by another which is a very reasonable assumption given that the molecules are in a gaseous phase. We also assume that the modulation applied by the electro-optic modulator to the laser field is accurately described by the term used in equation 3.9.

To extend this work we could use the experimental apparatus to map out the change in laser-induced fluorescence over the parameter space shown in the contour plots. Then the model could be adapted to include a magnetic or electric field which might be useful when we need to trap the molecules. Small alterations could also be used to make the model applicable to other molecules.

Chapter 4

Exciting the repump transition

4.1 Introduction

In the preceding chapter, we established that we can achieve a reasonable rate of scatter addressing the main cooling transition: $X^1\Sigma^+(v'' = 0; F'' = 3/2, 5/2) \leftrightarrow A^1\Pi(v' = 0; F' = 5/2)$. However, as discussed in chapter 2, in order to do this we have to close the transitions to higher lying vibrational states: $X^1\Sigma^+(v'' = 1, 2; F'' = 3/2, 5/2) \leftrightarrow A^1\Pi(v' = 0, F' = 5/2)$. In this chapter I describe the design and construction of the laser system we use to excite the $X^1\Sigma^+(v'' = 1; F'' = 3/2, 5/2) \leftrightarrow A^1\Pi(v' = 0; J' = 1; F' = 5/2)$ transition, at 480.6 nm. The preliminary results of using this laser to probe the transition are also shown.

4.2 Building the laser system

Prior to this work, we did not have a suitable laser system at 480.6 nm needed to repump population out of $v'' = 1$. I now describe the development of this laser system.

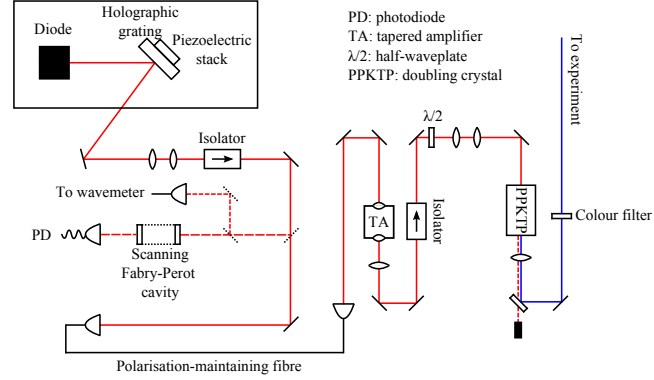


FIGURE 4.1: The system which produces 480.6 nm light to address the $X^1\Sigma^+(v'' = 1; J'' = 1) \leftrightarrow A^1\Pi(v' = 0, F' = 5/2)$ transition. The drawing of the TA shows two lenses, which are housed in the chip mount and couple the beam into and out of the chip.

4.2.1 System design

To produce light at 480.6 nm we use the apparatus shown schematically in figure 4.1. A laser diode (QPHOTONICS QLD-960-150S) produces light with a centre wavelength of 961.3 nm. The diode produces 30 mW of power in an external-cavity diode laser (ECDL) arrangement. Outside the extended cavity, the light is divided along three branches, which are sent to: a wavemeter, a Fabry-Perot cavity, and a fiberport. Around 25 mW enters the fiberport and is coupled into a polarisation-maintaining optical fibre. After the fibre, we amplify the power to approximately 1.0 W with a tapered-amplifier (TA) chip (M2K Laser TA-0950-2000). We then double the frequency with a periodically-poled doubling crystal to produce light at 480.6 nm, which we then send to the experiment.

4.2.2 ECDL

The ECDL set-up is shown in figure 4.2. The diode is operated in an external cavity, formed by the diode's facet and a diffraction grating, which provides feedback for a single mode. We follow the design described in [69], where the diffraction grating is

used in the Littrow configuration. In this arrangement, the first order of diffraction is reflected back into the diode and enhances the gain of the cavity at its own frequency, which forces the diode to lase on a single longitudinal mode. The entire apparatus is housed in an aluminium enclosure. The enclosure sits on a large, aluminium base which rests on highly stable optics mounts on the optical table. The base and enclosure form a relatively stable environment in which to operate the laser diode, free of dust, and undisturbed by instantaneous changes in the ambient conditions (pressure or temperature fluctuations, for example).

The laser diode itself is housed in a standard adjustable mirror mount from Thorlabs, with the diffraction grating attached to a plate on the fixed part of the mount opposite, as shown in figure 4.2. We adjust the coarse angle that the diode facet makes to the diffraction grating using the screws on the mirror mount. For the fine control we use the piezo to which the grating is glued. By changing its extension we can incrementally alter the position of the grating, and so, fine tune the frequency of the lasing mode, by changing the length of the external cavity formed between the cavity and the diode.

The initial alignment procedure is as follows. We first set the drive current to just below the threshold for lasing (26 mW) and then adjust the coarse angle of the diffraction grating with the mirror mount controls. Observing the reflection from the grating which leaves the box on a phosphorescent card, we see a significant increase in output light when the first order diffraction is being returned to the diode and it begins to lase on a single mode. To achieve this single-mode operation it has usually only been necessary to adjust the vertical angle of the grating, since the horizontal angle of the grating can be used to select between many different longitudinal modes, all of which will lase single-mode. At this point the drive current can be increased to the usual operation current (199 mA), provided that the optical power within the external cavity does not exceed the damage threshold of the diode facet (around 150 mW is known to be acceptable).

Once the diode has been made to produce radiation on a single longitudinal mode there can be as much as 30 mW outside of the external cavity set-up. The frequency of the mode can be selected by coupling the light to the wavemeter and adjusting

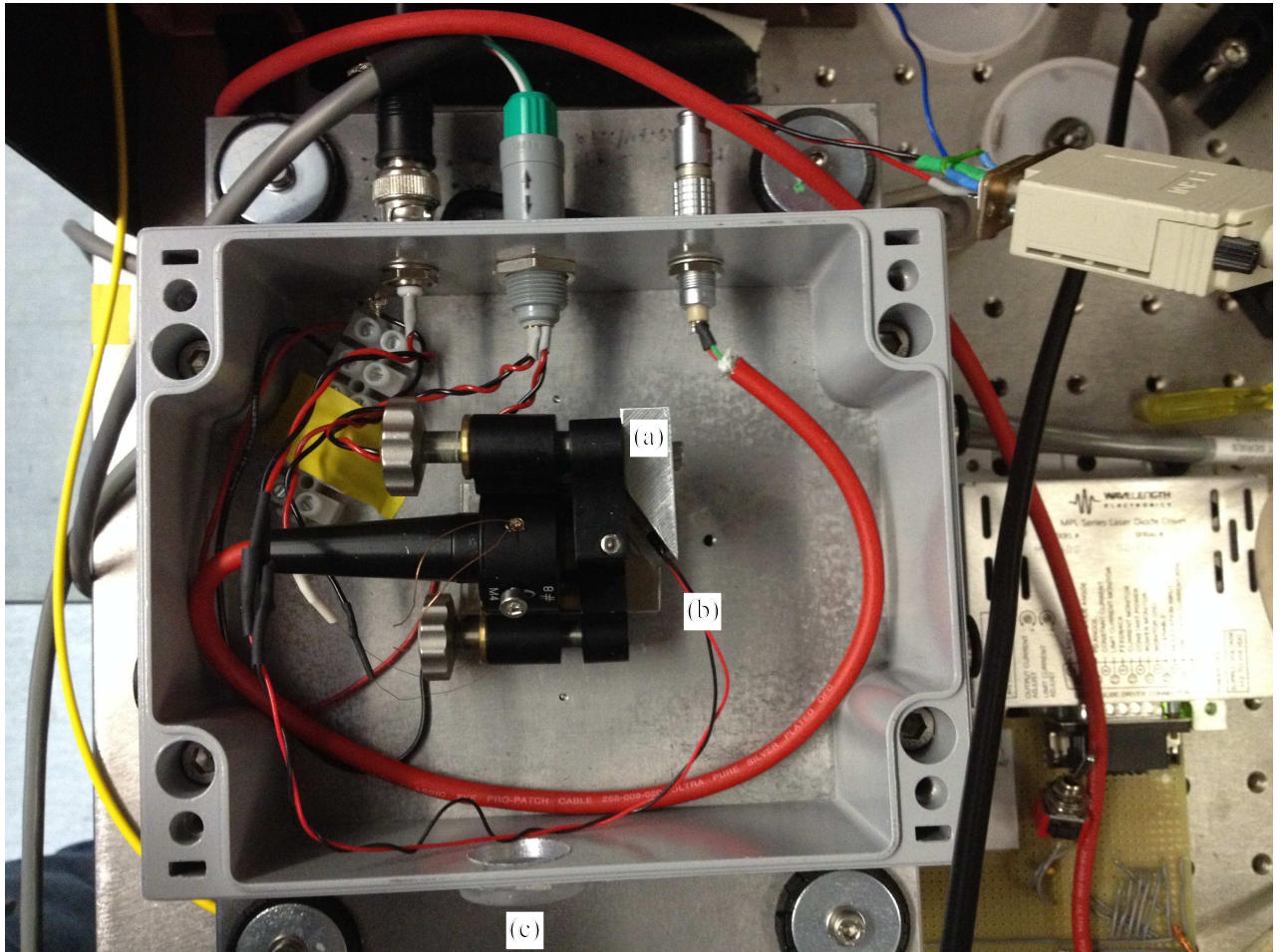


FIGURE 4.2: The external-cavity diode laser set-up in its enclosure with the lid removed. The thick cable with red shielding supplies power to the diode located in the mirror mount. The small aluminium piece (a) fixed to the adjoined part of the mount supports the holographic diffraction grating, used to ensure single-mode operation of the system. The red and black wires (b) apply a voltage to the piezoelectric stack which adjoins the grating and the aluminium mount. The beam leaves the enclosure through the window (c) at the bottom of the image.

the horizontal angle of the diffraction grating. As the horizontal angle is changed, the coupling to the wavemeter (and other fibre-optics) has to be adjusted. There is a single mirror outside the enclosure which can be used to compensate for changes in the output beam angle. The piezo that moves the grating gives fine frequency control over a narrow frequency range, typically about 1 GHz. Usually, the diode will lase on several longitudinal modes at once. By changing its temperature we vary its extension, and can change the gain profile to allow a single longitudinal mode to dominate over the others. As the laser power on this mode increases, the feedback from the diffraction grating eventually causes it to become the only mode present.

We control the temperature of the diode through a Peltier effect thermo-electric cooler which is sandwiched between the base of the mirror mount and the aluminium base. The control loop which sets the current, and therefore the heating rate, receives feedback from a thermistor housed in the casing of the diode mount. The temperature control loop is much more effective if the thermistor is housed close to the diode. Initially, we had located it at the base of the mirror mount, adjacent to the surface which the Peltier cooler is in contact with, but this caused the temperature to be unstable, as the feedback to the cooler relied only on the relatively quick change close to the surface in contact with it, while the rest of the mirror mount took much longer to thermalise to the setpoint. Careful positioning of the thermistor and testing of the amount of proportional gain used in the feedback loop is essential to ensure good frequency stability.

To check the frequency stability of the laser we look at its transmission through a scanning Fabry-Perot cavity, where we sometimes observe a periodic fluctuation in the frequency. The period of these fluctuations can be used to diagnose the source of the noise. Fluctuations which have a period of a few fractions of a second, to several seconds, are normally associated with the temperature-control loop, and can be removed by properly setting the proportional gain. Fluctuations on a smaller timescale would normally be associated with electronic noise and suggest improperly shielded cables, although we have also found that particular current drivers can be a source of electronic noise.

The wires for the piezo, the diode, the thermistor, and the Peltier cooler enter the enclosure through connectors which do not allow the flow of air to disrupt the internal environment, and are grounded at the enclosure. The optical output of the ECDL leaves the enclosure through an anti-reflection coated window, which also serves to isolate the environment of the diode from the ambient conditions in the lab. An optical isolator outside the housing of the diode laser protects the diode from high-power reflections, which could damage the diode facet, or introduce frequency noise to the lasing mode.

4.2.3 Tapered amplifier

We have about 12 mW of power in the seed light, after the fibre. The loss in power (from 25 mW) is mostly due to the higher order transverse modes of the beam produced by the diode, which cannot be coupled into the fibre. 10 mW of 961.3 nm light would only give about 0.3 mW at the doubled frequency (according to the manufacturer we expect to achieve a normalised efficiency of $1\text{--}1.2\%\text{cm}^{-1}\text{W}^{-1}$ and we have a 30 mm crystal) so we have to amplify the power before doubling. To do this we use a tapered amplifier (TA) chip in which a driving current maintains a population inversion to act as a gain medium for the input beam. The input, or seed, light enters the medium and stimulates the emission of photons with the same longitudinal mode. This increase in intensity risks damaging the output facet of the chip, so it is tapered to allow the power to be dispersed over a wider area. This tapering gives the output beam different divergences along its horizontal and vertical axes, which have to be corrected by lenses after the TA.

The TA chip is supplied already mounted on a copper block which dissipates the heat generated in the chip. We locate this small mount in our own mount, shown in figure 4.3, which also contains lens mounts for coupling the light into and out of the chip. The aspheric lenses are contained in threaded mounts which allow them to be brought closer to, or further from, the chip. The mount design does not limit the travel of these threaded lens-containers so care must be taken not to allow the lenses to come into contact with the chip when they are being positioned. To stabilise the temperature of the chip we include a Peltier cooler underneath the mount that sits

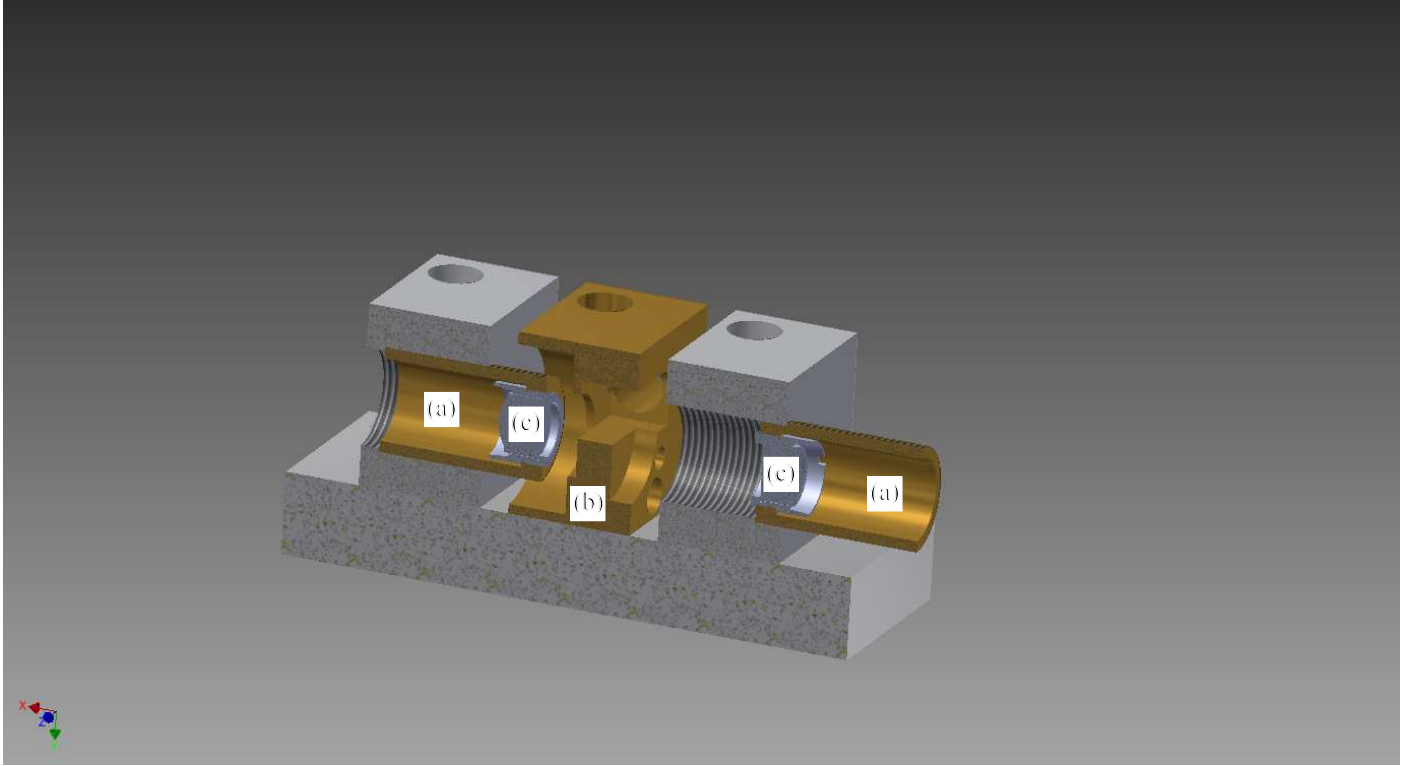


FIGURE 4.3: A rendering of the TA mount in section. The mount is machined from a piece of aluminium, and consists of a base with two raised frames, which hold the threaded lens-mounts (a). The TA chip sits in a gold-coated copper frame (b) between the lenses. In this figure, the aluminium is shaded grey and the gold-coated copper appears bronze. The threaded lens-mounts are shown with lenses (c) inside. The TA chip itself is not shown.

on a large aluminium block. The thermistor used to control the cooling is glued into a hole in the base of the mount. We enclose the mount with acrylic plates on top and at the sides to prevent damage to the TA chip by airborne particles. The current drivers for the Peltier and the TA itself feed into the enclosure through a small gap. The TA has a single connector, the base and mount are the connection to the anode.

To begin to align the TA the spatial mode of the seed light has to be matched to the mode supported by the chip. By far the easiest way to do this, is to run the TA without seed light at low current to produce some light by amplified spontaneous emission (ASE), and then to position the input lens so that it collimates this light. The TA can be driven up to 2.0 A without a seed before there is risk of damaging the input facet. The path of the ASE beam and the seed beam can be overlapped using the two beam-steering mirrors between the fiberport and the TA. Once the seed

light begins to be well coupled to the chip, the alignment can be further improved if the lens at the output is used to collimate the light there, and then the alignment of the input beam is adjusted while monitoring the output power on a power meter. To collimate the output we use two lenses: the aspheric lens in the threaded mount, and a cylindrical lens after the TA. The aspheric collimates the beam in the vertical axis, which rapidly diverges after the TA, and causes the beam to come to a focus in the horizontal. The cylindrical lens is used to collimate the beam in the horizontal. Once the seed light is well aligned and the output beam has been collimated the current driving the TA can be increased. Some careful adjustment of the seed light may be needed to optimise the input after the current is set to the desired level.

After the alignment procedure has been followed, the beam from the TA can have as much as 1 W of power with 3.5 A of driving current. A second optical isolator has to be placed after the TA to protect the chip from accidental reflections of the high-power output beam.

4.2.4 Doubling crystal

The amplified beam from the TA is used to drive second-harmonic generation in a 1 mm x 2 mm x 30 mm doubling crystal, made of periodically-poled potassium titanyl phosphate (PPKTP, manufactured by Raicol). The crystal is housed in a mount containing a resistive element, used to heat the crystal. We find that the doubling efficiency for 480.6 nm is optimal at 54.7 °C. The periodically-poled crystal produces light at double the frequency of the fundamental, and has an estimated conversion efficiency of 3 % W⁻¹, for a 3 cm-long wafer. The polarisation mode of the fundamental is matched to the crystal axis using a half-wave plate. A pair of beam-shaping lenses after the waveplate match the transverse mode of the beam to the crystal. A lens on the output side of the doubling crystal collimates the output beam. At the output there is light at both the fundamental and doubled frequencies, so we use a dichroic mirror to selectively reflect the doubled beam and pass the remaining fundamental light on to a beam stop. A coloured-glass filter, which has a high transmission at the doubled wavelength, further reflects or absorbs any remaining light at the wavelength of the fundamental. The doubled

light passes on to the vacuum chamber and intersects the molecular beam. The detection apparatus is unchanged from that used in chapter 2, except that we do not split the fluorescence from the molecules into two paths, and instead detect with a single PMT.

4.2.5 Testing the system

To measure the passive frequency-stability of the laser system, we monitor the frequency using both a wavemeter and a scanning Fabry-Perot cavity, which we built following the design in [69]. The wavemeter shows up frequency changes that are larger than about 100 MHz, whereas the scanning cavity is sensitive to frequency fluctuations at the 1 MHz level. We observed a frequency drift of about 600 MHz per hour. This is typical of ECDL systems when their frequency is not locked to a stable reference.

The intensity we need at 480.6 nm is determined by the scattering rate that we hope to achieve. In a two-level system, we can maximise spontaneous emission if we are at the saturation intensity, defined by $I_{\text{sat}} = \pi \hbar c / (3 \lambda^3 \tau)$, where λ is the wavelength of the transition, and τ is the lifetime for the radiative broadening of the upper state. For the $v'' = 1 \leftrightarrow v' = 0$ transition, the saturation intensity is 1.44 mW cm^{-2} . So, with a beam 5 mm in diameter, we would need to have 280 μW of power. However, the scattering rate we can achieve for a given intensity decreases when we have a system involving more than two states. In our case, there are four sublevels to each ground vibrational state and we expect to need closer to 10 mW of power in the beam to achieve a reasonable scattering rate, following the calculation in [70].

The intensity of the light generated at the frequency of the second harmonic is proportional to the square of the intensity of the fundamental, so the conversion efficiency is extremely sensitive to the intensity of the incoming beam. We have to control the divergence of the beam so that its spatial mode has the maximum possible overlap with the crystal. This is achieved by having the beam come to a waist at the centre of the crystal and the Rayleigh range be half the length of the

TA current / A	961.3 nm power after amplification / W	480.6 nm power / mW
1.0	0.080	0.03
2.0	0.45	0.64
3.0	0.85	2.47
3.5	1.05	3.4

TABLE 4.1: Optical power for varying TA drive current. The TA is seeded with 12 mW at 961.3 nm.

crystal. The pair of lenses before the doubling crystal is used to reshape the beam to attempt to meet these conditions.

A measurement of the optical power at various points in the set-up is shown in table 4.1. The optical power after the TA is not as high as the chip should achieve for the input we have (the quoted output power is 1.4 W for 3.0 A and 2.0 W for 3.5 A). This is due to the design of the TA mount, in which the position of the two coupling lenses can only be varied along the axis of the beam, not in the plane perpendicular to it. Better input coupling and imaging can be achieved with a v-shaped mount, which allows the lenses to be positioned with greater freedom, at the cost of a more difficult alignment procedure.

With the mode of the beam well matched to the crystal we would expect to see up to around 30 mW of 480.6 nm light, for 1 W of input power, though we see only a tenth of this. In order to assess how well we match the mode to the crystal volume, we have profiled the transverse distribution of intensity with a CCD camera (Allied Vision Technologies Marlin F-033B), which faces the beam coming from the TA. The intensity profile at 70 mm from the second beam-shaping lens is shown in figure 4.4. The figure shows that the beam coming from the TA does not have a Gaussian distribution of intensity but contains some component of higher-order Gaussian modes. This makes it difficult to match the beam waist and divergence to the ideal for the crystal. When we image the beam profile at different distances from the second beam-shaping lens we obtain a series of profiles which should allow us to map the divergence of the beam and measure its waist. Figure 4.5 shows the profile at 140 mm from the lens. This is roughly where the doubling crystal is. However, in practice we find that the complicated beam shape makes it difficult to extract the information we need from the beam profiles, and to match the beam

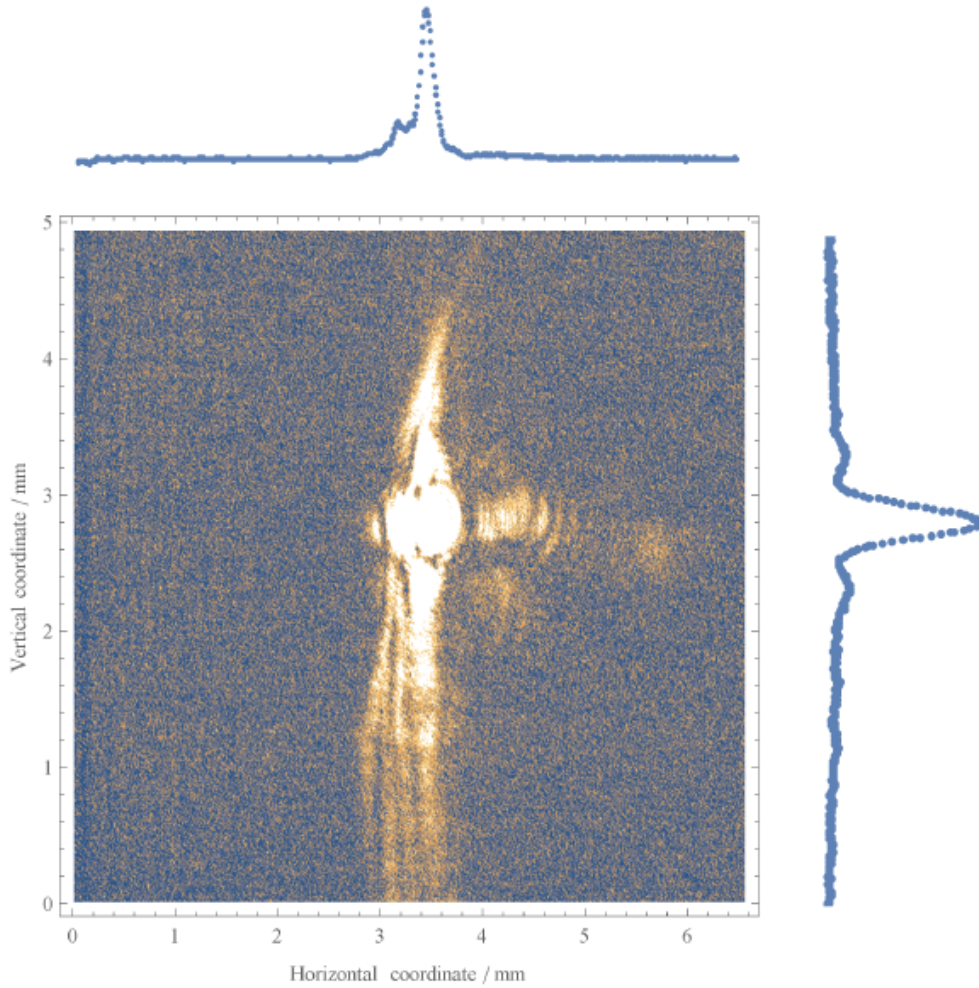


FIGURE 4.4: The intensity profile of the beam from the TA, 70 mm from the second beam-shaping lens before the doubling crystal. The beam profile is clearly not well modelled by a Gaussian intensity distribution, due to the imaging optics after the TA. The line-profiles show intensities for a single horizontal (or vertical) coordinate close to the centre of the spot.

mode to the crystal volume. The alignment of the TA with respect to its input and output coupling optics is critical for control over the mode of the beam, and the restriction in the placement of the aspheric lenses reduces the quality of the beam we can produce. In this case, the best solution would be to change the design of the TA mount to one which allows greater precision in the placement of these lenses.

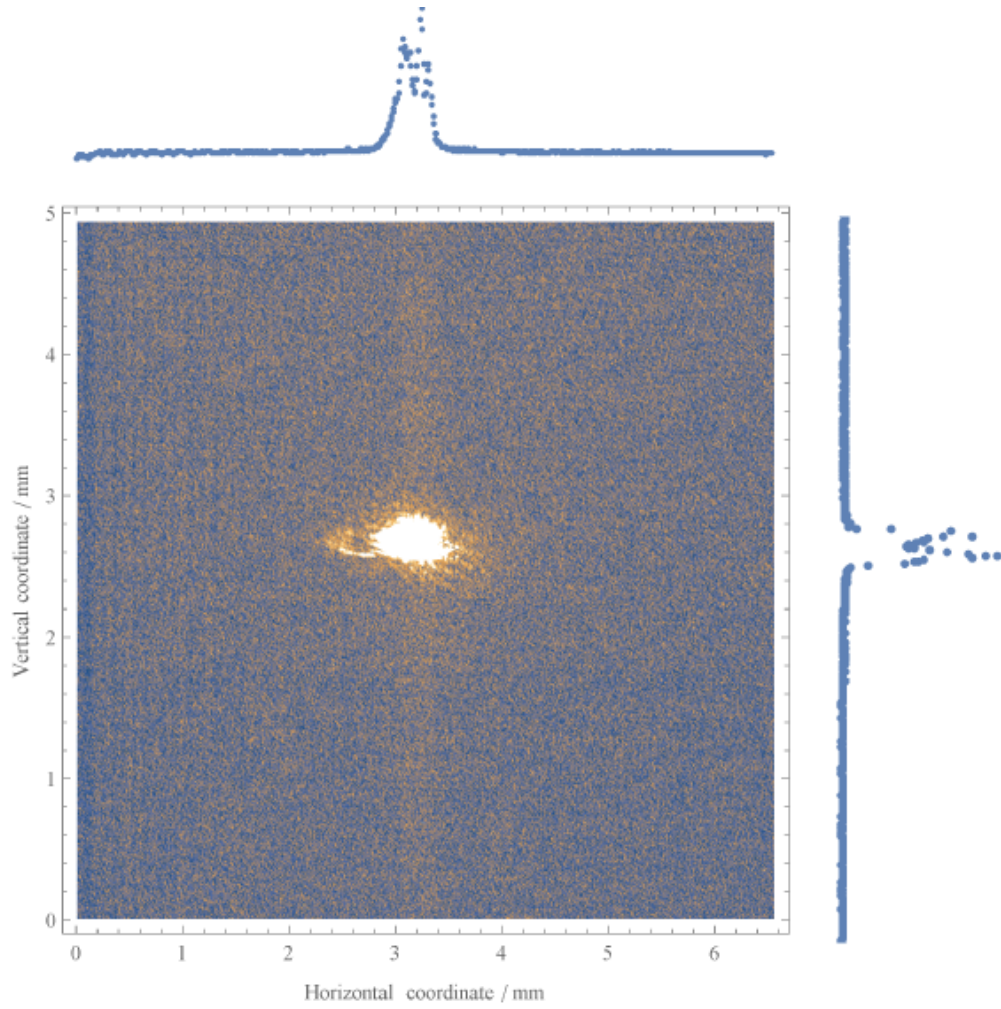


FIGURE 4.5: The intensity profile of the beam from the TA, 140 mm from the second beam-shaping lens before the doubling crystal. The beam profile is clearly not well modelled by a Gaussian intensity distribution, due to the imaging optics after the TA. The line-profiles show intensities for a single horizontal (or vertical) coordinate close to the centre of the spot.

4.3 Results

We have used the laser system described in the preceding section to excite population in the first excited vibrational level of the ground electronic state on the $A^1\Pi(v'' = 1, J'' = 1) \leftrightarrow X^1\Sigma(v' = 0, J' = 1)$ transition. This is the repump transition to be used to laser cool the molecules. It is difficult to make an accurate estimate of the population in the first excited vibrational state without doing significant work to characterise the probe beam inside the vacuum chamber. However, we can expect the molecules to follow the Boltzmann distribution inside the valve and before expansion. Since the gas is stored at room temperature there should be roughly equal occupation of the ground and first excited vibrational states. In fact, since we believe the supersonic expansion does not greatly affect the distribution of vibrational states (although it does have a large effect on the translational and rotational temperatures) the same should be true in the expanded molecular beam. To detect the effect of the excitation we place a filter in front of the PMT, isolating fluorescence from the 433.2 nm $A^1\Pi(v'' = 0, J'' = 1) \leftrightarrow X^1\Sigma(v' = 0, J' = 1)$ transition, which is the primary decay route from the $A^1\Pi(v'' = 0, J'' = 1)$ excited state. The filter allows us to detect the decay of the molecules from the excited state but exclude light scattered directly from the laser beam. The laser frequency is stepped by controlling the voltage sent to the piezo supporting the diffraction grating. We can scan the frequency over 140 MHz using only the piezo before the diode begins to lase on more than one longitudinal mode. A wider scan range can be achieved by adding a feed-forward control to the diode current.

The spectrum we observe scanning the laser over the transition is shown in figure 4.6. The $v' = 0$ spectrum is scaled so that the y-axis appears 300 times less than it actually is to facilitate comparison of the frequency. The structure of the two spectra should be the same because they share the same excited state and the hyperfine structure is dominated by that of the excited state. The resolution is worse for the $v' = 1$ due to the lower signal-to-noise ratio.

We measure the laser-induced fluorescence versus laser power by leaving the laser frequency fixed on the central peak in figure 4.6 and placing a variable neutral density filter in the path of the 480.6 nm beam. Another beamsplitter sends a

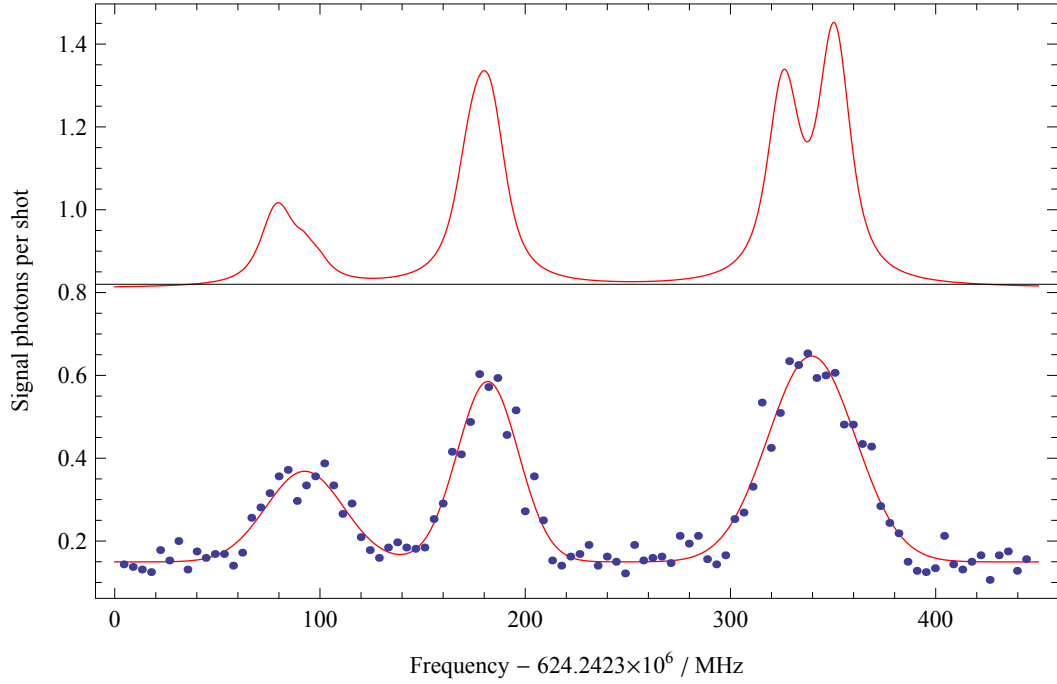


FIGURE 4.6: The lower part of the figure shows the data for and a fit to the frequency spectrum obtained by exciting the $A^1\Pi(v'' = 1, J'' = 1) \leftrightarrow X^1\Sigma(v' = 0, J' = 1)$ transition. In the upper of the figure the $(v'' = 0) \leftrightarrow (v' = 0)$ spectrum reported in chapter 2 has been reproduced for comparison. The y-axis is correct for the lower plot, the upper plot has been rescaled to fit so that the y-axis scale reads 300 times less than the true value, i.e. the amplitude of the largest peak is approximately 200.

fraction of the probe light to a photodiode so that we can record its relative intensity. Figure 4.7 shows the response of the signal as the beam intensity increases.

4.4 Conclusion

We have built a system to excite the 480.6 nm transition, tested its performance, and shown that it can be used to excite the $X^1\Sigma^+(v'' = 1; F'' = 3/2, 5/2) \leftrightarrow A^1\Pi(v' = 0; F' = 5/2)$ transition. Currently we are not able to saturate the transition but it should be possible to do this by using a TA mount which allows greater freedom in the placement of the imaging optic, in order to produce a beam shape that is more suitable for coupling into the doubling crystal.

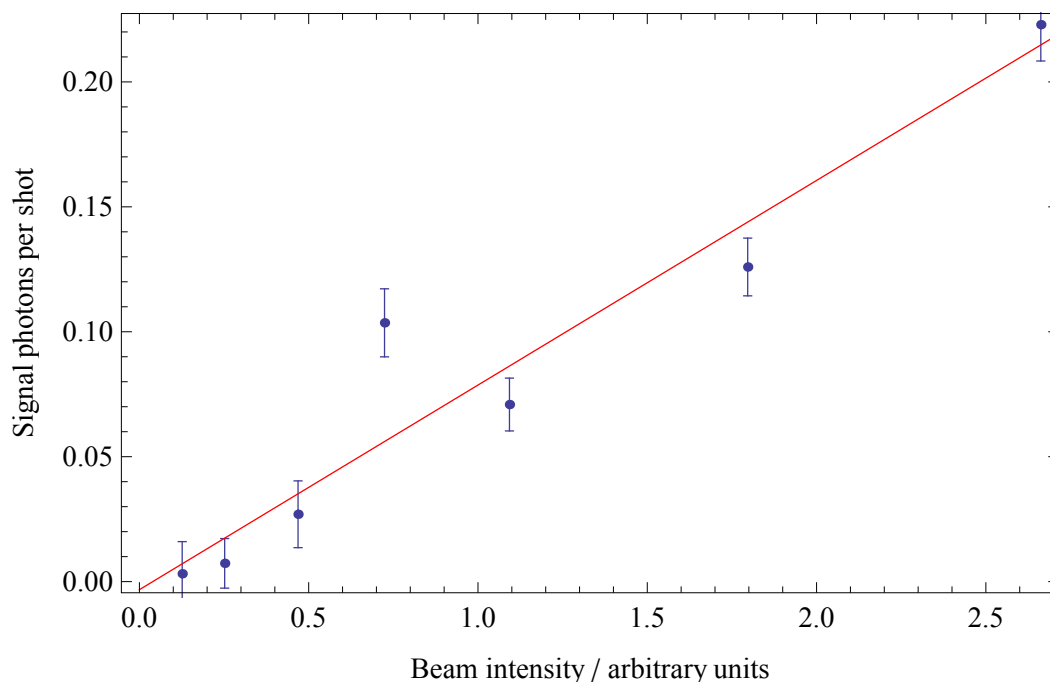


FIGURE 4.7: The variation of the fluorescence signal with increasing beam intensity. The red line is a linear fit to the data. The signal increases linearly because the beam intensity is not sufficient to come close to saturating the transition.

The process of designing, assembling and testing an apparatus of this type requires many different tools and skills. The benefit to having completed the procedure from start to finish, in particular achieving a blue wavelength, is that we not only have a system specific to BH but that we know we could very easily use the same experimental tools to produce a variety of other wavelengths if we needed to consider other molecules or for trapping. We can also reliably tune the existing system over a few nanometres which improves its applicability.

The development of the repump laser could also be used to trial a set-up in which the main cooling beam counterpropagates with the molecular beam while the repump crosses it transversely. This may have advantages over other set-ups as it cools the transverse degree of freedom over the same region as the main pump operates. Ultimately this could lead to a well-collimated sample for trapping.

This system could easily be adapted with any other diode laser to address further vibrational states of the BH molecule. This would be necessary to complete the

slower for the experiment and can now be achieved relatively quickly.

Chapter 5

Outlook

5.1 Progress towards a laser cooling set-up for slowing BH

The results we have produced so far show us that with a single laser frequency we would only be able to scatter an average of 75 photons before our molecules enter a different vibrational state. However, with just two lasers addressing $v'' = 0$ and $v'' = 1$ our measured branching ratios show that we would scatter 1000 photons on average (probability 0.5 following a Poisson distribution for the number of scattering events) before losing molecules to $v'' = 2$. With a third laser to address the transition from $v'' = 2$, the molecules will scatter more than 14000 photons before being lost to a higher-lying vibrational state. We have shown that we can excite two of the transitions of interest, and we have demonstrated the technical ability to address the third, as it lies very near to the wavelength that our repump laser produces. It should be possible to achieve a good intensity in our repump beam with the changes to the design that we have suggested. We have also demonstrated that, by modulating the frequency of the exciting field, we can improve the scattering rate. This chapter is concerned with the direction which the research can now take based on these results. We discuss the possibility of slowing the molecules to rest and the design of a Zeeman slower.

With the two laser frequencies that we currently have, we can scatter on average 1000 photons from each molecule. This corresponds to change in velocity of 77 m s^{-1} . If we add another repump laser on the $A^1\Pi(v' = 1) \leftrightarrow X^1\Sigma^+(v'' = 2)$ transition, then we increase both the number of photons scattered and the velocity change by a factor of 10. This would be sufficient to slow the molecules to rest from their present speed in the supersonic beam. As the molecular velocity changes, the Doppler shift of the radiation will also change, meaning that the radiation is no longer resonant with the molecular transitions. To counterbalance this effect, we can use the Zeeman shift of the molecular energy levels under the action of an external magnetic field. The Zeeman slower would take advantage of the strong Zeeman effect in the excited state and very weak Zeeman effect in the ground state, which greatly simplifies the required spectrum of laser light. This is an advantage of the simple structure of BH compared to the molecules that have so far been cooled.

In order to slow the molecules for trapping, we have to determine the magnetic field which will counteract the Doppler shift at all points on the path of the molecular beam, and then generate this field.

5.2 The design of a Zeeman slower

5.2.1 Introduction

Zeeman slowers [7] are used extensively to decelerate atoms to the low velocities needed for capturing in a magneto-optical trap. The Zeeman slower produces a magnetic field that is tailored so that the Zeeman shift of the laser cooling transition exactly compensates the Doppler shift of the counter-propagating laser. This Doppler shift changes as the atoms slow down, and so a specific magnetic field profile is needed. A Zeeman slower has never been applied to molecules, mainly because of the complexity of the Zeeman shifts of the many states involved in the laser cooling. The simple structure of the BH molecule avoids this complexity, and Zeeman slowing seems possible.

To design the Zeeman slower we first have to specify the conditions of the slowing experiment. The magnetic field profile in this section is designed for a preliminary demonstration of the slowing effect using the apparatus we have. We assume that we could have molecules with an initial velocity of 450 m s^{-1} , by seeding the diborane in a heavier carrier gas, and assume that we only have two laser frequencies. To demonstrate deceleration by 77 m s^{-1} that this entails, we would need a slower to be 1.6 m in length. The design field that we show is slightly smaller than this, at 1.2 m, as we would like to be able to demonstrate some slowing without a large change to the experimental apparatus.

To generate the desired field we can use either a series of coiled copper wires passing current, centred on the molecular beam axis, or pairs of permanent magnets on opposite sides of the beam. The choice of the method of generation has various implications: the current-carrying wires need the electronics to drive the current, as well as water cooling, if they dissipate a large amount of energy as heat. The two different methods also affect the direction of the magnetic field vector. The electromagnetic coils generate a magnetic field along their axis, collinear with the molecular beam, while the permanent magnets would give a field that crosses the beam and is perpendicular to it. Since we are able to continuously modulate the direction of the polarisation vector, neither alignment of the magnetic field will lead to a dark state. Without the modulation we can drive all components of the ground state if we have linearly polarised light, as long as the polarisation vector is not aligned with the magnetic field. Considering the implementation, we find the permanent magnet slower to be less experimentally challenging, so the design here assumes a permanent magnet slower.

5.2.2 Ideal field

To find the ideal field we have to calculate the Zeeman shift in the excited and ground states of the molecule, and make the difference in transition frequency between these two states match the Doppler shift. If we can maintain the resonance condition, then we know the scattering rate that we expect to be able to achieve, and that sets the acceleration that the molecules are subject to. The field profile

is then calculated by assuming that we can maintain a constant acceleration along the decelerator.

The Zeeman shift of the upper state is mostly due to the interaction between the magnetic field and the magnetic moment associated with the electronic orbital angular momentum, $\mathbf{B} \cdot \mu_{\mathbf{L}}$. The Zeeman shift ΔW_{Zeeman} , is given according to Brown and Carrington [56] equation (9.5):

$$\Delta W_{\text{Zeeman}} = g_L \mu_B B \frac{\Lambda^2}{J(J+1)} M_J. \quad (5.1)$$

The magnetic g-factor associated with the electronic orbital angular momentum, g_L , should be close to one; it typically only differs from 1 by a few parts in a thousand. For the excited $A^1\Pi$ state, we have $\Lambda = \pm 1$, and $J = 1$. So we have

$$\Delta W_{\text{Zeeman}} = \frac{1}{2} g_L \mu_B M_J. \quad (5.2)$$

The Zeeman shift for the $M_J = \pm 1$ levels is 7 GHz T^{-1} . The Zeeman shift in the ground state is due to the interaction between the external magnetic field and the magnetic moments associated with nuclear spin and rotation. The nuclear magnetic moment of BH is estimated to be around $3\mu_N B$, so the shift would be 23 MHz T^{-1} . If we produce BH with an initial velocity of 450 m s^{-1} then the peak magnetic field would have to be 0.15 T in order to compensate the Doppler shift. This is a very reasonable field to produce. At 0.15 T the Zeeman shift of the ground state is only 3 MHz , and so is small enough that we can neglect it.

The dependency of the magnetic field profile on the axial coordinate, z , can be written as a function of the initial velocity of the molecules, v_0 , the acceleration, a , which we know, and the transition frequency in the rest frame of the molecule, ω_0 . To do this we have to equate the changes in the transition frequency due to the Doppler and Zeeman shifts. The change in the transition frequency due to the Zeeman shift is given by the difference between the shifts in the upper and lower states, $\mu B/\hbar$, where $\mu = 1/2\mu_B - 3\mu_N$. The magnetic field can then be written in terms of the axial coordinate.

$$\frac{\mu B}{\hbar} = \frac{v}{c} \omega_0, \quad (5.3)$$

$$\Rightarrow B = \frac{\hbar \omega_0 v}{\mu c}, \quad (5.4)$$

$$\text{and } v^2 = v_0^2 + 2az, \quad (5.5)$$

$$\Rightarrow B = \frac{\hbar \omega_0 v_0}{\mu c} \sqrt{1 + \frac{2az}{v_0^2}}. \quad (5.6)$$

To decelerate the molecules we aim to maintain the maximum possible rate of scatter, which we estimate to be approximately $R = 0.086 \times 7.8 \text{ MHz}$, given the number of levels involved in the system. This gives an acceleration of $\hbar R / (\lambda M)$, where M is the molecular mass. This would give us an acceleration of $51\,500 \text{ m s}^{-2}$, but we have to include an efficiency parameter between 0 and 1, which describes how well the experimentally achieved field matches the design field. If we set this parameter to 0.5, then we can accommodate an average scattering rate which is half of the maximum that could be achieved on this transition, and we gain some freedom in the precision with which we must define the field. Our maximum acceleration will then be $25\,750 \text{ m s}^{-1}$. To slow the molecules to rest from their initial velocity of 450 m s^{-1} we would then need to build a slower 3.9 m in length. The magnetic field profile we aim to produce, given by 5.6, is shown in figure 5.1.

The field in figure 5.1 tapers to zero at the end of the slower. This design assumes that the laser frequency is tuned to be resonant with the molecules in their own rest frame. If we wanted to slow the molecules and then continue to manipulate them with a magnetic field, we could detune the laser from resonance and allow the magnetic field to cross zero before they are at rest. We have designed the slower for an initial demonstration of the deceleration, but we should be able to include some flexibility in the design, so that the magnets can be repositioned.

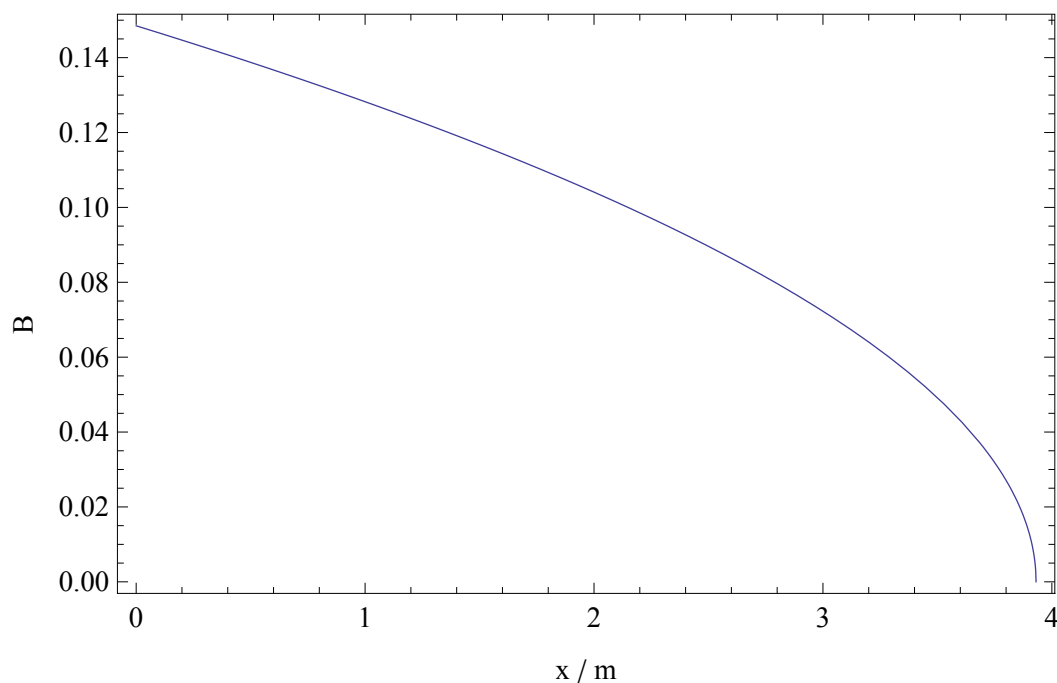


FIGURE 5.1: The magnetic field profile that would maintain the resonance condition as the molecules are slowed from 450 m s^{-1} .

5.2.3 Modelling the magnetic field

To produce the magnetic field shown in figure 5.1 we would use a series of magnet pairs of varying separation, centred on the beamline. We model the field produced by a series of bar magnets using the Radia package for *Mathematica* (by ESRF). This package can be used to simulate the field due to a bar magnet of a given material and dimension. The procedure to find the optimal separation of the magnet pairs follows.

We first make an approximate analytical model of the field due to a series of bar magnets. To do this, we treat each bar magnet as a magnetic dipole. The field due to a single dipole is well known, and the field due to a set of dipoles is just the vector sum of the field from each. We generate an analytical function that represents the field along the axis of the slower, leaving the transverse separation between each pair of dipoles as free parameters. Then we fit this function to the ideal field, varying the separations until we find the best fit. We have to fix the number of

magnet pairs to use, and the axial separation between the pairs, before fitting. The dipole function is useful to us because it has a relatively simple functional form, so it can be used to solve for the spacings fairly quickly. However, it does not render an accurate picture of the field due to a series of bar magnets.

The Radia package can be used to simulate the magnetic field due to a bar magnet, at the cost of greater computational resources. In order to generate a function which can be fitted from this field profile we have to make an interpolating function representing the bar magnet. Figure 5.2 shows the z-component of the magnetic field due to a 30 mm x 30 mm x 60 mm bar magnet, simulated in Radia. Figure 5.3 shows the interpolating function used to reproduce this data. The discrepancy between the Radia field and the interpolated field is below 1 μ T, except near to the magnet edge. Since the molecules would be travelling along a line a few times 10 mm from the magnet, this should not be a problem.

A series of these interpolating functions is fit to the ideal field, with only the spacings of the magnet pairs as free variables. Here, we use the spacings obtained in fitting the dipole function as initial estimates. Once the fitting procedure is completed we can use Radia to calculate the field due to the full set of bar magnets at the spacings found.

The z-component of the magnetic field at the centre of the slower due to a series of 118 magnet pairs is shown with the ideal field in figure 5.4. The components of the magnet field in the x- and y-directions are negligible. Each pair of magnets is separated from the next by 3 mm in the x-axis and the magnets are all of the same dimension: 30 mm x 30 mm x 60 mm. Simulating the magnets under these conditions we can easily reproduce the ideal field, which is also shown in figure 5.4 for comparison. The magnet pairs reproduce the field particularly well in the middle of the slower and less so at the ends. This is shown in figure 5.5, where the difference between the ideal and simulated fields is plotted.

The difficulty in matching field at the ends (particularly the start) of the slower is due to the discontinuity which occurs where the series of magnets ends. At all other points in the slower, there are contributions to the field from the nearest magnet pair, and from others displaced in either direction on the x-axis. However,

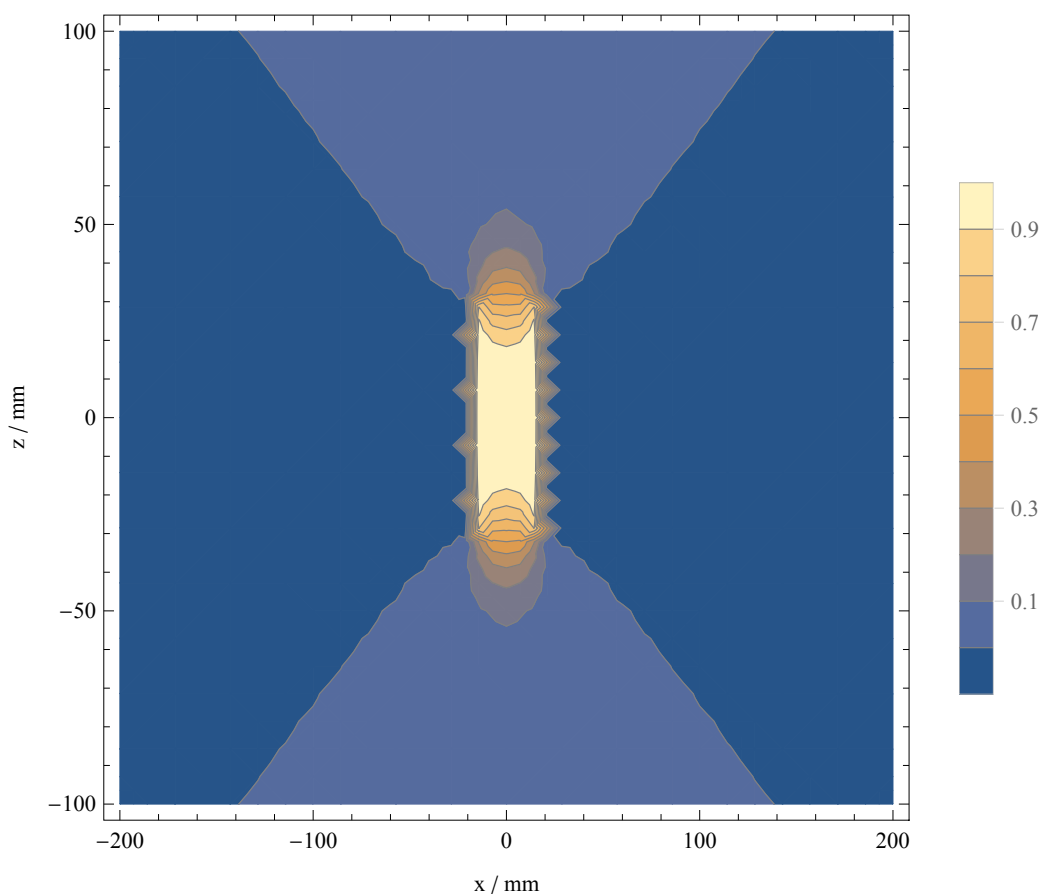


FIGURE 5.2: The magnetic field profile arising from a single 30 mm x 30 mm x 60 mm bar magnet computed in the Radia package. The field profile is in units of tesla.

at the end of the slower there are fewer magnets contributing to the field, and the profile varies less smoothly. The absolute discrepancy is usually around 0.001 T, which would result in the transition being less than one natural linewidth from the ideal frequency, and does not pose a problem for the slower. At the start of the slower, the discrepancy is as much as 0.01 T. To counteract this additional magnets should be added to either side of the slower. The same fitting procedure should be able to find the correct spacings.

The error introduced by the fitting procedure is not known but should be very small. When we use the interpolated function with separations from the fit, the resulting field matches the ideal field very well.

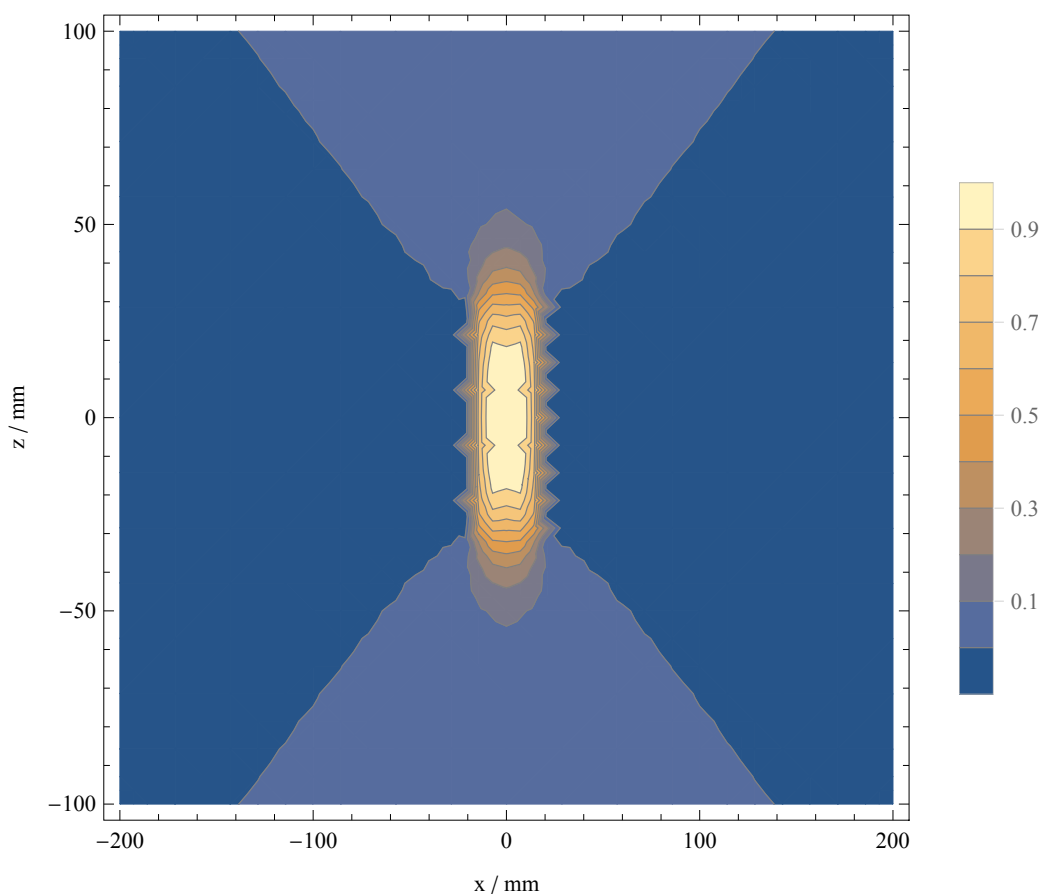


FIGURE 5.3: The magnetic field profile arising from a single 30 mm x 30 mm x 60 mm bar magnet computed using an interpolating function from data generated in Radia. The field profile is in units of tesla. The discrepancies between the interpolated field and the field calculated by Radia are greatest close to the surface of the magnet.

5.2.4 Actual design

Following the design which has been simulated we would consider building a Zeeman slower similar to the one described in [71], shown in figure 5.6. Here the magnets are mounted on threaded screws which allow careful adjustment of the position. The magnet spacings obtained from our fitting procedure are plotted with the distance along the slower in figure 5.7. The smallest spacing is greater than 120 mm, which is large enough to allow the vacuum tube (whose outer diameter is typically only

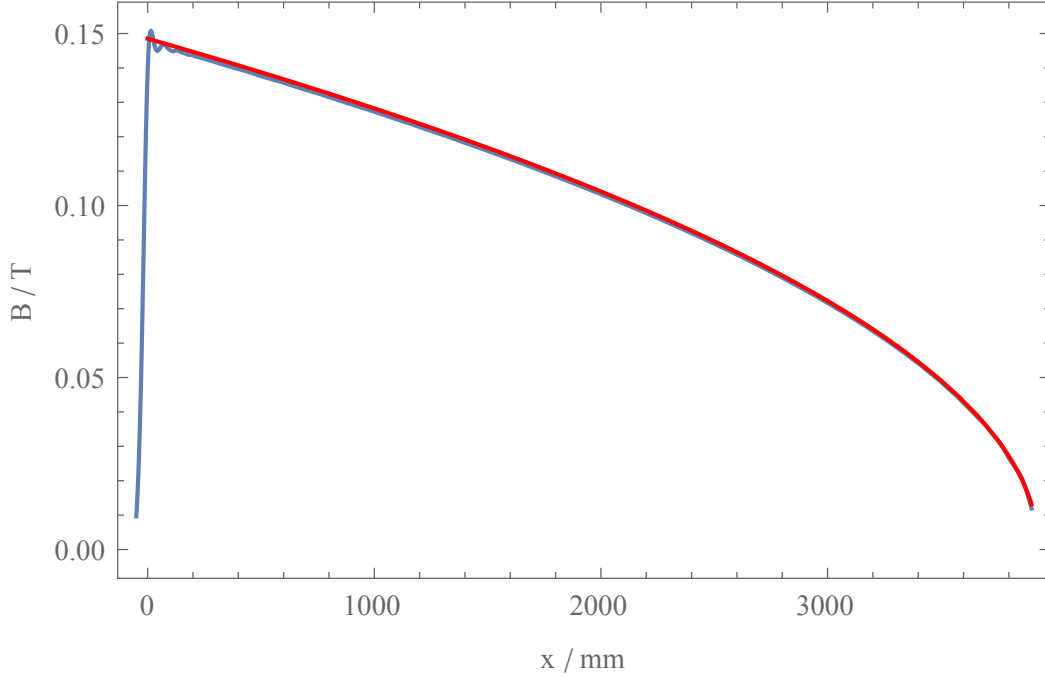


FIGURE 5.4: The magnetic field profile at the centre of the slower produced by a series of 118 pairs of magnets (blue). The magnet pairs spacings were determined by the fitting procedure described in the text and the field is simulated using Radia. The ideal field is shown in red.

20 mm) to pass between them. The tube could be made from aluminium, a non-magnetic material which will not cause any change to the field profile. The magnet positions could easily be adjusted to optimize the field profile as they would be outside the vacuum chamber.

We may choose to use fewer magnets, or magnets of a different dimension. It may also be necessary to prototype the Zeeman slower in order to find the separation between magnet pairs that the design can tolerate.

Once the slower has been built and the correct magnetic field profile obtained, it can be tested. The easiest test would be first to build just the first 1.6 m of the slower which can be used with a single repump frequency, and demonstrate 77 m s^{-1} of slowing. Eventually the slower could be extended to its full length of 3.9 m, although an alternative option would be to cool the supersonic valve, or use a buffer gas source so that the initial velocity is lower.

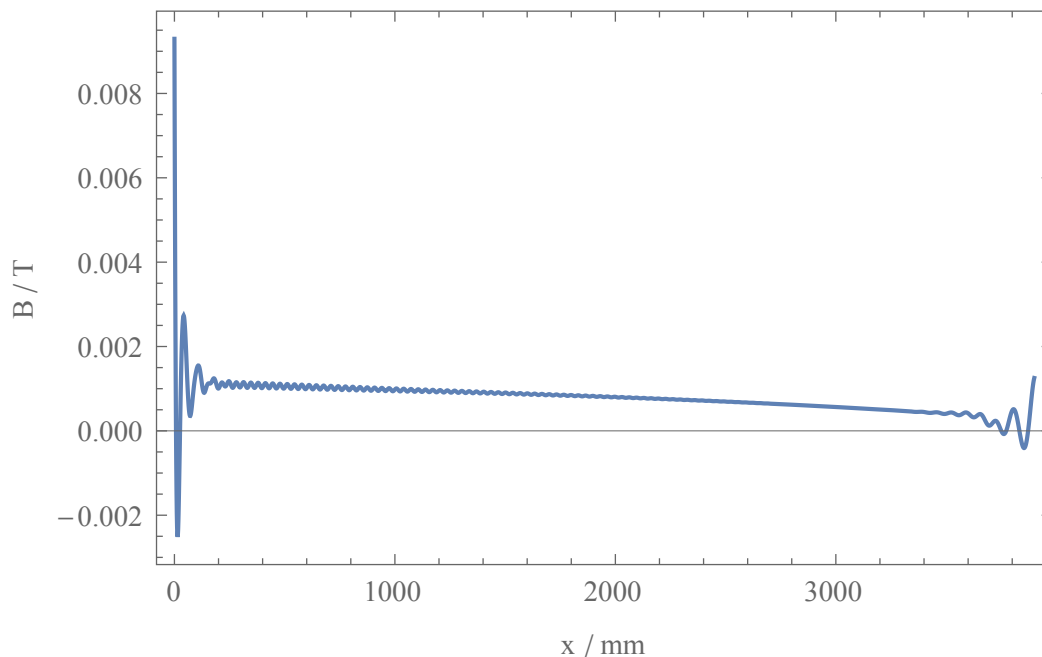


FIGURE 5.5: The difference between the ideal and simulated fields.

5.3 Conclusion

BH has been suggested by di Rosa [42] as a possible candidate for laser cooling. The results obtained in the second chapter indicate that BH is a good choice of molecule for laser cooling on the $A(v' = 0) \leftrightarrow X(v'' = 0)$ Q(1) transition with just two laser frequencies. The hyperfine structure of the levels was also confirmed in order to establish a clear understanding of the molecule. In the third chapter we saw through modelling the interaction between the molecular system and the optical field semi-classically that we can predict a high scattering rate if we excite to $F' = 5/2$ and modulate the polarisation at a frequency near 1 MHz. We built the apparatus to apply this modulation, along with diagnostics to measure the effect of the modulation on both the polarization and frequency of the light. We then demonstrated that the modulation does indeed increase the fluorescence rate of the molecule as expected.. The fourth chapter details work to produce light at the repump frequency to excite the $X^1\Sigma^+(v'' = 1; F'' = 3/2, 5/2) \leftrightarrow A^1\Pi(v' = 0; F' = 5/2)$ transition and the tests of this system.

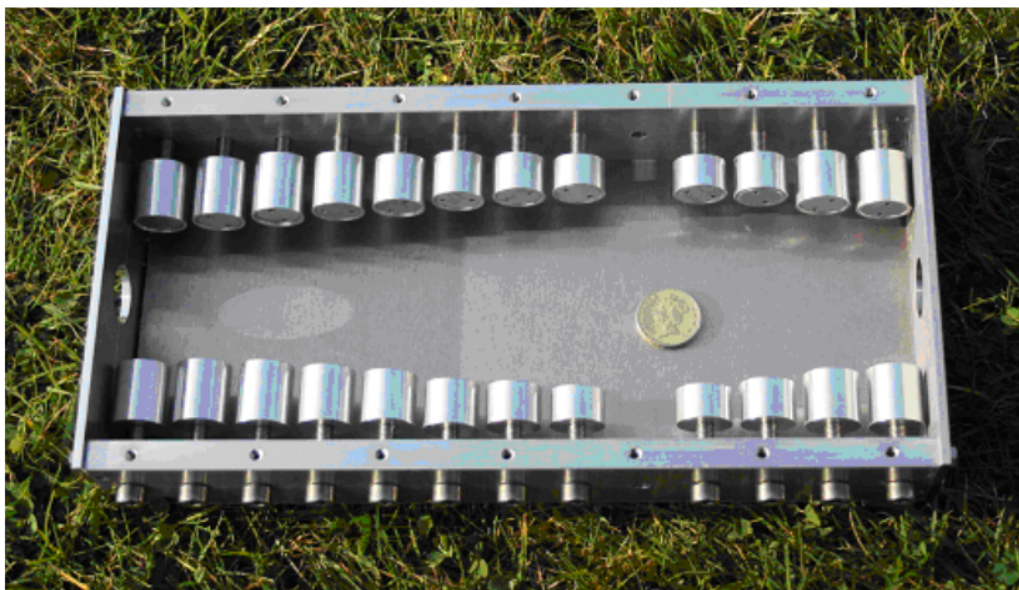


FIGURE 5.6: A Zeeman slower previously constructed at the Blackett laboratory to slow strontium atoms.

In order to bring the molecules to rest the pump and repump laser will have to be counter-propagated with the molecular beam. The pump laser should be counterpropagating, but the repump laser could be made to cross the molecular beam in the transverse direction. The Zeeman slower design will need to be implemented, this may require a small change to the vacuum apparatus, and the magnet pair spacings will have to be optimised through successive iterations of the slowing cycle. To trap the molecules it will be necessary to first investigate the interaction of the molecules with the trapping light by modelling the interaction and it may then be possible to design a magneto-optical trap.

It remains for us to address the issue of the divergence of the molecular beam. As the beam is slowed along its axis it will diverge and spread out over a large area which will make a trapping experiment difficult. We might be able to rectify this if we investigate cooling transverse to the beams direction of propagation with the repump laser.

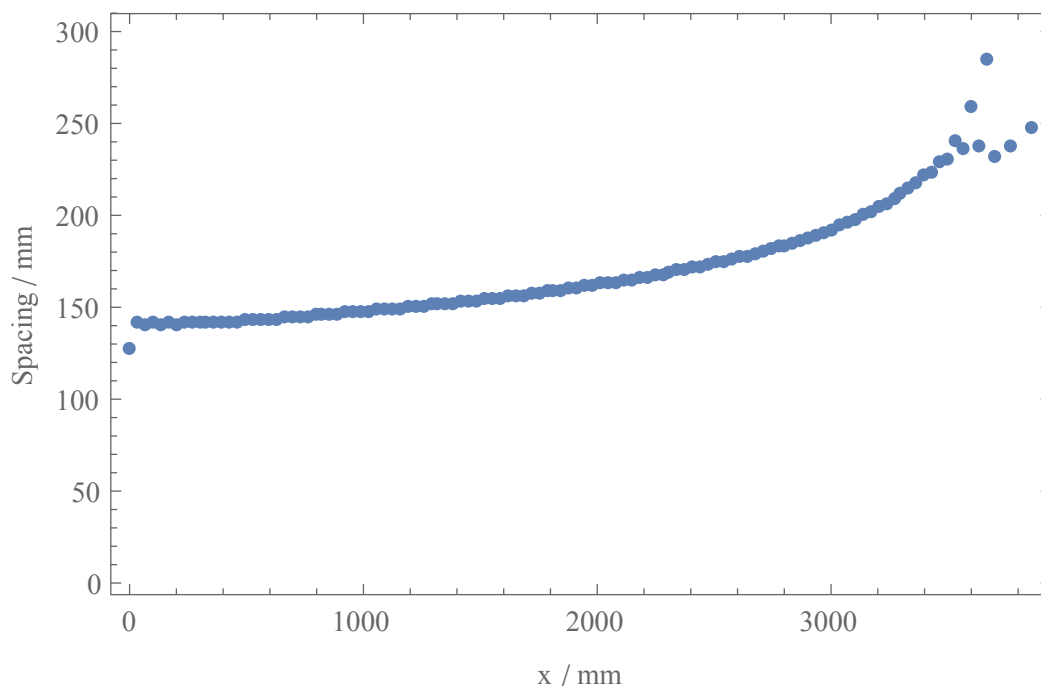


FIGURE 5.7: The spacing between magnet pairs. The odd behaviour around 3.6 m suggests that we could use fewer magnets here to produce the same field in this region.

Ultimately we aim to trap the molecules in a magneto-optical trap, where we would expect the molecules to reach a temperature of $30\text{ }\mu\text{K}$, or if polarisation-gradient cooling is effective, the recoil temperature of $4\text{ }\mu\text{K}$.

We have established the groundwork for a laser cooling experiment for a new molecule beginning with its production and expansion into a supersonic beam. The molecules cycling behaviour has been investigated through spectroscopy and experiments using an electro-optic modulator to vary the polarisation of the probe beam. We have been successful in producing light at the repump frequency using a compact system capable of achieving reasonable power. Further effort could find success in producing a trapped source of molecules with a relatively small amount of work. Alternatively, the experiment could be used to trial transverse cooling before proceeding to slow the molecules.

Appendix A

Appendix

A.1 Solving the Liouville equations in Mathematica

The solutions to the Master equation which describes the molecule-light interaction give the time-evolution of the unperturbed molecular states as long as the problem is amenable to the separation of timescales described in Cohen-Tannoudji [52]. Namely, that the spontaneously emitted photon makes an insignificant change to the laser field, which is true in our case, and that the spontaneously emitted photon doesn't interact with another, which is also true in our case.

To calculate the time-dependence of the unperturbed molecular states we have to solve the Master equation,

$$\frac{d\rho(t)}{dt} = \frac{1}{i} [\mathbf{H}_i, \rho] + \Gamma\rho. \quad (\text{A.1})$$

The rate of change of the density operator, ρ , is given by the commutator of the interaction Hamiltonian, $\mathbf{H}_i$, with the elements of the density operator. The damping term, Γ , contains all of the information about the bath of oscillators which are not included in the computation, i.e. the unoccupied modes of the radiation field. It also brings about the decay of excited electronic states by spontaneous emission.

Details of the term used to describe the optical field are given in chapter 3. We solve the equations with an initial condition that spreads the population equally among the ground states at $t = 0$.

A.2 Liouville equations

Rather than reproduce all 324 equations for the time dependence of the elements of the density matrix, I will include the typical examples for different elements from different sections of the density matrix here. Those which haven't been reproduced can be assumed to contain similar terms. The variables are those used in chapter 3. The states labelled 1–12 are the ground states, while the excited states are 13–18.

A.2.1 Ground-state population

$$\begin{aligned}
\dot{\rho}_{1,1}(t) = & \Gamma \left(\frac{1}{3} \rho_{13,13}(t) + \frac{1}{5} \rho_{14,14}(t) + \frac{1}{6} \rho_{15,15}(t) \right) \\
& + \Omega_R \left(\rho_{1,13}(t) \left(-0.144338i + 0.144338 \exp \left(-\frac{1}{4} i \phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4} i \phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \right. \\
& + \rho_{1,15}(t) \left(0.0456435i + 0.0456435 \exp \left(-\frac{1}{4} i \phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4} i \phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \\
& + \rho_{13,1}(t) \left(0.144338i + 0.144338 \exp \left(\frac{1}{4} i \phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4} i \phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \\
& \left. + \rho_{15,1}(t) \left(-0.0456435i + 0.0456435 \exp \left(\frac{1}{4} i \phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4} i \phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \right)
\end{aligned} \tag{A.2}$$

A.2.2 Ground-state coherence

$$\begin{aligned}
\dot{\rho}_{1,2}(t) = & \Omega_R \left(\rho_{1,14}(t) \left(-0.111803i + 0.111803 \exp \left(-\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \right. \\
& + \rho_{1,16}(t) \left(0.0790569i + 0.0790569 \exp \left(-\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \\
& + \rho_{13,2}(t) \left(0.144338i + 0.144338 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \\
& \left. + \rho_{15,2}(t) \left(-0.0456435i + 0.0456435 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \right) \quad (\text{A.3})
\end{aligned}$$

A.2.3 Coherence term

$$\begin{aligned}
\dot{\rho}_{1,18}(t) = & -\frac{1}{2}\Gamma\rho_{1,18}(t) \\
& + \Omega_R \left(\rho_{1,11}(t) \frac{e^{\frac{iE_{11}t}{\hbar}}}{2\sqrt{42}} \left(-\exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) + i \right) \right. \\
& + \rho_{1,4}(t) \left(0.144338i - 0.144338 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \\
& + \rho_{13,18}(t) \left(0.144338i + 0.144338 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \\
& + \rho_{15,18}(t) \left(-0.0456435i + 0.0456435 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \\
& \left. \right) + (\omega_0 - \omega) \rho_{1,18}(t) \quad (\text{A.4})
\end{aligned}$$

A.2.4 Excited-state coherence

$$\begin{aligned}
\dot{\rho}_{18,17}(t) = & -\frac{1}{2}\Gamma\rho_{18,17}(t) \\
& + \Omega_R \left(-\rho_{11,17}(t) \frac{e^{-\frac{iE_{11}t}{\hbar}}}{2\sqrt{42}} \left(i + \exp \left(-\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \right. \\
& + \rho_{18,10}(t) \frac{e^{\frac{iE_{10}t}{\hbar}}}{\sqrt{105}} \left(-\exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) + i \right) \\
& + \rho_{18,12}(t) \frac{e^{\frac{iE_{12}t}{\hbar}}}{2\sqrt{42}} \left(i + \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \\
& - \rho_{4,17}(t) \left(0.144338i + 0.144338 \exp \left(-\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \\
& \left. \rho_{18,3}(t) \left(0.111803i - 0.111803 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \right) \quad (\text{A.5})
\end{aligned}$$

A.2.5 Excited-state population

$$\begin{aligned}
\dot{\rho}_{18,18}(t) = & -\Gamma\rho_{18,18}(t) \\
& + \Omega_R \left(-\rho_{11,18}(t) \frac{e^{-\frac{iE_{11}t}{\hbar}}}{2\sqrt{42}} \left(i + \exp \left(-\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \right. \\
& \rho_{18,11}(t) \frac{e^{\frac{iE_{11}t}{\hbar}}}{2\sqrt{42}} \left(-\exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) + i \right) \\
& - \rho_{4,18}(t) \left(0.144338i + 0.144338 \exp \left(-\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} - \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} + \frac{i\phi}{2} \right) \right) \\
& \left. + \rho_{18,4}(t) \left(0.144338i - 0.144338 \exp \left(\frac{1}{4}i\phi e^{-it\delta_{\text{EOM}}} + \frac{1}{4}i\phi e^{it\delta_{\text{EOM}}} - \frac{i\phi}{2} \right) \right) \right) \quad (\text{A.6})
\end{aligned}$$

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