# Making and Manipulating Cold Calcium Monofluoride Molecules

Master Thesis submitted at the University of Stuttgart by **Ole Einar Prochnow** 

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Stuttgart, November 30th, 2023

Ole Einar Prochnow

# Deutsche Zusammenfassung

Neuste Fortschritte bei der Laserkühlung von Molekülen haben den Weg für eine neue Generation von Experimenten zur Forschen an ultrakalten, molekularen Quantengasen geebnet. Dabei hat sich gezeigt, dass insbesondere das Molekül Kalziumfluorid sehr gut für solche Experimente geeignet ist, da es eine für die Laserkühlung günstige Struktur besitzt und mögliche chemische Verluste bei niedrigen Temperaturen durch Mikrowelleneinstrahlung effektiv verhindert werden können.

In dieser Arbeit wird der Aufbau, die Optimierung und die Charakterisierung einer Quelle von CaF-Molekülen beschrieben, welche den Startpunkt für ein neues Experiment zum Laserkühlen von CaF auf ultrakalte Temperaturen bildet. Dabei ist CaF ein Radikal, das nicht natürlich vorkommt und deshalb speziell für das Experiment erzeugt werden muss. Zusätzlich müssen die Moleküle vorgekühlt werden, da die komplexen Laserkühlverfahren nur funktionieren, wenn die Moleküle speziell im Grundzustand  $X^2\Sigma^+(\nu = 0, N = 1)$  präpariert sind.

Mit unserer neuen Quelle erzeugen wir CaF durch Laserablation eines CaF<sub>2</sub>-Targets, bevor es durch Kollisionen mit dem Buffergas Helium auf Temperaturen von etwa 4K gekühlt wird. Unsere Quelle bietet mehrere Möglichkeiten zur direkten Messung der internen Zelldynamik, welche sonst schwierig theoretisch zu beschreiben ist. Beispielsweise bietet der Aufbau die Möglichkeit der Messung der Flugrichtung des Molekülstrahls. Dabei stellen wir fest, dass der Strahl für die gemessenen Heliumflussbereiche gerade verläuft. Zusätzlich messen wir den Wirkungsquerschnitt zwischen CaF und Helium und charakterisieren den Thermalisierungsvorgang der Moleküle während des Buffergaskühlens. Die Zelle erzeugt einen reproduzierbaren kalten Strahl aus CaF-Molekülen und stellt damit die Grundlage für nachfolgende Laserkühlexperimente dar.

# Abstract

Recent advances in cooling techniques for molecules have paved the way to a new generation of experiments exploring ultracold molecular quantum gases. Calcium monofluoride (CaF) in particular is a molecular species of interest in this context, because of its suitability for direct laser cooling and the availability of shielding techniques to mitigate chemical losses.

This thesis describes the construction, optimization and characterization of a source of cold CaF molecules that forms the starting point for a new experimental setup aiming to cool CaF into the ultracold regime. CaF is a radical that does not occur naturally and therefore has to be produced specifically for the experiment. In addition, for the elaborate laser cooling and trapping schemes to work efficiently the CaF molecules have to be precooled to achieve a significant population in the  $X^2\Sigma^+(\nu = 0, N = 1)$  ground state.

In our new source, CaF molecules are created via laser ablation of a  $CaF_2$  target and buffer gas cooled by collisions with helium to temperatures on the order of 4 K. The internal dynamics of buffer gas sources are notoriously difficult to understand, and the presented source allows for several angles of interrogation of the cell dynamics. As an example, we measure the molecular beam pointing direction and find that the beam is going straight for the investigated flow regimes. Furthermore we present measurements of the collisional cross-section between helium and CaF and the thermalization process of the molecules during buffer gas cooling. We find that the source reliably creates a beam of cold CaF molecules, providing the starting point for future laser cooling and slowing experiments.

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# 1 Introduction

### 1.1 Advances in Laser Cooling and Trapping of Molecules

The cooling of atomic gases with the help of light forces emerging from laser radiation was first proposed in the 1970s by Hänsch and Schawlow [1]. The proposals were initially intended to increase the accuracy of atomic spectroscopy at the time, as colder gas temperatures would mitigate the disturbing effect of Doppler broadening. In 1978 the first successful application of such ideas was demonstrated with the laser cooling of magnesium ions to temperatures below 40 K [2]. In the following years laser cooling methods were greatly enhanced and expanded upon, resulting in techniques like the three-dimensional Doppler- and sub-Doppler cooling [3] and Zeeman slowers able to decelerate atomic beams [4]. Further refinements eventually allowed for the trapping of neutral atoms in the form of a magneto-optical trap [5], which was previously only possible for charged particles like ions. The progress ultimately culminated in the first creation of a Bose-Einstein condensate in 1995 with Wieman, Cornell [6] and Ketterle [7] receiving the Nobel prize for this achievement.

Today, laser cooling and trapping techniques have become the standard tool of atomic and molecular physics. The heavily refined methods have enabled a wide variety of new applications in the field, from atomic clocks with an accuracy of  $5 \cdot 10^{-19}$  [8] to precision measurements of the fundamental constants in nature [9] and neutral atom-based concepts for quantum computers [10]. Confinement of atoms into optical lattices paved the wave for atom-based simulations of quantum systems [11], allowing for the investigation of among others the thermalization of quantum systems [12] as well as magnetic phenomena [13].

Ultracold molecules present an intriguing alternative to atoms. Their additional internal degrees of freedom result in an even richer system to investigate, allowing for more accurate measurements or even completely new possibilities. This includes the search for the predicted electron's electric dipole moment [14–16], quantum simulations based on the dipolar interactions between molecules [17, 18] and research into cold collisions and quantum chemistry [19, 20].

The increased complexity that results in this rich set of possible applications however also heavily complicates the laser cooling of molecules. Until the discovery of some diatomic molecular species as possible laser cooling candidates in 2004 molecular laser cooling had been considered too impractical to implement [21]. It took another six years until the first successful laser cooling of strontium monofluoride (SrF) by DeMille *et al.* [22], 32 years after the first laser cooled atoms. Since then, however, the field of cold molecules has undergone a similar explosion as the field of ultracold atoms before it. The first molecular MOT was demonstrated in 2014,



Phase Space Density of Laser Cooled Molecules

Figure 1: Progress of the phase space density of laser cooled molecules in recent years. Adapted from [24].

also by DeMille [23] and with SrF. Since then, additional molecular species were successfully cooled and trapped, including calcium monofluoride (CaF) [25] and yttrium monoxide (YO) [26]. Furthermore, molecular laser cooling has even been extended to the first polyatomic molecules [27–29]. In addition to direct cooling of molecules, significant progress has also been made in forming ultracold molecules from pairs of ultracold atoms. This has recently lead to the first formation of quantum degenerate Fermi gases of molecules [30–32].

### 1.2 Towards Molecular BECs and Supersolids

A milestone in the field of ultracold molecules that has not been reached yet is the creation of a molecular BEC. Bose-Einstein condensation of a gas occurs when the de Broglie wavelength of the matter waves of the particles in the gas is equal to the interparticle spacing, which is equivalent to phase space density of order unity. In atoms this is typically achieved via sympathetic or evaporative cooling [33, 34]. Applying these techniques to molecules however usually leads to high collisional losses [35, 36] as soon as a certain cloud density is reached. Consequently, so called shielding techniques which prevent molecules from coming close enough to each other to induce losses have been of particular interest for achieving higher and higher phase space densities. Shielding can be achieved in a number of ways, having already been successfully demonstrated using microwaves [37] and static



Figure 2: (a) Phase diagrams of a molecular BEC for different scattering lengths  $a_s$ , particle numbers N and dipolar lengths  $a_{dd}$ . Depending on the parameters, a BEC (b) can transform into various supersolid phases, including droplet arrays (c), honeycomb (d), stripes (e), labyrinth (f) and pumpkin patterns (g). Adapted from [39].

electric fields [38]. Due to these advances in molecular laser cooling the maximal achievable phase space density of a molecular cloud has continued to grow in recent years, as can be seen in Figure 1, and the implementation of such shielding techniques is expected to be able to push the phase transition to Bose-Einstein condensation.

A molecular BEC would also pave the way for a young field of research: The exploration of supersolid phases in ultracold quantum gases. Dipolar interactions between particles and quantum fluctuations can give rise to exotic states of matter emerging from a BEC. One such state, quantum droplets that spontaneously form out of a BEC, was already shown experimentally for dysprosium atoms [40]. The emerging droplet structures have supersolid properties, which means that they are both superfluid and crystaline at the same time [41]. The formation and observation of these droplets is possible due to the magnetic dipole moment of dysprosium. The magnetic dipole moment of atoms however is relatively weak. Molecules on the other hand possess a comparatively strong permanent electric dipole moment that would allow for the exploration of other supersolid phases besides droplets.

Simulations by Schmidt et al. [39] show that a molecular BEC could give rise to a wide variety of supersolid states depending on the s-wave scattering length and dipolar interaction strength of the molecules. Some of these states are depicted in Figure 2. Here molecules could provide yet another advantage over atoms: Besides their generally stronger dipolar interactions, both the dipolar interaction strength as well as the s-wave scattering length can be tuned by applying a DC and AC electric field, respectively. Tuning these parameters would allow for the exploration of the full phase diagrams of dipolar quantum matter in ways not realizable with magnetic atoms.

# 1.3 The Contents of this Thesis

Motivated by the recent advances in the field of molecular laser cooling we aim to create a molecular BEC of CaF and ultimately explore the supersolid phases. Before any laser cooling, trapping and eventual Bose-Einstein condensation can be achieved, however, a reliable source of cold CaF molecules has to be set up. This thesis will describe the construction process of such a source as well as characterize the efficiency of the source for varying parameters. Finally, first experimental results are examined as to whether the apparatus performs as intended.

# 2 Theoretical Background

### 2.1 Laser Cooling

Laser cooling is an important tool in the field of atomic and molecular physics. Neutral particles can be slowed, cooled and trapped due to the forces emerging from the interaction between a light field and atoms or molecules. Although it is not actually realized in the scope of this thesis it is of vital importance to understand the concepts, capabilities and especially prerequisites of laser cooling to motivate key aspects of the experiment, like the choice of molecule or method of molecule creation. The following section is mostly based on [42], except when noted otherwise.

#### 2.1.1 The Scattering Force

To explain the concept of particle-light interaction and the scattering force we assume an idealized two-level atom with ground state  $|g\rangle$  and excited state  $|e\rangle$  with excitation energy  $\Delta E = \hbar \omega_0$ . The system can interact with radiation in three ways, illustrated in Figure 3.

First, it can absorb a photon to transition from the ground state to the excited state. The photon energy has to be nearly equal to the energy difference  $\Delta E$ .

An atom in the excited state can spontaneously decay back to the ground state by emitting a photon, which occurs after the life time  $\tau$  of the excited state. Decay can also be provoked with a resonant photon in a process called stimulated emission. The momentum of the photon is transferred to the particle during absorption or emission.

The key to laser cooling is the fact that the momentum transfer from absorption is pointed towards the photon propagation direction, while the momentum transfer from spontaneous emission is pointed towards a random direction.

Let us now assume coherent photons from a laser, counterpropagating to the direction of motion of the atom. Each time a photon is absorbed by the atom, the photon transfers its momentum  $\hbar \mathbf{k}$  to it. The atom in the excited state decays back to the ground state at a rate given by  $\Gamma = \tau^{-1}$ . The momentum kicks gained from the spontaneous emissions point in random directions and therefore the average momentum gained from multiple emission cycles is zero. As soon as the particle is back in the ground state, it can absorb a new photon and the cycle begins anew. The particle will experience an overall force called the scattering force  $F_{\text{scatt}}$  given



Figure 3: The three possible light-matter interactions in an idealized two-level atom. **a**) The system is excited from the ground state  $|g\rangle$  to  $|e\rangle$  under the absorption of a photon with momentum  $\hbar \mathbf{k}$  and energy  $\hbar \omega_0$ . **b**) After a characteristic lifetime  $\tau$  the system decays to  $|g\rangle$  under spontaneous emission, emitting the photon in an arbitrary direction. **c**) The emission of a photon can be induced with a resonant photon via stimulated emission. The system relaxes to the ground state  $|e\rangle$  and the emitted photon is identical two the initial one.

by the product of the scattering rate with the photon momentum

$$\mathbf{F}_{\text{scatt}} = \hbar \mathbf{k} \, \Gamma \rho_{22}, \tag{2.1}$$

where  $\rho_{22}$  is the fraction of particles in the excited state. The force points in the same direction as the laser. An expression for  $\rho_{22}$  can be found by solving the optical Bloch equations, which describe the interaction of light with a two-level system. In the steady state, the population of the excited state is given by

$$\rho_{22} = \frac{1}{2} \frac{\Omega^2 / 2}{\delta^2 + \Omega^2 / 2 + \Gamma^2 / 4},$$
(2.2)

where  $\Omega$  is the Rabi frequency of the transition and  $\delta = \omega - \omega_0 - \mathbf{k} \cdot \mathbf{v}$  is the detuning of the system, which is given by the difference of the laser frequency  $\omega$  to the resonance frequency of the transition  $\omega_0$  in addition to the Doppler shift due to the velocity v of the particles. The scattering force is strongest when there is no detuning  $\delta = 0$ , which means that a certain laser frequency is only resonant with a specific velocity class with respect to the direction of the laser.

It becomes apparent that a single laser beam at frequency  $\omega$  is not enough to cool a cloud of atoms. For one, the force only acts in one direction. Additionally the scattering force depends on the particle velocity v with respect to the photon propagation direction. If the laser is resonant ( $\delta = 0$ ) it will strongly scatter photons off of the particles which in turn increases the detuning due to the change in velocity v. This will continue to weaken the scattering force until the laser is so far off resonant that the slowing effectively stops.

#### 2.1.2 Doppler Cooling

In order to reduce the velocities of an ensemble of particles in all directions, so called Doppler cooling is employed. Doppler cooling a laser cooling scheme that is able to dampen velocities of the particle cloud in potentially all spatial dimensions, effectively reducing the overall temperature of the cloud. In Doppler cooling, two counterpropagating laser beams are overlapped with each other. The lasers are now red detuned, which means that  $\omega$  is deliberately lower than the resonance frequency  $\omega_0$ . The overall detuning  $\delta$  may still be zero for certain velocity classes of atoms as the corresponding positive Doppler shift counteracts the redshift. The faster the particle, the stronger the Doppler shift it experiences.

Due to the geometry of the setup, this effect works in both directions. A particle moving in the same direction as the laser will instead experience a negative Doppler shift. This means that the laser is shifted even further out of resonance, making an absorption process exceedingly unlikely. Thus the heating effects of the scattering force are always smaller than the cooling effects.

This cooling scheme can be generalized to three dimensions by setting up three pairs of counterpropagating laser beams, one for each spatial dimension. The overall force can be approximated to be linearly dependent on the particle's velocity

$$\mathbf{F}_{\text{Dopp}} \approx -\alpha \mathbf{v} \tag{2.3}$$

for small velocities  $\mathbf{v}$ , which can be seen in Figure 4. All particles are slowed down with a damping constant  $\alpha$ . Because this happens regardless of the particle's direction of motion, this process effectively cools an ensemble of particles, since the temperature of an ensemble is dependent on the average velocity of its particles. Doppler cooling is limited by the fact that spontaneous emission events transfer a finite momentum to the particles. While the average momentum transfer of spontaneous emission vanishes over many emission cycles, this still induces a finite temperature. The lowest temperature achievable with Doppler cooling is the Doppler temperature

$$T_{\rm Dopp} = \frac{\hbar\Gamma}{2k_{\rm B}}.$$
(2.4)

Even lower temperatures can be achieved with more complex cooling schemes like Sisyphus cooling [43]. Additionally, using the dependence of the Zeeman shift on the magnetic field allows for the creation of position-dependent light forces which can be used to trap neutral particles in a magneto-optical trap (MOT) [5].

The previously described laser cooling schemes assumed an idealized two-level system where particles can only cycle between the ground and a single excited state. Although real atoms and molecules are far more complicated than this idealized case, the general principles can be extended to these multi-level systems.



Figure 4: The Doppler force  $F_{\text{Dopp}}$  for different particle velocities v. The Force always acts in the opposing direction of the particle's velocity, creating a cooling effect when applied in all three dimensions. For small v the force is appproximately linear.

# 2.2 Energy Structure of Molecules

Molecules are made up of multiple atoms held together by chemical bonds. In addition to the electronic degree of freedom found in atoms, molecules have multiple nuclei and their interactions that have to be taken into account. This leads to additional degrees of freedom resulting in a richer, more complex energy structure. This chapter will go through all relevant contributions to the energy structure of diatomic molecules in order of energy scale and is based on [44] and [45].

#### 2.2.1 Electronic Levels

As with atoms the eigenstates and eigenenergies of electrons in molecules can be calculated by solving the Schrödinger equation. However even the simplest molecular case, a diatomic molecule with a single electron, cannot be solved analytically. The eigenenergies of the electronic states can be approximated very well with the Born-Oppenheimer approximation, which separates the motion of the electron and the nuclei due to the great mass difference between them. Instead of solving multiple coupled Schrödinger equations for all particles in the system, the positions of the nuclei are assumed to be fixed and only the Schrödinger equation for the electron in a static potential arising from the nuclear positions is solved.

The solutions to this equation are the electronic states and corresponding eigenenergies of the molecule. They are labelled with Latin letters  $\{X, A, B...\}$  indicating the ground state, first excited state, second excited state and so on.

To fully describe an electronic state however one needs to take into account its spin as well as the orbital and total angular momenta. In atoms, both the spin and angular momentum operators  $\hat{S}$  and  $\hat{L}$  commute with the atomic Hamiltonian  $\hat{H}_{atom}$ because of its spherical symmetry. The Hamiltonian of a diatomic molecule  $\hat{H}_{mol}$ is no longer spherically symmetric meaning that S and L are not good quantum numbers. Instead the projections of  $\hat{S}$  and  $\hat{L}$  on the internuclear axis, labelled  $\hat{\Sigma}$ and  $\hat{\Lambda}$  respectively, are used. The final quantum number needed to fully describe an electronic state of a molecule is the projection of the total angular momentum onto the internuclear axis, which is given by  $\Omega = |\Sigma + \Lambda|$ . This leads to a molecular term symbol of the form

$$n^{2S+1}|\Lambda|_{\Omega},\tag{2.5}$$

where n is the label of the electronic state with the multiplicity 2S+1.  $|\Lambda|$  provides the state's angular momentum in units of  $\hbar$  with possible values  $|\Lambda| = \{0, 1, 2...\}$ given by Greek letters  $\Sigma, \Pi, \Delta$ .... For states with  $|\Omega| = 0$ , an additional subscript  $\pm$  indicates the state's parity.

#### 2.2.2 Rovibrational Levels

The Born-Oppenheimer approximation allows for the decoupling of electronic states and eigenenergies from other molecular motions like vibrations and rotations. The total energy  $E_{\rm mol}$  of a molecular state is given by the sum of electronic, vibrational and rotational contributions

$$E_{\rm mol} = E_{\rm el} + E_{\rm vib} + E_{\rm rot}, \qquad (2.6)$$

with each contribution treated separately.



Figure 5: The first few vibrational energy levels for the ground and first excited states and corresponding internuclear potentials of a diatomic molecule. Around the equilibrium position  $R_0$  the potential is approximately harmonic, leading to eigenstates and energies similar to the harmonic oscillator for small vibrational quantum numbers  $\nu$ . For higher vibrational excitations, the eigenstates become more distorted and the spacing between them smaller due to the anharmonicity of the potential. Adapted from [46].

#### 2.2.3 Vibrational Levels

In diatomic molecules, vibrations refer to oscillations of the internuclear distance around the equilibrium position  $R_0$ . A proper description the vibrational motion requires a solution of the Schrödinger equation for a potential corresponding to the forces between the two nuclei, those being the internuclear electrostatic repulsion and the long-ranged Van der Waals-attraction. The form of such a potential energy landscape can in general not be described analytically. The potential is similar to a harmonic oscillator around the equilibrium position, but it gets distorted further away from it. The vibrational eigenenergies can be described by a series of the form

$$E_{\rm vib}(\nu) = \hbar\omega_{\rm e}\left(\nu + \frac{1}{2}\right) - \hbar\omega_{\rm e}x_{\rm e}\left(\nu + \frac{1}{2}\right)^2 + \dots , \qquad (2.7)$$

depending on the vibrational quantum number  $\nu$ . The first term of the equation corresponds to the energy of a simple quantum harmonic oscillator with eigenfrequency  $\omega_{\rm e}$  while all further terms accounts for the anharmonicity of the potential with  $x_{\rm e}$  being the first order anharmonicity constant. Figure 5 shows the first few vibrational levels for the ground and first excited state of a diatomic molecule. Due to the anharmonicity of the internuclear potential, the lower vibrational levels are nearly equally spaced, while the spacing decreases for large  $\nu$ .

#### 2.2.4 Rotational Structure

Aside from vibrations, another degree of freedom in diatomic molecules is the rotation around an axis perpendicular to the intermolecular axis. As a first order approximation one can consider the molecule to be a rigid, linear rotor, where the internuclear distance does not change due to the rotation. In the case of a classical rotor the rotational energy is

$$\tilde{E}_{\rm rot} = \frac{\tilde{N}^2}{2I} = \frac{\tilde{N}^2}{2\mu R^2},\tag{2.8}$$

with the angular momentum  $\tilde{N}$ , the moment of inertia I, the average internuclear distance R and the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{2.9}$$

with  $m_1$  and  $m_2$  being the respective masses of the two atoms of the molecule. In the quantum mechanical description the classical angular momentum N is replaced with the angular momentum operator  $\hat{N}$ . Analogous to atomic angular momentum operators, the eigenvalues can be obtained by applying the square of the operator to the eigenfunction, leading to the rotational energies

$$E_{\rm rot}(N) = \frac{\hbar^2 N(N+1)}{2\mu R^2}$$
(2.10)

scaling with the rotational quantum number  $N = \{0, 1, 2...\}$ .

The previously established rotational energy can be extended by correction terms which account for the centrifugal change of the internuclear distance due to highly excited rotational states. This results in a new term for the rotational energy

$$E_{\rm rot}(N) = \frac{\hbar^2 N(N+1)}{2\mu R^2} - \frac{\hbar^4 N^2 (N+1)^2}{2\kappa \mu^2 R^6} + \dots , \qquad (2.11)$$



Figure 6: A vector diagram of the different angular momentum coupling schemes described by Hund's cases (a) and (b). The dotted lines imply the precession of an angular momentum around the axis. From [46].

where  $\kappa$  is the bond stiffness constant.

Just like every electronic state has a vibrational sub-level for every vibrational quantum number  $\nu$ , every vibrational level itself has a rotational sub-level for every possible rotational quantum number N.

#### 2.2.5 Coupling of Angular Momenta and Hyperfine Structure

Like in atoms the various angular momenta in molecules couple to each other directly or indirectly. In addition to the electron's spin and angular momentum the molecule's rotation also has to be considered when forming the total angular momentum.

The so-called Hund's cases differentiate between different angular momentum coupling schemes. The different coupling configurations arise due to the relative strength of the various couplings of the angular momenta in comparison to each other. Here, cases (a) and (b) are of particular interest as they describe the ground and first two excited states of CaF which are typically used for laser cooling and trapping. The coupling schemes of the Hund's cases (a) and (b) are illustrated in Figure 6.

#### Hund's case (a)

Hund's case (a) describes a state with a strong spin-orbit coupling between the electron's angular momentum  $\hat{L}$  and its spin  $\hat{S}$ . Additionally,  $\hat{L}$  couples strongly to the internuclear axis forming the combined projection of spin and angular momentum  $\hat{\Omega} = \hat{\Lambda} + \hat{\Sigma}$ . In turn  $\hat{\Omega}$  couples weakly to the molecules rotation  $\hat{R}$  to form the total angular momentum  $\hat{J}$ . Good quantum number for a state described

by Hund's case (a) are  $\Lambda$ , S,  $\Sigma$ , J and  $\Omega$ .

#### Hund's case (b)

Hund's case (b) describes a state where spin-orbit coupling is weak compared to the molecule's rotation. Here the electron's angular momentum  $\hat{L}$  first couples with the molecule's rotational angular momentum  $\hat{R}$  to form  $\hat{N} = \hat{L} + \hat{R}$  which in turn couples with the spin  $\hat{S}$  to form the total angular momentum  $\hat{J} = \hat{N} + \hat{S}$ . Good quantum number are  $\Lambda$ , N, S and J. It should be noted that states with no spin-orbit coupling, for example when  $\Lambda = \Sigma = 0$ , are usually described with Hund's case (b).

#### Hyperfine Structure

If either of the molecule's nuclei possesses a non-zero nuclear spin, the electron's total angular momentum  $\hat{J}$  and nucleus' nuclear spin  $\hat{I}$  couple to form the new total angular momentum  $\hat{F} = \hat{J} + \hat{I}$ . The possible values for F are F = |J - I|, ..., |J + I|. For the ground state of CaF  $X^2\Sigma$  we have  $J \in \{1/2, 3/2\}$  and I = 1/2, therefore the possible hyperfine states are  $F \in \{0, 1^-, 1^+, 2\}$ .

#### 2.2.6 Transitions and Selection Rules

Up until this point we have seen how the complexity of even the simplest class of molecules results in a vast number of different energy states described by molecular term symbols, vibrational, rotational and hyperfine quantum numbers. Just like in atoms, electronic transitions between these levels follow a set of selection rules. These are of particular interest for laser cooling as they describe to which states a molecule can be excited, and arguably even more important for laser cooling, decay to.

#### **Electric Dipole Transitions**

An electric dipole transition describes the effect of an electron changing its quantum mechanical state under the influence of an electric field. This can happen in two different ways we have already examined in chapter 2.1: Either the electron changes from a state of lower energy to one higher energy via the absorption of a photon or it decays from higher to lower energy by emitting a photon. The probability of such a process happening depends on the wavefunctions of the initial and final state and can vary drastically, in a lot of cases even vanishing completely. The probability P of an electric dipole transition in a diatomic molecule can be expressed as the absolute square of the so called transition dipole moment. It is given by [47]

$$P_{ik} = |\mathbf{M}_{ik}|^2 = \left| \int \psi_i^* \mathbf{p} \, \psi_k \, \mathrm{d}\tau_{\mathrm{el}} \mathrm{d}\tau_{\mathrm{N}} \right|^2, \qquad (2.12)$$

with indices *i* and *k* indicating the initial and final state and  $M_{ik}$  being the transition dipole moment. Here  $\psi_i$  and  $\psi_k$  are the wavefunctions of the initial and final state, p is the molecules overall dipole operator and  $d\tau_{el}$  and  $d\tau_N$  indicate integration over all coordinates for the electron and both nuclei, respectively. Under the Born-Opphenheimer approximation one can decouple the nuclear wavefunction into an electronic and a nuclear part

$$\psi = \psi_{\rm el} \cdot \phi_{\rm N}.\tag{2.13}$$

This allows for the splitting of the transition dipole moment into two parts

$$\mathbf{M}_{ik} = \int \phi_{\mathrm{N},i}^{*} \left[ \int \psi_{\mathrm{el},i}^{*} \mathbf{p}_{\mathrm{el}} \psi_{\mathrm{el},k} \, \mathrm{d}\tau_{\mathrm{el}} \right] \phi_{\mathrm{N},k} \, \mathrm{d}\tau_{\mathrm{N}} + \int \psi_{\mathrm{el},i}^{*} \left[ \int \phi_{\mathrm{N},i}^{*} \mathbf{p}_{\mathrm{N}} \phi_{\mathrm{N},k} \, \mathrm{d}\tau_{\mathrm{N}} \right] \psi_{\mathrm{el},k} \, \mathrm{d}\tau_{\mathrm{el}}$$
(2.14)

The second part of the equation vanishes for  $i \neq k$  because of the orthogonality of the electronic wavefunctions

$$\int \psi_{\mathrm{el},i}^* \psi_{\mathrm{el},k} \,\mathrm{d}\tau_{\mathrm{el}} = \delta_{i,k},\tag{2.15}$$

which leaves us with just

$$\mathbf{M}_{ik} = \int \psi_{\mathrm{el},i}^* \, \mathbf{p}_{\mathrm{el}} \, \psi_{\mathrm{el},k} \, \mathrm{d}\tau_{\mathrm{el}} \cdot \int \phi_{\mathrm{N},i}^* \phi_{\mathrm{N},k} \, \mathrm{d}\tau_{\mathrm{N}}$$
$$= \mathbf{M}_{ik}^{\mathrm{el}} \cdot \int \phi_{\mathrm{N},i}^* \phi_{\mathrm{N},k} \, \mathrm{d}\tau_{\mathrm{N}}. \qquad (2.16)$$

The first part of the equation is just the purely electronic transition dipole moment analogous to the atomic case while the second part of the equation is the overlap integral of the nuclear wavefunctions of the two states. While the latter only increases or decreases the probability of a certain transition, the electronic transition dipole moment between the initial and final state is only non zero under certain conditions, which are known as selection rules, and can be summarized as

$$\Delta P = \pm 1, \quad \Delta J = 0, \pm 1 \text{ except } J = 0 \to J' = 0, \quad \Delta m_J = 0, \pm 1$$
 (2.17)

Note that changes to the rotational quantum number are included in the total angular momentum section rule as N is a part of J. This means that during an electronic excitation (or decay) the rotational quantum number may change by  $\Delta N = 0, \pm 1$  as long as no other selection rule is violated. Decay processes that change the rotational quantum number represent one of the major challenges of molecular laser cooling as molecules may not end up in the same ground state used for the cooling transition.

Rotational transitions are divided into so called branches. Transitions that lower the rotational quantum number  $N \to N' = N - 1$  are called R-branch, while the opposite  $N \to N' = N + 1$  are called P-branch transitions. Finally, the Qbranch contains all transitions without a change to the rotational quantum number  $N \to N' = N$ .

#### Vibronic Transitions and Frank-Condon Factors

There is no selection rule governing changes to the vibrational quantum number resulting from electric dipole transitions, meaning that any vibrational level can be excited and decay to any other vibrational state. While this means that no potential cooling transition can be truly closed, the problem instead comes down to finding a transition with such a high chance of decaying back to the initial state that molecules can be effectively cooled before being lost to the cycle. A suitable transition for laser cooling must be able to cycle through the involved states thousands of times before decaying into a state that is no longer resonant to the laser frequency.

When a molecule is excited to a higher electronic state the resulting new electron orbitals will change the overall electric potential of the molecular system. In diatomic molecules this will generally induce a more antibonding character, meaning that both the potential curve as well as the equilibrium distance  $R_0$  shift further away from the nucleus' position.

The Frank-Condon principle suggests that the masses of the nuclei are so much heavier than the electrons that they remain stationary during the electronic transition. Only after the transition do the nuclei move to their new equilibrium positions which can excite a vibration. This also suggests that the electron statistically prefers transitions between vibrational wavefunctions that are similar to each other, for example if the corresponding wavefunctions have a maximum at a similar internuclear distance R.

Calculating the probabilities of vibronic transitions can be done analogously to equations 2.12 to 2.16. Here we split the electronic wavefunction from equation 2.13 into another, vibrational part that is dependent on the internuclear distance

and there on the nuclear coordinates **R**.

$$\psi = \psi_{\rm el} \cdot \psi_{\nu}(\mathbf{R}). \tag{2.18}$$

Following the previous calculations then leads us to a transition dipole moment

$$\mathbf{M}_{ik}^{\nu,\nu'} = \mathbf{M}_{ik}^{\mathrm{el}} \cdot \int \psi_{\nu i}^* \psi_{\nu' k} \, \mathrm{d}\tau_{\mathrm{N}}$$
$$= \mathbf{M}_{ik}^{\mathrm{el}} \cdot S(\nu,\nu')$$
(2.19)

containing the purely electronic transition dipole moment as well as the overlap integral  $S(\nu, \nu')$  between the vibrational wavefunctions of the initial state with  $\nu$  and final state with  $\nu'$ . The transition probability is then proportional to the absolute square of the overlap integral  $|S(\nu, \nu')|^2$ , which is called the Frank-Condon factor. Decay probabilities from an excited vibrational state  $\nu'$  to a vibrational ground state  $\nu$  are given by the branching ratios

$$B_{\nu,\nu'} = \frac{\omega_{\nu,\nu'} |S(\nu,\nu')|^2}{\sum_{\tilde{\nu}} \omega_{\nu',\tilde{\nu}} |S(\nu',\tilde{\nu})|^2},$$
(2.20)

where  $\omega_{\nu,\nu'}$  is the corresponding frequency of the vibrational transition. Effective laser cooling of molecules usually requires both a transition with a high Frank-Condon factor as well as repumper lasers that bring molecules lost to other vibrational states back into the cooling cycle.

### 2.3 Calcium Monofluoride

Calcium monofluoride (CaF) is a diatomic molecule made out of a single calcium and fluorine atom held together by an ionic bond. It belongs to a class of earth alkaline fluorides which are particularly interesting for laser cooling because of their comparatively convenient level structure, possessing transitions with highly diagonal Frank-Condon factors, alongside SrF [48], BaF [49] and MgF [50]. For our project, CaF was chosen because of its especially good Frank-Condon factors, low mass of 59 amu and laser transition wavelengths in the visible spectrum, where high power lasers are commercially available. In addition, it has a strong dipole moment of 3.08 D which is a key feature in efforts to realize novel supersolid phases of matter. Finally, CaF is an already well established molecule with multiple groups routinely laser cooling and trapping it for further research, e.g. in the field of dipolar interactions (See [51–54]).

The electronic ground state of CaF  $X^2\Sigma^+$  is described by Hund's case (b). Coupling of the fluorine atom's nuclear spin I = 1/2 to the total angular momentum



Figure 7: The energy levels of CaF relevant in the experiment. The bold, colored lines indicate the transition wavelengths while the wiggly lines indicate the respective Frank-Condon factors. The inset shows the hyperfine splitting of the  $X^2\Sigma^+(\nu = 0, N = 1)$  ground state.

gives rise to a hyperfine structure, splitting all electronic ground states with a rotational quantum number bigger than zero into four hyperfine manifolds. The total splitting spans about 150 MHz and has to be addressed for cycling when driving transitions from the ground state.

The other two important states for this experiment are the first and second excited states, described by the term symbols  $A^2\Pi_{1/2}$  and  $B^2\Sigma^+$ , respectively. Both of these states split into two hyperfine sublevels. The  $A^2\Pi_{1/2}$  state's splitting around 5 MHz is not resolved [55], while the  $B^2\Sigma^+$  state has a splitting of about 20 MHz.

In CaF, both the  $X^2\Sigma^+(\nu=0) \rightarrow A^2\Pi_{1/2}(\nu=0)$  as well as the  $X^2\Sigma^+(\nu=0) \rightarrow B^2\Sigma^+(\nu=0)$  transition possess good Frank Condon factors, corresponding to a 97% and 99.8% chance to decay back into the initial vibrational level respectively.

Typically, the former is used as the cooling transition for a magneto-optical trap while the latter is chosen for slowing of the molecular beam. Additional transitions between different vibrational levels are driven as repumpers for the main cooling and slowing transition.

Decay into wrong rotational sublevels can be eliminated by choosing a transition that can only decay into a single state because all other decay channels are forbidden by transition rules. In CaF this is realized by driving transition not from the absolute ground state but instead the first rotationally excited state  $X^2\Sigma^+(\nu =$ 0, N = 1). Because the parity of state must change and  $\Delta J = 0, \pm 1$  in a dipole transition, a molecule in either of the two excited states  $A^2\Pi_{1/2}(\nu = 0, J = 1/2)$ and  $B^2\Sigma^+(\nu = 0, N = 0)$  can only decay back to  $X^2\Sigma^+(\nu = 0, N = 1)$ . Such transitions are called rotationally closed.

A state diagram of CaF with all relevant states, transition wavelengths and Frank Condon factors can be seen in Figure 7.

### 2.4 State Population

The main cooling and slowing transitions driven in our experiment both start from the  $X^2\Sigma^+(\nu = 0, N = 1)$  electric ground state. These are the same transitions driven for absorption spectroscopy in this thesis. Because of this, all molecules that start out in a different state, even if its just a different rotational or vibrational level, are effectively lost from the spectroscopy scheme. Molecules differ from atoms in the sense that the thermal energy of an ensemble can not only be stored in translational movement but also in rotational and vibrational motion. The chance of finding a molecule with energy E in a thermal equilibrium with a temperature T is given by the Boltzmann distribution [56]

$$P(E,T) = \frac{g_n \exp\left(-\frac{E}{k_{\rm B}T}\right)}{\sum_i g_i \exp\left(-\frac{E_i}{k_{\rm B}T}\right)},\tag{2.21}$$

where  $k_{\rm B}$  is Boltzmann's constant and  $g_n$  is an additional factor accounting for a possible degeneracy of states with energy E. The equations denominator sums of all possible energy levels of the system.

Calculating this probability distribution for vibrational levels is relatively straight forward. The energy levels are dependent on the vibrational quantum number  $\nu$ and given by equation 2.7. Vibrational states are not degenerate, therefore  $g_n$ simply equals one.

For rotational levels the degeneracy has to be taken into account. The exact form of the degeneracy factor  $g_N$  depends on the specific state, here an example will be given for the ground state of CaF. Each rotational level with quantum number



Figure 8: Occupation probabilities of the electronic ground state of CaF as a function of the ensemble temperature for different vibrational and rotational quantum numbers.

N has (2N + 1) degenerate sub-levels [56]. The overall distribution for rotational level population is then given by

$$P(N,T) = \frac{(2N+1)\exp\left(-\frac{E(N)}{k_{\rm B}T}\right)}{\sum_{i}(2i+1)\exp\left(-\frac{E(i)}{k_{\rm B}T}\right)},$$
(2.22)

with the rotational energies E(N) given by equation 2.11. Figure 8 shows occupation probabilities of the lowest vibrational and rotational states for different temperatures. It becomes apparent that while nearly all molecules are in the  $\nu = 0$ vibrational state even at room temperature, having a high portion of CaF in the first excited rotational state N = 1 requires a rotational temperature below 10 K. Before any kind of laser cooling scheme can be employed, the CaF molecules have to first be created and sufficiently cooled, which in our experiment is realized with a buffer gas source.

### 2.5 Buffer Gas Cooling

The most common method of producing atomic vapors in atom experiments is to use an effusive source such as an oven. With molecules this is usually not possible. For one, particles generated by effusive sources tend to have temperatures on



Figure 9: A schematic of a typical buffer gas cell. Molecules are first created with the ablation of molecules from a target. The newly formed, hot molecules are thermalized via collisions with a cold helium which acts as the buffer gas. The thermalized molecules are then extracted out of the cell aperture and form the molecular beam.

the order of  $10^3$  K [57]. However, the molecular states required to close a photon scattering cycle are nearly unpopulated at temperatures this high. Furthermore, for many molecules including CaF, it is not possible to build effusive sources. As a radical, CaF is highly reactive and does not naturally occur as a monofluoride, making an oven source impossible. Instead, experiments with cold molecules typically begin with a buffer gas cell.

Buffer gas sources can offer a slower and colder molecular beam with comparatively higher flux. The concept of buffer gas cooling has been pioneered by John Doyle's group at Harvard [58] and is now a well established technique for creating cold molecules. The working principle is the dissipation of the thermal energy of the laser-ablated molecules via elastic collisions with a cold inert gas. Typically helium is used as a buffer gas due to its low reactivity and the fact that it remains gaseous at low temperatures, resulting in a high rate of purely elastic collisions with the target molecular species. The thermalization process between the buffer gas and target species takes place in a copper cell with a temperature of 4 K. The basic template of a buffer gas cell is shown in Figure 9. In a buffer gas source molecules of the target species have to be fully thermalized before being extracted out of the cell aperture. The number of collisions N between a molecule and the buffer



Figure 10: The temperature  $T_{\rm mol}$  of a CaF molecule in relation to the number of collisions N with helium atoms. It takes around 60 collisions before the CaF molecules reach a temperature of about 5 K.

gas atoms necessary to cool down the target species to a temperature  $T_{\rm mol}$  can be estimated by treating all particles as hard spheres. The change in temperature per collision event can then be approximated as [59]

$$\frac{\mathrm{d}T_{\rm mol}}{\mathrm{d}N} = \frac{-2m_{\rm mol}m_{\rm He}}{(m_{\rm mol} + m_{\rm He})^2} (T_{\rm mol} - T_{\rm He}), \qquad (2.23)$$

where  $T_{\text{He}}$  is the temperature of the buffer gas and  $m_{\text{mol}}$  and  $m_{\text{He}}$  are the masses of the target and buffer gas species, respectively. This differential equation has an exponential solution of the form

$$T_{\rm mol} = T_{\rm He} + (T_{\rm i} - T_{\rm He}) \exp\left(-\frac{2m_{\rm mol}m_{\rm He}}{(m_{\rm mol} + m_{\rm He})^2}N\right),\tag{2.24}$$

where  $T_i$  is the initial temperature of the target species. Figure 10 shows a theoretical example of this thermalization process for the configuration present in our experiment, with CaF as the target species and He as the buffer gas. The temperature chosen for the helium buffer gas is  $T_{\text{He}} = 4 \text{ K}$  while the initial temperature of the ablated CaF molecules is set to  $T_i = 10^4 \text{ K}$ , which is a typical value for ablation products.

We consider the molecules to be thermalized when they reach a temperature of  $T_{\rm mol} = \sim 5 \,\mathrm{K}$  which happens after around 60 collision processes. We can now estimate the thermalization length  $L_{\rm T}$ , which gives a measure of the average distance travelled by a molecule before fully thermalizing, as

$$\sqrt{N_{\rm T}}\lambda_{\rm S} < L_{\rm T} < N_{\rm T}\lambda_{\rm S},\tag{2.25}$$

with  $N_{\rm T}$  being the number of collision events before thermalization and  $\lambda_{\rm S}$  the mean free path of the molecules between collision events. For low densities of the target species the mean free path is just

$$\lambda_{\rm S} = \frac{1}{n_{\rm He}\sigma_{\rm mol,He}},\tag{2.26}$$

where  $n_{\text{He}}$  is the density of the helium gas in the cell and  $\sigma_{\text{mol,He}}$  is the collision cross-section between buffer gas and target species.

Buffer gas cells usually have dimensions of a few centimeters in length and diameter, which is enough to have the molecules thermalize, assuming typical collisional cross-sections of  $\sigma_{\rm S,B}$  10<sup>-14</sup> cm<sup>2</sup> [59] and helium densities corresponding to a flow of 1 SCCM [57].

Another important consideration for buffer gas cells is the diffusion time  $\tau_{\text{diff}}$ . The diffusion time provides a timescale for the diffusion of molecules inside the cell, the main loss mechanism being collisions with the cell wall. Upon colliding with the cell wall, molecules can either chemically react with it or freeze upon it. Either way, the molecule is lost for the extraction process.

In the experiment this will be noticable in the form of an exponential decay of the molecule signal. The diffusion time is the given by [57]

$$\tau_{\rm D} = \frac{16}{9\pi} \frac{A_{\rm cell} \,\sigma_{\rm CaF, He} \,n_{\rm He}}{\overline{v}},\tag{2.27}$$

where  $A_{\text{cell}}$  is the surface area of the cell's internal cross-section and  $\overline{v}$  is the mean thermal velocity of the helium atoms inside the cell. Generally, higher buffer gas densities and therefore flows increase the amount of extracted molecules, however flows too high might extract them before they can fully thermalize.

# 3 Setup and Construction

Making and probing cold calcium monofluoride molecules requires a complex experimental setup. The following chapter goes through all of the major parts making up the whole apparatus, describing their design and function in the setup, as well as what devices were used and how they can be communicated with. Since the measurements described below, a number of upgrades to the experimental setup have been implemented and relevant upgrades have been specified in the text. The experimental setup was designed by P. Groß.

### 3.1 Buffer Gas Cell

The buffer gas cell is the heart of the experimental apparatus. Inside the cell, CaF molecules are created and thermalized before forming molecular beam. Our design is based on cells from other groups that have successfully buffer gas cooled molecules [60]. In the following, the direction in which the molecular beam is pointing is called the forward direction.

The cell is made out of high purity copper for optimal thermal conductivity. The cell is made of a 30x30x40 mm block with a central bore with a diameter of 10 mm. The resulting bore is the main chamber in which ablation and thermalization occur. The backside of the cell features a hole with a diameter of 3 mm to allow a slowing and probing laser to pass through the cell. This for alignment purposes and to reduce the heat load on the cell. At the front of the cell, the central bore is covered with a copper plate with an aperture with a diameter of 3 mm. There are two additional holes through the cell perpendicular to the flow direction. Further to the front two 3 mm wide holes provide optical access through the cell which can be used to probe the molecules via absorption spectroscopy. Further back, a 5 mm bore serves as the opening for the ablation laser into the cell. On the opposite side, the ablation target is mounted in the cell with a M10 thread. A picture of the buffer gas cell as well as a render showing the cell's interior can be seen in Figure 11.

Two different methods of creating CaF molecules are typically used: Ablation from a salt target and ablation from a metal target with the additional usage of sulfur hexafluoride (SF6) gas. The first and simpler method makes use of a calcium diffuoride (CaF<sub>2</sub>) salt target. Ablating material from the salt target not only produces CaF<sub>2</sub> but also Ca, F and CaF. The other method uses a pure calcium metal target in combination with a SF<sub>6</sub> gas source. Here the laser pulses ablate only calcium atoms which then react with the SF<sub>6</sub> present in the cell to form CaF. During the work described in this thesis the salt target method was used almost exclusively as it was easier to initially get to work while still producing enough



Figure 11: a) The buffer gas cell as seen from the outside. The parts depicted are as follows: (1) Helium gas port (2) SF6 gas port (3) Ablation laser window (4) Temperature sensor (5) Copper skimmer plates (6) Exit window for slowing laser. b) A top-down view into the cell. Parts not depicted in a) are designated in the figure.

molecules for good absorption spectroscopy signal. It should be noted however that other groups working with CaF suggest that the  $SF_6$  method may provide a better molecule yield and longer target lifetimes [24].

While the  $CaF_2$  salt target only requires a He supply line, the Ca metal target requires both a He and an  $SF_6$  supply line. Our buffer gas cell can be operated in both ways and therefore has two access ports for gas lines. While the exact buffer gas cell dynamics are hard to simulate and estimate, both gas ports are angled in such a way that the emerging gas flow hits directly onto the target surface, with the helium flowing from the back to the front of the cell. Because the helium is used to thermalize the CaF molecules, the helium temperature should be around 4 K. The cooling of helium is realized by simply cooling the copper line used for its transport. This is mainly done with so-called cold fingers, which are copper cylinders around which the gas line is wound and brazed. The cold fingers are connected to the cold plates and provide thermal contact between the copper line and cryostat. The  $SF_6$  line on the other hand should have as little thermal contact with the cell or cryostat as possible as  $SF_6$  freezes at about 209 K [61] at atmospheric pressure, which decreases even more in a vacuum. In an earlier iteration of our setup, the  $SF_6$  line was directly connected to the cell which lead to the gas freezing inside of the line and eventually completely clogging it up. The consequential evaporation of the frozen  $SF_6$  during the next warm-up of the cell can be seen as an increase in the chamber pressure depicted in Figure 12.



Figure 12: The pressure inside the vacuum chamber for different cell temperatures during a warm-up process. When the melting temperature of a frozen gas species is reached the gas will begin to evaporate. The pressure increases until the outgassing eventually becomes slower than the pumping of the turbo pump. This can be clearly seen for both nitrogen and the SF<sub>6</sub> gas. SF<sub>6</sub> begins to melt at about 209 K at atmospheric pressure [61]. Due to the vacuum, the melting already sets in at a temperature of 155 K.

As a workaround, the connection between cell and gas line is now given by a small tube made out of Vespel, a vacuum-compatible plastic with very low thermal conductivity. With this configuration the temperature of the  $SF_6$  line never falls below 240 K, enabling continuous  $SF_6$  supply.

Two small copper pieces at the front and side of the cell are used as skimmer plates to cut off the parts of the emerging molecular beam with the biggest transversal velocities. Both plates as well as the inside surface of the 4 K radiation shield are coated with charcoal. The reason for this is to get rid of excess helium and keep the pressure in the experiment low, as charcoal becomes an exceptional binder of helium at temperatures below 20 K [62]. Should the temperature of the charcoal go above 20 K it will begin to release the helium again. As the binding capabilities of charcoal eventually saturate under extensive helium exposure, the setup is left to warm up every night before it is cooled down again in the morning.

# 3.2 Cryogenic Setup

The cryostat in the experimental setup is used to reduce the temperature of the buffer gas cell and the buffer gas supply line to around 4 K. Furthermore, it cools the radiation shields which protect the cell from thermal radiation. Our cryostat<sup>1</sup> is a closed cycle cryostat and consists of a cold head and a compressor unit. An advantage of this cryostat compared to more traditional models that cool by using a helium bath is that the helium is directly recycled in the compressor. Therefore it is not necessary to refill the helium supply on a regular basis. Resupplying helium is only needed after long usage times when small leaks in the internal helium cycle lead to a big enough pressure drop.

The excess heat generated by the cooling process is dissipated via cooling water cycling through the compressor unit. We use an additional chiller<sup>2</sup> as an intermediate piece between the cryo compressor and the universitie's cooling water, so that the compressor has its own cooling water cycle with the chiller.

The cryostat has two stages to which we connect cold plates: The lower stage is designed to reach a temperature of 40 K and has a power of 35 W, while the upper stage can reach temperatures around 4K and has a power of 1.5W. The lower stage holds the outer layer of radiation shields. This intermediate layer called the 40 K-shield protects the 4 K-stage from the thermal radiation of the vacuum chamber. As the power of thermal radiation scales with the fourth power of the temperature it is particularly important to keep the immediate surroundings of the coldest parts in the experiment at similarly low temperatures. The shield is made of polished brass because of its good reflectivity and thermal conductivity and sits on top of an aluminum plate. Better thermal contact between cold head, cold plate and 40 K-shield is ensured by thin layers of vacuum thermal grease on the contact surfaces. To make sure the buffer gas cell reaches its intended temperature, a second radiation shield and cold plate is placed on top of the upper cryostat stage. Both the cold plate as well as the shield are made from copper for optimal thermal conductivity even at low temperatures. Notably, in a previous iteration of the setup this cold plate was made of aluminum, and this iteration did not manage to reach a cell temperature of 4 K. This can be attributed to the much lower thermal conductivity of aluminum compared to copper. The inner shield, made from copper, provides an additional layer of protection from the thermal radiation of the outer 40 K-shield to ensure that the buffer gas cell inside reaches temperatures as low as possible. On the bottom of the upper stage cold plate sit seven cold fingers which are used to cool down the helium. A pre-cooling stage containing three cold fingers is placed on the lower stage cold plate. The large number of

<sup>&</sup>lt;sup>1</sup>Sumitomo SRDK Series Cryocooler

<sup>&</sup>lt;sup>2</sup>Thermo Scientific System 1 Heat Exchanger


Figure 13: A cross-section of the cryostat inside the vacuum chamber. The cryostat cools down the cell and radiation shields through the corresponding cold plates.

cold fingers is higher than usual, but it was chosen to absolutely make sure the helium reaches the necessary temperatures. Figure 13 shows a cross-section of the vacuum chamber and cryo cold head. Three silicon diode temperature sensors<sup>3</sup> are placed on different parts inside the chamber. They measure the temperature at the lower and upper cold plates as well as the buffer gas cell itself. The data is read out with a temperature controller<sup>4</sup> that is also able to control two heater cartridges via PID loops, which control the temperature of the upper and lower cold plate. Both the temperatures as well as the pressure inside the chamber can be monitored by the laboratory computer.

In a typical cooldown process, the cell and 4K-shield sitting on the upper cryo stage initially cool down slower than the 40 K-shield on the lower stage. The cooling rate of the 40 K shield eventually slows down around 100 K. In contrast, the cooling rate of the cell and the 4 K stage increases for lower temperatures. Cooling from 50 K to 3 K typically only takes about five minutes. This increase of the cooling rate can be attributed to the increasingly good thermal conductivity

<sup>&</sup>lt;sup>3</sup>CryoCon S950

<sup>&</sup>lt;sup>4</sup>CryoCon Model 24C



Figure 14: A typical cooldown process of the experimental apparatus. The 40 K-shield initially cools down faster before slowing down, slowly approaching a final temperature around 40 K. Both the cell and 4 K-shield increase their cooling rate for lower temperatures because of the thermal properties of copper. They reach a final temperature around 2.9 K.

of copper at low temperatures, which both the cell and the 4K-shield are made of. At temperatures below 100 K, the thermal conductivity of copper greatly increases, reaching a maximum around 10 K [63]. The lowest temperatures achieved are about 2.9 K for both the 4K-shield and the cell. Generally speaking, the experiment can be run as soon as the cell has a temperature around 4 K, which usually happens after about two hours. The exact temperature of the 40 K-shield is not important as long as its thermal radiation is low enough for the cell inside to reach its intended temperature. The temperature evolution during a typical cooldown process is shown in Figure 14.

## 3.3 Vacuum Chamber

The vacuum chamber consists of two main CF200 pieces made of stainless steel. The buffer gas cell is located inside the upper area of the vacuum chamber, so that nearly all modifications of the internal experimental setup can be performed without having to disassemble the whole chamber.

The vacuum chamber is equipped with multiple flanges granting optical, electrical and gas line access to the devices inside. Two gas line feedthroughs on the lower chamber piece deliver helium and SF6 to the buffer gas cell while two electric feedthroughs allow for the readout and control of internal temperature sensors and heaters. Two windows on opposite sides of the upper vacuum chamber piece grant the ablation laser and probe beams for absorption spectroscopy optical access to the buffer gas cell.

The vacuum is created with a turbo pump<sup>5</sup> attached to the lower chamber piece. The pump requires a fore-vacuum of at most 30 mbar before being able to operate, so a diaphragm backing pump<sup>6</sup> is attached to the turbo pump. The connection between fore- and turbo pump can be manually closed with a valve. An additional emergency valve automatically closes the same connection if power to it is cut, so that the vacuum is not lost in the case of a power outage. The internal pressure is monitored with a pressure gauge<sup>7</sup> sitting at the top of the chamber and can be read out either via with the experiment control computer. Typical pressure regimes for the chamber are about  $10^{-7}$  mbar. When the setup is cooled down with the cryostat, however, drops to below  $5 \cdot 10^{-9}$  mbar, below the limits of the pressure gauge. This is due to all depositions and dirt on the parts' surface areas freezing solid, strongly reducing any outgassing processes. Figure 15 shows the whole source chamber as seen from the outside.

<sup>&</sup>lt;sup>5</sup>Pfeiffer Vacuum HIPACE 300H

<sup>&</sup>lt;sup>6</sup>Pfeiffer Vacuum MVP 040-2

<sup>&</sup>lt;sup>7</sup>Pfeiffer Vacuum PKR 261



Figure 15: The source chamber as seen from the outside. The depicted parts are as follows: (1) Pressure Gauge. (2) Future exit of the molecular beam.
(3) Inlet and outlet windows for probe beam and ablation laser. (4) Electrical feedthroughs. (5) Turbo pump. (6) Ablation laser outcoupler.
(7) Mirror system for ablation and probe beam alignment.



Figure 16: A schematic of the lens system used to focus the ablation laser pulse on the target. An initial diverging lens with a focal length of  $f_{\rm L1} = -100 \,\mathrm{mm}$  expands the beam from a 3 mm to a 7.5 mm diameter before a converging lens with  $f_{\rm L2} = 250 \,\mathrm{mm}$  recollimates the beam. The distance between the first two lenses is 150 mm. Finally, another converging lens with  $f_{\rm L3} = 400 \,\mathrm{mm}$  focuses the beam down to a diameter of 70  $\mu$ m.

## 3.4 Ablation Laser System

We use a pulsed Nd:YAG laser<sup>8</sup> to ablate the material from the target surface and eject it into the cell. The ablation laser emits 5-7 ns long laser pulses at a wavelength of 1064 nm with a power of up to 28 mJ within a single pulse. Although it can achieve pulse repetition rates up to 15 Hz, we operate at a repetition rate of only 1 Hz in the experiment since the measurement frequency of the presented experimental iteration is limited by data read-out processes and to reduce the heat load of the cryostat.

The laser pulse has to be focused on the target to achieve maximized ablation. This is realized with a tube-system connecting the laser head with a breadboard at the height of the cell. A three lens setup for collimation is built into the tube-system, expanding the pulses from a diameter of 3 mm to 7.5 mm before focusing it to a width of about 70  $\mu$ m roughly 400 mm behind the last lens. A schematic of the lens system can be seen in Figure 16. The lens positions can be adjusted on the order of a few centimeters by screwing them in the internal thread of the tubes. This is particularly important for the final lens which focuses the beam as its position determines the focus point inside the cell. A poorly aligned focus point can lead to strongly reduced ablation or damage to the cell windows.

The final mirror in the tube system is of particular importance to the setup, as it determines which spot of the target is hit. As has been reported from other ex-

<sup>&</sup>lt;sup>8</sup>Continuum Minilite I



Figure 17: The ablation laser alignment setup. Two stepper motors are attached to the screws of a mirror mount to precisely control the target spot hit by the ablation laser. The letters **H** and **V** indicate which screw moves the beam in the horizontal and vertical axis, respectively.

periments with cold molecules, the amount of ablated CaF molecules per ablation pulse significantly varies based on the spot hit by the laser. In addition, spots with an initially good yield seem to worsen after a few hundred to thousand ablation laser shots. This necessitates a certain flexibility with regard to the targeted spot. Neither the cell nor the target within are visible from the outside, making manual spot adjustment by hand impossible. A solution to this problem is the motorization of the mirror screws via stepper motors. The implementation described here is based on the concept developed in the BaF experiment of our group [64]. In this configuration each adjustment screw of a mirror mount is being controlled by a stepper motor. Figure 17 shows the ablation laser alignment setup on the mirror mount<sup>9</sup>. The stepper motors are controlled with a microcontroller<sup>10</sup>, allowing for very precise adjustment of the mirror mount screws. A default position designating the center of the target can be set by manually calibrating the setup when the

 $<sup>^{9}</sup>$ Thorlabs KCB2/M

 $<sup>^{10}\</sup>mathrm{Arduino}$  UNO R3

vacuum chamber is open. This also enables the conversion between motor steps and actual spot walking distance on the target. The spot is adjusted by inputting the target coordinates into a python script. This can also be used to automate the process of searching for spots with good molecule yield by letting the ablation laser position scan over a grid on the target and measuring the amount of generated molecules via absorption spectroscopy (see section 4.1) at each spot.

## 3.5 Laser Systems

In our experiment we detect molecules and investigate the properties of the molecular beam via absorption spectroscopy. In principle, any transition of CaF can be used for the purpose of absorption spectroscopy. Typically, the  $X^2\Sigma^+(\nu = 0, N =$  $1) \rightarrow A^2\Pi_{1/2}(\nu = 0, J = 1/2)$  transition is used. For one, the exceptional Frank-Condon factor of this transition makes absorption processes more likely, making the absorption signal stronger. Furthermore, a large portion of CaF molecules are in the ground state of this transition after thermalizing with the buffer gas.

The transition  $X^2\Sigma^+(\nu = 0, N = 1) \rightarrow A^2\Pi_{1/2}(\nu = 0, J = 1/2)$  is driven by a laser at 606 nm and is typically used as the cooling transition in MOTs [24, 51, 65]. In the following, this laser is called the *A*-state laser. The wavelength is hard to achieve with semiconductor materials, which is why a frequency doubling scheme is employed: The power of a seed laser running at a wavelength of 1212 nm is increased using a fiber amplifier. The amplified light is then frequency-doubled via second-harmonic generation (SHG) to 606 nm. For the *A*-state laser system we use a commercial seed laser<sup>11</sup> in conjunction with a commercial fiber amplifier and SHG unit<sup>12</sup>. The system can operate at a peak power of 2.2 W [66].

Initially the A-state laser was intended for use in absorption spectroscopy. The A-state system however was lost during a transit for repair, so instead the laser driving the  $X^2\Sigma^+(\nu = 0, N = 1) \rightarrow B^2\Sigma^+(\nu = 0, N = 0)$  had to be used as a backup.

This transition is driven at 531 nm and typically used to slow a beam of CaF molecules. Like the X-A transition it has highly diagonal Frank-Condon factors and can therefore be used just as efficiently for the purpose of absorption spectroscopy. In the following, the laser running at this wavelength is referred to as the B-state laser. Although this wavelength is achievable by conventional laser diodes, they cannot output the power required in the experiment which is on the order of a Watt. Instead, the B-state laser also operates using second-harmonic generation. Here the seed laser is self-built with a commercial fiber amplifier<sup>13</sup> and

<sup>&</sup>lt;sup>11</sup>Toptica DL Pro

<sup>&</sup>lt;sup>12</sup>MPB VRFA-P-2000

<sup>&</sup>lt;sup>13</sup>Keopsys CYFA-PB

SHG crystal<sup>14</sup>. This system can operate at a peak power of 1 W. The *B*-state laser system's exact specifications are described extensively in [67].

The laser systems are monitored on a wavemeter<sup>15</sup> and a cavity, which can be used to lock the laser with a stability of < 2 MHz over a time scale of several hours using a scanning transfer cavity lock [68].

<sup>&</sup>lt;sup>14</sup>HC Photonics SHVIS-MD<sup>15</sup>Bristol Instruments 671 Wavelength Meter

# 4 Source Characterization

## 4.1 Setup for Absorption Spectroscopy

The properties of the molecular ensemble inside the buffer gas cell can be probed with absorption spectroscopy. A laser beam tuned to one of the many molecular transitions of CaF, in our case the *B*-state laser, passes through the cell and gets absorbed by molecules if the light is resonant with the transition. This results in a time-dependent light transmission which is monitored with a photodiode.

Unlike most experiments with cold molecules in buffer gas cells, the presented setup is able to probe for molecules at two different positions. One beam path goes directly through the cell while the other one is positioned just in front of the cell aperture. This enables direct monitoring not only of the extracted portion of the molecules, but by performing absorption spectroscopy at both positions simultaneously the molecular beam pointing can be determined. The pointing of the beam is crucial to ensure that the molecules arrive at the exact position needed, for example a MOT.

The probe beam going through the cell passes through the dichroic mirror which directs the ablation laser onto the target. On the other side of the setup the probe beam transmissions are detected on amplified photodiodes. To filter out stray light from the ablation laser 950 nm bandpass filters are put in front of the photodiodes. The absorption spectroscopy setup can be operated in the inverse direction by switching the positions of the photodiodes and the outcoupler of the probe light. Figure 18 shows a simplified version of the optical setup for absorption spectroscopy. After its creation by the ablation laser pulse CaF will quickly dissipate within the cell, either by making contact with the cell surface or by simply being extracted through the cell's aperture. Accordingly, the measured absorption signals are equally short, usually only a few milliseconds long. The measurement of the absorption traces, which is recorded with Red Pitayas<sup>16</sup>, is triggered by the ablation laser. Only the first few milliseconds of data are taken.

Further information like the molecules' temperature or a possible drift of the molecular beam in a particular direction can then be extracted by scanning over a frequency range around the transition. For this the probe laser is first taken out of the lock so its frequency can be tuned. The probe laser frequency can be changed by applying a voltage to the seed laser's piezo crystal. This enables spectroscopy scans over several 100 MHz, which is enough to probe the Doppler-broadened peak of the X-B transition.

<sup>&</sup>lt;sup>16</sup>Red Pitaya STEMLab125-14



Figure 18: The spectroscopy setup including the inside of the vacuum chamber and a simplified version of the optical setup. The probe laser is split into two beams with a 50/50-beam splitter to probe both inside the cell as well as in front of the cell aperture. The probe light is filtered with bandpass filters to remove traces of the ablation laser before being detected with photodiodes PD-1 and PD-2. The signal is read out with a Red Pitaya.



Figure 19: A set of absorption traces recorded for varying frequencies around resonance. The brown trace with the strongest absorption was taken on resonance. Frequency spectra for different velocity classes of molecules can be formed by evaluating the absorption traces during different time frames. The inset plot shows the spectrum of the  $X^2\Sigma^+(\nu = 0, N =$  $1) \rightarrow B^2\Sigma^+(\nu = 0, N = 0)$  transition for the time frame indicated by the main plots orange area. The measurement was taken with a helium flow of 0.6 SCCM and a probe beam intensity of 40  $\mu$ W.

## 4.2 Signal Characterization

A typical absorption signal is shown in Figure 19. It has a characteristic shape which provides insight about the internal dynamics of the buffer gas cell. When the ablation laser pulse strikes the target surface a cloud of hot CaF molecules is released into the cell. Immediately afterwards the absorption is still low as most hot molecules are in rotational and vibrational levels which are not adressed with the probe laser. Absorption rapidly increases as both more molecules reach the area of the probing beam and collide with the helium buffer gas, thermalizing to the  $X^2\Sigma^+(\nu = 0, N = 1)$  ground state, before the absorption maximum is reached. In the following milliseconds, the molecules either exit the cell through its aperture or diffuse to the cell walls. The absorption signal decays exponentially until no molecules are left in the probe region. A typical time scale for an absorption trace in our experiment on resonance is roughly 2 ms.

More information about the molecules can be obtained by performing a frequency scan instead of just recording a single absorption trace. In experiments with a constant atom or molecule source this is usually done by simply scanning the probe laser frequency. As the diatomic molecules and therefore absorption signals are both pulsed and short lived, this is not possible. Instead a trace is being recorded for each particular probe laser frequency. Before the next trace is recorded, the frequency is shifted. Typically multiple traces are recorded at each frequency interval and averaged to account for possible fluctuations of molecule production. By plotting the absorption of the various traces at a specific time a frequency spectrum of the transition can be created. It is useful to create multiple such spectra for different time frames. The earliest parts of the signal correspond to absorption by the fastest molecules, which reach the probe regions first. Early molecules are typically not thermalized. On the other hand, the later parts of the traces correspond to the slower molecules, which have thermalized to some degree with the buffer gas. Thus a set of spectra for molecules of different velocity classes can be created, one of which can be seen in Figure 19.

As a wide variety of information about the molecules and the internal dynamics of the buffer gas cell can be gathered out of these traces and spectra, it is of particular importance to understand and optimize the absorption signals in relation to the varying factors of the experiment, like ablation laser power, target spot and helium flow. A well-optimized absorption trace can reach up to 95% absorption in the experiment, significantly reducing relative noise and therefore possible error of the measurement.

If the probe beam is tuned to resonance, the strength of the absorption signal is proportional to the amount of CaF molecules in the  $X^2\Sigma^+(\nu=0, N=1)$  state in the probe beam region for small absorption powers, as stated by the Beer-Lambert law. Most absorption powers recorded in the experiment exceed the limit however. We still try to optimize absorption values to their maximum, but it should be kept in mind that the recorded data can no longer be used to infer information about the number of CaF molecules as the Beer-Lambert law is no longer applicable to our system.

#### 4.2.1 Target Spot and Ablation Power

Both the chosen ablation spot on the target as well as the ablation laser power strongly affect the resulting absorption signal as they influence how many CaF molecules are created. Our salt targets are created by pressing pulverized CaF<sub>2</sub> into disks with a diameter of 5 mm and a thickness of 2-3 mm. Although the targets should be homogeneous, the heights of the traces in the buffer gas cell are strongly



Figure 20: The results of a target scan. The upper half of this target produced no signal, while the lower half possesses good areas with strong signal.

dependent on the ablation spot. This is in agreement with observations from other experiments [69]. On a typical target some areas provide a good signal, some a weaker one while others seemingly produce no measurable amount of molecules at all. Shooting at spots with no signal for a few hundred shots sometimes seems to "activate" the spot, albeit with a usually weak resulting absorption signal.

Even good spots typically decay over time. Some spots provide a strong and constant absorption signal for thousands of ablation laser shots without any apparent decrease in signal quality, only stopping when the ablation laser has presumably shot completely through the target. Other spots may start out with a good signal but the peak absorption decays over time. Like the overall molecule yield, if and how strong the decay at a specific spot is seems to be completely arbitrary. Searching for spots with a stable, constant signal therefore becomes of great importance for a good measurement, especially when conducting a frequency scan. A target spot decaying during a frequency scan will falsify the resulting spectrum.

To find a good ablation spot, we tune the probe laser to resonance and use the motorized mirror setup to perform a target scan (see section 3.4). This results in



Figure 21: Peak absorption inside the buffer gas cell for different fractions of the maximal pulse energy. Fractions below 0.2 were examined but no signal could be recorded. Measured on resonance with a probe beam power of  $20 \,\mu W$ .

a map of the target which indicates what areas provide a high molecule yield. An example of such a target scan can be seen in Figure 20.

The spot is then set to one of the good areas and checked if any immediate signs of spot decay can be observed. If a spot stops providing signal, for example if the laser has completely shot through the target, or begins to decay the spot has to be changed. If a spot begins to decay, choosing a spot within a distance of 0.5 mm often recovers a decent signal.

Just like the target spot, ablation laser power influences if any and how many molecules are created within the cell. The ablation laser power can be tuned with a lever with the highest configuration corresponding to a power of 28 mJ within a pulse. As the exact relation between the lever setting and actual pulse energy is not given we arbitrarily measure the peak absorption of a constant spot and on resonance frequency for certain fractions of the lasers maximal pulse energy  $E_{max}$ ,



Figure 22: Peak absorption inside the buffer gas cell for various flows of helium. Measured on transition resonance with a probe beam power of  $5 \,\mu$ W.

which is depicted in Figure 21.

Fractions below 0.2 produced no measurable signal at all. For higher pulse energies the peak absorption value seems to increase linearly, before seemingly plateuaing for fractions above 0.7. We assume that a certain pulse energy has to be reached before the resulting ablation process is strong enough to create CaF molecules out of the salt target. This power seems to be reached for about 70 % of the ablations laser's maximal power, explaining the plateauing effect. We generally operate the ablation laser at maximal power.

#### 4.2.2 Helium Flow Rate

The B-state laser used for absorption spectroscopy, is only resonant with molecules in the  $X^2\Sigma^+(\nu = 0, N = 1)$  ground state, which is only significantly populated for low rotational temperatures. CaF is cooled to this state via collisions with cold



Figure 23: Absorption traces recorded both inside and in front of the cell. The absorption has been normalized to the arbitrary value one for better comparison between the shapes.

helium atoms in the buffer gas cell. The flow rate of helium into the cell changes the helium density and therefore mean free path of CaF molecules between collisions. If the helium flow is too low, molecules might not fully thermalize before either diffusing or being extracted out of the cell. This results in a weakened absorption. Furthermore, since the probe region is about 10 mm further forward than the ablation region, a low buffer gas flow allows the molecules to diffuse to the cell walls before they can be probed. The relation between helium flow rate and absorption signal strength in our experiment can be seen in Figure 22.

The signal remains stable for flows above 0.3 SCCM. Below this point however the signal strength rapidly decreases as molecules fail to thermalize to the required rotational temperatures in the probe region. While the exact flow rate does not seem to have a significant influence on the signal strength as long as the threshold of 0.3 SCCM has been exceeded, the preferable flow used to operate the experiment depends on more factors than just the signal strength. Higher flow rates tend to extract more molecules out of the cell. While absorption data taken in front of the cell is strongly fluctuating and more unreliable than inside of the cell, generally only flows above 0.6 SCCM generate good absorption traces outside the cell. This



Figure 24: Recorded onset times of the absorption signal outside of the cell for two separate measurements. The errors of the onset times are large because of the low signal outside of the cell. For low flows the onset time changes significantly between measurements, which is assumed to be caused by the different spots used to make these measurements.

flow value is comparable to values found in other experiments which employ a buffer gas cell for CaF [70].

Figure 23 shows an exemplary comparison of traces recorded inside of the cell and outside of it, just in front of the cell aperture. Not surprisingly, the bulk of the absorption trace in front of the cell arrives slightly delayed compared to the signal inside the cell, as the molecules have to travel further to reach the second probe region. The signal takes longer to decay, which can be interpreted as later molecules flying slowly out of the cell. Note that for the figure both traces have been normalized to make differences in shape more apparent. In the actual experiment, a peak absorption of about 80% inside the cell typically results in a peak absorption of around 15-20% in front of it, as long as the helium flow is big enough to carry molecules out of the cell. This comparatively low signal is also the reason for the huge error for the trace in front of the cell.

The outcoupling time is a measure of the time it takes the molecules to leave the cell in the form of a molecular beam. Because the beginning of the signal is measured at almost the same time both in and outside the cell, we instead look at the onset time it takes the signal to reach half of its maximal value. Figure 24 shows recorded outcoupling times for different flow regimes from two separate measurements. Aside from the large error the measurement has because of the low absorption signal in front of the cell, the recorded onset times for low flows vary strongly between the two measurements. As the target spot was changed between the measurements, we cannot exclude that the chosen spot also has an effect on the cell dynamics and therefore outcoupling time. Typically, the recorded onset times are below 0.3 ms however. For a more accurate measurement of the outcoupling times the measurement should be repeated with higher probe beam powers in front of the cell to decrease noise and more trace averages on resonance frequency.

## 4.3 Spectroscopy Results

#### 4.3.1 P and R-Branch Transitions

Besides its usage for absorption spectroscopy the *B*-state laser's main purpose in the experiment will be the slowing of the emerging molecular beam of CaF by driving the  $X^2\Sigma^+(\nu = 0, N = 1) \rightarrow B^2\Sigma^+(\nu = 0, N = 0)$  transition. This is the first transition in the P-branch which contains all transitions where the rotational quantum number decreases by one. The *B*-state laser is able to tune its wavelength to to the next P-branch transition  $N = 2 \rightarrow N = 1$  as well as the first R-branch transition  $N = 0 \rightarrow N = 1$  without heavy modification of the laser. The Q-branch does not exist for X-B transitions as both the ground and excited state are  $\Sigma$  states. The parity of  $\Sigma$  states is given by  $P = (-1)^N$  [46], which means that for Q-branch transition were N does not change the parity is the same for ground and excited state, making the transition forbidden.

The energy spacing between the different rotational levels in CaF is on the order of 20 GHz, so the overall spacing between the three states achievable with the *B*-state laser is about 60 GHz. For a given temperature, driving current and piezo voltage combination the *B*-state laser can only scan a frequency range around 2.5 GHz. Because of this limitation and the energy spacing between rotational levels only frequency ranges a multiple of 20 GHz away from the  $N = 1 \rightarrow N = 0$  transition were scanned. The resulting overall spectrum is depicted in Figure 25. The measured spectra of the transitions are compared with a simulated spectrum calculated with a software developed within our group [49]. The simulation is using the molecular



Figure 25: Measured spectrum of the lowest P-, and R-branches achievable with our laser system, including the slowing transition  $X^2\Sigma^+(\nu = 0, N = 1) \rightarrow B^2\Sigma^+(\nu = 0, N = 0)$  corresponding to P(1  $\rightarrow$  0). Plotted in orange is the simulated spectrum of the recorded transitions. Note that the measured spectrum has been shifted by -310 MHz to account for our wavemeter offset.

constants of CaF measured by Dulick *et* al. [71]. By explicitly checking the rubidium D-lines and comparing the resonance frequencies to literature values [72, 73] we measure a systematic offset of +310 MHz for our wavemeter. This offset is taken into account by shifting the measured data of the branches by this amount. We estimate the resonance frequency of our measured transitions by fitting a sum of four Gaussians to the recorded spectrum, corresponding to the hyperfine sublevels of the  $X^2\Sigma^+$  ground state. The frequency position of the peak attributed to the hyperfine quantum number F = 0 is considered the resonance frequency of the transition. Table 1 shows both the measured and simulated resonance frequency used as the slowing transition in CaF experiments, other groups have shared their resonance frequency as well, which are included in the table. It should be noted that even with our wavemeter correction, disagreements between the measured and simulated values on the order of a GHz exist. These disagreements extend

Transition	Note	f [GHz] $-$ 564 THz	$\Delta f$ [GHz]
$P(1 \rightarrow 0)$	Measured	$582.11 \pm 0.03$	
$P(1 \rightarrow 0)$	Simulated	582.61	+0.50
$P(1 \rightarrow 0)$	Tarbutt $[65]$	581.3	-0.81
$P(1 \rightarrow 0)$	Doyle $[24]$	582.695	+0.585
$P(2 \rightarrow 1)$	Measured	$560.80 {\pm} 0.03$	
$P(2 \rightarrow 1)$	Simulated	561.93	+1.13
$R(1 \rightarrow 0)$	Measured	$622.46 {\pm} 0.03$	
$R(1 \rightarrow 0)$	Simulated	623.76	+1.30

Table 1: Measured and simulated resonance frequencies f for the first two P-branch and first R-branch transition, as well as the deviation  $\Delta f$ . For P(1  $\rightarrow$  0) values of other groups are included.

even to the measured values of other groups, with the Doyle and Tarbutt groups disagreeing with each other by about 1.4 GHz. The cause of this are most likely absolute wavemeter offsets of the groups' wavemeters. Although our wavemeter was checked and corrected in terms of the offset, this was only done for a wavlength of 780 nm. The offset may be changing for different wavelengths.

#### 4.3.2 Thermalization

As the molecules have to be initialized into the  $X^2\Sigma^+(\nu = 0, N = 1)$  state, the experimental setup has to allow for the thermalization of the molecules within the buffer gas cell before they form the molecular beam. As all commonly employed laser cooling and trapping schemes use this state as the ground state, molecules populating other states are effectively lost from the experiment. We have seen in section 2.4 that having a significant fraction of molecules in specifically the first excited rotational state requires them to thermalize to a temperature on the order of 5 K.

We can estimate the temperature of the molecule ensemble and examine their thermalization process by evaluating the frequency spectra for different times after the ablation. In general, molecules belonging to the fastest velocity classes will reach the probing region of the absorption spectroscopy the fastest, corresponding to the beginning of and initial rise in the absorption traces. Accordingly, the later parts of an absorption trace belong to molecules of slower velocity classes. How well the molecules have thermalized at this point depends on the number of collisions with helium atoms they experienced when entering the detection region, as can be seen in figure 10. Typically, the earliest and therefore fastest molecules have undergone the a smaller of collisions at the time of their detection, resulting



Figure 26: a) A set of spectra from the first  $200 \,\mu s$  of an absorption trace. Each spectrum corresponds to the molecules detected during a  $39 \,\mu s$  interval. Earlier spectra are significantly Doppler broadened as the corresponding molecules have not fully thermalized yet. b) An examplary fit to a recorded spectrum. The shape of the spectrum is composed of the four Gaussian hyperfine components of CaF, which have fixed distances and relative heights in relation to each other.

in a higher temperature compared to the slower molecules that have had more time to thermalize.

Higher temperatures result in a stronger Doppler broadening of the transition. The measured spectra will consequently be broadened for the fastest velocity classes in the beginning of an absorption trace as they have not yet fully thermalized. Figure 26 shows the measured spectra for different times after the ablation. Later spectra will continue to narrow until a final temperature has been established in the slowest molecules.

A value for the temperature can be obtained by fitting a sum of Gaussians to the measured frequency spectra. The  $X^2\Sigma^+(\nu = 0, N = 1)$  ground state contains four hyperfine sublevels with equal width that have to taken into account for the fit, with fixed frequency distances given in Figure 7 and a relative signal strength ratio of 5:3:1:3 for peaks with F = 2, 1<sup>+</sup>, 0 and 1<sup>-</sup> respectively. The hyperfine splitting of the excited state  $B^2\Sigma^+(\nu = 0, N = 0)$  is small compared to the splitting of the ground state and therefore has only little influence on the form the the resulting spectrum. It is therefore ignored in the context of this approximation. An examplary fit to a measured spectrum is shown in Figure 26. By setting the gaussian width  $\sigma$  obtained by the fit equal to the Doppler broadening  $\sigma_{\rm D}(T)$  one can obtain the approximate temperature of the molecules

$$\sigma \approx \sigma_{\rm D}(T) = \sqrt{\frac{k_{\rm B}T}{m_{\rm CaF}\lambda_0^2}} \quad \Leftrightarrow \quad T = \frac{m_{\rm CaF}\lambda_0^2\sigma^2}{k_{\rm B}}, \tag{4.1}$$

where  $k_{\rm B}$  is Boltzmann's constant,  $m_{\rm CaF}$  the mass of CaF and  $\lambda_0$  the resonance wavelength of the transition. Here it should be noted that we approximate the width of the individual hyperfine peaks to be strictly equal to the Doppler broadening. While Doppler broadening is the dominant contribution to a peak's overall width, other broadening effects like power broadening and the natural linewidth of the transition also play a part in it. The resulting temperatures should therefore not be understood as the real temperatures of the corresponding molecules, but rather an upper limit to the temperature.

Plotting the temperatures extracted from the spectra fits for a multitude of different time frames of the absorption trace allows for a visualization of the molecular thermalization process, which is shown in Figure 27. The first molecules arrive in the detection region about 130  $\mu$ s after the ablation laser trigger. These molecules have not fully thermalized yet and have a temperature of about 400 K, however the uncertainty at these time frames is very high, because the early spectra are noisy and strongly Doppler broadened which reduces the accuracy of the fits. The molecules continue to thermalize and cool down at an approximately exponential rate. After 220  $\mu$ s the absorption trace typically reaches its maximum. At that point, most molecules have reached a temperature of  $(10.4 \pm 1.5)$  K. Note that the probe region is about 1 cm away from the cell aperture, so molecules will continue to thermalize until they exit the cell. Later molecules will continue to cool down until all are either diffused or extracted. The relative error for late molecules is increased because of the weakening signal of the absorption trace, but an estimate of the final temperature established for the slowest molecules is about  $(6 \pm 2.5)$  K. The actual average temperature of the molecules shortly before being extracted out of the cell will most likely be somewhere between the two previously stated values, which is within the requirements we set for the apparatus. It should be noted that the temperatures calculated here are strictly speaking purely translational temperatures. Previous works have shown, however, that buffer gas cooling tends to thermalize translations and rotations simultaneously and at comparable rates with roughly equal final temperatures [74, 75].

A more accurate value for the rotational temperature of the molecule ensemble can be obtained by comparing the relative heights of the absorption peaks for multiple rotational transitions. The relative heights should be proportional to the population of the rotational ground state of the corresponding transition, and this way a rotational temperature can be reconstructed (see Figure 8). In our case, this was not possible because in CaF neighbouring rotational transitions are so far



Figure 27: Calculated upper limit of the temperature of the buffer gas cooled molecules for different times after the ablation. The first molecules detected have had the least time to thermalize and therefore have a high temperature. At the peak of the absorption trace molecules have reached a temperature of  $(10.4 \pm 1.5)$  K, but will continue to thermalize until being extracted. Later molecules will continue to cool down until they are either extraced out of the cell or diffuse to the cell walls. This measurement was taken with a helium flow of 0.6 SCCM and a probe beam intensity of 40  $\mu$ W.

apart from each other (see section 4.3.1) that the laser had to be manually tuned to a new transition by changing its temperature. The amount of time needed for this significantly changed other parameters in the experiment like the quality of the target spot, making the relative measured absorption strengths unreliable. In addition, the recorded absorption traces are too strong to directly compare, as the Lambert-Beer law looses its validity for absorption this high.

#### 4.3.3 Collisional Cross-Section

The collisional cross-section  $\sigma_{\text{CaF,He}}$  between CaF and He can be estimated by investigating the diffusion time of the molecules for different helium flows. Equation

2.27 suggests a linear dependence of the diffusion time  $\tau_{\rm D}$  on the helium density inside the cell of the form

$$\tau_{\rm D} = \frac{16}{9\pi} \frac{A_{\rm cell} \,\sigma_{\rm CaF, He}}{\overline{v}} \cdot n_{\rm He} = a \cdot n_{\rm He}. \tag{4.2}$$

The mean speed  $\overline{v}$  of helium atoms inside the cell is given by

$$\overline{v} = \sqrt{\frac{8k_{\rm B}T}{\pi m_{\rm He}}},\tag{4.3}$$

where T is the temperature of the helium gas that we assume to be about as cold as the buffer gas cell and cold fingers, with an additional error accounting for a possible heating during collisions with the CaF molecules, so  $T = (3.5 \pm 0.5) K$ . The helium density inside the cell can be approximated by assuming steady state, so the helium outflow out of the aperture is considered the same as the inflow  $f_{\rm in}$ through the gas line. The helium density is then given by [57]

$$n_{\rm He} = \frac{4f_{\rm in}}{A_{\rm aperture}\overline{v}},\tag{4.4}$$

where  $A_{\text{aperture}}$  is the cross-section surface area of the cell aperture. The diffusion time of traces made with varying helium flow rates is the extracted by fitting an exponential decay of the form

$$f(t) = P_0 \cdot \exp\left(-\frac{t}{\tau_{\rm D}}\right) \tag{4.5}$$

to the decaying end of the absorption traces. Figure 28 shows the extracted diffusion times for helium densities corresponding to the flow rate at which the measurement was taken. The data points are fitted with a linear function as suggested by equation 4.2. The previous approximation of the helium density technically assumed higher flow rates than the ones used for measurement. To account for the possible error we add an offset to the linear fit function.

The slope of the linear fit is proportional to the cross-section  $\sigma_{\text{CaF,He}}$ . Rearranging equation 4.2 finally leads to

$$\sigma_{\text{CaF,He}} = \frac{9\pi}{16} \frac{\overline{v} a}{A_{\text{cell}}} = (6.2 \pm 1.4) \cdot 10^{-15} \,\text{cm}^2.$$
(4.6)

This value is lower than the measured cross-sections of other monofluoride molecules like BaF ( $\sigma_{\text{BaF,He}} = 27 \cdot 10^{-15} \text{ cm}^2$  at 4 K [69]) and YbF ( $\sigma_{\text{YbF,He}} = (20.3 \pm 7.5) \cdot 10^{-15} \text{ cm}^2$  at 20 K [75]) and above some lighter molecules like BaH ( $\sigma_{\text{BaH,He}} = (3.1 \pm 0.2) \cdot 10^{-15} \text{ cm}^2$  [76]). It should be noted that the expected true error for



Figure 28: Diffusion times of absorption traces for varying helium densities inside the cell. A linear function is fitted to the data as equation 4.2 suggests a linear relationship between the values. The corresponding measurements were taken with a probe beam power of  $5 \,\mu$ W.

this value is bigger than the one stated, which is only the resulting error of the diffusion time fits and uncertainty in helium temperature. A number of additional errors that are hard to quantify and were therefore not taken into consideration quantitatively, like target decay and measuring in flow regimes where the above approximations start breaking down. For a more accurate value, the measurement should be retried with higher flow rates around 1-100 SCCM, which were not accessible with our flowmeter.

#### 4.3.4 Beam Pointing

An important aspect of the buffer gas cell and resulting molecular flow dynamics is the angle under which the molecular beam exits the cell. As the ultimate figure



Figure 29: a) A schematic of the measurement setup. Both the inside and the front of the cell are probed from opposite directions. Counterpropagating beams in the actual setup are overlapped, but are shown side-by-side for clarity. b) Schematic sketch of absorption peaks detected in the measurement setup. The colors of the peaks correspond to the respective beams shown in a). If the molecules have a velocity in a certain transversal direction, the resonance frequencies of the spectra will differ for counterpropagating beams due to the Doppler shift. The effect of this shift is exaggerated for clarity of the illustration. The true resonance frequency for a straight molecule beam  $\omega_0$  is given by the mean of the resonance frequencies of opposite sides. The Doppler shift of the molecules can be calculated by taking the difference between a measured resonance frequency and  $\omega_0$ .

of merit of the presented setup will be the molecule number in a MOT, the beam pointing is critical, as it directly impacts the loading of a MOT. The fluoresence setup has not been realized at the time of this thesis, so the exact shape of the molecular beam and a possible angled pointing can not be accurately determined. We can however measure the transversal movement of the beam by comparing the Doppler shifts for opposite directions perpendicular to the forward velocity of the molecules.

For this we measure frequency scans to generate the corresponding spectra for different times during the trace. The resonance frequency of the spectra is extracted by fitting the hyperfine substructure of the transition, analogous to section 4.3.2. The spectroscopy setup is then reversed, with the probe beams going through and in front of the cell in the opposite direction. If the molecules have a velocity in a



Figure 30: A measurement of the transversal velocities of the molecules, both for different helium flows and times after the ablation trigger. The figure on the left depicts the velocities inside the cell. Horizontal black lines denote the flow values for which the measurement was performed. The values in between these flow values are interpolated linearly. Velocities up to 27 m/s are measured in both directions, heavily dependent on the flow rate. The figure on the right depicts the transversal velocities at the cell aperture where a molecular beam has already formed. Velocities are small and flow dependent. For flows between 0.65 and 0.8 SCCM the beam is exactly straight.

certain transversal direction, the measured resonance frequencies will be different for the two probe direction because the molecules will experience different Doppler shifts. The true resonance frequency  $\omega_0$  of a straight molecule beam is then given by the mean of the resonance frequencies of the two directions. A schematic of the beam setup as well as an overview of the different measured resonance frequencies is depicted in Figure 29.

The overall Doppler shift is calculated by subtracting one of the measured resonance frequencies from the true resonance frequency  $\omega_0$ . Transforming this Doppler shift  $\omega_D$  into a corresponding transversal velocity  $v_{\text{trans}}$  with

$$v_{\rm trans} = \frac{\omega_{\rm D}}{\omega_0} c, \tag{4.7}$$

were c is the speed of light allows for a measurement of the molecules average transversal velocity. Because the internal cell dynamics are dependent on the helium flow and might change the molecules' transversal velocity the measurement is taken for different flow regimes. Figure 30 depicts the molecules' average transversal velocity for different flow regimes and times during an absorption trace, both inside and in front of the cell.

It should be noted that the measurement inside the cell does not describe a molecular beam, but rather the transversal velocity of the overall ensemble of CaF molecules in the probe region. Heavy dependence of both the strength of the drift as well as its direction on the helium flow can be observed, implying strongly changing flow dynamics for different flow regimes. Transversal velocities of up to 27 m/s in both directions are recorded.

The transversal velocity at the cell aperture provides a more relevant picture of the molecular beam movement as the molecules outside the cell no longer thermalize with the buffer gas and the cell walls. Transversal velocities recorded here are lower than inside the cell as molecules with high transversal velocities are less likely to pass through the aperture without colliding with the cell wall and diffusing. The transversal velocities are positive for most flows, indicating that the molecular beam might have a slight inclination towards the right of the beam propagation direction. For helium flows between 0.65-0.8 SCCM the molecules' transversal velocity is close to zero, the beam is straight in this flow regime. The calculated error for the transversal velocities, however, is on the order of 5-10 m/s, meaning that the molecular beam will experience a bigger spread during propagation just from its finite temperature than any transversal drift measured here. With this and the signal dependence on flow rate (see 4.2.2) in mind we typically operate the experiment with a flow of 0.8 SCCM unless specifically needed otherwise.

## 4.4 Target Decay and Cell Cleaning

The amount of produced molecules per ablation pulse is strongly dependent on the target spot. Spots degrade over time, with the number of ablated molecules per pulse decreasing. Due to the accumulation of ablated dust, the entire buffer gas cell setup decreases in performance over long periods of use.

Typically, this will result in recorded absorption traces becoming more noisy and their peak absorption weakening, even for good spots. Additionally, decay of individual spot seems to happen at an accelerated rate and it becomes increasingly hard to find spots with no or very little decay. Other groups have found that the forward velocity of the molecular beam exiting the cell increases the longer a cell and target have been in use [24]. The problem seems to be common to the usage of salt targets (CaF<sub>2</sub>), while targets made of metal (utilizing a chemical reaction with the SF<sub>6</sub> gas) are reported to last much longer with consistent molecule yield. Although the exact reasons for the increased forward velocity are not well understood, this suggests that the accumulation of CaF<sub>2</sub> dust on the inner cell walls



Figure 31: a) A look into the cell from the front. A thin film of CaF<sub>2</sub> dust has accumulated inside after the cell has been used extensively for two months.
b) The inner side of the cell's front plate. Dust sticks to the copper surface.

hampers the thermalization process, causing the molecules to leave the chamber at higher velocities and temperatures. Consequently it is necessary to open the vacuum chamber roughly every six weeks to swap the target and clean the cell.

Figure 31 shows the interior of a cell that has been in use for two months.  $CaF_2$  dust has accumulated on all surfaces inside the cell, sticking to the copper in the form of a thin film. Some of the dust even managed to leave the cell through the aperture and small gaps between cell and windows, falling onto the cold plate. Dust particles also stick to the cell windows as illustrated in Figure 32. In some cases the windows have been soiled so heavily that we were not able to clean them anymore and had to replace them. The target, also depicted in Figure 32, shows heavy signs of use. At multiple spots on the lower half the target has been completely shot through until the ablation laser reached the vacuum glue used to attach the target to the copper holder. This target is the same as the one used in the target scan in Figure 20. As the upper half of the target depicted in the scan showed little to no signal we have only rarely shot at it, which is why it is still mostly intact in the picture.

A typical cleaning procedure first involves the disassembly of the buffer gas cell. The majority of the dust accumulated on the cell's copper parts and cold plate is



Figure 32: a) A  $CaF_2$  salt target after two months of use. Multiple spots in the lower half of the target have been completely shot through by the ablation laser, revealing the black vacuum glue underneath. Slight misalignment of the stepper motor setup has led to some shots hitting the glue and copper holder towards the edge of the target. b) and c) Dust deposits on the ablation laser window and probe beam windows, respectively. In some cases the dust sticks to the windows so strongly that the windows have to be replaced.

initially removed with wipes soaked in isopropyl alcohol. Special care has to be taken as to not accidentally get dust particles into the lower parts of the vacuum chamber, as they could get sucked into and damage the turbo pump during the next pump down. Next, the cell inside is polished anew. Finally, the cell parts are put into an isopropyl alcohol bath and ultrasonic cleaner to remove any lingering dust or grease deposits. Cell windows with only slight signs of use can be cleaned with optical cleaning equipment and reused, while dirtier ones have to be replaced entirely.

## 5 Summary and Outlook

In this thesis a source for a beam of cold CaF molecules was constructed, characterized and optimized. A vacuum chamber was constructed to provide the necessary environment for the creation of CaF. The setup of an ablation laser system allowed for the creation of CaF molecules by hitting a CaF<sub>2</sub> target with a pulsed beam. For this the beam was focused onto the target with a lens system. Additionally, a motorized mirror system was constructed to accurately and reproducibly control where the ablation beam hits the target.

A buffer gas cell was set up to cool the ablated CaF molecules to rotational states required for the optical cooling and trapping schemes planned for the experiment. For this, a closed cycle cryostat was installed into the vacuum chamber, cooling both the cell and helium buffer gas to a temperature of about 3 K. A setup for absorption spectroscopy using the  $X^2\Sigma^+(\nu = 0, N = 1) \rightarrow B^2\Sigma^+(\nu = 0, N = 0)$ transition at 531 nm was built, able to probe molecules both within as well as in front of the cell. Using this setup we are able to produce CaF molecules that thermalize to a temperature of at most  $(6.0\pm2.5)$  K, which is within the requirements we set for the apparatus.

The strength of the absorption signal was investigated in relation to the helium flow, ablation laser power and target spot. We found that ideal conditions for absorption traces are flows above 0.3 SCCM, as well as maximal ablation laser power. Furthermore we note that molecule production is strongly dependent on target spot. Spot signal decays over time, making a regular change of the spot necessary.

Besides the aforementioned transition corresponding to the first transition of the P-branch  $(N = 1 \rightarrow N = 0)$ , we were able to observe the next P-branch transition  $P(N = 2 \rightarrow N = 1)$  as well as the first R-branch  $R(N = 0 \rightarrow N = 1)$ . By comparing the transition frequencies with simulated data we made sure the initial transition indeed is the correct transition used for slowing.

Comparing Doppler-shifts in the molecular spectra from opposite directions allows for a measurement of a potential transversal drift of the molecules. With this we found that for the helium flow regime of 0.65-0.8 SCCM the molecular beam emerging from the cell leaves the cell straight without a drift to a certain direction. Finally, by extracting the diffusion times of absorption traces for varying flow rate we were able to estimate the collisional cross-section between CaF and He to be  $\sigma_{\text{CaF,He}} = (6.2 \pm 1.4) \cdot 10^{-15} \text{ cm}^2$ .

The measurements presented here have provided a basis for the further construction of a molecular MOT with a high molecule number. In particular, the several possible angles to examine the buffer gas cell via absorption spectroscopy allow for the examination of aspects of the internal cell dynamics that were previously



Figure 33: A render of the planned experimental setup. On the right the current setup with the source chamber can be seen. The next steps would be the setting up the transversal cooling chamber and afterwards the main MOT chamber.

often subject to educated guesses. This is especially useful for the immediate next goal of the experiment, which is to compare the molecular species CaF and BaF side-by-side within our buffer gas cell with a dual-species target. Our setup allows for the detection of both species at the same time, both inside and in front of the cell. This enables for a direct comparison between molecule thermalization, extraction speed and dynamics between the two species.

In the future, further improvements to the setup could be made by replacing the salt target used currently with a metal target in conjunction with  $SF_6$  gas. Other groups have suggested that this significantly increases the molecule yield and life-time of the source [24].

The next steps in the experiment would be setting up of a transversal cooling chamber, followed by the main chamber for the MOT, a design sketch of which can be seen in Figure 33. The molecular beam created by the source chamber described in this thesis can then be slowed and focused by decreasing the molecules transversal velocities via 2D Doppler cooling in the transversal cooling chamber, before finally being trapped by the MOT.

# 6 Appendix

## Molecular Constants of CaF

Table 2 provides the molecular constants used for the calculation of the state populations in section 2.4 and the simulated transitions in section 4.3.1. Note that the rotational constants are dependent on the vibrational quantum number. As an example, the first rotational constant  $B_{\nu}$  is given by

State	Constant	Value $[cm^{-1}]$		State	Constant	Value $[cm^{-1}]$
$X^2 \Sigma^+$			· · ·	$B^2\Sigma^+$		
	$T_e$	0			$T_e$	18841.309
	$\omega_e x_e$	2.908			$\omega_e x_e$	3.143
	$\omega_e y_e$	0.0081			$\omega_e y_e$	0.0095
	$B_e$	0.343715			$B_e$	0.342604
	$D_e$	$4.21 \cdot 10^{-7}$			$D_e$	$4.66 \cdot 10^{-7}$
	$lpha_e$	$2.453 \cdot 10^{-3}$			$lpha_e$	$2.63 \cdot 10^{-3}$
	$\gamma_e$	$6.2 \cdot 10^{-6}$			$\gamma_e$	$6.3 \cdot 10^{-6}$

$$B_{\nu} = B_e - \alpha_e \left(\nu + \frac{1}{2}\right) + \gamma_e \left(1 + \frac{1}{2}\right)^2 + \dots$$
 (6.1)

Table 2: Electronic state energy as well as vibrational and rotational constants for CaF for the ground state  $X^2\Sigma^+$  and second excited state  $B^2\Sigma^+$ . Constants are taken from [71].

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