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Intense slow beams of heavy molecules to test fundamental symmetries

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**Intense slow beams of heavy molecules to
test fundamental symmetries**

Cover description: *few heavy molecules overwhelmed by lighter atoms*

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and engineering

van swinderen institute for
particle physics and gravity

This work is part of a research program VIDI 680-47-519 funded by the Dutch Research Council (NWO) and done at the Van Swinderen Institute for Particle Physics and Gravity, part of the University of Groningen.

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PhD Thesis

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on the authority of the
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and in accordance with
the decision by the College of Deans.

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1

Introduction

The standard model of particle physics (SM) is considered to be the most successful theory in physics, describing all observations in experiments up to date [1], but there are still facts which cannot be accounted for in this model. For that reason new theories beyond the Standard Model (BSM) have emerged in order to explain some of these phenomena. A few of these shortcomings of the Standard Model are listed below. The SM:

1. Has no solution to the hierarchy problem [2]
2. Does not explain the number of particle generations[3]
3. Has a large number of free parameters [4]
4. Has no description of the "missing" mass in the universe, the so-called "dark matter" [5, 6, 7]
5. Has a strong CP problem (θ parameter) [8, 9]
6. Has no explanation for the observed universal baryon/lepton asymmetry [10]

Among others, the range of validity of the SM can be tested by looking for CP violation effects beyond the Standard Model, where C and P represent the charge conjugation and parity operators $\hat{C}$ and $\hat{P}$, respectively.

Charge conjugation (C), Parity (P) and Time-reversal (T) are three discrete symmetries in the SM. Let $|\Psi(x, t, q)\rangle$ be a particle state, where x , t and q represent space, time and charge, respectively —then the charge conjugation and parity operations result in:

$$\hat{C} |\Psi(x, t, q)\rangle = |\Psi(x, t, -q)\rangle \quad (1.1a)$$

$$\hat{P} |\Psi(x, t, q)\rangle = |\Psi(-x, t, q)\rangle \quad (1.1b)$$

In the same way a time-reversal operation T can be defined with the corresponding operator $\hat{T}$:

$$\hat{T} |\Psi(x, t, q)\rangle = |\Psi^*(x, -t, q)\rangle \quad (1.2)$$

A quantum field theory such as the Standard Model requires that eigenfunctions to the $\widehat{CPT}$ operation are even [11]. That is why CP symmetry violation is assumed to imply T violation and written here as CP/T.

Symmetry conservation can hold for the separate or another combination of C, P and T operations. The mechanism or property governing $|\Psi\rangle$ to look for here should not yield a state equivalent to the initial state after a combination of C and P operations or after a T operation.

The first experiment that showed the violation of CP symmetry was a measurement performed on the products of decaying neutral kaons [12]. This CP violation mechanism can be described within the SM. The CP violation mechanism contained in the SM is not sufficient to account for the observed baryon asymmetry if the initial state of the universe was symmetric. Typically BSM theories contain new phases and mechanisms for additional CP violation, resulting in observables such as a permanent electric dipole moment of the electron (eEDM) or any other fundamental particle. As a result of an electric dipole moment (EDM), a fundamental particle would acquire an additional energy in an electric field. The Hamiltonian H of the interaction is:

$$H = -\mathbf{d}_e \cdot \mathbf{E} - \boldsymbol{\mu} \cdot \mathbf{B}, \quad (1.3)$$

where $\mathbf{d}_e$ is an eEDM, $\mathbf{E}$ an electric field, $\boldsymbol{\mu}$ the magnetic dipole moment of the electron and $\mathbf{B}$ a magnetic field. A sensitive measurement of $\mathbf{d}_e \cdot \mathbf{E}$ requires large electric field, since current experiments have set stringent limits on the size of $\mathbf{d}_e$.

The eEDM predicted by the most up to date BSM models and measurements is less than 10^{-29} ecm [13]. To measure such a small eEDM above experimental noise level using a bare electron, one needs to generate an electric field that is technologically not feasible at the moment. Instead it has been found that the measurement sensitivity for an EDM of electrons in heavy atoms is enhanced by factors between $\sim 10^3$ and $\sim 10^4$ when the atoms are maintained in an external electric field of $\sim \text{kV/cm}$ [14, 15, 16]. In case of diatomic polar molecules like BaF and YbF the enhancement can even reach $\sim 10^6$ [17, 18].

Given the discovery of the eEDM enhancement in atoms and molecules around the year 1965 and the fact that polar molecules can be slowed down and trapped using external electric field [19, 20, 21], polar molecules are attractive for experiments. Sensitivity to small eEDMs requires limiting statistical uncertainties. To minimize statistical uncertainty, a large number of slow molecules (see Chapter 4) and a large interacting electric field for the molecules are required. Having slow molecules allows for long eEDM-electric field interaction and long measurement times required for decreasing statistical measurement uncertainties (see Chapter 2).

A large number of slow molecules can be obtained by means of a cryogenic buffer gas molecular source (cryogenic source) [22]. A cryogenic source, as described in Chapter 3, is based on a hydrodynamic expansion of a cold inert gas entraining molecules of interest, cooling the molecular thermal degrees of freedom in the process. Such a source can produce a large number of internally cold molecules in a relatively slow beam, permitting a relatively long interaction time. With a cryogenic source it is expected that it is possible to produce $\sim 10^9$ molecules in the molecular state of interest with a velocity of 180 ± 50 m/s every 100 milliseconds [23].

Combining the cryogenic source with a Stark decelerator [24, 25] (described in Chapter 7), molec-

ular beams from the cryogenic source can be made slower to reach velocities around 30 m/s. This low velocity will allow for molecules interacting with a strong electric field for a time of ~ 5 ms [23]. Measuring the eEDM with sufficiently intense molecular beams of BaF coming from a cryogenic source and travelling at 30 m/s can result in a statistical eEDM upper limit of $\sim 10^{-30}$ ecm. Setting a lower upper limit on the eEDM will contribute to reducing the parameter space of current and new BSM Models.

The effort for measuring an eEDM in BaF is done within a collaboration of two institutes: Laser-Lab, Department of Physics and Astronomy (Vrije Universiteit) and Van Swinderen Institute for Particle Physics and Gravity (VSI) (University of Groningen). VSI is a university partner of the Dutch National Institute for Subatomic Physics (Nikhef). The collective name of this Nikhef research program is NL-eEDM [23]. In the initial phase of the NL-eEDM measurements, parts of the setup have been built and tested. Two initial stages of the complete setup will be presented and discussed in this thesis, namely the cryogenic source and the travelling-wave Stark decelerator. The emphasis will be on the cryogenic source, as that is the new component build for this work. The final eEDM measurement will be performed on BaF molecules. Due to the availability of laser infrastructure from previous experiments [24, 25, 26], the cryogenic source was optimized for measurements on SrF in our laboratory. The fact that the energy level structure of SrF is comparable to that of BaF, made it attractive to test the molecular source using SrF molecules. The design and building of the cryogenic source, the coupling to the Stark decelerator and the experimental results using SrF, will be presented in this thesis.

Thesis Outline

This thesis is about building, testing and characterising a cryogenic source to create cold and slow molecules that can be used for an eEDM measurement. Chapter 2 gives a brief theoretical treatment of how the NL-eEDM program is relevant for measuring CP violation beyond the SM and the principles behind a sensitive measurement of an eEDM. The principles behind the cryogenic source, the design considerations of the construction and the source itself are discussed in Chapter 3 together with a characterisation of the operation conditions. After the molecules are produced, they are detected. The methods used for detection and results of their application are presented in Chapter 4. In Chapter 5 and Chapter 6 a systematic study is presented of the performance of the source, for two precursor materials: SrF₂ in Chapter 5 and Sr in Chapter 6. After the molecular beams are created in the source, they will be accelerated to lower speeds using a travelling-wave Stark decelerator. Using a modest deceleration from 190 to 150 m/s and guiding speeds of 0, 80 and 190 m/s, the coupling of the molecular beam from the source into the decelerator is tested and characterised in Chapter 7. Finally a summary and outlook of this work is given in Chapter 8.

2

CP/T Violation: Theory and Measurement

The Standard Model predicts that all interactions between fundamental fermionic particles are mediated by bosonic force carriers.

Fermions						Bosons									
Leptons			Quarks			Electro-weak			Strong						
particle	mass (GeV/c ²)	electric charge	particle	mass (GeV/c ²)	electric charge	Particle	mass (GeV/c ²)	electric charge	particle	mass (GeV/c ²)	electric charge				
e electron	5.1x10 ⁻⁴	-1	u up	2.2x10 ⁻³	+2/3	γ photon	0	0	g gluon	0	0				
ν_e electron neutrino	<225x10 ⁹	0	d down	4.7x10 ⁻³	-1/3	W^-	80.4	-1	<div>scalar boson</div> <table><tr><th>Particle</th><th>mass (GeV/c²)</th><th>electric charge</th></tr><tr><td>H^0 Higgs</td><td>125.2</td><td>0</td></tr></table>	Particle	mass (GeV/c ²)	electric charge	H^0 Higgs	125.2	0
Particle	mass (GeV/c ²)	electric charge													
H^0 Higgs	125.2	0													
μ muon	0.1	-1	c charm	1.3	+2/3	W^+	80.4	+1							
ν_μ muon neutrino	<19x10 ⁻⁵	0	s strange	95x10 ⁻³	-1/3	Z^0	91.2	0							
τ tau	1.8	-1	t top	173	+2/3										
ν_τ tau neutrino	<18.2x10 ⁻³	0	b bottom	4.2	-1/3										

Figure 2.1: Fermions, bosons and their properties in the Standard Model of elementary particles [27]. The fermions consist of leptons and quarks. Interactions involving leptons are mediated by the electro-weak and the scalar boson, while the electro-weak, the scalar and the strong bosons mediate interactions involving quarks.

The accomplishments of the standard model are outstanding and all its predicted particles where discovered. A table of the SM particles is shown in Figure 2.1, together with their mass and charge.

The SM does allow for CP violation. In the quark sector, the weak force allows for the mixing of quark flavours via the Cabibbo-Kobayashi-Maskawa mechanism given by the unitary CKM matrix [28]. This CP violation mechanism also contributes to CP violation in the lepton sector [29, 30, 31]. Similar to the CKM mechanism, neutrinos transitioning between different mass eigenstates is also an allowed mechanism that generates CP violation. The latter mechanism is known as the Pontecorvo - Maki - Nakagawa - Sakata (PMNS) mechanism [32, 33, 34, 35].

Another possible mechanism for CP violation within the SM is found in the strong interactions between quarks. The strong interactions are described by the so called field theory of Quantum Chromodynamics (QCD). QCD contains a CP-violating parameter θ , which is tuned to $\sim 10^{-9}$ [9]. The smallness of θ is known as the strong CP problem. To solve the strong CP problem Roberto Peccei and Helen Quinn introduced a new dynamical CP-conserving field, resulting in a new particle —the axion [9, 36]. The axion is also considered to be a candidate for dark matter [37] and is expected to suppress CP violation in the strong interactions. Up to now there is no experimental evidence for the axion [38].

2.1 Electric Dipole Moments

A potential source of CP violation beyond the Standard Model is a permanent electric dipole moment of a Standard Model particle, such as the electron or neutron/quarks. The upper limit for an eEDM is estimated to be $|d_e| \simeq 10^{-38}$ ecm due to contributions from the CKM mechanism at the 4-loop level [39]. For the neutron, the upper limit CKM quark mixing contribution was calculated to be $|d_n| \simeq 10^{-32}$ ecm [40]. Current electron and neutron EDM measurement methods are not sensitive enough to measure small non-zero values at the orders of the CKM EDM contributions. This implies that any non-zero measurement now would require physics beyond the Standard Model.

In general an elementary particle with a permanent electric dipole moment $\mathbf{d}$ violates both T and CP symmetry. The Hamiltonian H of a subatomic fermion containing only spin $\mathbf{S}$ and an EDM $\mathbf{d}$ placed in a electromagnetic field, is given by:

$$H = -d \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} - \mu \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{B}, \quad (2.1)$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic field, respectively and μ is the magnetic dipole moment strength of the particle and d its electric dipole strength.

The EDM is in the same direction as $\mathbf{S}$, because if that was not the case, a particle ‘spinning’ around its centre of mass would average any off-axis moment to zero and there would be no measurable EDM or spin. Maybe even more fundamental, the Pauli exclusion principle would allow for at least three or four electrons in the lowest atomic orbital. This has never been observed —the latter observation thus demands that the EDM and the spin have the same quantum number $|\mathbf{S}|$. Both the spin and an EDM are intrinsic properties of elementary particles.

Performing separate C, P and T operations on the Hamiltonian yields:

Figure 2.2: Charge conjugation (C), parity (P) and time-reversal (T) operations performed on a fundamental particle with a permanent EDM $\mathbf{d}$ and spin $\mathbf{S}$.

$$\hat{C}(H) = -d \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} - \mu \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{B}. \quad (2.2a)$$

$$\hat{P}(H) = +d \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} - \mu \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{B}. \quad (2.2b)$$

$$\hat{T}(H) = +d \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} - \mu \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{B}. \quad (2.2c)$$

(2.2) shows that the Hamiltonian only changes when P and T are applied, this means that P and T are violated in the used configuration. Figure 2.2 shows C, P, and T operations performed on a particle with a permanent spin and EDM. Using CPT invariance, T violation also implies that the combined CP symmetry is violated here.

Figure 2.3: Generic examples of Feynman diagrams showing how typically CP violating phases (δ_L and δ_R) enter beyond the Standard Model interactions at the 1-loop level [30]. Further description in the main text

On the theory side there are proposed models for BSM physics [41, 42, 43, 44]. Figure 2.3 shows generic 1-loop diagrams contributing to a fermion EDM, predicted by gauge theories beyond the standard model [30]. f_L and f_R are chiral opposite fermions such as the left- and right handed electrons, while B represents a (BSM) boson such as a scalar electron in supersymmetric models or a Higgs particle in Higgs models [30]. δ_L and δ_R are CP violating phases and $\tilde{f}$ a fermion.

2.1.1 Measuring Electric Dipole Moments with Atomic Systems

We present the formal description of the molecular/atomic system including an eEDM. Starting with diamagnetic atoms: measuring EDM's of diamagnetic atomic systems allows for probing the EDM of the nucleus, because the contribution from an eEDM vanishes—any two electrons cancel each others EDM contribution in the system. The resulting atomic/molecular EDM is expected to be dominated by contributions from CP-violating (QCD) interactions within the nucleus and an eventual net nuclear EDM [45]. Interactions between the nucleus and the surrounding electrons can also add to the measured EDM. The latter contributions are usually parametrized as dimensionless scalars C_S , C_P and C_T [45]. Table 2.1 shows current lowest measured values of eEDMs and atomic EDMs from some atomic systems.

Table 2.1: Historical table of several eEDMs and EDMs measured in atomic systems. Where applicable 'stat' and 'syst' in the uncertainties refer to statistical and systematic errors of the measured value.

observable	system	result	year	reference
eEDM	Cs	$(-1.5 \pm 5.5 \pm 1.5) \cdot 10^{-26}$	1989	[46]
eEDM	TlF	$(-2.1 \pm 3.5) \cdot 10^{-25}$	1991	[47]
eEDM	Tl	$(6.9 \pm 7.4) \cdot 10^{-28}$	2002	[48]
eEDM	YbF	$(-2.4 \pm 5.7_{\text{stat}} \pm 1.7_{\text{syst}}) \cdot 10^{-28}$	2011	[49]
eEDM	PbO	$(-4.4 \pm 9.5_{\text{stat}} \pm 1.8_{\text{syst}}) \cdot 10^{-27}$	2013	[50]
eEDM	Ra	$(-0.5 \pm 2.5_{\text{stat}} \pm 0.2_{\text{syst}}) \cdot 10^{-22}$	2015	[51]
EDM	Hg	$(-2.20 \pm 2.75 \pm 1.48) \cdot 10^{-30}$	2016	[52]
eEDM	HfF ⁺	$(0.9 \pm 7.7_{\text{stat}} \pm 1.7_{\text{syst}}) \cdot 10^{-29}$	2017	[53]
eEDM	ThO	$(4.3 \pm 3.1_{\text{stat}} \pm 2.6_{\text{syst}}) \cdot 10^{-30}$	2018	[13]
EDM	Xe	$(-2.1 \pm 6.4) \cdot 10^{-28}$	2019	[54]

Paramagnetic Atoms

With paramagnetic atomic systems, one is expected to be predominantly sensitive to the EDM of the unpaired electron(s) within the atomic system [55], but again here CP-violating interactions between electrons and the nucleus can add to a measured EDM signal. The next derivations are based on [55, 56]. In an external electric field $\mathbf{E}$, the non-relativistic Hamiltonian of a neutral atomic system in electrostatic equilibrium is given by:

$$H_0 = \sum_i \frac{p_i^2}{2m_i} + \sum_{i \neq j} \frac{q_i q_j}{2r_{ij}} + \sum_i q_i V(\mathbf{r}_i), \quad (2.3)$$

where i and j are elementary particle indices, r_{ij} is the distance between particle i and j , q_i and q_j are the charges of particle i and j and $V(\mathbf{r}_i)$ the electrostatic potential of the external field $\mathbf{E}$ at the position of particle i . p_i is the linear momentum of particle i and m_i its rest mass. The

electric Hamiltonian corresponding to possible individual subatomic particle EDM interactions is given by the sum of the individual EDM interactions of the particles with $\mathbf{E}$:

$$H_{edm} = - \sum_i d_i \frac{\mathbf{S}_i}{|\mathbf{S}_i|} \cdot \mathbf{E}(\mathbf{r}_i), \quad (2.4)$$

where d_i is the EDM of particle i and $\mathbf{E}(\mathbf{r}_i)$ the external electric field at position $\mathbf{r}_i$. The former Hamiltonian can be rewritten as the result of a commutator:

$$H_{edm} = \left[\sum_i \frac{d_i \mathbf{S}_i}{q_i |\mathbf{S}_i|} \nabla_i, H_0 \right]. \quad (2.5)$$

Using H_{edm} as a small perturbation to H_0 , the expectation of the EDM Hamiltonian over the eigenstates $|\Psi\rangle$ of the system is given by:

$$\langle \Psi | \left[\sum_i \frac{d_i \mathbf{S}_i}{q_i |\mathbf{S}_i|} \nabla_i, H_0 \right] | \Psi \rangle = 0, \quad (2.6)$$

which implies shielding of the eEDM interaction with $\mathbf{E}$ (Schiff's theorem [57]). $|\Psi\rangle$ is an eigenstate of (2.3). In other words, an atom in an external electric field rearranges its charge configuration such that the time average electric field inside the atom is cancelled. Schiff himself, suggested four mechanisms that can invalidate the above argument [55, 58, 57]:

1. The particles have finite size and structure due to non-electrostatic forces.
2. There are spin dependent contributions to the forces.
3. There are relativistic corrections to the particle interactions.
4. The particle spin direction is correlated with the electric field.

For measurements on an eEDM, the dominant mechanism is the relativistic correction to the electron interactions in paramagnetic atomic systems. Consider a one-electron atom. Then its relativistic Hamiltonian is given by the Dirac equation:

$$H_D = \beta m_e c^2 + c \boldsymbol{\alpha} \cdot \mathbf{p} - eU(\mathbf{r}), \quad (2.7)$$

where:

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \quad (2.8)$$

$U(\mathbf{r})$ is the total electric potential of the external field and the nuclear electric field at the position of the electron $\mathbf{r}$, e is the electron charge magnitude, $\mathbf{p}$ is the electron's momentum and m_e the electron mass. By inserting H_D for H_0 in (2.5) one obtains:

$$H_{edm} = \left[-\frac{d_e \mathbf{S}}{e |\mathbf{S}|} \beta \cdot \nabla, H_D \right] + 2i \frac{d_e}{e} c \beta \gamma_5 |\mathbf{p}|^2, \quad (2.9)$$

where γ_5 is the fifth Dirac matrix, d_e the eEDM and c the speed of light. The expectation value of the first term in (2.9) vanishes, similar to (2.6), so that:

$$\langle H_{edm} \rangle = \langle \Psi | -d_e \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} - d_e(\beta - 1) \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} | \Psi \rangle. \quad (2.10)$$

The same arguments for obtaining (2.5) and (2.6) from (2.4) can be used here to deduce that the expectation value of the first term in (2.10) is zero, leading to:

$$\langle H_{edm} \rangle = \langle \Psi | d_e(1 - \beta) \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \mathbf{E} | \Psi \rangle. \quad (2.11)$$

This shows an effective multiplication of the eEDM interaction with the field. For the relativistic effects to be significant, the electron requires speeds close to the speed of light. The electrons speeds are higher if they are close to the nucleus [59], where the total electric field $\mathbf{E}$ can be approximated by $\mathbf{E} \approx Ze/r^2 \hat{\mathbf{r}}$, with Z the number of protons in the nucleus.

$$\langle H_{edm} \rangle \approx \langle \Psi | d_e(1 - \beta) \frac{Ze}{r^2} \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \hat{\mathbf{r}} | \Psi \rangle. \quad (2.12)$$

In the relativistic limit, the effect of an external field can be considered as a small perturbation, resulting in the atomic state $|\Psi\rangle$ becoming an admixture of eigenstates of the unperturbed Hamiltonian H_0 . An external electric field induces an electric dipole in the atom, whose interaction Hamiltonian with the field is given by:

$$\Delta H = aeE\hat{y}, \quad (2.13)$$

assuming that the field points in the y -direction with strength E and $a \ll 1$. Later on a will be set to 1 for the correct ΔH .

The eigenstates of H_{edm} can be written as a MacLaurin expansion in eigenstate $|\psi_n\rangle$ of the unperturbed Hamiltonian, where $n \in \mathbb{N}$ is the principal quantum number of the eigenstate. Similar to [56], one can write:

$$|\Psi\rangle = |\psi_n\rangle + a |\psi_n^{(1)}\rangle + a^2 |\psi_n^{(2)}\rangle + \dots, \quad (2.14)$$

The indices noted by superscripts (k) with $k \in \mathbb{N}$ indicate the k^{th} order correction to $|\psi_n\rangle$. As the first order correction has the largest contribution and for simplicity, the expansion will be approximated to first order.

$$|\Psi\rangle = |\psi_n\rangle + a |\psi_n^{(1)}\rangle. \quad (2.15)$$

The first order corrected wave function is given by:

$$|\psi_n^{(1)}\rangle = \sum_m \frac{\langle \psi_n | aeE\hat{y} | \psi_m \rangle}{\mathcal{E}_n - \mathcal{E}_m} |\psi_m\rangle \delta_{nm}, \quad (2.16)$$

where $\mathcal{E}_n$ is the energy eigenvalue of state $|\psi_n\rangle$ and $m \in \mathbb{N}$, resulting in:

$$|\Psi\rangle = |\psi_n\rangle + a \sum_m \frac{\langle\psi_n| aeE\hat{y}|\psi_m\rangle}{\mathcal{E}_n - \mathcal{E}_m} |\psi_m\rangle \delta_{nm}. \quad (2.17)$$

Knowing that $\langle\psi_n| H_{edm} |\psi_n\rangle = 0$, $\langle H_{edm} \rangle$ can be written as:

$$\langle H_{edm} \rangle = \langle \Psi | H_{edm} | \Psi \rangle \approx E d_e \sum_m \frac{\langle\psi_n| e\hat{y}|\psi_m\rangle \langle\psi_m| (1-\beta) \frac{Ze}{r^2} \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \hat{\mathbf{r}} |\psi_n\rangle}{\mathcal{E}_n - \mathcal{E}_m} \delta_{nm} + c.c., \quad (2.18)$$

where a has been set to 1 to reflect the proper ΔH . Introducing the notation $|n, \ell\rangle$, where ℓ is the angular momentum quantum number. The atom is initially prepared in the state $|n, s\rangle$. The energy eigenstates of opposite parity are then given by $|m, p\rangle$, then (2.18) becomes:

$$\langle H_{edm} \rangle \approx E d_e \sum_m \frac{\langle n, s | e\hat{y} | m, p \rangle \langle m, p | (1-\beta) \frac{Ze}{r^2} \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \hat{\mathbf{r}} | n, s \rangle}{\mathcal{E}_{n,s} - \mathcal{E}_{m,p}} \delta_{nm} + c.c. \quad (2.19)$$

Note that in a multi-electron atom, one has to do the above summation over all the electrons.

One can rewrite (2.18) to:

$$\langle H_{edm} \rangle \approx A \times E \times d_e = E_{\text{eff}} d_e, \quad (2.20)$$

Where A is the so called enhancement/suppression factor of the external electric field E .

$$A = \sum_m \frac{\langle n, s | e\hat{y} | m, p \rangle \langle m, p | (1-\beta) \frac{Ze}{r^2} \frac{\mathbf{S}}{|\mathbf{S}|} \cdot \hat{\mathbf{r}} | n, s \rangle}{\mathcal{E}_{n,s} - \mathcal{E}_{m,p}} \delta_{nm} + c.c. \quad (2.21)$$

One can see that if one compares a direct measurement of an eEDM on the electron with an eEDM measurement on a single electron atom, using an electric field $\mathbf{E}$, one is a factor A more sensitive when using the atom. The radius of the n^{th} electron orbit is given by [60]:

$$\begin{aligned} r_n &= \frac{4\pi\epsilon_0\hbar^2 n^2}{Ze^2\mu} \\ &= \frac{n^2\hbar}{Z\mu_0 c\alpha}, \end{aligned} \quad (2.22)$$

where μ is the reduced mass of the nucleus and the electron, α the fine-structure constant, ϵ and μ_0 are the electric and magnetic permeability of space, respectively. Inserting (2.22) into (2.21) for $|\mathbf{r}|$ and writing β explicitly results in:

$$A \approx \chi \cdot \begin{pmatrix} 0 & 0 \\ 0 & 2 \end{pmatrix} \alpha^2 Z^3, \quad (2.23)$$

where χ is a measure for the polarization of the atom.

Equation (2.23) is an approximation not only because perturbation theory was used, but also because only the m -dependency of the orbital radius was taken into account. Its (small) p -dependency in state $|m, p\rangle$ was discarded. From (2.21) it can be concluded that if the states of opposite parity become closer in energy, it results in a higher dipole interaction energy $\langle H_{edm} \rangle$ and thus a larger sensitivity to an eEDM. The same holds for atoms with larger masses. It is good to realise that the enhanced EDM also contains contributions from CP-violating processes involving the nucleons, beside the eEDM [30].

The treatment above is applicable to paramagnetic atoms. For diamagnetic atoms finite size effects play a more prominent role compared to relativistic effects, leading to an atomic eEDM more sensitive to the nucleus EDM instead of the eEDM. Diamagnetic atoms have been used for measurement on the nuclear EDM, for example in Xenon [54]. Although not treated above, hyperfine interactions in diamagnetic atoms can also lead to a non-zero contribution of d_e to the measured EDM [61]. Typical values for A in atoms are between 10^3 and 10^4 [14, 15, 16].

Molecules

In diatomic molecules the enhancement factor A can be even higher than in atoms due to the presence of closely lying rotational energy states of opposite parity or so called Λ and Ω doubling [62, 58]. The latter conditions enhance the eEDM sensitivity via the denominators in (2.18) and (2.21). Enhancement factors of $\sim 10^6$ are reached [17, 18].

All measurements performed on the eEDM up to now yielded a limit to its value, which constrains proposed theories beyond the Standard Model. Figure 2.4 shows the experimental upper limits on the eEDM obtained using molecules and the eEDM regimes of several proposed beyond the standard model theories. The aimed upper limit of the NL-eEDM project and the Standard Model range are also shown.

2.2 The NL-eEDM Measurement Setup

The NL-eEDM project aims at an eEDM measurement using BaF [23]. The experimental setup for the NL-eEDM project is shown in Figure 2.5.

Starting from left to right: A cryogenic source produces beams of BaF molecules in a quantum state suitable to be decelerated in a travelling-wave Stark decelerator [24, 21, 25]. After the source, an electrostatic guide [63, 64] is used to guide the molecules into the decelerator. The molecules, which have been decelerated to ~ 30 m/s by the decelerator, are laser cooled to decrease their transverse velocity spread. At the state preparation stage the molecules are prepared in a superposition quantum state with optimal sensitivity for an eEDM. The molecules continue into the interaction zone where there are both a static electric and magnetic field $\mathbf{E}$ and $\mathbf{B}$, respectively.

Figure 2.4: Theoretical and experimental limits on an eEDM, together with the eEDM domains of several BSM physics models and the Standard Model. The experimental limits are set by measurements on Tl atoms and YbF, HfF⁺ and ThO molecules. The aimed limit of the NL-eEDM program is also shown. Adapted from figure by David DeMille.

Figure 2.5: A schematic depiction of the planned NL-eEDM experimental setup, with the number of expected molecules (N) and the expected fields-molecules coherent interaction time (τ) at the relevant stages [23].

Figure 2.6: A particle with electric dipole moment $\mathbf{d}$ and spin $\mathbf{S}$ in a) a static electric field $\mathbf{E}$ and b) in a static electromagnetic field consisting of $\mathbf{E}$ and $\mathbf{B}$.

If an electron with magnetic dipole moment μ and EDM d_e is placed in a static electric field $\mathbf{E}$, it will be polarized. Its EDM will undergo a precession with frequency ω_{d_e} around the electric field axis, as shown in Figure 2.6a. If a parallel magnetic field is added, the particle's spin precession adds to the total precession frequency ω with ω_μ , see Figure 2.6b. The precession frequencies associated with the two different precessions are given by:

$$\omega_{d_e} = \frac{1}{\hbar} A d_e |\mathbf{E}|, \quad \text{electric dipole moment} \quad (2.24a)$$

$$\omega_\mu = \frac{g_s}{\hbar} \mu_B |\mathbf{B}|, \quad \text{magnetic dipole moment,} \quad (2.24b)$$

with g_s = the so called electron g-factor[65] and μ_B the Bohr magneton. After an interaction time τ between the field and the particle's EDM and magnetic dipole moment, the total precession angle θ_+ is:

$$\theta_+ = (A d_e |\mathbf{E}| + g_s \mu_B |\mathbf{B}|) \frac{\tau}{\hbar} \quad (2.25)$$

After setting the magnetic field $\mathbf{B}$ antiparallel to the field $\mathbf{E}$, the precession angle becomes:

$$\theta_- = (A d_e |\mathbf{E}| - g_s \mu_B |\mathbf{B}|) \frac{\tau}{\hbar} \quad (2.26)$$

Taking the difference of (2.25) and (2.26) we find the dipole moment d_e :

$$d_e = \hbar \frac{\theta_+ + \theta_-}{2 |E_{\text{eff}}| \tau}, \quad (2.27)$$

where (2.20) has been used.

The precession angles are manifested as phase changes in the quantum state of the molecule (or atom) during interaction with the field. The difference between the phases (2.25) and (2.26) is usually the observable measured in experiments [49, 13, 66, 23]. In the NL-eEDM setup, phase change develops as follows:

Before the molecules enter the interaction zone, one prepares the molecule in a superposition of two angular momentum projections $m_f = 1$ and $m_f = -1$. The molecules then go through the interaction zone where both a uniform electric and magnetic field are present. During their time in the interaction zone the molecular state acquires a phase difference $\theta = \omega\tau$. At the optical detection stage, the molecules are transferred from the superposition state to energy eigenstates for a fluorescence measurement. The probability to find the molecule in a particular energy eigenstate is $\cos^2(\omega\tau) = \cos^2(\theta)$, so that the measured signal Φ is given by:

$$\Phi \propto \cos^2(\theta) \quad (2.28)$$

From Φ the precession angle θ can be extracted. Using (2.27), an eEDM or its upper limit can be obtained*.

2.2.1 Statistical Error and Electron Electric Dipole Moment Sensitivity

The statistical uncertainty in such a measurement originates from the shot-noise of measuring the precession frequency ω on molecules, given by [67]:

$$\delta\omega \geq \frac{1}{\tau\sqrt{X}}, \quad (2.29)$$

where X is the number of molecules. The beams of molecules enter the interaction zone every Δt , during measurements this cycle is being repeated for a measurement time t_m . Let N be the number of molecules entering the detection zone every Δt , then:

$$X = \frac{N}{\Delta t} \cdot t_m \quad (2.30)$$

Equation (2.31) then becomes:

$$\delta\omega \geq \frac{1}{\tau\sqrt{\dot{N}t_m}}, \quad (2.31)$$

where $\dot{N} = N/\Delta t$ is the number of molecules per measurement cycle—equivalent to the number of molecules per shot.

Because the eEDM is given by (2.27) the error in the d_e is given by :

$$\delta d_e \geq \frac{\sqrt{(\delta\theta_+)^2 + (\delta\theta_-)^2}}{2|E_{\text{eff}}|\tau} \approx \frac{\hbar\delta\omega}{|E_{\text{eff}}|} = \frac{\hbar}{|E_{\text{eff}}|\tau\sqrt{\dot{N}t_m}} = \frac{\hbar}{|E_{\text{eff}}|\tau\sqrt{\dot{N}t_m}}. \quad (2.32)$$

The choice for using BaF for the NL-eEDM measurements is based on its relatively large mass, it can be produced in a relatively safe environment and crucially the fact that it can be decelerated

*One has to be aware of false EDM signals originating from moving charges ($\mathbf{v} \times \mathbf{B}$) and other systematic errors.

with the available decelerator in our laboratory. Using heavier candidates such as RaF [68, 69] requires relatively strict and costly safety measures. Although heavier molecules such as YbF and ThO have been used to measure the eEDM, the combination of the cryogenic source and the decelerator should allow for long enough eEDM-field interaction times and enough molecules to obtain an eEDM (upper limit) smaller than the current upper limit with ThO molecules (see Figure 2.4).

An experimental limit anticipated for the NL-eEDM experiment can be translated into a mass limit of a new boson on the order of TeV for a two loop process and even higher for one loop or tree level processes as shown in Figure 2.7.

Figure 2.7: Energy scales which would be probed with different upper limits of an eEDM (electron-EDM), according to several beyond the Standard Model physics models —Multi-Higgs, Supersymmetry and Leptoquarks. Adapted from [23].

3

Creating Molecular Beams

Creating a large number of molecules is indispensable for the experiment. Key features of the molecular beam source are a high molecular yield, low beam velocity and low spatial and temporal spread. The quantum state of the molecules produced in the source is important for detection and further stages of the experiment.

Other requirements are that the created molecular beams must not produce clusters at cryogenic temperatures* —more specifically, temperatures around 20 K. The molecules will be created inside a cell, kept close to 20 K —external supply of molecules is not possible due to the likelihood of them freezing before arriving in the cell. Furthermore, the molecules should thermalize and flush out of the cell by a buffer gas (neon) flowing through the cell and exit to form a beam. The creation of molecules by laser ablation causes a heat load on the cryogenic cell, which needs to be controlled. Thermalisation of the molecules with the buffer gas to 20 K requires a minimum buffer gas density. The experimental conditions such as the cell temperature and buffer gas flow rate should be kept stable and recorded for a consistent performance. Details of the setup built for this work are set out in this chapter and properties of the expected molecular beams are discussed.

*temperatures below 120 K [70]

3.1 Producing Molecules

Figure 3.1: Four stages of laser ablation: spallation, threshold evaporation, stationary evaporation, stationary evaporation + melt ejection. Each stage from left to right is accompanied by an increase in ablation energy [71].

At the start of a molecular beam is the production process of the molecules. The preferred method in this work is laser ablation of a solid target. It has been extensively used in molecular beam experiments containing alkali earth metals such as CaF [72, 73], BaF [72, 74], and in particular for producing SrF [75, 24, 25]. During laser ablation an intense laser beam is incident on a target. Typically pulses from a Nd:YAG laser are used. For solid targets, four different stages of laser ablation have been recognized (illustrated in Figure 3.1) [71]. The first type is ablation through spallation, this occurs primarily in brittle materials: an initial material ejection gives rise to more material being ejected from the target due to stress in the target. In non-brittle materials spallation is also possible via the expansion of ablated material plasma and the recoil of ablated products. During threshold evaporation the ablation happens close to the point where evaporation of the material is initiated. At this stage, most of the energy applied is used for heating the material up to the point where evaporation starts. The ablation yield at this stage is relatively small. The next stage is stationary evaporation, this stage yields a continuous production of material plasma and vapour during the ablation process. Although more molten material accumulates inside the resulting hole (grey), the vapour pressure inside is not high enough to eject molten material out of the hole. During stationary evaporation and melt ejection the laser energy is high enough to create enough vapour inside the hole, capable of ejecting molten material out of the hole. The resulting products of this last stage are vapour, plasma and molten material. It is not known at which ablation fluences/energies these stages are reached for SrF—these stages can influence the molecular beam characteristics. The preferred stage, regarding efficient use of the ablation yield, is stationary evaporation.

Molecule formation is achieved by ablating two different targets: one containing SrF₂ and the other containing Sr metal. The two processes are schematically depicted in Figure 3.2. When ablating a target containing SrF₂, reactions within the created plasma occur, resulting in SrF among other reaction products. This method has been used in [75, 25, 24] to produce SrF molecules. When laser ablating a Sr metal target, a reactant containing fluorine is required to produce SrF. Halogen containing molecules are known to react with alkaline earth atoms [76]

Figure 3.2: Two methods of producing SrF: As a product of laser ablating a) SrF_2 or b) Sr metal, while mixing with SF_6 gas.

to form Alkaline Earth Halides. The reactant chosen is SF_6 , which is introduced during the ablation process and SrF is formed. The reaction dynamics is still a subject of investigation. For BaF production from Ba metal ablation combined with SF_6 , a supersonic source has been built at VSI [77]. At the LaserLaB in Amsterdam, as part of the NL-eEDM collaboration, possible reaction pathways are being investigated [78, 76]. One of the possible reactions leading to SrF is given by [76, 79]:

A similar pathway is expected for the creation of BaF [80]. Another possible product of the reactions is SrF₂ [80].

The frequency of the ablation laser also influences the molecular yield. A laser frequency dependence of the negative ion yield was observed in [78] from the reactions of Ba and SF₆. The frequency dependence limits the efficiency of converting laser power to ion yield. Similar limitations have been reported in [81]. Regarding the yield of neutral species, it was shown in [82] that the yield of YbOH can be multiplied with one order of magnitude if the $1^1S_0 \rightarrow 3^1P_1$ transition in Yb is driven. The latter transition increases the reaction cross section of Yb with reactants H₂O and H₂O₂. Such an enhancement might be achievable for SrF and BaF.

Typically the ablation threshold is lower for Ba and Sr metal targets compared to BaF₂ and SrF₂ targets, because the alkaline earth metals have lower melting and boiling points compared to the alkaline earth Halides. Typical temperatures of the ablation products are between $\sim 10^3$ and $\sim 10^4$ K [83, 84]. A higher ablation threshold for BaF₂ compared to Ba has been shown in [72] and in this work it will be shown for SrF₂ and Sr.

3.2 Molecular Beam Formation

How to create a molecular beam will be discussed next. One way to create a molecular beam is by letting molecules in a pressurised cell escape through a small orifice in the cell towards a region of lower pressure. The principle behind the creation of molecular beams in this work is illustrated in Figure 3.3. The laser ablation methods discussed in the preceding subsection are applied to create molecules in the interior of the cell. The cell is pressurised by a continuously flowing buffer gas into the cell. The newly created molecules diffuse into the buffer gas and are carried out of the cell through an orifice of diameter D . In our experiment,

Figure 3.3: molecular beam formation principle.

^{20}Ne gas is used as a buffer gas, because of its low condensation temperature. This gas is monatomic and because its cell volume density far exceeds that of the ablated products, the beam dynamics can be described in terms of the neon atoms.

The mean free path λ_b of the buffer gas in the cell determines the flow regime of the outgoing beam. There are two limiting regimes of flow: effusive and supersonic. The mean free path is given by [83]:

$$\lambda_b = \frac{1}{\sqrt{2}n_b\sigma_{bb}}, \quad (3.2)$$

where σ_{bb} is the collisional cross section between the buffer gas atoms, n_b is the buffer gas number density in the cell. For an ideal gas it holds that:

$$n_b = \frac{N_b}{V} = \frac{p}{k_B T}, \quad (3.3)$$

where N_b is the number of buffer gas atoms in the cell of volume V , p the pressure inside the cell, T the buffer gas temperature and k_B the Boltzmann constant. The number of buffer gas atoms and ablation products flow out of the cell per second $\mathcal{F}_{out}$, is given by [83]:

$$\mathcal{F}_{out} = \kappa^{-1} \frac{1}{4} n_b \langle v_{exit} \rangle A_{exit}, \quad (3.4)$$

where κ is an orifice shape-dependent parameter, $\langle v_{exit} \rangle$ the average beam forward velocity at the exit and A_{exit} the cross section of the cell exit along the beam line. For any orifice shape κ can be roughly estimated by the Knudsen expression:

$$\kappa \approx (3/16) \left(A_{exit} \int_0^l \frac{p}{A^2} dl \right), \quad (3.5)$$

where ρ is the periphery (outer circumference) of the orifice, A the cross section of the orifice at position l along the the molecular beam axis. Here A_{exit} can be interpreted as the cross section at the orifice base and is included to be canceled in equation (3.4).

Assuming a steady flow is reached in the cell, the buffer gas flow rate into the cell equals the gas flow rate out—the total flow rate out is then given by:

$$\mathcal{F}_{out} = \mathcal{F}_{in}, \quad (3.6)$$

where $\mathcal{F}_{in}$ is the number of buffer gas atoms flown into the cell per second, (3.4) can then be rewritten as:

$$n_b = \mathcal{F}_{in} \frac{4\kappa}{\langle v_{exit} \rangle A_{exit}}. \quad (3.7)$$

For an orifice with a very short length along the beam line, the exact value for κ is 1. For other orifice geometries the values of κ [83] have been calculated. With the help of (3.7) and (3.2), the mean free path of the molecules can be calculated.

The collisional cross section between buffer gas atoms can be approximated in a hard sphere model by [85]:

$$\sigma_{bb} = 4\pi r_b^2, \quad (3.8)$$

where r_b is the atomic radius. The atomic radius can be estimated by the van der Waals radius, which for neon is given by $r_b \approx 1.54 \cdot 10^{-10}$ m [86], leading to $\sigma_{bb} \approx 3 \cdot 10^{-15}$ cm².

One of the goals of this work is the production of beams with velocities ~ 150 m/s. The applied buffer gas flow rate in our experiment ranges between 3 and 40 sccm[†], corresponding to $5 \cdot 10^{-8}$ and $7 \cdot 10^{-7}$ m³/s. Taking f_V as the neon flow rate in m³/s and ρ_{ne} the mass density of neon (≈ 0.84 kg/m³ [87]) at room temperature and invoking (3.6) leads to:

$$\mathcal{F}_{out} = \frac{f_V \rho_{ne}}{m_b} \quad (3.9)$$

The mass of a neon atom is given by $m_b = 3.32 \cdot 10^{-26}$ kg. From (3.9) it follows that the flux is: $1.3 \cdot 10^{18} < \mathcal{F}_{out} < 16.9 \cdot 10^{18}$ neon atoms per second. Using a cell exit radius of $r = 2.25$ mm (3.7) with $\kappa = 1$, $\langle v_{exit} \rangle = 150$ m/s and the flow rate between 3 and 40 sccm, the number density becomes:

$$\sim 2.1 \cdot 10^{21} < n_b < \sim 28 \cdot 10^{21} \text{ m}^{-3} \quad (3.10)$$

From (3.2) the mean free path for the atoms is then estimated to be:

$$\sim 0.1 < \lambda_b < \sim 1 \text{ mm} \quad (3.11)$$

[†] 1 sccm = mln/min = 1 cm³/min

One should realise that the average velocities, $\langle v_{exit} \rangle$, used in the above analysis is not the terminal velocity of the beam—in the hydrodynamic and supersonic limits collisions near the cell exit will boost the beam velocity further, the actual $\langle v_{exit} \rangle$ is lower.

In the experiment collisions between buffer gas atoms in the cell are assumed to be the dominant type of collisions. The mean free path of the molecules with the background atoms can be estimated by [88]:

$$\lambda_x = \frac{1}{n_b \sigma_{bx} \sqrt{1 + m_x/m_b}} \quad (3.12)$$

σ_{bx} is the collision cross section between the buffer gas and the molecules, m_x is the mass of a single molecule. A common approximation is $\sigma_{bx} \approx \sigma_{bb}$ [88].

Using (3.2), one can rewrite (3.12) to:

$$\sim 0.05 < \lambda_x = \frac{\sqrt{2} \lambda_b}{\sqrt{1 + m_x/m_b}} < \sim 0.6 \text{ mm}, \quad (3.13)$$

where the following substitutions were made: $m_b = 3.32 \cdot 10^{-26} \text{ kg}$, $m_x = 1.78 \cdot 10^{-25} \text{ kg}$ for the masses of neon and SrF and (3.11). The effusive and supersonic regimes are characterised by the mean free path λ through [83]:

$$\begin{aligned} \lambda_b &\gg D \text{ (effusive)} \\ \lambda_b &\ll D \text{ (supersonic)}, \end{aligned} \quad (3.14)$$

where D is the orifice diameter or its typical length scale. Because in the experiment the orifice diameter is 4.5 mm, (3.11) and (3.13) show that the flow regime of the beam is between the effusive and supersonic regime, but closer to the supersonic regime.

When the molecules are introduced into the cell, they diffuse throughout the cell volume. The maximum time τ_{cell} that molecules spent in the cell can be approximated by the time necessary for the cell content to be refreshed. This time τ_{cell} can be estimated by:

$$\tau_{\text{cell}} = \frac{V \cdot n_b}{\mathcal{F}_{\text{out}}} \quad (3.15)$$

With the cell volume $V \approx 1.3 \text{ cm}^3$, (3.15) results in the molecules spending $\sim 2 \text{ ms}$ in the cell, before all escaped.

From the buffer gas particle density n_b and the cell temperature, the pressure in the cell can be estimated using (3.3). In case the cell is held at 20 K, which is the typical cell temperature during the experiment, it follows that the pressure p in the cell is given by $\sim 4 \cdot 10^{-3} < p < \sim 120 \cdot 10^{-3} \text{ mbar}$. It is expected that the approximate parameters derived in this subsection should lead to molecular beams with velocities between 100 and 200 m/s.

3.3 Cooling Molecules

During production of the molecules, their temperature, the cell temperature and the buffer gas temperature increases due to the energy deposition of the ablation laser. One of the requirements on the molecular source is that the extracted molecular beam has a temperature at which most or a significant fraction of the molecules occupy a molecular state of interest. At the same time the carrier gas pressure has to be sufficient for thermalisation and beam formation.

The neon vapour pressure for the temperature range used in our experiments is given in Table 3.1. The distribution over the lowest rotational states for SrF in thermal equilibrium with the carrier gas can be extracted from simulations [89] (shown in Figure 3.4 for 4 and 20 K).

Table 3.1: Vapor pressure of ^{20}Ne at different temperatures [90]

T (K)	p (mbar)
16.42	2.07
17.10	4.17
18.28	11.42
19.12	21.69
20.00	39.64
21.03	75.51
22.14	141.77
23.04	213.50
24.01	334.85
25.17	529.40

An additional cooling mechanism is the expansion of a molecular beam from a relatively high pressure region to a region of lower pressure. The molecules have three different ways of storing their energy: the energy can be stored in translational, rotational and vibrational degrees of freedom. These three degrees of freedom are cooled through collisions with the buffer gas, but their rate of cooling differs due to their different collisional cross sections, σ_{trans} , σ_{rot} and σ_{vib} , respectively. In general it holds that [91]:

$$\sigma_{\text{trans}} > \sigma_{\text{rot}} \gg \sigma_{\text{vib}}. \quad (3.16)$$

The rotational state of the molecules are noted by N . As the beam's temperature gets lower, the population in the lower rotational states increases. From Figure 3.4 it is clear that if the molecules can be cooled down further, more molecules will be in the state of interest, $N = 1$. Cell temperatures around 4 K can be achieved if helium is used as a buffer gas [75], however pumping the gas load out of the setup and the thermalisation time become the limitations.

Figure 3.4: Simulation of rotational state population of SrF at rotational temperatures of 20 and 4 K [89].

3.3.1 Buffer Gas Cooling

Immediately after ablation, the hot molecules, diffuse into the neon buffer gas and start to collide with the colder neon atoms. A hard sphere model is used to derive that the temperature T of the molecules after n collisions with the buffer gas is given by (see Appendix A):

$$T(n) = (T_0 - T_{bg}) \exp \left[-\frac{2m_x m_b}{(m_x + m_b)^2} n \right] + T_{bg}, \quad (3.17)$$

where T_0 and T_{bg} are the initial molecule and buffer gas temperatures, respectively. m_x and m_b are the molecule and buffer gas atom masses respectively. This simplified treatment does not take in consideration the fact that the buffer gas molecules can significantly heat up during the ablation process. For a more complete analysis, a mechanism for the initial heating and cooling of the buffer gas can be added to the model. An initial heating and afterwards exponential cooling mechanism for helium as a buffer gas (to cool YbF) has been added and its parameters fitted to data in [92].

Figure 3.5 shows the decrease of the molecule translational temperature as function of the number of collisions with a buffer gas temperature of 20 K. Using SrF with neon buffer gas results in cooling within 1% of the target temperature after ~40 collisions. In case of BaF ~54 collision are needed to achieve the same. Using ^4He as the buffer gas to cool SrF means that significantly more (156) collisions are necessary to reach within 1% of the buffer gas temperature.

Figure 3.5: Estimated temperature vs collision curve for SrF and BaF molecules, using buffer gasses helium (He) and neon (Ne).

The collision rate of the molecules f_c^x can be estimated by:

$$f_c^x = \frac{\bar{v}_x}{\lambda_x}, \quad (3.18)$$

where $\bar{v}_x$ is the mean velocity of the molecules in the cell.

$$\bar{v}_x \approx \sqrt{\frac{8k_B T}{\pi m_x}}. \quad (3.19)$$

Leading to the temperature dependent molecule - atom collision rate:

$$\begin{aligned} f_c^x(T) &\approx \frac{\bar{v}_x}{\lambda_b} \frac{\sqrt{1 + m_x/m_b}}{\sqrt{2}} \\ &= \sqrt{\frac{8k_B}{\pi}} \frac{\sqrt{1/m_x + 1/m_b}}{\sqrt{2}\lambda_b} T^{1/2} \\ &= \beta T^{1/2}. \end{aligned} \quad (3.20)$$

Where equation (3.19) has been used and:

$$\beta = \sqrt{\frac{8k_B}{\pi}} \frac{\sqrt{1/m_x + 1/m_b}}{\sqrt{2}\lambda_b}. \quad (3.21)$$

Collision rates are estimated for different buffer gas flow rates in two cases: one where neon of 20 K is used to thermalize the SrF molecules and in the other case helium of 4 K is used for the thermalisation. The collision rates as function of the number of collisions experienced by the molecule are shown in Figure 3.6. The collision rates are one order of magnitude higher when helium is used instead of neon.

Figure 3.6: The SrF - buffer gas collision rate as function of the number of collisions already experienced when a): neon is the buffer gas and b): helium is the buffer gas. Buffer gas flow rates 3, 10, 20, 30 and 40 sccm are applied.

The molecules in the cell are extracted out of the cell through beam formation, two competing processes are involved in the extraction of the molecular beam: once the molecules are formed they can diffuse towards the cell walls and freeze on them. On the other hand the beams should be thermalized before extraction from the cell. Knowing that there are 40 collisions needed, the total time necessary for thermalisation, τ_{th} , is then:

$$\begin{aligned}\tau_{th} &= \frac{1}{\beta} \sum_{n=1}^{40} T(n)^{-1/2} \\ &= \frac{1}{\beta} \sum_{n=1}^{40} \left((T_0 - T_{bg}) \exp \left[-\frac{2m_x m_b}{(m_x + m_b)^2} n \right] + T_{bg} \right)^{-1/2} \\ &\in [\sim 0.02, \sim 0.2] \text{ ms.}\end{aligned}\tag{3.22}$$

The final result in (3.22) indicates the thermalisation times for 40 and 3 sccm respectively.

The typical time for a molecule to diffuse to the cell walls is $\sim 1\text{-}10$ ms [22]. Using the above, then according to (3.22) the higher the flow rate, the less molecules diffuse to the walls and a larger fraction of the molecules can be extracted out of the cell. The buffer gas is cooled on its way to the cell by colder parts in the experimental setup and it is not guaranteed that at high flow rates, the neon atoms have thermalized sufficiently with the cold parts before reaching the cell.

3.3.2 Expansion Cooling

The buffer gas undergoes an expansion at the orifice of the cell. In the supersonic regime, expansive cooling results in an additional decrease of the beam temperature—in favour of a higher beam velocity. The analysis below is based on [83]. The beam consists almost entirely of buffer gas and so the expansive cooling will be discussed in terms of the buffer gas. At the high pressure conditions of supersonic flows, the effects of heat transfer and viscosity are negligible, instead the flow can be viewed as isentropic and adiabatic. Under these circumstances the energy of the total mass is conserved during the expansion. The total energy of the beam with mass m is the sum of the enthalpy and the kinetic energy of the beam, or:

$$E_{ss} = h(x, T) + \frac{1}{2} m \langle v \rangle^2, \tag{3.23}$$

where $h = U + pV$ with U the molar enthalpy at position x from the beam origin along the beam line, p the pressure and V the beam volume. Furthermore T is the beam temperature at position x , $\langle v(x) \rangle$ the average kinetic energy of the buffer gas particles at position x , E_{ss} is a constant.

It follows that with initial position $x_0 = 0$, beam temperature T_0 and velocity v_0 that:

$$h(0, T_0) + \frac{1}{2} m \langle v_0 \rangle^2 = h(x, T) + \frac{1}{2} m \langle v \rangle^2, \tag{3.24}$$

In the limiting case where the expansion is from a relatively high pressure region to vacuum, $T \ll T_0$ and $v_0 \ll v$, the conservation described in (3.23), implies that the maximum velocity is given by:

$$\langle v \rangle_{max} = \sqrt{\frac{2h(0, T_0)}{m}}. \quad (3.25)$$

For a gas of constant pressure molar heat capacity c_p held at temperature T , it holds that the enthalpy is given by $h(x, T) = c_p T(x)$ resulting in:

$$\langle v \rangle_{max} = \sqrt{\frac{2c_p T_0}{m}}, \quad (3.26)$$

where T_0 is the beam temperature at the cell exit and can be approximated with the cell temperature. For an ideal monatomic gas such as neon, it holds that: $c_p = 5/2R$, where R is the gas constant ($8314.36 \text{ J kmol}^{-1} \text{ K}^{-1}$). The isentropic nature of the gas expansion yields that:

$$\frac{p}{\rho^\gamma} = \text{constant} \quad (3.27)$$

Before and after the expansion. ρ is the mass density of the beam, $\gamma = 5/3$ for a monatomic ideal gas and p the gas pressure.

Assume p_0 , T_0 and ρ_0 are the pressure, temperature and mass density of the gas just before expanding. Similarly p_1 , T_1 and ρ_1 are the same parameters after the expansion, then according to (3.27):

$$\frac{p_0}{\rho_0^\gamma} = \frac{p_1}{\rho_1^\gamma} \Rightarrow \frac{\rho_0}{\rho_1} = \left(\frac{p_0}{p_1} \right)^{1/\gamma} \quad (3.28)$$

Using the ideal gas law $p = \rho RT$ and (3.28), one can derive that:

$$\frac{p_0 T_1}{p_1 T_0} = \frac{p_0^{1/\gamma}}{p_1^{1/\gamma}} \Rightarrow \frac{T_0}{T_1} = \left(\frac{p_0}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (3.29)$$

Because the exponent of the last term in (3.29) is positive for an ideal monatomic gas, one can see that decreasing the pressure in an adiabatic isentropic flow leads to a decrease in beam temperature. The net forward velocity of the molecules traversing the cell exit is aimed along the beam direction. While traversing the relatively narrow cell exit, the atoms undergo many collisions resulting in a forward boost of the beam velocity. Because the molecule density is very low compared to the buffer gas density, it means that atom-atom collisions are practically responsible for the total boost. As the beam travels further the buffer gas dilutes due to its divergence and the collisions cease—at that point the forward velocity becomes stagnant. At which time the stagnant velocity is reached and what its final value becomes, depends on the flow regime [93].

3.4 Experimental Apparatus

An experimental overview of the cryogenic source setup is shown in Figure 3.7 and can be divided in the following four parts: cooling, heating and isolation, molecules production and beam formation, and the beam detection.

To maintain the cell at cryogenic temperatures, a two stage pulse tube cryocooler is used, it has a warm (~ 30 K) and cold (~ 5 K) stage. The cell is mounted to the cold stage. A cylindrical aluminium heat shield is thermally connected to the warm stage to reduce the heat load on the cold stage. Around the cold stage a cylindrical copper heat shield is attached to reduce the heat load on the cell. Temperature sensors are used to monitor the temperature at different locations in the source. A PID feedback system with resistive heaters is used to control mainly the temperature of the cell, but also the temperature of the two stages and the aluminium shield when there is a need to heat up the setup. To keep the vacuum chamber under adequate vacuum conditions a turbo molecular pump (Pfeifer TC 400, not shown) is used.

Figure 3.7: Schematic overview of the experimental setup of the cryogenic source. The cryocooler and a zoom in of the cell are displayed. In the cell an ablation laser pulse ablates a rotating target. The products from the target are mixed with SF₆ to form molecules. The molecules are flushed out through the cell exit by a continuous neon flow into the cell. The fluorescence detection of molecules is illustrated. Heaters and temperature diodes are placed at strategic positions in the setup. For the rotating target the rotation mechanism is visible and the different lines for gas flow into the cell are also shown. Further description is given in main the text.

3.4.1 Cooling, Heating and Thermal Isolation

The cryocooler

The largest component in the setup is a two stage cryocooler, details about the operation principles can be found in [94, 95]. The first and second stage of the cryocooler reach temperatures of 26 K and 4 K respectively during operation, depending on the mass and heat load on them. The higher the heat load the higher the final temperature on the stages. The cryocooler is a commercially available two stage pulse tube cryocooler (RP-082B2S) from Sumitomo Heavy Industries.

A schematic overview of the pulse tube cryocooler is shown in Figure 3.8, where **B** and **C** are two tubes filled with helium and **A** is a tube consisting of regenerator material. The typical pulse tube cooling cycle is given in [94]:

Figure 3.8: A schematic view of a two-stage pulsetube cryocooler. Its working principles are described in the main text.

The rotating valve rotates to allow compressed helium through the supply line into the main line, through **A** into **B** and **C**. From regenerators **b** and **c** compressed helium also flows into **B** and **C** and out again at low pressure via regenerators **A**, **b** and **c**. The small helium reservoirs **R_B** and **R_C** are used for regulation of the pressure inside **A** and **B**. Due to helium expansion and compression and flow through the heat exchangers a net amount of heat can be removed through the helium flowing back. The back flow occurs via the rotating valve and the return line into the helium reservoir **He**. This cycle will be repeated until the temperatures on both sides

of the regenerator material are equal or the heat load adds as much energy as the cooling cycle can remove. According to manufacturer specifications the cooling capacity of the cold stage is 0.9 W when it reaches a temperature of 4.2 K and 35 W for the warm stage at 45 K. Under normal working conditions, the warm and cold stage reach temperatures of 26 K and 3–4 K respectively. The advantage of using this type of cryocooler is that vibrations from the rotating valve are decoupled enough from the warm and cold stage and do not interfere with the molecular beam production and measurement processes. The decoupling is possible because the main line is a flexible gas line.

Cooling the cell

Connected to the cold stage is the cell in which molecules are produced. The cell temperature has to be kept around 20 K. Because the temperature of the warm stage is too high, the second stage is the logical choice for thermal connection. The cell temperature will also reach around 4 K, but can be controlled using a 50 W/ 50 Ω resistive cartridge heater (cryocon CC-3039-001), referred to as heater in Figure 3.7, and a temperature controller (Cryocon model 26). The temperature controller reads out a silicon temperature diode (cryocon s950-BB) and increases or decreases the current through the resistive heater depending on the temperature readout. The current through the heater is regulated via an inbuilt PID feedback system in the temperature controller. The heater is thermally anchored to the cell and heats up the cell to the desired temperature. The cell is not directly mounted to the cold stage, but indirectly via a copper cell mount. Between the mount and the cell, there are polyether ether ketone (PEEK[‡]) washers used, to reduce their contact surface. In this way it is easier to keep the cell temperature at ~20 K. Because the PEEK washers worked well, there was a need for an extra thermal anchor from the cell to the mount, which can be seen in Figure 3.7.

Cooling the neon line

Anchored to the warm stage and the cold cell is the fill line for neon buffer gas. The fill line is a tube partly made of copper and partly made of stainless steel, it transports neon into the cell from a gas bottle at room temperature. The idea is that the neon cools down during the transport, such that when it arrives in the cell it already has a similar temperature as the cell. The warm stage provides the first stage of cooling and the remainder is provided by the cell itself. To prevent the neon line from cooling below the cell temperature, the stainless steel (316 L stainless steel) parts of the line are strategically placed at parts where the neon line is prone to external thermal loads. Copper segments are placed where good thermal conductivity is desired, and are made of oxygen-free high thermal conductivity (OFHC) copper.

Cooling the SF₆ line

The SF₆ line transports room temperature SF₆ into the cell—it is a ~0.5 m long tube with a diameter of 1 mm. Cooling of this line is undesirable, but occurs due to the connection with the cell and occasional contact with other cold parts of the setup. The line is made of PEEK which has a low thermal conductivity. The plug of the line into the cell is made of a thick layer of PEEK. The melting point of SF₆ is around 220 K, at this temperature its vapour pressure is ~1 bar [96]. Minimizing thermal contact between the line and the cold parts is essential for transporting SF₆ into the cell. To make sure the SF₆ does not freeze in the line, a constantan[§] wire with a diameter of 0.3 mm and high electrical resistivity is guided through the inside of the PEEK tube. One end of the wire is connected to one pole of a power supply, the other end

[‡]PEEK is a material with a low thermal conductivity of ~0.25 W·m⁻¹·K⁻¹ at room temperature

[§]resistivity of constantan at room temperature ~50 · 10⁻⁸ Ohm · m

is anchored to the cell (grounded). The exterior of the cryostat and the remaining pole of the power supply are connected to the same ground to complete the circuit to the power supply. A current through the constantan wire, keeps the SF₆ line at the desired temperature. Applying a power of 2.5 W (5 V, 0.5 A) proved to be enough to prevent freezing of SF₆ in the line. The warm SF₆ presents an extra heat load on the cell, but the cooling power of the cold stage is enough to keep the cell temperature below 10 K (measured 9.3 K).

Heat shields

In order to reduce the thermal load from radiation on the 4K stage a cylindrical aluminium heat shield is fit ed and thermally connected around the warm stage. Similarly, a shield, made of copper, is connected to the cold stage to shield the cell further from remaining external thermal radiation. The warm and cold heat shields attached to the cryocooler are shown in Figure 3.9. To allow entrance for laser light, the target motor, and exit of the molecular beam there are holes made in the shields. The total area comprising the holes in the cold shield is $\sim 10 \text{ cm}^2$. Excluding the holes, the total surface of the shield is $\sim 618 \text{ cm}^2$. To estimate the heat load on the cell the Stefan-Boltzmann law will be used:

$$P_{\text{rad}} = \epsilon \sigma T^4, \quad (3.30)$$

where P_{rad} is the emitted power per square meter, ϵ the emissivity of the radiating material, $\sigma = 5.67 \cdot 10^{-8} \cdot \text{W} \cdot \text{m}^{-2} \text{K}^{-4}$ is the Stefan-Boltzmann constant and T the temperature of the radiating body. The heat load Q on a surface of area A is given by:

$$Q = \epsilon_{\text{cell}} P_{\text{rad}} \cdot A, \quad (3.31)$$

where ϵ_{cell} is the emissivity of the polished copper cell. The efficiency of the heat shields can be calculated as:

$$\eta = 1 - \frac{Q_s}{Q_0}, \quad (3.32)$$

where Q_s and Q_0 are respectively the heat loads with and without the heat shields attached. The cold shield, made of polished copper, reaches a temperature of around 5 K. Using equation (3.30) the thermal radiation from the cold shield (copper) is then $\sim 0.2 \text{ W/m}^2$. Radiation through the holes in the shields is mostly due to the temperature of the objects inside the laboratory, typically 290 K. Assuming full radiation, room temperature radiation is $\sim 400 \text{ W} \cdot \text{m}^{-2}$. The surface of the cubic cell is approximately 72 cm^2 , about 14% of it is subjected to room temperature radiation and 86% to cold shield radiation. Using the above equations, the total heat load Q_{cell} on the cell is estimated to be $\sim 16 \text{ mW}$. The resulting shielding efficiency η is $\sim 99\%$. Making the holes smaller would seem to be beneficial to the heat shielding, but during operation of the source heat load from the SF₆ line, target ablation and heating of the cell become the dominant contributions to the heat load on the cell. Solely heating the SF₆ line approximately doubles the temperature of the cell with the heat shields protecting it, making extra shielding futile.

[¶] $\epsilon_{\text{cell}} \approx 0.04$ [97]

(a)

(b)

(c)

Figure 3.9: a): Copper shield attached to the cold stage, shielding the cell inside from black-body radiation. The opening in the shield to allow to exit of the molecular beam is sealed here with aluminium tape. b): The top half of the aluminium shield attached to the warm stage, shielding the upper part of the setup. The left half of the copper shield is removed to reveal part of the cell and cell mount. c): Complete radiation shielding by the aluminium shield. An extra copper shield is placed at the top to shield openings in the aluminium shield.

Another useful function of the heat shields is to act as a cryopump for background gases. Background gases with melting temperatures higher than the shields will attach to the shields when encountered. This gives an extra pressure reduction in the vacuum chamber—on top of the turbo molecular pumps in use. The vacuum chamber is evacuated down to a pressure around 10^{-8} mbar. This pressure can be maintained for several days of operation with the neon gas load. Cryopumping speeds up the process of reaching the final pressure and during the experiments it is mostly responsible for maintaining the low vacuum chamber pressure as neon is flushed in. With cryopumping it takes less than 3 hours to reach the final chamber pressure. Occasions of buffer gas saturating the shields have been reported [73], such that less and less particles can attach to it. Increasing the shield temperature above the buffer gas melting point and pumping the gas out using the turbo pump solves this issue. In the work described here this was not an issue. Both the warm and cold shield have other particles frozen on them, e.g. water, oxygen, nitrogen and dust.

3.4.2 Molecule Production and Beam Formation

The cell

Production of molecules is established inside the cell. In the cell the target is ablated with a pulsed 1064 nm Nd:YAG laser (INLITE II-20, Continuum). The ablation laser wavelength is set to 532 nm (green) for visibility—there was no difference in yield between 1064 and 532 nm. The cell is a hollowed out 9 cm³ copper cube, with a shape that is aimed at optimizing the extraction of molecules out of the cell and was designed in collaboration with Stefan Truppe and Michael Tarbutt of Imperial College London. They already demonstrated its success in producing short (240 μ s) pulsed molecular beams of CaF [73]. The outer and inner cell geometry are shown in Figure 3.10. Five openings lead to the cell volume. Two are used for separate inflow of neon and SF₆ gas. In Figure 3.10a one can also see the PEEK plug (SF₆ in) that is used for the SF₆ line input to the cell. The anchoring of the copper neon line (Ne in) around the cell is visible.

There is an opening for the insertion of a cylindrical solid target. One opening is for the entrance of an ablation laser, this opening is elongated with a tube. The tube opening is closed off with a sapphire glass window of 0.4 mm thickness and a diameter of 7.5 mm (Edmund Optics) at the laser entrance. The tube minimizes coating of the glass window by ablation products—coating of the window would attenuate the ablation energy on the target. The remaining opening is the cell exit of diameter 10 mm. On top of the cell a transition adapter is installed. The adapter reduces the cell exit to 4.5 mm and can be replaced to create a different cell exit geometry.

A separate hole in the cell is used to plug in a resistive heater. This hole does not lead to the cell interior—to improve the heater's thermal conductivity to the cell, thermal paste (Apiezon N) is applied inside the hole. For alignment of the target and the ablation laser, a small opening opposing the ablation laser entrance is made in the cell. The opening for the target is sealed on one side with aluminium tape to prevent buffer gas flow out of it.

To reduce turbulent flow of the buffer gas near the exit in the cell, a copper plate with a conic shaped hole is used as an adapter in front of the cell exit.

Figure 3.10:

a): outer geometry of the cell, with the purpose of the different parts noted. b): cross sections of the cell from one side view (with adapter) and c): cross sections of the cell from different side (without adapter).

This particular adapter geometry gradually changes the exit radius from 10 mm to 4.5 mm over a 2 mm distance along the beam path. The geometry reduces turbulent flow near the cell exit as reported in [98]. The adapter is shown in Figure 3.11. The exit of the adapter became black/grey because of the deposition of SrF_2 on it from earlier measurements with a SrF_2 target. The white grains above the black parts are remnants of oxidized Sr. Furthermore, to enhance thermal contact between the cell and the adapter, thermal paste is applied around the cone edges. The thermal paste also helps to reduce leakage from the adapter edges. The cell is continuously flushed with cold neon gas to thermalize and carry the produced molecules out of the cell in the form of a beam. Experiments with the setup have shown that if the cell is maintained at at least 16 K, a molecular beam is observed.

Target

The target is attached to a target holder that is continuously rotating during the experiment. Rotating delays wearing off the target at a single location—it also prevents the target from overheating at a single location. The rotation mechanism is a rotating stepper motor (Smaract SR-4011-HV Rotation Stage) to which the target holder is magnetically attached. The cylindrical target is ~1.5 cm long and has a diameter of 0.5 cm, the rotation speed of the target can be

Figure 3.11: Adapter with conic shaped exit, used in front of the cell exit (this side towards cell exit). Also visible in Figure 3.10.

chosen. The SrF_2 target is a mixture of 10% boron and 90% SrF_2 moulded to a cylindrical shape. For more cohesion and water removal, the target is heated at around 800°C in an oven for approximately 20 minutes. The boron is added for better cohesion of the target. The Sr metal target is cut out of a larger sample of Sr metal and machined to form a cylindrical rod. After a few hours of rotation and ablation, an ablation trace can be identified on the target as shown in Figure 3.12 for a Sr target. The crack seen here in the target is accidental and occurred during the target preparation.

Figure 3.13: Cell interior a): before and b): after ablation.

Due to the threading in the threaded plate, the target will move up and down while being rotated by the rotation motor, creating a spiral trace along the target. During ablation of the target, the cell walls are coated by ablation products, possibly reducing the cooling efficiency of the cell walls on the buffer gas. If the buffer gas is cooled sufficiently before entering the cell, the effects on the cooling of molecules can be minimized. Figure 3.13 shows the inside of the cell before and after 30 to 40 hours of ablation of a strontium target. After ablation the cell volume is partially filled with oxidized strontium, making regular maintenance required when using high ablation energies—at low ablation power longer periods between maintenance work are achieved.

Figure 3.12: Ablation trace on a Strontium target.

Figure 3.13 shows the inside of the cell before and after 30 to 40 hours of ablation of a strontium target. After ablation the cell volume is partially filled with oxidized strontium, making regular maintenance required when using high ablation energies—at low ablation power longer periods between maintenance work are achieved.

Because the target can rotate up and down and the target motor has environment dependent uncertainties in its motion, the target can sometimes rotate out of the threaded plate either down or up. If the threading on the target holder is too long, the target can be pushed away from the the rotation motor and lose its magnetic attraction to the motor—in that case the target holder can fall down due to gravity. To prevent the target from moving out of the threading, the length of the threaded region on the target holder was adjusted to be similar to the target length. Figure 3.14 shows a bottom view near the target motor.

Another way the target can fall down is when the target gets stuck, but the rotation motor keeps rotating. There are only two magnetic contact points between the holder and the motor.

When there is no overlap between the contact points on the holder and those on the motor it will result in detachment of the holder from the motor. This last mechanism for detachment is solved by a copper structure, referred to as target catcher, attached on the same platform as the motor. As soon as the target holder falls down it will fall on the catcher, which is just ~ 2.5 cm away from the motor platform. The distance between the magnets on the target holder and the motor is enough for the target holder to be attracted and attach to the motor again. If the target holder threading is beyond the threaded plate from the top, then one might damage the aluminium sealing on top of the cell and the fl w in the cell will be redirected upwards instead of the direction of the cell exit—no molecular beam was observed in that case.

Gas flow and ablation

Ablation is performed with a pulsed Nd:YAG laser running at ablation rate 10 Hz at ablation energies between 1.2 and 33 mJ per pulse. The diameters of the ablation spots used in this experiment are 0.5 and 1 mm. Neon fl ws into the cell at fl w rates between 3 sccm and 40 sccm, while the SF_6 fl w rate is set to 0.5 sccm. The fl w rate of the neon is controlled with a 0-50 sccm fl w controller (Bronkhorst, M19201817A) and the SF_6 fl w rate by a 0-9 sccm fl w controller (Bronkhorst, M18202321A). They are both connected to a data acquisition and feedback system. Using the neon and the SF_6 fl w rates in these regions have proven to result in SrF molecular beams.

Figure 3.14: Bottom view of the experiment's vacuum chamber, showing the rotation motor.

3.4.3 Beam Detection

The detection of the molecular beams is performed using laser induced fluo escence (LIF) detection and absorption detection. Figure 3.7 shows the LIF detection scheme at the right hand side of the figure. The molecular fluo escence can occur at all possible angles, but in this scheme it is only collected from the regions shown using three lenses and two mirrors. The two lenses close to the molecular beam are opposite each other in order to detect photons going down or up. The downward fluo escence collected at the lower lens is refle ted upwards by a mirror at the bottom in order to be collected by the two upper lenses. The upper lens focuses the collected light into a photomultiplier tube (PMT) (Hamamatsu H7422P-40), which is connected to a data acquisition and feedback system. On its way to the PMT the fluo escence light is fil ered to allow only wavelengths between 632 and 634 nm through. A more elaborate treatment of the detection methods will be given in Chapter 4.

3.5 Operational Conditions

In this section the typical working conditions of the source are described. In Figure 3.15 the build experimental setup is shown together with the length scale, ablation laser, PMT, and a pressure gauge with which the pressure is measured inside the vacuum chamber. The chambers where absorption and LIF detection are performed will be referred to as the absorption chamber and LIF chamber, respectively. Most of the components described in the former section are not visible since they are inside the vacuum chamber. The measurement outcomes given in this section are as read out from the temperature controller and pressure gauge. These give their output with a high resolution.

Figure 3.15: External view of the experimental setup. The output of the ablation laser is guided via mirrors into the vacuum chamber. In the vacuum chamber the output hits a rotating target. The resulting molecular beam intersects with a detection laser beam ~ 31 cm further and below the PMT which records part of the resulting laser induced fluorescence. The detection laser beam enters from the other side of the chamber. The pressure in the vacuum chamber is recorded by a pressure gauge at the top of the chamber. Absorption detection is performed in the absorption chamber and fluorescence detection (LIF) in the LIF chamber.

Temperature stabilization

The temperature of the cell is stabilized by both the cryocooler and a resistive heater, and controlled by a temperature controller reading out a temperature diode attached to the cell. To measure the temperature at different parts of the source, silicon temperature diodes (cryocon s950-BB) are used and placed at the locations shown in Figure 3.7. Typical cool down temperature curves of the cell and other parts of the setup are shown in Figure 3.16a. The bottom of the cold shield reaches a temperature of ~ 4 K, while at the same time the bottom of the warm shield reaches a temperature around 30 K (not shown). The cell cools down to ~ 4 K. It takes around 3 hours and 15 minutes to reach these terminal temperatures.

Figure 3.16: a): temperature evolution of several parts in the setup during cool down of the cryocooler. b): stability of the cell temperature when heated to 17 K, during laser ablation and without ablation.

Using the temperature controller with built-in PID feedback system, the temperature of the cell is monitored and controlled. The typical stability of the cell temperature over time is shown in Figure 3.16b. The left hand side (green) shows the evolution while the ablation laser is on, while on the right hand side (red) the ablation is off. The variation in the cell temperature is below 10^{-2} K during ablation and in the absence of ablation. The sharp peak around 0.6 hours occurs just after the ablation was switched off due to the delayed reaction of the PID feedback system in the temperature controller. In both cases, there is SF_6 and neon flowing into the cell, and the SF_6 line is being heated. The cell temperature is acquired every ~ 2 seconds—20 times slower than the ablation rate and resulting in undersampling of the temperature measurements.

Figure 3.17: Histograms of the cell temperature deviation from the setpoint as read from the temperature monitor/controller. a): Cell temperature deviation at 3, 10 and 20 sccm neon flow rate. The legend on the right indicates different set temperatures in Kelvin b): Cell temperature deviation at set temperatures 16, 22 and 28 K, the legend on the right indicates different neon flow rates in sccm. c): Cell temperature deviation at ablation spot sizes 0.5 and 1 mm, the legend on the right indicates different ablation laser energies.

The distribution of temperature deviation away from the set temperature at different experimental conditions is shown in Figure 3.17. From the above data it can be concluded that overall the cell temperature is stable within $\sim 10^{-1}$ K above a set temperature of 16 K. Figure 3.17a shows that below 16 K, the stability deviates relatively far away from the set point compared to the deviation for set temperatures of 16 K and above. Below 16 K the relatively large deviations

are biased towards temperatures above the set temperature.

Vacuum chamber pressure

Figure 3.18 and Figure 3.19 show the stability of the vacuum chamber pressure at different conditions. One can conclude that the pressure in the chamber is stable under typical working conditions even as the neon flow rate is being increased. This indicates that the cryopumping by the heat shields works well.

Figure 3.18: Histograms of the pressure in the vacuum chamber as read from the pressure gauge at different neon flow rates and cell temperatures 17 and 20 K.

Figure 3.19: Histograms of the pressure in the vacuum chamber as read from the pressure gauge at different cell temperatures and ablation energies 24 and 12.1 mJ.

Ablation energy and neon flow rate stability

The stability of the ablation energy, the neon flow rate and the SF₆ flow rate were not measured in this work. The manufacturers specifications were used. The uncertainty of the pulse-to-pulse ablation energy is according to the manufacturer (Continuum) 4% at the wavelength used in this work, 532 nm. The energies at which the ablation laser is operated lie between 1.6 and 33 mJ and would give variations of ± 0.06 and ± 1.32 mJ respectively.

Both flow controllers were made by manufacturer Bronkhorst. The flow rate precision of the neon flow controller is given by the manufacturer as 0.5% of the readout and 0.1% of the full scale (50 sccm). For the SF₆ flow rate precision the manufacturer gives also 0.5% of the readout and 0.1% of the full scale (9 sccm). On top of the former flow rates uncertainties there is also a $\pm 0.06\%$ full scale error from the used voltage supply (Labjack T7 pro). The full scale of the Labjack T7 output is 0 to 5 V. The same holds for the full scale of the flow controllers.

3.6 Data Acquisition and Feedback System

To record and control parameters in the setup a data acquisition system (DAQ) was built. At the heart of the system are three commercially available data acquisition devices (Labjack T7 Pro) or in short T7 [99]. With this device 14 input analogue channels for voltages between -10 and 10 V can be read out from devices such as flow controllers and pressure gauges. To provide analogue output signals to for example flow controllers, there are two channels available for voltages between 0 and 5 V. There are 4 high speed edge counters available, with a counting frequency of 40 MHz. A schematic view of the data acquisition system of the source is shown in Figure 3.20.

The upper T7 (T7-1) is used for counting the PMT pulses on the high speed counter channel CIO2 and fast readout of the photodiode (PD) signal on analogue input channel AIN2. Although there are more channels on the T7s, only the channels used are noted. A trigger signal of 100 kHz is sent to the DAQ devices for external control of the acquisition rate. Beside the PMT and PD signal, the trigger of the ablation laser on channel DAC0 is also registered as 1 in case there is a detection or 0 when there is no trigger detected. The latter makes it possible to synchronise the detection data with the ablation shots during analysis. Although the external acquisition's trigger is 100 kHz, the maximum acquisition rate is ~ 33 kHz as three channels are being registered. The high speed counters count the number of detected edges in an input signal. To enable the PMT registered photons to be counted their signal shape had to be altered: First the signal is amplified with a pre amplifier (pre-amp) of 26 dB (Becker & Hickl HFAC-26dB), this amplified signal is converted to square signal of 15 ns width with a pulse discriminator (Physik. Institut Heidelberg, D435). The T7 was unable to distinguish such narrow pulses and so a gate generator (Physik. Institut Heidelberg, G43) was connected to the signal and converted the pulse width to 40 ns, but the output is a NIM (Nuclear Instrumentation Module/standard logic processor) signal. The NIM signal was converted to a TTL (transistor-transistor-logic) signal with a level converter (Physik. Institut Heidelberg, L49A). The pulses in the resulting signal were successfully counted by the T7.

The upper T7 is also used to send an analogue signal via channel DAC0 to the neon flow con-

Figure 3.20: Data acquisition and control system scheme, described in the main text.

troller in order to set the flow rate. After a set point voltage has been supplied a response signal of the flow controller is registered at channel AIN0. From this response signal the actual flow rate is calculated. For both the applied and response signal it holds that the maximum is 5 V. This maximum voltage is also the upper limit of the flow controller and channel DAC0. Their lower limit is 0 V. The middle T7 (T7-2) is used for the generation of two 20 Hz square wave signals on analogue outputs DAC0 and DAC1, relatively shifted by 225 μ s. The two signals are used as triggers for the flash lamp and Qswitch of the Nd:YAG ablation laser, the 225 μ s is the Qswitch delay after the flash lamp is triggered. Similar to the neon flow controller on T7-1, T7-3 controls the flow rate of SF₆ into the cell. Furthermore, the pressure gauge signal is read out by T7-3. The GND and SGND channels are used to connect the electric grounds of the different devices to a single ground.

Via Ethernet connections from the T7's to a personal computer (PC), using an Ethernet switch in between, the data stored in the T7's buffers is read out and stored on the PC in a home-made data format for later analysis. The temperature controller (M26, cryocon) and temperature monitor (M14, cryocon) are directly connected to the switch. The relevant temperatures registered by them are read out and stored on the PC in real time. With home-made programs using python and lua scripts, data acquisition and feedback is controlled via the PC. The detection laser stabilisation setup is a sub-acquisition system by itself and will be treated in Section 4.3.

3.7 Conclusion

The experimental setup for the production of SrF beams was build. Using a combination of commercial and home built data acquisition and feedback hardware and software, it was possible to stabilize and measure the experimental parameters such as the cell temperature and the buffer gas flow rate. From the measurements, it is shown that the setup can be operated at cell temperatures between 16 and 28 K with the average temperature deviations below 10^{-2} K, while ablating a target and flowing SF₆ of ~ 220 K into the cell—below 16 K, cell temperature's deviation from the set temperature increases to $\sim 10^{-1}$ at 14 K. The heat shields used to protect the cell against thermal radiation are able to reduce the heat load on the cell by $\sim 99\%$ to ~ 20 mW. The pressure in the vacuum chamber stays around 10^{-8} mbar during operation. The rotation motor used for target rotating is shown to enable effectively homogeneous target usage. Initially the target would cease translational movement once the target holder's threading would escape from the threaded plate via the top or bottom, but suitable adjustments marginalised this issue. One of the adjustments was the removal of threading on the target holder, effectively limiting the upward and downward target movement. The target catcher turned out to be very useful in making sure that the target did not detach from the rotation motor, but always stay in reach of the motor. The inner cell becomes dirty (as was shown in Figure 3.13b) after just 30-40 hours of use at high ablation energies and maintenance has to be performed to recover from a low molecular yield. In [73] months of usage without maintenance was reported—there seems to be some room for improvement regarding extension of the target use without maintenance. It was possible to create molecular beams by either ablating a solid target containing Sr or SrF₂ and in the next chapter the molecule detection methods and their application will be presented.

4

Detecting Molecules

Laser induced fluorescence (LIF) and absorption detection are widely used and proven methods for the detection of atoms and molecules. In case of LIF, the molecules passing through a laser beam are detected by their induced fluorescence. This provides for a quantitative state selective characterisation of the molecules. Absorption of photons by the molecules provides for an alternative detection. The application of the two methods will be described in this chapter. Expanding on an already existing setup in the laboratory, molecular beams are being detected using both LIF and absorption detection simultaneously. Because of the large number of states in a molecule and the presence of the molecules for a time longer than the excited state lifetime, cycling effects have to be taken into account for a quantitative determination of the number of molecules. Furthermore, by changing the frequency of the detection light, the setup allows for the addressing of different hyperfine states. The principle behind the detection scheme, the detection setup and the results from using this setup, are discussed in this chapter.

4.1 Molecular Level Structure

For detection, molecular energy transitions are employed in this work, in particular between the lowest two electronic states of SrF. Several rotational states within the lowest vibrational state of these two electronic states of the SrF molecule can be addressed. For the heteronuclear SrF molecule, the lowest state is the $X^2\Sigma^+$ state and the first electronically excited state is the $A^2\Pi_{1/2}$ state. The vibrational states are labeled by the vibrational quantum number v . The rotational states will be noted by the rotational quantum number N .

Figure 4.1: Hund's cases relevant for SrF. S is the total electron spin of SrF, L is the total angular momentum and $J = L + S$, Λ and Ω are the respective projections of S , L and J on the internuclear axis. N is the rotational angular momentum of the molecule [100]. K is the total angular momentum excluding spin.

There are four types of angular momentum in a free molecule, namely electronic spin (S), nuclear spin (I), orbital angular momentum (L) and the rotation of the molecule as a whole (N). The couplings of the different angular momenta to a set of 'good' quantum numbers are state dependent and for the $A^2\Pi_{1/2}$ and $X^2\Sigma^+$ states of SrF are best described by the so called Hund's cases (a) and (b), respectively. Hund's cases (a) and (b) are illustrated in Figure 4.1. The rotational angular momentum N is also shown. The rotational quantum number N , associated with the strength of N is used to label the rotational state of the molecule in the ground state

The nuclear spin I has not been considered yet. It gives rise to the hyperfine structure. The total angular momentum $F = J + I$ describes the spectrum. Since the nuclear spin of ^{88}Sr is $I_{\text{Sr}} = 0$, the nuclear spin of ^{19}F of $I_{\text{F}} = 1/2$ determines the hyperfine structure. For more details on the molecular structure and notation the reader is referred to [100].

Part of the molecular energy structure of SrF is shown in Figure 4.2. The solid black arrow indicates the transition primarily employed in the measurements throughout this thesis. The blue arrows indicate the possible decay transitions with their Franck-Condon factors noted [101]. The hyperfine energy structure for $N = 1$ is explicitly shown [102].

Figure 4.2: Relevant energy structure of SrF . Σ and Π represent the projection of the electronic orbital angular momentum on the internuclear axis for the X and the A electronic state, respectively. The superscript '2' stands for the total spin multiplicity given by $2S+1$. In both states $S = 1/2$, resulting in a multiplicity of 2. The letter v represents a vibrational state, N the rotational state, J the total angular momentum without the nuclear spin, F the total angular momentum and p denotes the state's parity. The energy differences between hyperfine states of $N = 1$ are also indicated.

4.2 Laser Induced Fluorescence and Absorption

The experiment was optimized for absorption detection and LIF via the transition $X^2\Sigma^+(v=0, N=1) \rightarrow A^2\Pi_{1/2}(v=0, J=1/2)$, but transitions from different rotational states N are also possible with the current setup.

Figure 4.3: Schematic representation of the optical setup for SrF detection. The light with a wavelength of 663.3 nm is required for the transition $X^2\Sigma^+(v=0, N=1) \rightarrow A^2\Pi_{1/2}(v=0, J=1/2)$ and produced by diode laser **DL1**. Light from **DL1** is split in to two parts. One part is sent to an electro-optic modulator **EOM** for the generation of sidebands to address the hyperfine structure of the transition. The other part of the light is sent to a Fabry-Perot cavity **cavity1** together with a helium-neon laser **HeNe** for frequency locking of **DL1**. Using optical feedback, the power of the sidebands is increased through the use of a secondary diode laser **DL2**. A tapered amplifier **booster** increases the power further. The amplified light is then send into the vacuum chambers where LIF and absorption detection are performed (see Figure 3.15). The measured signals are processed by a data acquisition and feedback system **DAQ & Feedback**. Several Faraday isolators **FI** are used in the setup for stable operation. With **cavity2** the frequency mode spectrum of **DL2** is monitored.

Figure 4.3 shows a schematic representation of the optical setup for preparation of the required laser light for detection. Light with a wavelength of 663.3 nm for the transition $X^2\Sigma^+(v=0, N=1) \rightarrow A^2\Pi_{1/2}(v=0, J=1/2)$ is produced by a laser diode (HL6545MG, Opnext) embedded in a tunable extended cavity diode laser setup **DL1**. The laser power can be increased by diode laser

DL2 of which the frequency is controlled by **DL1** through optical feedback. A custom made tapered amplifier (Toptica Photonics BoosTA_00267) **booster** provides for higher power levels.

Two scannable Fabry-Perot cavities, **cavity1** and **cavity2**, are used for monitoring the frequency mode spectrum of the diode lasers. Each cavity has two semi-transparent curved mirrors, and at their exit there are photo diodes attached to read out the outgoing light intensity. The output of **cavity1** is used for frequency stabilisation of the light from **DL1** (see Section 4.3). According to the manufacturer, the finesse of **cavity1** is ~ 250 . The mirrors in **cavity2** have a reflectivity of $r > 0.999$ in the wavelength region 600 - 980 nm and have a curvature radius of 1 m, resulting in the finesse of **cavity2** to be ≥ 1770 . The finesse F for **cavity2** was calculated from the following equation:

$$F = \frac{\sqrt{\pi} r}{1 - r} \quad (4.1)$$

The cavity **cavity2** provides for a higher frequency resolution. The cavity **cavity1** is used in combination with a stable helium-neon (HeNe) laser to acquire information on the frequency stability of the diode laser **DL1** so that the laser frequency can be stabilised in frequency via a feedback system. Fine-tuning of the laser is discussed in Section 4.3.

A wavelength meter **WLM** (HighFinesse WS6) is used to measure the wavelength of the light. The light is guided to two detection regions—namely the LIF chamber, where fluorescence spectroscopy is performed and the absorption chamber, where absorption spectroscopy is done. Both chambers are connected together in the same vacuum system.

The resulting signals from both cavities photodiodes, the PMT (**PMT**) and the photodiode (**PD**) are sent to a data acquisition and feedback system (**DAQ & Feedback**) to be stored and analysed. The latter is described in Section 3.6 and Section 4.3.

Figure 4.4: A schematic view of the fluorescence and absorption detection laser beams crossing the molecular beam (blue circles) from the cell. Absorption detection is done 5 mm after the cell exit and the fluorescence detection 31.1 cm after the cell exit.

The positions of the detection laser relative to the cell is illustrated in Figure 4.4.

Figure 4.5: EOM transmission measured from the transmission of **cavity2**, when the EOM (**EOM**) is a) off and b) when it is on.

For simultaneous excitation of all hyperfine components of the $N = 1$ state, four frequency sidebands are required. The frequency differences between the hyperfine states are shown in Figure 4.2. An electro optical modulator (EOM) **EOM** (JENOPTIK PM660) in the optical setup is employed to provide evenly spaced frequency sidebands.

A sinusoidal voltage $V = V_0 \sin(2\pi \cdot f_{SB} \cdot t)$ is supplied to the EOM. This writes a phase modulation onto the electro-magnetic wave, which results in sidebands separated by $f_{SB} = 42.5$ MHz. At $f_{SB} = 42.5$ MHz a good overlap of the hyperfine structure is possible. Figure 4.5 shows a measured spectrum of **cavity2** with the EOM on and off. With a modulation amplitude of $V_0 = 5$ V the amplitude of the signal in Figure 4.5a becomes distributed over the newly created sidebands as shown in Figure 4.5b. This method of amplifying a multi-frequency laser beam from an EOM with a secondary diode laser (**DL2**) is similar to what was done in [103].

4.3 Frequency Stabilisation

The laser determining the optical frequency in the optical setup is **DL1**. The laser diode produces light with wavelengths between 652 and 664 nm. A diffraction grating stabilizes the frequency and can be tuned to the molecular transition frequency.

The diode and grating are embedded in an external cavity diode laser in Littrow configuration (ECDL) [104, 105, 75] (Figure 4.6). The angle θ and the cavity length of the ECDL determine the output frequency and permits stable single mode operation of the ECDL. The cavity length can be modified with a Piezo element attached at the backside to push against the grating holder. On a long time scale the frequency is sensitive to pressure and temperature changes in its environment and mechanical drifts. To reduce the thermal variation in the system, a Peltier element is used to control the temperature of the diode, this element is installed beneath the main stage and thermally anchored to it. A copper block forms the base of the installation and acts as a heat sink through which excess heat from the system can be dumped and it is thermally anchored to the backside of the Peltier element. To further reduce unwanted environmental effects, the laser construction is shielded by an aluminium enclosure. The temperature of the Peltier element is controlled by a diode laser controller (**DLC**) (Moglabs, DLC-202). A Faraday isolator (**FI**)

Figure 4.6: Illustration of the design of **DL1**. An external cavity diode laser (ECDL) in Littrow configuration with a piëzo driven diffraction grating to select the desired frequency at the output. The coupling of the laser output into **cavity1** is also illustrated, together with the data acquisition and laser control devices

is used to prevent light coupling back into the diode, which can lead to unwanted optical feedback and unstable frequency output.

To compensate for frequency drifts, a computer controlled feedback system similar to [106] was built to alter the ECDL cavity length with the Piëzo via the DLC. The output of the diode is guided into a confocal scanning Fabry-Perot cavity (Thorlabs SA200-5B) (**cavity1**). After the semi-transparent output mirror of the cavity, a photo diode (**PD1**) measures the transmitted light. The voltage output of the photo diode is read out using an Analog-to-Digital Converter (ADC) from a data acquisition card (**DAQ card**). In the same cavity, light from a commercial stabilized helium-neon (**HeNe**) laser (Thorlabs HRS015B) is coupled (Figure 4.3). The HeNe laser has a specific stability of 1 MHz drift over 60 minutes. **cavity1** is used as an optical spectrum analyser (OSA). While scanning the cavity length L , a resonance for the confocal cavity arises when the following condition holds:

$$4L = n \cdot \lambda, n \in \mathbb{N}, \quad (4.2)$$

where the distance $4L$ refers to the fact that due to the cavity geometry and laser alignment a photon in the cavity traverses the cavity 4 times before arriving back at its initial position.

The frequency difference between consecutive resonances is called the free spectral range (FSR) and is given by:

$$FSR = \frac{c}{4L}, \quad (4.3)$$

where it has been used that $\lambda = 4L/n$ and c is the speed of light in the medium (air) in the cavity.

Figure 4.7: A measured spectrum of the scanning Fabry-Perot cavity **cavity1**. HeNe resonances (labelled mode n and mode $n+1$) at scan times t_0 and t_1 correspond to two resonances of the HeNe laser **HeNe**, differing by 1 FSR. The peak at scan time t_d corresponds to diode laser **DL1**. T_{01} is the time difference between the two **HeNe** resonances and T_d the time difference between the first **HeNe** resonance and the **DL1** resonance.

For the cavities used in this work $FSR = 1500$ MHz. Figure 4.7 shows the spectrum of **cavity1**, with its corresponding resonances noted by their source lasers. The horizontal axis indicates the time scale on which the cavity scanning was driven.

A variation of the frequency of the laser light will result in a change of the relative position of the resonances. These variations are expected to be caused by temperature and pressure variations and mechanical drifts, all with different typical time scales. Assuming the cavity parameters are constant over time, the horizontal coordinates of the HeNe resonances (t_0 and t_1) are expected to be stable over time with the same stability as the HeNe laser. A variation of the cavity properties will vary t_0 , t_d and t_1 , but as long as the diode laser follows the pattern of the HeNe resonances, the frequency is considered stable in this work. The latter is a reasonable assumption that the wavelength difference between the HeNe and the diode laser is relatively small. **cavity1** is stable enough for relevant time scales (~ 1 hour). To transfer the stability of the **HeNe**

laser to **DL1**, the two stable HeNe resonances are used as references and **DL1** resonance coordinate t_d will be locked to the relative time difference between the HeNe resonances T_{01} . The parameter to be locked is noted as ζ and given by:

$$\zeta = \frac{T_d}{T_{01}}. \quad (4.4)$$

The parameter ζ is continuously measured and whenever it deviates from a setpoint ζ_0 , a voltage proportional to the deviation from ζ_0 is applied to the Piëzo element at the back of the grating. This voltage V_{fb} is given by:

$$V_{fb} = \kappa_{\delta\zeta} \cdot \delta\zeta, \quad (4.5)$$

where $\delta\zeta = |\zeta - \zeta_0|$ and $\kappa_{\delta\zeta}$ is a $\delta\zeta$ dependent parameter that determines how strong the feedback is. The position of the grating is then slightly changed, adjusting the output wavelength until $|\delta\zeta|$ falls within a desired accuracy. A homebuilt LabVIEW program executes the stabilisation. The parameters κ , ζ_0 and the desired locking accuracy can be set. For more stable behaviour in the stabilisation frequency, the program reduces $\kappa_{\delta\zeta}$ automatically (linearly) with increasing $|\delta\zeta|$ and decreases in a similar way if the $|\delta\zeta|$ increases. The LabVIEW program records and saves the spectral data from the cavity, from which ζ and V_{fb} are determined. V_{fb} is applied via an (ADC) to the Piëzo.

Because the free spectral range represents the frequency difference between the HeNe peaks, the scan time can be converted to relative frequency with:

$$\text{relative frequency} = \frac{t_{\text{scan}} - t_0}{T_{01}} \cdot FSR, \quad (4.6)$$

where t_{scan} is the cavity scan time. Figure 4.8 shows the scan time spectrum of Figure 4.7 converted to a frequency spectrum.

Figure 4.8: Spectrum of **cavity1** (as shown in Figure 4.7) in terms of the relative frequency.

Variation of the spectral position of the reference HeNe resonances and the diode laser resonance relative to their initial spectral positions are shown in Figure 4.9. The diode laser is locked to the reference from the HeNe laser by actively keeping $\delta\zeta$ constant. The deviation of the frequency with $\delta\zeta$ is shown in Figure 4.10 for the frequency stabilised diode laser. The feedback gain has been determined from stability measurements.

Figure 4.10 shows the result of a measurement of the frequency deviations δf away from the locking point as function of time. The definition of δf is given by:

$$\delta f = \frac{|t_d - t_0|}{T_{01}} \cdot FSR, \quad (4.7)$$

The locking accuracy was set to be within 2 MHz of a desired setpoint. The deviations away from the locking point are consistently below 2 MHz and have a full-width-half-maximum spread of

Figure 4.9: Variation of the spectral position of the **HeNe** laser modes (n) and ($n+1$) and the **DL1** laser mode in the Fabry-Perot cavity **cavity1** due to thermal and pressure drift of the cavity length

Figure 4.10: a): Frequency deviation δf of the locked diode laser **DL1** from the desired locking point. The laser was locked to be within 2 MHz of the desired locking point. b): Histogram of the deviations.

~ 0.15 MHz. Lower deviations are possible, but one becomes more sensitive to faster fluctuations and more frequent demand for a feedback voltage V_{fb} . The application of feedback can cause additional instability if the feedback is not synchronised well with the fast frequency fluctuations, so there is a limit to the locking accuracy. From experience in the lab, the most stable behaviour was found to be at accuracies between of 1 and 2 MHz.

A low locking strength is applied when the laser frequency is relatively far away from the setpoint and increases as the feedback brings the laser frequency closer to its setpoint. This feature allows for automatic correction if the laser is significantly disturbed, without mode hopping. If the laser frequency falls within the desired accuracy no feedback is provided. In practice the locking strength will keep oscillating between a few values, depending on the desired accuracy, when the deviations are close to the desired accuracy.

To study spectral properties of molecules, the locking program has the flexibility to scan the setpoint ζ_0 between two points with the step size set by the user. The laser locking system has been in use for several years now and is typically locked for several hours of experiment time. One frequently occurring limitation to the locking is the cavity length drift, which changes the spectral positions of all the resonances simultaneously, to an extent that they sometimes move out of the data acquisition time interval. Once they move out of this interval they cannot be tracked and thus not be locked. This is being corrected manually once in a while (~ 1 hour) by

adjusting the offset in the length of the cavity. Automating this process in the future would remove this inconvenience.

4.4 Spectroscopy of Rotational States

The $X^2\Sigma^+(v=0, N=1) \rightarrow A^2\Pi_{1/2}(v=0, J=1/2)$ is observed using laser induced fluorescence by recording the fluorescence as function of the laser frequency over a range of 30 GHz. With the same LabVIEW program used for frequency stabilization, the setpoint ζ_0 as defined in Equation 4.4 was scanned. With the setpoint the detection laser (**DL1**) frequency is also scanned at regular intervals. During the scan the fluorescence from consecutive molecular beams was continuously measured.

Figure 4.11: Measured Hyperfine structure spectrum of rotational states a) $N=1$ and b) $N=2$. ζ_0 represents the varying locking setpoint of the laser stabilisation software.

The measurements performed have confirmed the hyperfine structure in the rotational states $N=1$ to 7. For every setpoint ζ_0 fluorescence is collected for ~ 5 minutes. Figure 4.11 shows the results for the $N=1$ and 2 states.

Figure 4.12: Molecular beam spectroscopy for rotational states $N = 1$ to 7 , approximated by a fit to multiple Lorentzian line shapes. f_{off} is the the offset of the laser frequency in MHz. The error bars are the standard deviation from the average of multiple measurements. The resonances are numbered from 1 to 4.

Figure 4.12 shows the different molecular signal strengths as functions of the detection laser frequency for $N = 1$ to 7 . The laser frequencies are given relative to an offset frequency f_{off} on a wavelength meter. The spectra in Figure 4.12 are approximated by Lorentzian distributions, given by:

$$S(f) = A \frac{\Gamma/2}{(f - f_0)^2 + (\Gamma/2)^2}, \quad (4.8)$$

where Γ is the full-width-at-half-maximum (FWHM) of the distribution and f_0 the centre frequency of the distribution, all in units of natural frequency. By comparing the frequency differences between the peaks in the spectra with literature values [107] and the spectrum simulating

software package PGOPHER [89], a rotational number N was assigned to each spectrum. The widths of the resonances are widened by power broadening.

The spectra permit the extraction of the rotational state dependent splitting of the J levels and the ground state hyperfine structure.

Figure 4.13: Estimated resonance frequencies of the hyperfine structure in rotational states $N = 1$ to 7, using the Lorentzian fits in Figure 4.12. On the vertical axis from bottom to top, the order of the data points corresponds to the resonance number 1 to 4.

Table 4.1: Estimated frequency differences (in MHz) between hyperfine levels of different rotational states N , extracted from the Lorentzian fits in Figure 4.12. The resonance numbers (1 to 4) are shown in Figure 4.12. The transition frequency for the hyperfine levels are given between brackets [107].

N	difference between hyperfin resonances		
	1 and 2	2 and 3	3 and 4
1*	31.9 ± 0.3 [41]	96.3 ± 2.7 [74]	28.6 ± 2.8 [55]
2 [†]	37.0 ± 0.7 [45]	152.6 ± 1.0 [140]	56.7 ± 1.0 [51]
3 [†]	45.7 ± 1.2 [45]	214.6 ± 1.8 [216]	55.5 ± 1.8 [52]
4 [†]	43.1 ± 1.3 [50]	281.8 ± 1.3 [289]	50.5 ± 1.0 [47]
5 [†]	42.1 ± 1.5 [47]	375.8 ± 1.5 [363]	57.3 ± 1.4 [51]
6 [†]	52.2 ± 2.4 [48]	428.4 ± 2.9 [437]	65.4 ± 2.3 [50]
7 [†]	55.4 ± 2.6 [47]	604.7 ± 3.1 [513]	71.7 ± 2.1 [49]

The extracted frequency difference between the consecutive hyperfin resonances are summarized in Table 4.1. The frequency differences between the measured hyperfin resonances for $N = 1$ do not match with literature and simulation. The reason for this has not been traced back and might be in the measurement process. The other results are closer to the PGOPHER simula-

*Values between brackets obtained from [107]

[†]Values between brackets obtained from PGOPHER [89]

tion outcomes. simulation results. The PGOPHER result for the $N = 1$ state is (in the same order as the columns of Table 4.1): 1 and 2: **52** MHz, 2 and 3: **69** MHz, 3 and 4: **44** MHz.

The population distribution over the rotational states N satisfies a Boltzmann distribution if the molecular beam has an equilibrium rotational temperature T_r . The distribution is then given by:

$$\text{pop}(N) = A(2N + 1) \exp \left[\frac{-B_0 N(N + 1)hc}{k_B T_r} \right], \quad (4.9)$$

where B_0 is the rotational constant of the $v = 0$ level, h is the Planck constant, c the velocity of light in vacuum (unit = cm/s), k_B is the Boltzmann constant, N the rotational state and A an amplitude constant.

From the rotational spectra data the population in each rotational state is obtained. Figure 4.14 shows the total population at different rotational states N . Fitting the data against Equation 4.9 shows good agreement. A rotational temperature of the molecules is estimated to be 9.30 ± 0.59 K, where $B_0 = 0.25 \text{ cm}^{-1}$ [108]. The $N = 7$ result has not been included, because it was not fully scanned over all hyperfine levels.

Figure 4.14: Population versus rotational state N , fitted to a Boltzmann distribution.

As the detection laser power is increased scattering of more photons by one molecule becomes possible.

Figure 4.15: a) Time-of-flight profiles and b) the molecular fluorescence at different detection laser powers. This shows that saturation has not been reached with the applied detection laser powers. The $1/e^2$ laser beam diameter was set to 1 mm for this measurement.

The molecular signal as function of the detection laser power has been measured using a $1/e^2$ laser beam diameter of 1 mm and the results are shown in Figure 4.15. As the laser power

increases so does the total signal, but no saturation is reached in the applied laser power range. It is thus possible to have a higher signal if one increases the laser power further.

Figure 4.16: a): Histogram of the molecular beam fluorescence. The signal is measured separately when the EOM was on and when it was off to show the effect of addressing the sidebands. b): The signal was also measured during time periods where no fluorescence was expected.

The fluorescence from the SrF beam has been measured on the $X^2\Sigma^+ \rightarrow A^2\Pi_{1/2}$ transition (Figure 4.16) with sidebands from the EOM (blue) and with a single laser frequency (black). The increase of factor ~ 8 shows that all hyperfine components can be addressed with optical sidebands. As expected no significant difference in the background signals was seen.

4.5 Counting Molecules

The number of molecules detected from the source can be deduced from both the fluorescence and absorption detection signals. Here we describe the quantitative evaluation from the experiment data.

4.5.1 Using Fluorescence Detection

In case of determining the number of molecules from the fluorescence detection signal, one has to know how many detected photons are scattered off a single SrF molecule. A simplification of the SrF energy spectrum to a three-level spectrum was made to arrive at an estimate for LIF and absorption detection measurements. The three level system consists of a ground, excited and a lost state noted as the accessible, excited and inaccessible state. Except for a small fraction of molecules $\mathcal{P}_{el}$ decaying from the excited state to the inaccessible state, the transitions into the inaccessible state are not detectable by the photon detection system (PMT). Once a molecule enters the inaccessible state it cannot be addressed any more by the detection laser. A more general approach which can in principle include all levels and transition moments is described in Appendix B.

The simplified three level energy structure is shown in Figure 4.17. Using a detection laser beam with a $1/e^2$ diameter of 3 mm and a power of 1 mW, the number of scattered photons per molecule is found to be around $N_s = 9.8$, assuming perfect overlap between the sidebands from the EOM and the hyperfine transitions in the $N = 1$ state of SrF (see calculation details in Appendix B). This assumption seems justified by the results shown in Figure 4.16, that switching on the sidebands yielded a ~ 8 times higher signal.

Figure 4.17: 3-level energy system based on the energy structure of SrF and the available detection laser in the current experimental setup. The respective probabilities for the decay channel to occur are also shown for each channel. The accessible state consists of all the states which can be excited by the laser. The excited state is the $A^2\Pi_{1/2}$ state and the inaccessible state consists of all the states to which the molecule can decay to but unable to be excited by the laser. The derivation of this figure is discussed in Appendix B.

According to the simplified model, using sidebands should increase the number of scattered molecules by a factor of about 7.5.

By dividing the number of detected photons by the number of scattered photons per molecule one obtains the number of molecules. Not all the photons scattered are detected by the LIF detection system and a number of correction factors have to be estimated. The number of detected photons is limited by: the detection efficiency of the PMT η_{dev} , only a fraction η_{opt} of the scattered light is transmitted via the collection optics into the PMT, only scattered light in a solid angle Θ_{sol} can be detected with the setup. Furthermore, the molecular beam spreads out transversely before reaching the LIF detection region. Only a fraction η_{cross} of the molecules are passing through the detection laser beam of $1/e^2$ radius $r_0 = 3$ mm.

Taking the number of scattered photons per molecule and the above mentioned limitations into consideration, the number of produced molecules M_{mols} can be estimated by:

$$M_{\text{mols}} = \frac{N_{ph}}{N_s} \frac{1}{\eta_{\text{cross}}} \frac{1}{\eta_{\text{dev}}} \frac{1}{\eta_{\text{opt}}} \frac{4\pi}{\Theta_{\text{sol}}}, \quad (4.10)$$

where N_{ph} is the total number of photons counted by the PMT. For typical molecular beams created in this work, a list containing the estimated values for the above mentioned parameters is shown in Table 4.2.

Table 4.2: Typical values for the parameters in equation (4.10). More on this table can be found in Appendix B

parameter	value
η_{dev}	0.33
Θ_{sol}	1.1 sr
η_{opt}	0.9
N_s	9.8
η_{cross}	$1.1 \cdot 10^{-4}$

The fluorescence signals representing the highest achieved fluorescence rates in this work for respectively Sr and SrF₂ ablation are shown in Figure 4.18. The figure shows around $\sim 10^6$ photons detected per shot for Sr and $\sim 10^3$ for SrF₂ ablation.

Figure 4.18: Number of detected photons versus ablation shots for Sr and SrF₂ ablation, obtained from fluorescence detection.

Using the methods in Appendix B, estimates for the number of molecules per steradian per shot $\mathcal{B}$ and the total molecular yield per shot M_{mols} in the $X^2\Sigma^+(v=0, N=1)$ state are given in Table 4.3. The number of molecules per steradian per shot $\mathcal{B}$ has been added here for comparison with other cryogenic sources.

Table 4.3: Estimated beam brightness and number of produced molecules in the state $X^2\Sigma^+(v=0, N=1)$ from both SrF₂ and Sr ablation.

	SrF ₂	Sr
$M_{\text{mols}} (\text{shot}^{-1})$	$\sim 10^6$	$\sim 10^9$
$\mathcal{B} (\text{sr}^{-1} \text{shot}^{-1})$	$\sim 10^7$	$\sim 10^{10}$

4.5.2 Absorption Detection

In case of absorption detection, the signal with the highest absorption was obtained from ablating a Sr target. An averaged absorption signal over ~ 3000 ablation shots is shown in Figure 4.19. This absorption signal was obtained while the sidebands were switched on. To calculate the number of molecules from the absorption signal, one has to calculate the Doppler shift for each sideband and their individual contribution to the absorption signal. To avoid such complication, the absorption signal should be measured at a single transition with the sidebands off. A method to obtain the number of molecules per shot for the latter case is presented in Appendix B, using two different absorption signals, representing the highest yields obtained with the ablation of a Sr target.

Figure 4.19: Absorbed fraction α of detection light versus time after Sr ablation, using absorption detection. This time-of-flight profile is averaged over ~ 3000 shot-to-shot time-of-flights. The maximum absorbed fraction is around 8%.

4.6 Conclusion

The laser light of the wavelength needed for detection, 663 nm, was produced using a home-made diode laser. Using a home built frequency locking system, it was possible to stabilise the diode laser frequency to a commercial stabilized helium-neon laser within 2 MHz. Part of the hyperfine structure of SrF was confirmed by using the frequency scanning functionality of the setup. The experimentally obtained rotational spectra from the $N = 1$ to 7 state were compared and found to be in agreement with the results from a spectrum simulating software package PGOPHER, except for the $N = 1$ case. The hyperfine splitting of the $N = 1$ rotational state did not yield the structure expected from literature. That is probably due to yet to identify problems during the measurements. The molecular beam's rotational temperature was determined from the measured signal strength of transitions originating from several rotational states.

Furthermore, the detected molecular signal was increased ~ 8 fold, using an electro optical modulator to address the hyperfine states of the $N = 1$ rotational state.

Estimating the maximum number of detected molecules in the $N = 1$ state, using LIF, resulted in $\sim 10^{10}$ molecules per steradian per ablation shot and a total of $\sim 10^9$ molecules per shot. This number of molecules satisfies the requirement of the NL-eEDM experiment, but it still should be investigated how to produce these molecules for a prolonged time. Such high yield as shown in Figure 4.18 could only be sustained for roughly half an hour before settings for the ablation process had to be adjusted in order to sustain the yield. Furthermore in light of the NL-eEDM

program the transfer of the finding from SrF production to BaF from a barium target has to be done. A comparison to results from other cryogenic sources is shown in Table 4.4.

Table 4.4: Yields reported from different buffer gas sources, with their beam velocities

Molecule	buffer gas	rate (Hz)	yield ($\text{sr}^{-1} \cdot \text{shot}^{-1}$)	velocity (m/s)	reference
SrF	He	1	$1 \cdot 10^{11}$	140	[88]
ThO	He	10	$3 \cdot 10^{11}$	160	[93]
ThO	Ne	10	$1 \cdot 10^{11}$	180	[93]
CaF	He	2	$5 \cdot 10^{10}$	150	[73]
SrF	Ne	10	$\sim 10^{10}$	$190^{\ddagger}$	This work

The CaF source has a similar cell design as the one used in this work. One can see that both sources produce a similar number of molecules, but at different molecular beam velocities.

[‡]The typical beam velocity was obtained after coupling the cryogenic source to a travelling-wave Stark decelerator, as treated in Chapter 7, and measure the resulting time-of-flight t profil .

5

Molecular Beam Properties from SrF_2 Ablation

In Chapter 4 it was shown by means of absorption and fluorescence detection that the cryogenic source produces molecular beams of SrF . In this chapter relevant characteristics of the produced molecular beams are determined. The characterisation is done by extracting information from measured time-of-flight (TOF) profile. In particular there are the molecular beam arrival time and its spread, yield and time variation of distributions resolved for the molecular quantum states. Other characteristics can be derived from the TOF, such as the beam velocity and its spread.

Measurements have been performed at a series of experimental conditions. Beams generated from SrF_2 ablation will be discussed in this chapter. The measurements will be extended to beams originating from Sr metal ablation, aided by SF_6 gas, in the next chapter—Chapter 6. We investigate how in particular the cell temperature, buffer gas flow rate, ablation energy and spot size affects the molecular beam properties. Changing the cell temperature can effectively be considered as changing the buffer gas temperature, assuming full thermalisation of the molecules, buffer gas and the cell. Due to the pulsed nature of the laser ablation process, the molecules arrive at the detection zone within a certain time interval and repeat periodically with the ablation repetition rate. Throughout the experiments an ablation rate of 10 pulses per second is maintained. The length of the ablation pulse and other experimental conditions are not covered in this work. Their effect might be important, but not all of them are accessible in the current experimental setup and/or left out of this work to be investigated at a later time. In Section 5.1 the characteristics of time-of-flight measurements are discussed. The extracted beam properties presented in Section 5.2 and in Section 5.3 molecular yields are presented. Finally conclusions based on the results of this chapter are given in Section 5.4.

5.1 Time-of-flight Profiles

TOF profiles are used as evidence for successfully creating molecular beams. The information extracted from the TOF profile allows for optimizing parameters of the source, in order to provide a slow, cold and intense molecular beam occupying a chosen quantum state. From these TOF profile transverse beam properties are not accessible. In some cases the TOF shows a distribution consisting of multiple distinguishable peaks in the arrival time. These peaks will be referred to as modes.

After molecular formation the molecules spent some time τ_{cell} in the cell, thermalizing with the buffer gas, to be finally entrained in the resulting molecular beam. Once out of the cell the molecules and the buffer gas have formed a mixed species beam. The beam then passes the detection zones. Although there might be several species originating from the ablation process, only the fluorescence from a selected transition is detected. Other species pass by without contributing to the TOF profile. Both the absorbed light registered by the photodiode and the photon count rate registered by the PMT trace out the molecular density overlapping their detection laser beams. The profile in Figure 5.1 shows that the densest part of the molecular beam arrives ~ 0.15 ms after target ablation in the absorption detection zone—5 mm away from the cell exit. The data in this figure was obtained from the ablation of a Sr metal target and is used here to mainly introduce the concepts related to the TOF analysis. For the SrF₂ ablation no simultaneous LIF and absorption detection data was available.

Figure 5.1: Time-of-flight (TOF) profiles obtained with respectively absorption detection, 5 mm after the cell exit, and fluorescence detection, 311 mm after the cell exit. Both signals shown are the average TOF profile, extracted from ~ 1000 ablation shots. The results were obtained at the following experimental settings target = Sr + SF₆, cell temperature = 17 K, neon flow rate = 9 sccm and SF₆ flow rate = 0.5 sccm.

TOF profiles obtained with the two available detection methods (absorption and fluorescence detection) from the same molecular beam are shown in Figure 5.1. The signal from absorption measurements shows a fluctuation for times larger than 1.5 ms due to electronic interference.

The average absorbed signal $\langle \alpha \rangle$, is given in terms of the absorbed fraction α of light by the molecules, obtained from N ablation shots:

$$\langle \alpha \rangle(t) = \langle \text{absorption fraction} \rangle(t) = \frac{1}{N} \sum_{n=1}^N \frac{\overline{bg_n} - \alpha_n(t)}{\overline{bg_n}}, \quad (5.1)$$

where $\overline{bg_n}$ is the time average background signal of the n^{th} TOF, $\alpha_n(t)$ is the time dependent absorbed signal after the n^{th} ablation shot.

Similarly, the average net fluorescence signal $\langle \text{pmt count} \rangle$, obtained from the photons counted by the PMT, pmt count, minus the background photons, is defined as:

$$\langle \text{pmt count} \rangle(t) = \frac{1}{N} \sum_{n=1}^N (\text{pmt count})_n(t) - \overline{bg_n}, \quad (5.2)$$

where $(\text{pmt count})_n(t)$ is the time dependent number of photons counted for the n^{th} ablation shot. The background signal is measured in a region of the TOF where no molecular signal is expected. The flight signal seen beyond 4 ms continues until the next ablation occurs after 100 ms. The average background $\overline{bg_n}$ is subtracted in the graphical representation.

As the molecules travel further, part of the beam reaches the fluorescence detection zone. At this time some of the molecules with large enough transverse velocities have spread out of reach for the fluorescence detection volume and will not be detected. Around 1.5 ms after target ablation the densest fraction of the beam arrives in the fluorescence detection volume. Moreover, the molecules that comprise the densest part arriving at the absorption detection zone are not necessarily the same molecules that will be detected as the densest part when arriving at the fluorescence detection zone. Broadening of the TOF profile is observed as the molecules travel from the absorption zone into the fluorescence detection zone. Faster and slower molecules spatially separate from each other as they travel through space and time, revealing the evolution of the TOF profile into a terminal profile.

With the obtained information from the TOF distributions the velocity v_0 corresponding to the maximum in $\langle \alpha \rangle(t)$ and $\langle \text{pmt count} \rangle(t)$ can be estimated. The arrival time is measured relative to the ablation time, so that the arrival time of the densest part at the absorption zone can be written as $t_{\text{ab}} \approx 0.15$ ms and its position from the exit of the cell is $x_{\text{ab}} = 5$ mm. Similarly for the fluorescence detection zone one can write $t_{\text{fl}} \approx 1.5$ ms and $x_{\text{fl}} = 31.1$ cm as the respective arrival time and position of the fluorescence detection zone.

There are then three simple methods to estimate the beam velocity.

1. One can use the absorption TOF resulting in

$$v_b \approx \frac{x_{\text{ab}}}{t_{\text{ab}}} \approx 33 \text{ m/s}. \quad (5.3)$$

2. Using the fluorescence TOF:

$$v_b \approx \frac{x_{\text{fl}}}{t_{\text{fl}}} \approx 207 \text{ m/s}. \quad (5.4)$$

3. It is also possible to combine both TOFs to obtain the following result:

$$v_b \approx \frac{x_{fl} - x_{ab}}{t_{fl} - t_{ab}} \approx 227 \text{ m/s.} \quad (5.5)$$

Assuming full thermalization of the molecules before extraction from the cell and using (3.19) leads to the beam velocity in the cell being $v_{cell} \sim 63 \text{ m/s}$. This is also the minimal molecular beam velocity. After the exit the velocity is expected to be boosted higher than $\sim 63 \text{ m/s}$, but instead (5.3) results in a lower beam velocity. The problem here lies in the erroneous calculation method—it was assumed that $\tau_{cell} \approx 0$, but the time spent by molecules inside the cell is not negligible. The maximal beam velocity is given by (5.5), 227 m/s . Using the minimal and maximal velocity, a lower and upper limit for τ_{cell} can be set. The arrival time t_{ab} is composed of the τ_{cell} and the time required to travel x_{ab} after the cell t_5 .

$$t_{ab} = \tau_{cell} + t_5 = \tau_{cell} + \frac{x_{ab}}{\langle v_5 \rangle}, \quad (5.6)$$

where $\langle v_5 \rangle$ is the average velocity of the molecules between the cell exit and the absorption detection zone. Inserting the minimal and maximal beam velocities results in the average time most molecules spent in the cell:

$$0.07 < \tau_{cell} < 0.13 \text{ ms.} \quad (5.7)$$

Approximations of the velocity become less accurate with decreasing measurement distance away from the cell. The above calculation means that an underestimation between $\sim 5\%$ and $\sim 10\%$ arises in the velocity calculation when the fluorescence TOF is used (5.4). In the next subsections the qualitative aspects of TOFs, obtained at different experimental conditions are discussed. All the next measurements described in this section are obtained from ablating a SrF₂ target.

5.1.1 Ablation Fluence

The ablation process is the initial step in the molecular beam formation. To see how the ablation energy deposition on the target influences the TOF, a set of experiments for different ablation fluences* have been performed. With the current experimental setup the fluence can be varied in two ways: via the ablation laser power output or via the ablation laser spot size on the target. In the experiment the most accessible handle is the ablation laser power. While varying the power a series of time-of-flight measurements have been performed at two different laser spot sizes.

Starting with a spot size of 0.5 mm on the target, the ablation laser power output was varied between 12 and 240 mW . This corresponds to ablation fluences between 0.6 and 12.2 J/cm^2 and deposition energies between 1.2 and 24 mJ . The results are given in Figure 5.2a. Switching to measurements at a 1 mm spot size, the power was varied between 67 and 330 mW or correspondingly, ablation fluences between 0.9 and 4.2 J/cm^2 and deposition energies between 6.7 and 33 mJ . Figure 5.2b shows the results of the latter experiment. For the 0.5 mm spot size

*Fluence is the intensity of energy deposition on the target, with units of J/cm^2 .

Figure 5.2: Fluorescence time-of-flight profiles using two different ablation spot sizes and several ablation fluences. The results were obtained with the following experimental settings: target = SrF_2 , cell temperature = 20 K, neon flow rate = 9 sccm.

measurements every TOF profile shown, was obtained from the average of ~ 2000 consecutive shot-to-shot TOFs, corresponding to ~ 3 minutes of measurements. At 1 mm spot size the integration and averaging was performed over ~ 3000 shots. Figure 5.2a shows that at a spot size of 0.5 mm, fluences of 6.2 J/cm^2 and lower produce relative symmetric molecular density distributions in time. Above 6.2 J/cm^2 a significant asymmetry becomes apparent. A similar behaviour can be observed for a spot size of 1 mm, but the asymmetry becomes visible above 2 J/cm^2 . In both cases the TOF distribution of the molecular beam becomes broader as the fluence increases. The increased energy deposition in the ablation products might be responsible for this behaviour.

As the fluence is increased the distributions become considerably asymmetric along the time axis—a second and even a third mode seemingly appears as part of the distribution for both spot sizes. The visible transition from a single mode to a multi-mode distribution occurs between 4.6 and 6.2 J/cm^2 and between 2.4 and 3.1 J/cm^2 for 0.5 and 1 mm spot size respectively. The transition appears for pulse energies between 9 and 12 mJ and between 12 and 16 mJ for the respective spot sizes. Furthermore, as the fluence and deposited energies increase, the most probable arrival time of the distribution decreases, hinting towards higher kinetic energies of SrF molecules. The multi-mode nature of the TOFs have been observed before in pulsed laser deposition (PLD) measurements: [109, 110, 111, 112, 113]. This behaviour was also observed in a supersonic molecular source [114].

Figure 5.3: Single shot time-of-flight profiles for a) 6.2 J/cm^2 and for b) 12.2 J/cm^2 . Both figures are extracted from the data used in Figure 5.2a

To explore the possibility of the multi-mode nature being a product of accumulated TOFs with varying arrival times of the peak, time-of-flight profiles of single shots, extracted from the data of Figure 5.2a, are shown in Figure 5.3. For both fluences it is visible that although the area under the distribution fluctuates, the modal shape of the TOF is maintained through all the shots—proving that the multi-modal distribution is not due to instability in the molecular beams arrival time.

Figure 5.4: Density plot of the time-of-flights, extracted from the first 500 shots used to build the TOF histogram in Figure 5.2a at 12.2 J/cm^2 .

A density plot displaying all time-of-flight profiles for the first 500 shots extracted from the 12.2 J/cm^2 data of Figure 5.2a are shown in Figure 5.4. From the first 10 ms it is visible that there are fluctuations in the molecule ablation yield. These fluctuations might give the impression that there are shifts in the arrival time. It is more likely that as the signal decreases, so do the edges of the distribution. Furthermore, there is a periodicity in the signal strength of ~ 50 shots or ~ 5 seconds, of which the origins will be discussed in Subsection 5.3.4.

Other research [115, 116] suggests that the multi-mode phenomena can be explained as follows:

1. The energy deposited by the laser is absorbed by the target surface, creating a plume of plasma consisting of neutrals, ions and electrons.
2. The plume expands with time and the lightest particles (electrons) diffuse outward faster than the ions, creating two separated charge regions with opposite charge. What naturally follows is an induced electric field between the two regions. If among the ions there are particles of different masses and/or charges, multiple charge and/or mass regions will be created apart from the neutrals, resulting in multiple modes.
3. The electric field accelerates the ions toward the electron region and decelerates the electrons. Away from the target surface the density of particles is relatively low, allowing the ions and electrons to oscillate between the two different regions until a collective velocity is reached.
4. Both the multi (charged) layers and their oscillatory nature contribute to the multi-mode nature of the molecular beam. Adding a background gas such as neon can alter the structure of these layers, depending on the background gas pressure [111].

If the induced electric field causes the oscillation and splitting of the ablated plume, then the splitting and oscillatory behaviour can be manipulated by the flow rate of SF_6 into the cell. Naturally one would expect the earliest arriving peak is correlated to ions with the most positive charge as they accelerate faster outward [111]. Furthermore, it was found that the wavelength of the ablation pulse determines the prominence of double layer effects—at shorter wavelengths (e.g. 532 nm) the double layer effects are more prominent compared to longer wavelengths (e.g. 1064 nm), due to higher ion yields at shorter wavelengths [111].

5.1.2 Cell Temperature

Subsection 5.1.1 revealed that the TOF mode structure depends on the energy deposition on the target. How the temperature of the buffer gas adds to the already complicated relation between TOF and ablation energy/fluence will be studied in this subsection by varying the cell temperature. The cell temperature is varied by varying the current through the resistive heater attached to the cell, this in turn varies the temperature of the cell. For all the experiments in this section the ablation laser energy was set to 19.1 mJ at a spot size to 1 mm—corresponding to a fluence of 2.4 J/cm^2 . The TOF signal is recorded from the molecular fluorescence. According to Figure 5.2b, two modes are expected in the TOF profile for these settings.

Figure 5.5 displays the TOF results from the cell temperature variations. The cell temperature is being lowered from 25 to 14 K in steps of 1 K, while maintaining the neon (buffer gas) flow rate at values 3, 10 and 20 sccm. For every temperature set point, the target is ablated ~2500 times and the average PMT count (pmt count) TOF profile is obtained from the resulting TOFs. At all neon flow rates a temperature dependent splitting of the TOF in two distinct modes is observed. As the cell temperature increases the two modes seem to merge into a single mode distribution.

The temperature dependence seems to be correlated to the buffer gas flow rate. As the buffer gas flow rate increases a higher cell temperature is required to enter the single mode regime. In the density plots of Figure 5.5, the projection of the total TOF signal over the course of the

Figure 5.5: 3D (left) and density (right) representations of time-of-flight profiles as function of cell temperature, at neon flow rates of Ne flow = 3, 10 and 20 sccm. Projections of the total profile are plotted on the top and right hand side of the density plots.

measurement is plotted on top. The integrated TOF signal as function of the cell temperature is projected on the right hand side of the main density plots. The arrival times of the different modes seems to converge to the average of their individual arrival times as the temperature is increased. Below 15 K the molecular signal vanishes, likely caused by freezing of the buffer gas inside the cell. From the projected signal on the right hand side of the density plot, it can be concluded that the total molecular signal increases with temperature until a saturation point is reached around 23 K.

5.1.3 Buffer Gas Flow

In the previous subsection, it was shown by varying the cell temperature at three different flow rates of buffer gas, that there is a significant effect of the buffer gas flow rate on the TOF profile of the molecular beam. In the next measurements the buffer gas flow rate is varied at several cell temperatures while the TOF is recorded from the molecular fluorescence.

Figure 5.6: 3D (left) and density (left) representations of time-of-flight profiles as function of the neon flow rate, at cell temperatures $T_{\text{cell}} = 16, 22$ and 28 K . Projections of the total profile are plotted on the top and right hand side of the density plots.

Similar to the experiments in Subsection 5.1.2, the ablation fluence is 2.4 J/cm^2 and the spot size set to 1 mm for all the experiments in this subsection. Also here two modes are expected in the TOF profile. For every flow rate set point ~ 2500 ablation shots are fired. Figure 5.6 shows a 3D plot (left) and a density plot (right) of the molecular beam TOF profile as function of the neon flow rate in the cell at different cell temperatures. The flow rate is changed in steps of 4 sccm.

The cell temperature dependence yield follows the same trend as in Subsection 5.1.2. At high cell temperatures the dual-mode structure becomes less apparent. From the above results and those in Subsection 5.1.2, it can be concluded that the mode distribution is strongly governed by a combination of buffer gas flow rate and cell temperature—increasing buffer gas flow rate increases the signal amplitude, decreasing the cell temperature lowers the signal and by increasing the flow rate, merging of the two modes occurs at higher cell temperatures.

Figure 5.7: Time-of-flight versus neon flow rate at cell temperature $T_{\text{cell}} = 22 \text{ K}$.

Even if reproducible trends are observed in the TOF when varying the cell temperature and buffer gas flow rate, the conditions of the target itself also play a large role. This cannot always be controlled in the experiment. As an example the TOF profile for a cell at temperature 22 K was measured on a different date compared to the one shown in Figure 5.6. All other conditions were similar, except that the target used for the former results was replaced and the neon flow rate step size set to 1 sccm. Figure 5.7 shows that the results are similar to those presented in Figure 5.6, but that the signal amplitude is now the highest for the earlier arriving mode, contrary to the earlier measurement. The variation in signal strength appearing along the flow rate axis, might be attributed to inhomogeneities of the target surface—similar to Figure 5.4a. The inhomogeneities might be introduced during the target preparation process or during the laser ablation and the target rotation.

5.2 Molecular Beam Properties

Considering that the source will be coupled to a Stark decelerator with a limited velocity acceptance in the next stage of the experiment [24, 25], a molecular beam of low velocity and small velocity spread is beneficial for maximal deceleration yield. In this section the influence of the experimental handles on these properties is studied. We present a model for the TOF profile in order to extract estimates for the molecular beam velocity, its spread and the translational beam temperature.

If the molecular beam is in thermal equilibrium it is expected that its velocity distribution can be described by a shifted Maxwell-Boltzmann distribution (SMB), which can be derived from the Boltzmann density distribution equation:

$$f(E)dE = A \cdot \exp \left[-\frac{E}{k_B T} \right] dE, \quad (5.8)$$

where E is the energy of the particle, A is a normalization constant, k_B the Boltzmann constant and T the molecular beam temperature. Substituting the kinetic energy of the particles for E and normalizing the integral, results in the Maxwell-Boltzmann velocity distribution for one dimension:

$$f(v)dv = \frac{1}{\beta\sqrt{\pi}} \cdot \exp \left[-\frac{v^2}{\beta^2} \right] dv, \quad (5.9)$$

and

$$f(v)dv = \frac{4}{\beta^3\sqrt{\pi}} \cdot v^2 \cdot \exp \left[-\frac{(v - v_0)^2}{\beta^2} \right] dv, \quad (5.10)$$

for 3 dimensions, where

$$\beta = \sqrt{\frac{2k_B T}{m}}, \quad (5.11)$$

and f is proportional to the spatial density of the particles, v is the velocity of the individual molecules, m their mass and v_0 is the molecular beam velocity here.

The absorption and the laser induced fluorescence provide for a signal which is proportional to the molecular fluence ϕ [117] and thus given by:

$$\phi(v)dv = \frac{B}{\beta^3\sqrt{\pi}} \cdot v^3 \cdot \exp \left[-\frac{(v - v_0)^2}{\beta^2} \right] dv, \quad (5.12)$$

where B is a constant to be adjusted to the measured fluence data.

The molecules that are able to reach the detection zone are assumed to have negligible velocities in the transverse directions compared to the longitudinal direction, as the size of the detection zone is $\sim 10^{-3}$ m and the detection zone distance from the cell exit is much further away. The velocity distribution is then reduced to a single dimension. For this case the one dimensional Maxwellian distribution in (5.9) will be assumed as the distribution for the number of molecules arriving at the detection zone. For this one dimensional model the flu equivalent is given by:

$$\phi(v_l)dv_l = \frac{B}{\beta\sqrt{\pi}} \cdot v_l \cdot \exp\left[-\frac{(v_l - v_0)^2}{\beta^2}\right] dv_l. \quad (5.13)$$

The subscript of v_l represents the longitudinal direction. Note that now β in (5.11) will only depend on the longitudinal temperature component $T_{||}$ inducing the transformation:

$$T \Rightarrow T_{||}. \quad (5.14)$$

In the experiment, not the velocity of the molecules, but the arrival time t of the photons is registered. The time for the photons to travel from the molecule to the PMT is negligible compared to the arrival time of the molecules in the detection zone. From this arrival time one can estimate $v_l = L/t$ and $v_0 = L/t_0$. L is the distance the molecular beam travelled before arriving at the detection zone. Using $dv_l = L/t^2 dt$, equation (5.13) becomes:

$$\phi(t)dt = X \frac{L^2}{t^3} \cdot \exp\left[-\frac{L}{\beta} \cdot \frac{t - t_0}{tt_0}\right]^2 dt, \quad (5.15)$$

where t_0 is the beam arrival time and X a constant to be adjusted to the data. In the limit where $t_0 \approx t$ i.e. in case the TOF measurements are done before the beam expands significantly, the SMB distribution can be approximated by a Gaussian:

$$\phi(t)dt = X \frac{L^2}{t_0^3} \cdot \exp\left[-\frac{L}{\beta} \cdot \frac{t - t_0}{t_0^2}\right]^2 dt. \quad (5.16)$$

Rewriting (5.16) in the general form of a Gaussian function:

$$\phi(t)dt = A \cdot \exp\left[-\frac{1}{2} \left(\frac{(t - t_0)^2}{\sigma_t^2}\right)\right] dt, \quad (5.17)$$

with the standard deviation in time σ_t given by:

$$\sigma_t = \sqrt{\frac{k_B T_{||} t_0^4}{m L^2}} = \frac{t_0^2}{\sqrt{2} L} \beta. \quad (5.18)$$

The above derivations are partly based on [118].

5.2.1 Error Estimation

For the best fit estimation of the data to (5.15) and/or (5.17), the Levenberg-Marquardt fitting algorithm [119] incorporated in the `scipy.optimize` package in Python is used [120]. This package also determines the errors in the estimated parameters t_0 , $T_{||}$, X or A together with a χ^2 value, which assumes the standard deviation on each data point to be unity. The latter simplification is good enough for our purpose, just to compare the relative goodness of fit of the SMB and Gaussian fit methods using the same experimental data.

From a general variation in velocity δv away from a measured velocity v , the variation in arrival time δt in terms of δv and v is given by:

$$\delta t = \frac{L\delta v}{v^2} \quad (5.19a)$$

$$\delta v = \frac{L\delta t}{t^2}. \quad (5.19b)$$

This results in a standard deviation in arrival time σ_t :

$$\sigma_t = \frac{L\sigma_v}{v^2}. \quad (5.20)$$

As described in the beginning of this chapter, molecular beam velocities can be estimated using the velocity of both the absorption and fluorescence signal. The fluorescence TOF will be used to estimate the molecular beam velocity. The velocity spread σ_{v_0} will be derived from a shifted Maxwell-Boltzmann or Gaussian fit to the TOF data and its translational temperature $T_{||}$ from (5.11) or (5.18). Whether to use the SMB or Gaussian distribution to fit the data is decided by which results in the best goodness of fit (χ^2) values. The fact that some molecules scatter more photons than others is considered to be negligible here. Gaussian distributions have been proven to describe narrow molecular pulses from supersonic beam sources very well [24, 25].

5.2.2 Ablation Fluence

In Subsection 5.1.1 it was shown in Figure 5.2 that the ablation fluence influences the time structure of the beam. The temporal spread is correlated to the velocity spread by equations (5.19) and (5.20). The spread can be expressed in terms of the translational temperature from (5.18) or (5.11). Up to an ablation fluence of 6.2 J/cm² in 0.5 mm spotsize a single Gaussian or shifted Maxwell-Boltzmann distribution suffices to estimate the molecular beam properties. Beyond that multiple modes appear.

Figure 5.8 displays Gaussian and shifted Maxwell-Boltzmann(SMB) functions fitted to fluorescence data for different ablation fluences. The figure shows that the SMB functions describe the data less accurately compared to the Gaussian functions. Beyond a fluence of 6.2 J/cm² multiple Gaussians are required to describe the TOF profile. There is a transition from requiring a minimum of one Gaussian, to two and finally three Gaussians to describe the data as the fluence is increased. Although more Gaussian components always provide a better description, the approach is useful to distinguish between different operation regimes of the source.

Figure 5.8: Gaussian and shifted Maxwell-Boltzmann (SMB) functions fitted to measured time-of-flight data at several applied ablation fluences. Above 6.2 J/cm^2 the profile cannot be described by a single Gaussian or SMB function and multiple functions of the same kind are used for the fit. The fits to data taken at low fluence (0.6 and 1.3 J/cm^2) are less reliable because of their low signal to noise ratio. The experimental settings are: ablation spot size = 0.5 mm , cell temperature = 20 K , Ne flow rate = 9 sccm , target = SrF_2 . The multiple components that comprise the Gaussian fit are also shown.

Interesting beam properties extracted from the (multi) Gaussian fit to the data are the most probable arrival time of the molecules t_0 and its spread σ_{t_0} , and the longitudinal translational beam temperature $T_{||}$. Other useful properties such as the beam velocity, v_0 and its spread σ_{v_0} , are derived assuming the molecules travel primarily longitudinal over a distance $L = 0.311 \text{ m}$ before reaching the fluorescence detection zone. The extracted beam properties are summarized in Figure 5.9 together with a plot of the χ^2 values of both fit to the data (Gaussian (Gauss) and shifted Maxwell-Boltzmann (SMB) function). The properties are extracted for all the components of the Gaussian fit. The goodness of fit values (χ^2 values) become worse as the molecular beam approaches the multi-modal regime. The χ^2 values can be used to estimate where a modal transition occurs. Although there are estimated properties for fluences below 3.4 J/cm^2 , they are less reliable compared to properties at higher fluences as the molecular yield is very low and difficult to fit properly. Furthermore, the velocity of the different modes in the beam are

Figure 5.9: Parameters derived from an analysis with Gaussian functions fitted to the fluorescence time-of-flight profiles at different ablation fluences. The estimated arrival time and its standard deviation t_0 and σ_{t_0} ; the estimated velocity and its standard deviation v_0 and σ_{v_0} ; the translational temperature $T_{\parallel}$ and the goodness of fit χ^2 values are shown. If multiple Gaussian modes appear at a certain fluence, multiple colours are used to indicate the different modes throughout the different graphs. Other experimental settings: ablation spot size = 0.5 mm, cell temperature = 20 K, Neon flow rate = 9 sccm and target = SrF_2 .

estimated to vary between 150 and 400 m/s with the fluence. The slowest component in the multi-fit is seemingly constant at ~ 150 m/s, regardless of the ablation fluence, while the other components are at higher velocities.

The molecular production process creates molecules in a number of molecular rotational states—this was shown in Chapter 4. To see how the beam properties evolve for different rotational states, measurements of the TOF for rotational states $N = 4, 5$ and 6 have been performed at different ablation fluences. The hyperfine structure of the rotational states was not considered in these measurements. Before each measurement the laser frequency was altered until the maximum yield was obtained for the rotational state N .

Figure 5.10: Time-of-flights fitted to multiple Gaussian (Gauss) and shifted Maxwell-Boltzmann (SMB) distributions at several ablation fluences and rotational states ($N = 4, 5$ and 6). The Gaussian components of the fit are also shown. Other experimental settings: ablation spot size = 1 mm, cell temperature = 20 K, Neon flow rate = 9 sccm and target = SrF_2 .

In Figure 5.10 the results of the measurements are shown. The modal transitions for all the states occur at similar fluences. The single to double mode transition appears between 2 and 2.4 J/cm^2 . The profile at 2.0 J/cm^2 already suggests a transition in the shape of one or more of the TOFs. The yield is notably different for the different states, more on this will be discussed in Section 5.3. It is visible that the lower the rotational state N , the higher the yield for fluences below 2.0 J/cm^2 . When the fluence is increased further the yields increase further, but become more similar for the different rotational states. This indicates an increasing rotational temperature with increasing fluence.

The molecular beam properties derived from the multiple Gaussian fit are summarized in Figure 5.11, for several rotational states the properties are shown—the colours refer to the state while the different arrival marker shapes distinguish the multi-mode components from each other. Based on their arrival times, the modes are marked as early, later and late in a separate legend. For all the measured molecular states, the properties follow the same pattern—the states, in order of increasing velocity, are $N = 4, 5$ and 6 for all the modes. Furthermore, it is shown that

Figure 5.11: Molecular beam properties derived from multiple Gaussian fits at different fluences for rotational states $N = 4, 5, 6$. The colour legend (upper left) refers to the rotational state, while the marker legend (upper right) refers to the multiple component relative arrival times.

higher fluences induce higher translational temperatures $T_{||}$ of the molecules. The higher the fluence the earlier the molecules arrive at the detection zone, with gradually decreasing arrival time spread. The modes differ in estimated arrival times and velocity, but are similar in the time and velocity spreads σ_{t_0} and σ_{v_0} respectively. Also the ratio between the estimated velocity and its spread are mode independent when the fluence is varied.

5.2.3 Cell Temperature

The data described in Subsection 5.1.2 will be analysed here. The molecular beam properties are calculated after each set of experimental parameters. First we analyse the cell temperature dependence of the molecular beam properties, while the neon flow rate into the cell is maintained at 3 sccm.

Figure 5.12: Neon flow rate: 3 sccm. Time-of-flight profiles (shaded areas) fitted separately with a two peak Gaussian and a two peak shifted Maxwell-Boltzmann (SMB) function. The neon flow rate is kept at 3 sccm, while the cell temperature is varied. The solid lines inside the shaded area are shifted Maxwell-Boltzmann components from the multi fit. The vertical scale is the same for all the TOF profiles.

A double mode structure is observed in the fluorescence TOF profile at all temperatures. The results of these measurements are fitted to both a double peak Gaussian and a double mode SMB distribution and are shown in Figure 5.12. The blue solid curves inside the shaded areas are tracing out the SMB fit components. The amplitudes of both peaks increase together with the total area under their curve, as the cell temperature increases up to around 23 K. The ratio between the mode amplitudes also changes with the cell temperature—with a higher magnitude for the early component at cell temperatures below 24 K. For higher cell temperatures the late component dominates. The short pulse at time ≈ 0 ms is the ablation laser light registered by the PMT—signalling the ablation pulse. As the cell temperature increases, the temporal overlap between the two components increases, up to what seems to be developing into their complete merger.

Figure 5.13: Neon flow rate: 3 sccm. a): Arrival times derived from the multi-mode shifted Maxwell-Boltzmann (SMB) distribution fit. The different markers are used to distinguish the arrival times of the two modes. b): The goodness of fit in the form of χ^2 , derived from both the SMB and Gaussian function fit is shown for comparison.

The arrival times of the two modes derived from SMB fitting are shown in Figure 5.13. The χ^2 values show that the SMB is a better fit to the data compared to the Gaussian fit, especially at higher cell temperatures.

Figure 5.14: a-0): **Neon flow rate: 10 sccm.** Time-of-flight profiles (shaded area) fitted to double Gaussian and shifted Maxwell-Boltzmann profiles at different cell temperatures, while maintaining the neon flow rate at 10 sccm. a-1): The corresponding goodness of fit values for both fits. b-0): **Neon flow rate: 20 sccm.** Time-of-flight profiles fitted to double Gaussian and shifted Maxwell-Boltzmann profiles at different cell temperatures, while maintaining the neon flow rate at 20 sccm. b-1): corresponding goodness of fit values. The solid blue curves in the time-of-flight plots are the SMB fit components.

Figure 5.14 shows the time-of-flight profile and their fit at neon flow rates of 10 and 20 sccm (left), together with their χ^2 values on their right. The same double mode structure seen before in the 3 sccm measurements, is also visible at both flow rates. As the flow rate is set to 20 sccm, the two mode structure is also visible but the degree of overlapping is less than at 3 and 10 sccm. The χ^2 plots show consistently a better goodness of fit for the SMB fit. A closer look at the TOF profile in Figure 5.14, seems to suggest the emerging of a third mode between the two fitted modes at cell temperatures above 19 K. For 10 sccm this can be seen between cell arrival times 1.5 ms and 1.8 ms. For 20 sccm a third mode can be seen to evolve in the same time interval at 21 K. The worsening goodness of fit are a good indication for the emergence or disappearance of modes in the TOF profile.

Using the SMB fit, other molecular beam properties such as the temporal spread σ_{t_0} and its translational temperature $T_{||}$ are derived. The lower beam temperatures are achieved for the late modes, while the opposite is true for the early modes. Figure 5.15 shows the derived properties at different cell temperatures and neon flow rates. The ratio between the arrival time and

Figure 5.15: Summary of molecular beam properties derived from the multi component shifted Maxwell-Boltzmann fit for selected cell temperatures at 3, 10 and 20 sccm buffer gas flow rate. For both the relatively early and late arriving modes the beam properties are derived. This figure contains a legend for the colours used (upper left) and one for the different markers used (upper right).

its spread is the same as the ratio between the beam velocity and its spread σ_{v_0}/v_0 and is also displayed. As the cell temperature increases, the arrival time of the modes converges towards a value close to 1.8 ms, equivalent to a velocity of ~ 180 m/s. The translational temperature $T_{\parallel}$ initially increase with the cell temperature, but after a cell temperature of 24 K the $T_{\parallel}$ decreases at all neon flow rates. For the late modes there is an interesting pattern showing the transition cell temperature for the beam to go from an increasing $T_{\parallel}$ to a decreasing $T_{\parallel}$ depends on the neon flow rate. The transition cell temperatures are 19, 21 and 23 K for neon flow rates 20, 10 and 3 sccm respectively.

5.2.4 Rotational States

Further analysis was performed on the influence of the cell temperature on the beam properties of molecules occupying the rotational states $N = 8, 4, 5$ and 6 . For these experiments the neon flow rate was set to 9 sccm and the ablation fluence to 2.0 J/cm^2 with an ablation spotsize of 1 mm.

Figure 5.16: Time-of-flight profiles (shaded area) fitted to double Gaussian and shifted Maxwell-Boltzmann profiles for the rotational states $N = 8, 4, 5$ and 6 . The cell temperature is varied, while the neon flow is maintained at 9 sccm. The vertical scale is different for each of the subfigures.

The different TOF profile in Figure 5.16 show the cell temperature effects on molecules in rotational states $N = 8, 4, 5$ and 6 . Their time-of-flight profile shape seems to be similar—the most significant difference comes from the relative change of the area under the consecutive profile.

Figure 5.17: Summary of beam properties derived from equation (5.15), while the cell temperature was varied and measurements performed in different rotational states. The colours refer to the rotational state and the markers to the relative arrival times of the two beam components—late and early.

Figure 5.17 shows that for all the rotational states, the beam properties follow the same pattern as function of cell temperature. There seems to be no significant difference between the beam properties for $N = 4, 5$ and 6 .

5.2.5 Buffer Gas Flow

The analysis on the properties of the cryogenic source beam are extended to varying the neon flow rate between 3 and 40 sccm at different cell temperatures T_{cell} , the results of these experiments are discussed in this subsection.

At a cell temperature of 16 K, a two mode structure is clearly visible in Figure 5.18. The signal here is lower than the fluorescence signals described at other experimental conditions in this section. As discussed before, this is probably because of the low vapour pressure of neon buffer gas at $T_{\text{cell}} = 16$ K. Furthermore, as the flow rate is varied the molecular beam is not stable, because the signal fluctuates in width, amplitude and arrival time of the modes without a clear pattern.

When the cell temperature is kept at 22 K and the flow rate is increased, the two mode temporal separation becomes clearly visible at 17 sccm and higher, as can be seen from Figure 5.19. This separated double mode seems to be emerging from a more overlapping structure. As the flow rate increases there is a sudden change of profile shape from 17 sccm on. Although a two mode fit seems an adequate fit, it is clearly visible that from 25 sccm a noticeable 'bump' is emerging

Figure 5.18: Gaussian and shifted Maxwell-Boltzmann double mode fits to time-of-flight data for different neon flow rates, while the cell temperature is kept at 16 K.

Figure 5.19: Gaussian and shifted Maxwell-Boltzmann double peak fits to time-of-flight data for different neon flow rates, while the cell temperature is kept at 22 K.

at the right hand side of the last arriving mode. Ideally one would like to account for a possible emerging third mode. A three mode SMB fit can be used, but its uniqueness cannot be guaranteed as the prominence of the third mode is relatively small. Nonetheless this emergence has

a significant influence on the accuracy of the extracted beam properties. The figure shows that with the emergence of a later arriving mode, the fitting of the second mode becomes poorer. Given the acquired knowledge from the TOF measurements with respect to the ablation parameters in Subsection 5.2.2 it is possible to conclude that an increased ablation fluence would likely enhance the emergence of the third peak. An increasing flow rate seems to enhance or induce the visibility of a more complicated mode structure.

Figure 5.20: Gaussian and shifted Maxwell-Boltzmann single peak fits to time-of-flight data for different neon flow rates, while the cell temperature is kept at 28 K.

For a cell temperature of 28 K, Figure 5.20 shows seemingly single mode TOF profiles as function of the neon flow rate.

The beam properties derived from the SMB fit at the different flow rates and cell temperatures are summarized in Figure 5.21. The general trend seems to be that as the flow rate increases, the arrival time difference between the modes, first increases and later it decreases slowly. For the single mode molecular beam at $T_{\text{cell}} = 28$ K, there is a transition from being a late mode to an early mode as the flow rate increases. The relatively larger uncertainties in the beam properties when $T_{\text{cell}} = 16$ K are also visible. Properties at the latter temperature show that the influence of the neon flow rate on the beam properties is small compared to data at higher temperatures. This could be due to the fact that the neon gas has a low vapour pressure [90] at this temperature and starts freezing more than actually flowing—and so adding more neon does not result in more flow. Here one can also see that the ratio between the mode velocity v_0 and its spread σ_{v_0} is almost independent of neon flow rate and cell temperature for all modes. The same holds for the velocity spread itself. The translation temperature of the molecules decreases at the higher neon flow rates, as one can expect at higher buffer gas densities. The higher $T_{||}$ values at 22 K are probably the result of inadequate fitting of the data (see Figure 5.19).

Figure 5.21: Beam properties derived from the SMB fits from Figure 5.19, Figure 5.20 and Figure 5.18, The colours refer to the cell temperatures at which the data was taken and the markers to the different beam modes.

5.3 Molecular Yield

Two requirements for the source are stable and high molecular beam yields. The different parameters of the setup are used to optimize the yield and its stability over time. The yield dependency on the ablation fluence, the cell temperature and the buffer gas flow rate will be presented here, using the data discussed in Section 5.2. Furthermore the effect of the cell temperature and ablation energy on different rotational state populations is also investigated. Molecular yields are obtained by integrating the time-of-flight signal as obtained from equation (5.2).

5.3.1 Ablation Fluence

The ablation spot size on the target together with the pulse energy affect the resulting yield—this has been found in Subsection 5.1.1. For spot sizes 0.5 and 1 mm the yields have been measured. At energies between 10 and 24 mJ a larger yield is obtained with the 1/2 mm spot size, but for higher energies both spot sizes result in similar yields. This can be seen from Figure 5.22. These results also contain uncertainties due to the deteriorating target surface, which have not been incorporated in the analysis.

Figure 5.22: Molecular yield in the $N = 1$ state as function of the ablation energy for spot sizes 1/2 and 1 mm. The error bars are the standard error.

Furthermore, it seems that the yield approaches saturation around 24 mJ, independent of spot size. With the ablation laser set to a spot size of 1 mm and varying the energy from ~1.2 to 24 mJ, corresponding to fluences of ~0.9 to 4.2 J/cm², measurements have been performed on how the yields of molecules in rotational states $N = 4, 5$ and 6 are affected. Figure 5.23 shows the yields in different rotational states as function of the ablation fluence.

Figure 5.23: Molecular yield as function of the ablation fluence for rotational states $N = 4, 5$ and 6. The ablation spot size is 1 mm.

The molecular states are populated equally to the same order. This is especially valid for states $N = 4$ and 5, the yield in state $N = 6$ is consistently lower. The figure shows a clear threshold behaviour for the molecular yield. Furthermore the yield saturates at high fluence providing a narrow range for the operational parameters. The measurements are done in such a way that the measurement sequence is repeated for every fluence, instead of keeping the rotational state constant and vary the fluence in one measurement series. This will reduce yield bias towards a single state.

The average yield per ablation shot has been measured and summarized in a yield histogram shown in Figure 5.24. For a spot size of 1 mm, energies below 12.1 mJ show little to no sign of molecule production. Comparing the latter with the yield at 0.5 mm spot size shows that the energy threshold for production is between 6.7 and 9.1 mJ. At 6.7 mJ there is no notable yield at 0.5 mm spot size. Figure 5.24b also shows a yield histogram, but with the spot size set to 1 mm and the yield in different rotational states. There is no notable yield at and below 1.2 J/cm^2 . Considering the shape of the distributions, if the molecular production and cooling is stable, a Gaussian distribution is expected. From Figure 5.24 and Figure 5.24b it is visible that as the ablation energy grows the signal becomes increasingly non-Gaussian. More on the yield stability will be discussed in Subsection 5.3.4.

(a) $N = 1$: Shot-to-shot yield at different ablation spot sizes and fluences.

(b) Spot size = 1 mm: Shot-to-shot yield histogram at different ablation energies and detected in rotational states $N = 4, 5$ and 6 . The color legend refers to the rotational state.

Figure 5.24

5.3.2 Cell Temperature

To see how the cell temperature influences the population in the molecular state $N = 1$, the yield has been measured as a function of cell temperature at several neon flow rates. The results are shown in Figure 5.25. For the individual modes in the multi-mode TOF distribution, the respective yields have been estimated using the area under the modes of the fit in Section 5.2.

Figure 5.25: a): Molecular yield versus cell temperature (T_{cell}) at neon flow rates 3, 10 and 20 sccm. b): The yield of the individual modes in the TOF are estimated from the SMB fit components. The order of the items in the colour legend from left to right represents the order of measuring.

The largest yield is obtained at 3 sccm, the yields at other flow rates are lower, but it could be due to target degradation—as the order of the measurements was 3, 10 and finally 20 sccm. Later measurements using absorption detection and presented in Chapter 7 show that the yield is higher at higher flow rates, thus resulting in the lowest yield at 3 sccm and the highest for 20 sccm. Up to $T_{\text{cell}} = 24$ K, the same trend is followed by all the three flow rates, the maximum yield is achieved at around 24 K for all the flow rates. The yield estimation of the individual modes is shown in Figure 5.25b. As the T_{cell} is increased at flow rates 10 and 20 sccm, the early component yield seems to become higher than the late one, but at 3 sccm there is no significant difference.

Figure 5.26: a): Molecular yield versus cell temperature T_{cell} detected at rotational states $N = 6, 5, 4$ and 8 . b): Yield of the individual modes in the time-of-flight, estimated from shifted Maxwell-Boltzmann (SMB) fit components.

The effect of the cell temperature on the population in different rotational states derived from the data is shown in Figure 5.26. The outcome suggests that a higher cell temperature increases the population in all states. The yield in $N = 5$ seems to fluctuate above 23 K. If the states are placed in order of decreasing yield the order becomes $N = 4, 5, 6, 8$ for all temperatures except at 25 K, where the population in $N = 5$ is the lowest. The order of the measurements performed by state is 6, 5, 4 and then 8. Compared to the results in Figure 5.23, these results again confirm that the order of decreasing particle production by population is 4, 5, 6. The early and late mode yields obtained from a double peak SMB fit are shown in Figure 5.26b. From this it is shown that the lowest measured rotational state $N = 4$ (lowest) is the most populated regardless of the cell temperature applied here.

5.3.3 Buffer Gas Flow

To thermalize the molecules, the number of collisions with the buffer gas is an important parameter, this parameter is proportional to the buffer gas density at a fixed cell temperature.

Figure 5.27: a): Molecular yield versus neon flow rate at cell temperatures 16, 22 and 28 K. b): Yield of the individual components in the time-of-flight, estimated from shifted Maxwell-Boltzmann (SMB) fit components.

If there is no freezing of the buffer gas, the density is assumed to be proportional to the flow rate into the cell. It partly determines how many molecules end up in the rotational states utilized for the yield measurements. The estimated yield as function of the neon flow rate at different cell temperatures is shown in Figure 5.27a. The two early and late mode yields, estimated from a double peak SMB fit, are shown in Figure 5.27b. From these plots it can be concluded that the yield saturates at a cell temperature dependent flow rate—higher cell temperatures require higher flow rates and provide higher yields.

5.3.4 Stability

Following the example of Figure 5.24, it is interesting to look at the shot-to-shot details, as they give insight into the stability of the yield. There are different time scales of the temporal variation of the molecular yield. Here we discuss first the time scales corresponding to the target rotation (1-10 s). From Figure 5.24 it was visible that the shot-to-shot yield distribution of detected photons by the PMT becomes increasingly wide as the ablation fluence increases. The distribution also becomes multi-modal. To see the stability of the yield, shot-to-shot yields have been measured for several experimental conditions.

The shot-to-shot fluorescence at different cell temperatures, while maintaining the neon flow rate at 3 sccm, is shown in Figure 5.28a. Figure 5.28b shows the yield at different neon flow rates, while the cell temperature is maintained at 28 K. A periodicity in the yield is visible in both figures, the period is independent of flow or cell temperature. The period corresponds to roughly the number of ablation shots fitted in the time the ablation target completes a up or down rotation cycle. This target rotation time is ~ 60 s or 600 shots.

Figure 5.28: a): Shot-to-shot yield vs cell temperature at a neon flow of 3 sccm.
 b): Shot-to-shot yield at a cell temperature of 28 K.

To see whether there is any influence on the yield stability in different rotational states, their shot-to-shot yield is plotted in Figure 5.29. Here the target rotation has been increased to ~ 1200 shots for a one way rotation down or up. Figure 5.29 shows that while the target is being ablated there is a reduction in yield, the gradient of this reduction seems to be the highest at $N = 6$, followed by $N = 4, 8$, and 5 . This relatively fast reduction has been observed whenever a new target has just been placed in the source.

Before these measurements the target was already used for an estimated 20 hours over several days, nevertheless there was still a decay of the yield on time scales of a minute as the target was getting used up. One explanation for this fast deterioration might be the fact that this target was judged to be softer than previous targets used, due to a shorter baking time. According to Figure 5.30 the background is reasonably stable during the measurements. There is only a small increase for the $N = 6$ measurement compared to the others. Furthermore, there is an obvious fine structure in the shot-to-shot PMT signal with a periodicity of ~ 100 shots or 10 seconds. The fine structure can be seen in all the measurements, on top of the ~ 1200 shots periodicity, but is more pronounced in the $N = 8$ measurement.

Histograms showing the distribution of the yield and background signal are displayed in Figure 5.31. From these results there seems to be no correlation between the shot-to-shot stability of the yield and the rotational state, as one would expect.

Figure 5.29: Number of net photon counts registered by the PMT after every ablation shot, from molecules in the $N = 4, 5, 6$ and 8 state. Experimental settings: cell temperature = 25 K , neon flow = 9 sccm , ablation energy = 15.8 mJ with spot size of 1 mm .

Figure 5.30: Number of background photon counts registered by the PMT after every ablation shot for molecules in rotational states $N = 4, 5, 6$ and 8 .

Figure 5.31: Histogram of photons counted in the a): signal and b): back-ground region by the PMT after every ablation shot, for rotational states $N = 8, 4, 5, 6$.

Figure 5.32: Shot-to-shot signal count at different ablation fluences and rotational states N .

To find out more about the periodic structures in the shot-to-shot pmt counts, the pmt counts for the signal at different ablation powers for different rotational states are shown in Figure 5.32. The graphs show the fine structure in all the plots, with the same periodicity. The structure is thus independent of state and ablation energy. It can be concluded that the lowest signal-to-fluctuation ratio in the yield is obtained at a fluence of 3.1 J/cm^2 with an ablation spot size of 1 mm.

The fluctuation periodicity of ~ 1200 can be related to the target rotation. One possible consequence of the target rotation is illustrated in Figure 5.33. In the illustration the target moves too much up and creates a new escape route for buffer gas inside the cell volume—this route is shorter than going through the cell exit. The consequence is that there is no or a weaker molecular beam observed. Another possibility is the ablation laser not or partly hitting the target, because the target is too much up and no or less molecules are created. Both scenarios could occur at the same time. The target can also move too much in the downward direction, in that case the ablation laser will also not hit the target, but no significant amount of buffer gas will escape, unless the target gets out of the cell. Possible solutions to the problems discussed above are a longer target or a shorter rotation domain for the target. The period of ~ 100 shots might be related to the step size resolution of the rotation (stepper) motor or target inhomogeneity.

Figure 5.33: Possible mechanisms behind the periodic yield instability, with period ~ 1200 shots or 2 minutes.

A remarkable TOF pattern was occasionally observed and is shown in Figure 5.34. This figure shows a yield periodicity closely corresponding to the target rotating up and down. From the projection on the right hand side of Figure 5.34a one can see that despite the varying TOF pattern, the shot-to-shot yield is relatively stable. For this measurement the cell temperature was set to 18 K and the neon flow rate to 9 sccm. Figure 5.34b shows a 3D interpolation of the same data. Figure 5.34c shows time-of-flight profile in the period between two ablation pulses (100 ms). Most molecules arrive within 5 ms after ablation, as can be seen in Figure 5.34a and Figure 5.34b. On the other hand, Figure 5.34c shows that there are occasional signal detections beyond 5 ms. This is probably due to the continuous flow of buffer gas through the cell, occasionally carrying with it dust and molecules left over in the (contaminated) cell from earlier ablation shots (see Subsection 3.4.2 and Figure 3.13). The background shown here will be compared to the background obtained after the ablation of Strontium in Chapter 6.

(a) density plot with every TOF the average of 100 TOFs

(b) 3d interpolation plot with every TOF the average of 100 TOFs

(c) Plot of all the TOFs between shot 352 and 551 extracted from a).

Figure 5.34

The stability of the shot-to-shot signal for different experimental parameters is summarized in Figure 5.35. The broader the profile, the less stable the yield. From the results one can conclude that there is a trade off between a high yield and a stable yield. Only at a cell temperature of 16 K, there seems to be no trade off, but the yield (integral under histograms) stays very low.

(a) Shot-to-shot yield at different cell temperatures for rotational states $N = 6, 5, 4$ and 8 .

(b) Shot-to-shot yield at different cell temperatures for neon flow rates $3, 10$ and 20 sccm.

(c) Shot-to-shot yield at different neon flow rates for cell temperatures $16, 22$ and 28 K.

Figure 5.35

5.4 Conclusion

Temporal evolution as measured by TOF profile revealed dynamics on different time scales due to the pulsed operation of the source. The multi-mode nature of the measured TOF profile is a remarkable result. Although the explanations from [115] and [116] have been adapted here, all investigations related to this phenomena, relied on measurements of ionic/charged species from laser ablation. A consequence of the multiple modes is that the beam velocity is not easily estimated by a Maxwellian or Gaussian fit of the TOF—beam modes arriving earlier or later relative to one another do not necessarily imply that their velocities are different. The behaviour of the modes is further complicated by their correlation with the buffer gas temperature and flow rate, which have been shown to have a significant impact on the number of observed modes and their properties. A velocity selective device can reveal more information about the beam velocities. An example of such a device is a travelling-wave Stark decelerator [24, 25]. To reduce the error in the velocity calculation more measurement points further downstream of the molecular beam are useful.

Although the mode velocities have been estimated using the fluorescence TOF simple relation $v_0 = L/t_0$, due to the multi-mode nature of the TOF profile it can not be concluded that the estimated velocities are the real velocities of the molecules. Since only the arrival time is measured it is possible that the velocities of the modes are not different from each other, but have simply different arrival times. In case of a single mode TOF, the error in the velocity calculation has been estimated to lie between 5% and 10 % using this simple method.

From the variation of the cell temperature it was observed that the molecular signal increases, even if theoretically the population in $N = 1$ is shown to decrease with cell temperature in Figure 3.4. This might be explained by the fact that at low cell temperatures the vapour pressure of neon is not high enough to efficiently cool the molecules in cell. At higher cell temperatures, the vapour pressure in the cell is higher and with it the buffer gas density, resulting in better cooling of the molecules. In future experiments one can increase the cell temperature for higher molecular signal until a maximum signal is obtained. Whether there will be formation of the desired molecular species, strongly depends on the ablation energy and spot size. The relationship is complicated, as before, by the interdependence of the molecular beam on buffer gas flow rate and temperature and the aforementioned ablation parameters.

For the stability of the molecular yield, it was shown that the stability decreases with the yield and for a spot size of 1 mm the highest signal-to-fluorescence ratio was found for a fluence of 3.1 J/cm^2 , corresponding to $\sim 24 \text{ mJ}$ ablation energy. At low ablation energies higher yields are obtained for a 0.5 mm spot size, but at higher energies the yields saturate and become similar to that of a 1 mm spot size. Regarding the buffer gas temperature, it was found that when the cell temperature is set at 16 K or lower, there is no consistent dependency on the flow rate and it might be caused by freezing of the buffer gas inside the cell. Measurements of the population and time-of-flight in rotational states $N = 8, 4, 5$ and 6 have revealed no significant differences in the derived beam properties.

The molecular yield shows saturation at both buffer gas flow rates and temperatures. For a double mode distribution it was found that both modes have similar yield dependencies on buffer gas flow rate and temperature.

Parameter	Value
Ablation energy (mJ)	24*
Ablation spotsize (mm)	1 and 0.5
T_{cell} (K)	24 - 25
Ne flow (sccm)	° 37

*Higher energies give equally high yields but with larger instability.

Figure 5.36: The optimal cryogenic source parameters for producing the highest yields measured 31.1 cm after the cryogenic source exit using SrF_2 ablation.

From the measurements on the source, the experiment parameters leading to the highest yields are summarized in Figure 5.36

6

Strontium Ablation

In Chapter 5 practically all the presented data and consequent analysis were all obtained from SrF_2 ablation experiments, except where mentioned otherwise. A short analysis of measurement data obtained from Sr metal ablation combined with SF_6 in the seed gas will be given in this chapter. Measurements on the influence of the cell temperature and the buffer gas flow rate on the beam properties have been performed. Yield instability will be investigated and compared to the yield instabilities found in the SrF_2 ablation method in Chapter 5. The analysis methods introduced in Section 5.2 will also be used here, in particular Gaussian and Shifted Maxwell-Boltzmann (SMB) distribution fitting. Data from absorption detection is available and are included in the analysis for the Sr metal ablation. The geometry of the detection of the molecular beam by fluorescence and absorption was laid out in Chapter 4.

6.1 Molecular Beam Properties

A typical density plot combined with its projections in time (top) and shot (right) illustrates the result of a molecular beam measurement (Figure 6.1). The projection on the right panel shows fluctuations in the yield. The fluence of the laser ablation pulse used for this experiment is 0.54 J/cm^2 , using an ablation spot size of 1 mm. Ablating the Sr target at this fluence already yields a higher signal compared to signals obtained at the highest fluence (4.2 J/cm^2) for ablation from SrF_2 for the same spotsize. The data in Figure 5.24a showed that there was no SrF beam formation below 1.5 J/cm^2 for SrF_2 . This means that the ablation threshold for Sr is lower compared to SrF_2 .

Figure 6.1: Density plot of the time-of-flight (TOF) measurements and their projections in time (top) and shot (right), showing the TOF for every shot taken during Sr metal ablation. The projection on the right, shows fluctuations in the yield. Experimental settings: cell temperature = 18 K, neon flow = 10 sccm, ablation energy = 4.3 mJ with a spot size of 1 mm.

To obtain the beam properties, the time-of-flight (TOF) profile of the beam are averaged for every 300 shots and a single peak shifted Maxwell-Boltzmann (SMB) distribution is fitted to the data (illustrated in Figure 6.2). The figure shows that the TOF profile is relatively stable over the number of shots, while its maximum varies. A direct comparison of the beam properties with SrF_2 is problematic as the ablation energy used for Sr is significantly lower than those typically used in SrF_2 ablation. Typically lower beam velocities are achieved with lower ablation energies. The results of the SMB fit are shown in Figure 6.3, where small variations in the beam properties can be seen over the number of ablation shots.

Figure 6.2: Time-of-flight (TOF) profiles from Figure 6.1, each shot represents the average 300 consecutive TOF profiles. Each profile is fitted to a shifted Maxwell-Boltzmann (SMB) distribution.

Figure 6.3: Beam properties derived from the shifted Maxwell-Boltzmann fit in Figure 6.2.

Figure 6.4: Time-of-flight (TOF) profiles for metal ablation, representing the average of 3000 TOFs. The TOFs are obtained from absorption and fluorescence, the fluorescence data is fitted to a Gaussian and a SMB distribution. Experimental settings: neon flow rate = 9 sccm, cell temperature = 17 K, ablation energy = 6.7 mJ at a spot size of 1 mm.

Figure 6.4 shows time-of-flight profile for another set of experimental parameters: neon flow rate 9 sccm, cell temperature = 17 K and an ablation energy of 6.7 mJ. The ablation spot size is maintained at 1 mm. The corresponding absorption detection signal is also included here. One can see that the fluorescence TOF profiles are not Maxwellian any more and also not Gaussian, although the Gaussian shows a better goodness of fit. From the fluorescence TOF profile the most probable velocity of the beam is around 200 m/s, faster than with the experimental conditions used for Figure 6.1. The faster beam could be explained by the higher energy deposition on the target from ablation.

6.1.1 Buffer Gas Flow

Figure 6.5 shows time-of-flight profiles at different neon flow rates while the cell temperature is held constant at 20 K. During these measurements the SF_6 flow rate could not be measured due to limitations in the data acquisition system. Furthermore, the area under the curves is not a good estimate for the yield in this measurement, because the detection laser power was significantly fluctuating in time. While the neon flow rate is increased, the peak structure transforms to contain more than two peaks. This is well visible for neon flow rates ≤ 27 sccm. Fitting this data with Gaussians or Maxwellian distributions demands a number of ≥ 4 individual distributions. This is beyond the scope of this work.

In SrF_2 measurements the multi-modal structure was also visible (Figure 5.2, Figure 5.8, Figure 5.10 and Figure 5.19). Under certain conditions a third peak has been observed, but not as pronounced as can be seen in Figure 6.6.

Figure 6.5: Time-of-flight (TOF) profiles as function of the neon flow rate. Each TOF consists of the average of 2500 TOF's from individual ablation shots. Experimental settings: ablation energy = 4.3 mJ with a spot size of 1 mm, cell temperature = 20 K.

Figure 6.6: Time-of-flight (TOF) profiles as function of neon flow rates 29, 31 and 33 sccm show the multi-modal structure. This data is also shown in Figure 6.5.

6.1.2 Cell Temperature

Maintaining the neon flow rate at 9 sccm while ablating with 6.7 mJ (1 mm spot size) resulted in two modes, similar to ablating with 4.3 mJ, as can be seen in Figure 6.5 and Figure 6.7. In Figure 6.7 the temperature of the cell is varied at a flow rate of 9 sccm. The double mode seems to be maintained. What changes, is the separation between the modes—as the temperature increases they merge into a single mode. It seems that the separation between modes is determined by the cell/buffer gas temperature and that the number of modes depends on the buffer gas flow rate and the ablation energy. For both Sr metal and SrF_2 ablation it holds that higher fluences result in more modes.

Figure 6.7: Time-of-flight (TOF) profiles as function of cell temperature, each TOF consists of the average of 2500 TOF's from individual ablation shots. *b)* is a continuation of *a)*, but at lower detection power. Experimental settings: ablation energy = 6.7 mJ with a spot size of 1 mm, neon flow rate = 9 sccm, target = Sr + SF_6 .

6.2 Stability

In this section it will be shown that the stability properties of a molecular beam resulting from Sr ablation are not different from those seen in SrF₂ ablation. The dominant instability is still periodic dips in the molecular signal with periods ~ 100 and 1200 shots.

Figure 6.8 shows an example of the signal (PMT counts) against the ablation shot number using an Sr target. Although less clear compared to the structure from SrF₂ (Subsection 5.3.4), it is also visible here and with a similar period of ~ 100 shots. The rougher repeating structure with periodicity of ~ 1200 shots, seen in SrF₂ ablation, is not visible in this measurement. It is possible that the higher signal obtained with the Sr target, reduces the fluctuations to a smaller fraction of the total signal, obscuring the variations seen in the lower SrF₂ ablation signals.

Data from absorption spectroscopy 5 mm after the cell exit have been obtained (Figure 6.9), for 1500 consecutive ablation shots. Each TOF in this plot is an average of 10 consecutive shot-to-shot TOFs.

Figure 6.8: Fluorescence from a molecular beam originating from ablating a Sr target combined with SF₆ gas, also displaying a periodic structure in the yield. Experimental settings: cell temperature = 18 K, neon flow rate = 10 sccm, ablation energy = 4.3 mJ with a spotsize of 1 mm.

Figure 6.9: Absorption time-of-flight signals from Sr metal ablation (1500 shots). Most molecules arrive within 0.5 ms after an ablation. Each data point results from the average of 10 ablation shots. Experimental settings: cell temperature = 17 K, ablation energy = 6.7 mJ with a spot size of 1 mm, neon flow rate = 9 sccm, SF₆ flow rate = 0.5 sccm.

In Figure 6.9 one can see the periodicity ~ 100 shots again as reported in Subsection 5.3.4. It is not clear what the origin is of the ~ 1 KHz background signal (parallel lines) —it probably indicates a data acquisition problem, but it was only present in a few measurements. Taking a closer look between shots 700 and 1000, shows that part of the detected signals seem to persist beyond 4 ms. Before drawing conclusions based on this latter extended signal, the fluorescence signal will be analysed to see if evidence of the signal can also be seen there.

Figure 6.10: Fluorescence signals corresponding to the absorption signal in Figure 6.9 showing no extended molecular signal beyond 4 ms.

After the molecules pass the absorption detection zone they are expected to appear at the fluorescence detection zone downstream. Figure 6.10 shows that is not the case for the extended signals seen in Figure 6.9 between shot 700 and 1000. It could be that these were heavy dust/ice particles mostly and under the influence of gravity did not reach the fluorescence detection zone, or that they were particles with large transverse velocities. The signal periodicity obtained from the absorption signal in Figure 6.9 is also visible in the fluorescence signal without the parallel lines in the background. Only the fine structure periodicity of ~ 100 shots is visible and not the rougher one of ~ 1200 shots—it might have something to do with the periodic vertical movement of the target (see Subsection 5.3.4).

Figure 6.11: Fluorescence versus the absorption yield, showing the correlation between the absorbed signal and the fluorescence signal.

To observe the correlation between the absorption signal and the fluorescence signal, the signals are plotted against each other in Figure 6.11. The plot reveals that the absorption signal 5 mm after the source is not one-to-one correlated to the fluorescence signal 31.1 cm after the source. For a single absorption value a broad band of different fluorescence yields are obtained. An explanation for this behaviour might be the fact that the fluorescence signal is in general more sensitive to fluctuations in the detection laser power. What can be said is that in general a higher absorption yield corresponds to a higher fluorescence signal, but not in a linear way. For small absorption this relation seems to be linear, but as the absorption increases the fluorescence tends towards saturation.

Apart from the ~ 100 shot periodicity seen in TOF measurements of SrF, the other typically larger signal periodicity seen in SrF₂ ablation measurements was also observed in the ablation of Sr targets. This larger periodicity related to the target (vertical) position reaching its limits is shown in Figure 6.12, where apart from the ~ 100 shot periodicity there is also a ~ 1200 shots periodicity visible. The ~ 1200 periodicity is correlated with the target reaching its position limits.

To compare the background of the molecular signal after Sr ablation with that from SrF₂ ablation shown in Figure 5.34a, Figure 6.13 shows the full fluorescence TOF pattern of the first 200 shots from Figure 6.12b. Compared to the background associated with molecular signals from SrF₂ ablation the Sr ablation process seems to be a 'cleaner' production process compared to SrF₂ ablation as shown in Figure 5.34a, or at least has a higher signal to noise ratio. The background seen in SrF₂ ablation might be related to the more brittle nature of the SrF₂ target. We investigated possible saturation of the PMT count rate at large SrF beam intensities. Here we placed a neutral density filter (ND3, 1:1000) in front of the PMT. We observe the same results and conclude that we did not saturate the PMT.

Figure 6.12: a): Density plot of Time-of-flight (TOFs) obtained from absorption spectroscopy. b): TOFs from the same experiment, but using fluorescence detection. c): 3d interpolation of the fluorescence data. Experimental setting: cell temperature = 17 K, ablation energy = 6. mJ with a spot size of 1 mm, neon flow rate = sccm, SF_6 flow rate = 2.5 sccm.

Figure 6.13: Time-of-flights of the first 200 shots, part of the data as also shown in Figure 6.12.

6.3 Conclusion

The Sr ablation yield is subject to similar instabilities as the SrF_2 target. Yield fluctuations with periods ~ 100 and ~ 1200 shots are observed. The instabilities are less pronounced with the Sr ablation due to higher yields obtained with the Sr target ($\sim 10^3$ times higher for the highest yields). It was found that lower ablation fluences are required for the Sr ablation, compared to SrF_2 , while higher molecular signal strengths are obtained. Multiple modes are manifested in the time-of-flight profile even more than seen in the SrF_2 data. The fact that multiple modes are encountered in many measurements makes it difficult to uniquely fit the data to obtain useful beam properties. Significantly less measurements are performed with the Sr target, leading to a shorter analysis compared to Chapter 5, where SrF_2 ablation was treated. Just like with SrF_2 ablation, also here it seems that the buffer gas flow rate and temperature are the determining factors regarding the number of observed modes.

7

Decelerating Molecules

In the setup for the NL-eEDM experiment the molecular beam from the cryogenic buffer gas source is coupled to a travelling-wave Stark decelerator for further deceleration of the molecules [25, 24, 21]. The sensitivity of the eEDM measurement depends on the number of molecules and their velocity. The cryogenic source produces molecules with speeds around 200 m/s. These molecules should be decelerated to ~ 30 m/s for the desired sensitivity in the NL-eEDM project. Achieving the optimal transfer of molecules from source to decelerator is a crucial step.

In this chapter the experimental parameters of the source will be varied and their effect on the molecular transfer from source to decelerator studied. The effect on molecular guiding and deceleration will be investigated. In Section 7.1 the principles of a travelling-wave Stark decelerator are presented, while in Section 7.2 the experimental setup is presented. The characterisation is based on arrival time distributions of molecules observed behind the ~ 4 m long decelerator. The measured absorbed fraction α and the average photons counted from the PMT $\langle \text{pmt count} \rangle$ are used here as defined in Section 5.1.

The time-of-flight t (TOF) results obtained with the experimental setup are presented in Section 7.3 and Section 7.4 presents the results on the transfer of molecular yield from the source to the decelerator, followed by a conclusion in Section 7.5.

7.1 Molecular Guiding and Deceleration Principles

When a polar molecule with an electric dipole moment $\mathbf{d}_{\text{SrF}}$ interacts with an external electric field $\mathbf{E}$, its internal rotational energy levels are shifted [121]. The energy shifts depend on the molecule's quantum state and the electric field the molecule resides in. In case of the diatomic molecule that can be described as a rigid symmetric top molecule, such as SrF in the electronic ground state, the rotational Hamiltonian is given by [122]:

$$H = H_0 - \mathbf{d}_{\text{SrF}} \cdot \mathbf{E}, \quad (7.1)$$

where H_0 is the rotational Hamiltonian without the presence of the electric field. For diatomic molecules in states where the angular momentum projection on the internuclear axis Λ is zero, H_0 is given by [122, 123].

$$H_0 = \frac{\hbar^2}{2} \frac{\hat{N}^2}{I_A}, \quad (7.2)$$

where $\hat{N}$ is the rotational angular momentum operator and I_A the moment of inertia. The Stark energy shifts due to the electric dipole interaction is given by [123].

$$\Delta \mathcal{E}(N, M) = \begin{cases} \frac{\mathbf{d}_{\text{SrF}}^2 E^2}{2\hbar c B} \frac{N(N+1)-3M^2}{N(2N-1)(2N+3)(N+1)}, & N > 0 \\ -\frac{1}{6} \frac{\mathbf{d}_{\text{SrF}}^2 E^2}{\hbar c B}, & N = 0 \end{cases}, \quad (7.3)$$

where M is the projection of the angular momentum N along the electric field axis: $M \in \{-N, -N+1, \dots, N\}$, resulting in a energy level splitting to $2N+1$ sub-levels. The rotational constant is given by $B = \hbar/(4\pi c I_A)$ [100]. The above energy shifts predict that the shifts will remain fully quadratic at all field strengths, but at large field strengths all the rotational level energies eventually decrease and the molecules become what is called high field seeking [24]. The counterpart of a high field seeking state is a low field seeking state. Molecules occupying a low field seeking state have their energy decreased only when the field decreases.

Eigenvalues of the Hamiltonian representing SrF in an electric field of different strengths were obtained from the spectrum simulation program PGOPHER and shown in Figure 7.1 [89]. From Figure 7.1, one can see that if the molecule is placed in a non-zero gradient field, it can be forced to a field minimum under the conditions that the molecule is in the low field seeking branches of the $N = 2$ curves. The largest force can be applied on molecules in the $M = 0$ state when the field is below ~ 60 kV/cm and not too close to zero field. Molecules in the low field seeking branch of the $N = 1$ curves can also be forced to field minima, but with smaller force and field below ~ 20 kV/cm. The higher the gradient is, the higher the force $F = -\nabla \mathcal{E}(E)$ on the molecules. This principle is used to create electric traps for polar molecules and is fundamental for the operation of the travelling-wave Stark decelerator [124, 125, 126].

The decelerator consists of 8 modules, each $\sim 1/2$ m long, coupled together. Each module consists of a series of stainless steel rings connected to 8 electrodes (made of tantalum). The electrodes and rings on a single module are shown in Figure 7.2a. Each electrode is connected to 42 rings. The rings have an inner diameter of 4 mm and are separated 1.5 mm from each other.

Figure 7.1: Stark shifts of SrF molecules in rotational states $N = 0, 1$ and 2 , residing in an electric field of strength $\mathcal{E}$. The blue lines mark the domain where the molecules are low field seeking (lfs), and the black lines the high field seeking (hfs) domain. The projection of N on the electric field axis is indicated as M .

Figure 7.2: a): Rings and electrodes of a single travelling-wave Stark decelerator module. b): Electric field minima formed along the decelerator.

During guiding or deceleration the molecules are trapped in a series of co-moving electrical traps, the molecules in these traps will be referred to as trapped molecules. To achieve trapping, a sinusoidal voltage is applied on the 8 electrodes. The voltage phase difference between consecutive electrodes is $2\pi/8$. The first 8 rings are each connected to one of the 8 electrodes, the same holds for the following eight rings and so on until there are 42 rings in one module. The decelerator can be operated in longitudinal guiding or deceleration mode. The voltages applied on the n^{th} ring to obtain any of the two modes is given by [25]:

$$V_n(t) = \begin{cases} V_0 \sin \left(-\frac{2\pi v_0 t}{\ell} + \frac{2\pi n}{8} \right), & \text{guiding} \\ V_0 \sin \left(-\frac{2\pi}{\ell} \left(v_i t - \frac{at^2}{2} \right) + \frac{2\pi n}{8} \right), & \text{deceleration} \end{cases} \quad (7.4)$$

where v_0 is the guiding velocity when guiding of molecules is desired and ℓ the distance between two consecutive rings of the same voltage (12 mm). v_i is the initial velocity from which to decelerate to a final velocity v_{fi} with deceleration strength $a = (v_i^2 - v_{fi}^2)/(2L_1)$. L_1 is the distance over which to decelerate. The maximum voltage amplitude V_0 in the current setup is 5 kV. A typical electric field pattern created along the rings in the decelerator is illustrated in Figure 7.2b. One can see the elliptical field minima in which the molecules can be trapped for guiding or deceleration. With a constant non-zero voltage applied to the rings only transverse confinement of molecules can be achieved. For more details on the travelling-wave Stark decelerator used in this work, the reader is referred to [25, 24].

7.2 Experimental Setup

The experimental setup used for the experiments to be described next is shown in Figure 7.3. The cryogenic source, described in Chapter 3, is connected to the decelerator's vacuum chamber and provides molecular beams to the 4 meter long decelerator. There is a 32.5 cm distance between the cryogenic source cell exit and the first decelerator ring, which sets the geometrical acceptance of the molecules to the decelerator. An electrostatic guide will be installed in the future to increase the acceptance [63]. Absorption detection is performed 5 mm after the cell exit to monitor the source production. Light-induced fluorescence (LIF) as described in Chapter 3 and Chapter 4 is used to detect molecules 18.1 cm after the last decelerator ring. Although the molecular beam exiting the decelerator is transversely colder than before entering, molecules still diverge out of the small fluorescence detection volume, because of the reduced longitudinal velocity.

Figure 7.3: Schematic experimental setup: molecules from the cryogenic source travel into the decelerator where they are trapped inside electric field minima. At the same time the molecules are decelerated or guided. The molecules are detected using absorption detection 5 mm after the cell exit. At a distance of 18.1 cm after the last ring of the decelerator, the outgoing molecular beam is detected using fluorescence detection.

The decelerator selects a molecular velocity class which can be guided or decelerated. The arrival time of the decelerated molecules at the fluorescence detection zone is estimated for an initial molecular beam velocity v_i and a final velocity v_{fi} as follows: Let L_0 be the distance be-

tween the exit of the cell and the first decelerator ring entered by the beam, v_i the initial beam velocity, L_1 the length of the decelerator, v_f the final beam velocity to achieve and L_2 the distance between the last decelerator ring and the LIF detection laser beam. The arrival time of the trapped molecules in the fluorescence detection region is then given by:

$$\begin{aligned} t_{\text{tr}} &= L_0/v_i + 2L_1/(v_f + v_i) + L_2/v_f \\ &= t_0 + t_1 + t_2 \end{aligned} \quad (7.5)$$

The individual terms have been split in to t_0 , t_1 and t_2 , referring to the times the molecule spends in the different regions of the setup: cell exit - first decelerator ring, first - last decelerator ring and last decelerator ring - detection zone, respectively. Setting $v_i = v_f$ in (7.5) results in the arrival time for guiding at velocity v_i . For all measurements in this chapter, in which the decelerator is switched on, the the ring voltage is set to $V_0 = 3$ kV.

7.3 Molecular Beams Through the Decelerator

After coupling the vacuum chamber of the source to the decelerator's vacuum chamber and aligning the exit of the source cell with the decelerator rings, measurements were performed on the behaviour of the coupled device.

7.3.1 Free Flight vs. Neon Flow

Starting with the decelerator switched off, the molecular signal is measured before and after the decelerator. For this measurement, the molecular beam was produced by ablating an Sr metal target while flushing the cell with SF_6 gas at 0.5 sccm. Even though the beam will have spread out considerably after such a large distance, the resulting molecular density was high enough to be measured from its fluorescence. The result of the TOF measurements are shown in Figure 7.4. When the neon flow is set to for example 21 sccm, the molecular beam starts with a distribution spread of ~ 0.4 ms full width at half maximum (FWHM) in the absorption detection zone and spreads out to a ~ 4 ms FWHM at the fluorescence detection zone, 4.533 m further. With an estimated velocity of ~ 240 m/s, this corresponds to a longitudinal expansion of the beam from ~ 10 cm to ~ 100 cm. For flow rates above 21 sccm, the multi-mode structure of the beam becomes visible in the absorption TOF profile with a second peak close to time = 1 ms. This peak is not seen in the fluorescence signal. The second peak signal is relatively small, the corresponding molecules have most likely already diffused transversely out of the detection domain or spread out longitudinally, averaging to a density of almost 0 before reaching the fluorescence detection zone.

Figure 7.4: a): Absorption signal 5 mm after the cell exit and b): Fluorescence signal acquired at 4.538 m after the cell exit. The solid blue lines in b) are shifted Maxwell-Boltzmann (SMB) fits to the fluorescence signals (see Section 5.2) at different neon flow rates. Other experimental conditions: cell temperature = 20 K, ablation energy = 6.7 mJ with spot size 1 mm, target = Sr = SF_6 , SF_6 flow rate = 0.5 sccm. These results were obtained without electric fields in the decelerator.

Figure 7.5: Beam properties derived from the shifted Maxwell-Boltzmann (SMB) fit (see Section 5.2) to the free flight fluorescence signal, 4.538 m after the cell exit, as shown in Figure 7.4b.

Molecular beam properties are derived from SMB distribution fit (see Section 5.2) to the data shown in Figure 7.4. The results are summarized in Figure 7.5. The beam's arrival time reduces with increasing fl w rate. After 11 sccm the beam spread is fairly stable with the fl w rate. When the fl w rate is increased from 3 to 37 sccm the beam velocity increases from ~ 200 to ~ 250 m/s. Comparing this figure and Figure 7.4 to Figure 5.21 shows that from the initial double mode distribution at 21 sccm seen in the absorption signal of Figure 7.4, only the single mode with a velocity comparable to that of the early arriving mode at 22 K (and 16 K) cell temperature in Figure 5.21 is detected.

An additional view on the evolution of the molecular beam is given by the density plots in Figure 7.6, added as reference for other data sets with the decelerator. In this figure projections of the data along the fl w rate and time axis are added. The projection along Ne fl w axis gives some insight into the trend of the total produced yield at different fl w rates. One can see that as the yield increases at the source, it saturates at ~ 15 sccm after the decelerator.

7.3.2 Guiding After Sr Ablation

Figure 7.7 and Figure 7.8 show molecular beam guiding at 190 m/s after Sr ablation. The figures show an apparent single mode structure TOF from absorption detection. After the decelerator a clear multi-mode TOF is visible for different neon fl w rates. For these measurements, the decelerator voltage amplitude was set to 3.0 kV. As before, the molecular signal increases with the neon fl w 5 mm after the cell exit. After the decelerator there seems to be a signal decrease

Figure 7.6: Density plots representing time-of-flight profiles for a): absorption detection and b): fluorescence detection while the decelerator is switched off. Same data as shown in Figure 7.4. The dashed line traces out the maxima of the absorption signal at different neon flow rates. Other experimental conditions: cell temperature = 20 K, ablation energy 6.7 mJ at 1 mm spot size, SF_6 flow rate = 0.5 sccm, target = SrF_2 .

at higher flow rates. There is an optimum reached around 15 sccm, below this flow rate the signal after the decelerator increases with the flow rate. According to (7.5), the expected arrival time of the trapped molecules after the decelerator is 24 ms, but from Figure 7.7b it is clear that the arrival time is beyond 24 ms and from Figure 7.8 it seems to even shift towards later arrival times. The remaining (non-trapped) molecules shift towards earlier arrival times as one would expect based on Figure 7.5. Later on this result will be compared to results from ablating a SrF_2 target.

Similar to the free flight case, the arrival time of the non-trapped beam fraction stagnates with increasing flow rate. The arrival time convergence is well visible in Figure 7.7b. In the case of zero voltage on the decelerator rings in Subsection 7.3.1 the molecular signal after the decelerator increases with the flow rate, here the signal decreases with the flow rate. Looking at the absorption detection signal in Figure 7.7a and Figure 7.8a one can see that starting from a neon flow rate of 4 sccm, the arrival time of the detected signal maximum increases with increasing flow rate until around 14 sccm. Beyond 14 sccm the arrival time of the signal maximum decreases and stagnates beyond ~30 sccm.

Figure 7.7: Density plots representing time-of-flight profiles for a): absorption and b): fluorescence while the decelerator is guiding at 190 m/s at different neon flow rates. The dashed line traces out the maxima of the absorption signal at different neon flow rates. Other experimental conditions: cell temperature = 20 K, ablation energy 6.7 mJ at 1 mm spot size, SF_6 flow rate = 0.5 sccm, target = Sr + SF_6 .

Figure 7.8: Time-of-flight signals a): before and b): after guiding at 190 m/s for different neon flow rates, the highlighted region indicates the arrival time intervals of the trapped molecules. Same data as shown in Figure 7.7.

7.3.3 Guiding and Deceleration vs. Neon Flow

Guiding

As a reference measurement for guided and decelerated molecules, a first measurement is performed at 80 m/s guiding. In the current setup 80 m/s corresponds to an estimated arrival time of 57 ms at the fluorescence detection zone. If the molecular beam is guided at this velocity, the expectation is that practically no molecules would be trapped and guided longitudinally in the moving field minima and no trap structure would be visible. A trap structure is manifested by a visible narrow dense signal region around the expected arrival time, as particles with a velocity close to 80 m/s would fall into the relatively narrow traps (minima) and pile up there, resulting in enhanced fluorescence. Molecules with significantly higher or lower velocities are not able to keep track of the electric traps formed by the decelerator, avoiding entrapment.

Figure 7.9: Density plots representing time-of-flight profiles, for guiding at 80 m/s at different neon flow rates. a): absorption 5 mm after the cell exit and b): fluorescence at 4.538 m after the cell exit. The dashed line traces the maxima of the absorption signal at different neon flow rates. Other experimental conditions: cell temperature = 17 K, $V_0 = 3.0$ kV, ablation energy: 24 mJ at a spot size of 1 mm, target = SrF₂.

Figure 7.9 shows results for guiding at 80 m/s with the cell temperature set to 17 K and $V_0 = 3.0$ kV, while the neon flow rate is varied. A multi-peak (3 peaks) distribution is now visible in the fluorescence signal. No molecular signal was observed beyond 40 ms and the TOFs in Figure 7.9 and Figure 7.10b were cut off there. The molecular signal produced by the source is lower now compared to when the decelerator was switched off, but the fluorescence signal is now higher. Although no longitudinal guiding occurs, there is transverse confinement by the electric field in the decelerator, possibly contributing to this larger signal after the decelerator. As the projected TOF at the top of Figure 7.9b and Figure 7.10b show, the guiding process reveals additional modes in the TOF. Modes at time ~ 23 ms and ~ 27 ms are clearly visible, one with a lower amplitude is visible around 22 ms and at least one more close to 32 ms arrival time. Looking at the absorption signal, the line tracing out the maxima is different compared to those seen in Figure 7.6a and Figure 7.7a, due to the presence of a significant second mode in the absorption TOF. Measurements performed by colleagues in our lab, have shown that the multiple modes seen in the signal after the decelerator have a decelerator ring voltage V_0 dependency [25, 77].

Figure 7.10 shows the TOFs corresponding to Figure 7.9 from both absorption and fluorescence.

Figure 7.10: Time-of-flight signals a): before and b): after guiding at 80 m/s for different neon flow rates. Same data as shown in Figure 7.9.

The absorption signal shows a multi-mode distribution emerging as the flow rate increases from 3 to 21 sccm.

From trials with different guiding velocities, it was found that guiding at 190 m/s yielded the highest detected signal of trapped molecules. The arrival times of these trapped molecules is equivalent to 24 ms.

Figure 7.11: a): absorption and b): fluorescence signals while guiding at 190 m/s at different neon flow rates. The dashed line traces out the maxima of the absorption signal at different neon flow rates. Other experimental conditions: cell temperature = 17 K, $V_0 = 3.0$ kV, ablation energy: 24 mJ at a spot size of 1 mm, target = SrF₂.

Figure 7.12: Time-of-flight signals a): before and b): after guiding at 190 m/s for different neon flow rates, the highlighted region indicates the arrival time intervals of the trapped molecules. Same data as shown in Figure 7.11.

When guiding the decelerator traps at 190 m/s, the TOF profile show a sharp peak at time ~ 24 ms, which corresponds to those molecules that travel at 190 m/s. Unlike with guiding from Sr ablation shown in Figure 7.7b, the molecules do arrive at the expected time of 24 ms here. A small peak can be seen arriving at ~ 15 ms, these could be emerging from a second mode in the molecular signal from the source. Remarkably, the TOF distribution as a whole became narrower (from the right hand side) compared to guiding at 80 m/s in Figure 7.9, although the absorption signal shows almost no difference from that at 80 m/s guiding. More investigations are needed to verify and explain this observation.

The narrowing of the molecular beam region (compared to guiding at 80 m/s) is also visible for flow rates between 3 and 21 sccm shown in Figure 7.12b. Around time = 15 ms, another molecular distribution arrives at the fluorescence detection zone.

Deceleration

To test the deceleration against the neon flow rate, a modest deceleration from 190 to 150 m/s will be performed at different neon flow rates. Using (7.5) with $L_0 = 0.367$ m, $L_1 = 4$ m, $L_2 = 0.193$ m, $v_i = 190$ m/s, $v_f = 150$ m/s, the decelerated molecular distribution is expected to arrive at $t_0 = 26.7$ ms at the fluorescence detection. The TOF profile are shown in Figure 7.13.

Figure 7.13: a): absorption and b): fluorescence time-of-flight signals while decelerating from 190 to 150 m/s at different neon flow rates. Other experimental conditions: cell temperature = 17 K, $V_0 = 3.0$ kV, ablation energy: 24 mJ at a spot size of 1 mm, target = SrF₂.

The molecular signal from absorption detection is lower than the ablation laser signal, this is visible from the absorption profile in Figure 7.13a and Figure 7.14a, because the signal is the highest close to time = 0 ms (when the ablation laser is triggered). The TOF projection on the top of Figure 7.13a shows this clearly. The fluorescence signal coming from the trapped molecules is relatively weak as shown in Figure 7.13b and Figure 7.14b, and their arrival time is between time = 26 and 27 ms. The predominantly 2 mode structure seen in guiding at 80 m/s is also visible here.

Figure 7.14: Time-of-flight signals a): before and b): after decelerating from 190 to 150 m/s for different neon flow rates. The highlighted region indicates the arrival time intervals of the trapped molecules. Same data as shown in Figure 7.13.

7.3.4 Guiding and Deceleration vs. Cell Temperature

Effects of the cell temperature on the guided and decelerated beams were also measured.

Guiding

Figure 7.15: Density plots representing time-of-flight profiles for a): absorption and b): fluorescence while the decelerator is guiding at 190 m/s at different cell temperatures. Other experimental conditions: neon flow rate = 9 sccm, ablation energy: 24 mJ at a spot size of 1 mm, target = SrF₂.

Figure 7.15a shows that at low cell temperatures more molecules are produced than at high

temperatures. This contradicts the results obtained in Section 5.2, where a higher cell temperature would yield a higher molecular yield. The reason for the difference in these observations is not clear. This could be some fluctuation in the source behaviour, but it is also possible that the current conditions of the source deviated from the conditions before. The same pattern is followed by the signal after the decelerator. Contrary to the measurements at different flow rates, the measurements at different cell temperatures yield similar behaviour between the absorption signal 5 mm after the cell exit and the fluorescence signal after the decelerator. This latter behaviour is clear from the right hand side projections in both plots of Figure 7.15. In Figure 7.15a and Figure 7.15b one sees a decrease of the molecular number, produced by the cryogenic source and the molecules traversing the decelerator when the cell temperature is increased. The reduction in molecular number could be due to less molecules being in the $N = 1$ state at higher cell temperatures. The same data is shown in Figure 7.16.

Figure 7.16: Time-of-flight signals a): before and b): after guiding at 190 m/s for different cell temperatures, the highlighted region indicates the arrival time intervals of the trapped molecules. Same data as shown in Figure 7.15.

Figure 7.16a shows individual TOF profile from absorption detection 5 mm after the cell exit. This shows that there is interference between the absorption signal and light from the ablation laser, or at least the reaction of the photodiode to the latter. The same behaviour was also observed in Figure 7.13.

Deceleration

For deceleration from 190 to 150 m/s TOF profile have been obtained at different cell temperatures, these are shown in Figure 7.17. The absorption signal shows the same behaviour as before. The molecule signal is relatively weak and with it also the trapped signal maximum, making it difficult to distinguish from the other non-trapped parts of the beam. Molecules are

expected to emerge at time ~ 26.7 ms. TOFs obtained from absorption and their corresponding fluorescence signal after the decelerator are shown in Figure 7.18.

Figure 7.17: a): absorption detection and b): fluorescence detection signals while decelerating from 190 to 150 m/s at different cell temperatures. Other experimental conditions: neon flow rate = 9 sccm, ablation energy = 24 mJ with spot size 1 mm, target = SrF₂.

Figure 7.18: Time-of-flight signals a): before and b): after decelerating from 190 to 150 m/s for different cell temperatures, the highlighted region indicates the arrival time intervals of the trapped molecules. Same data as shown in Figure 7.17.

7.3.5 Arrival Time Regions of Trapped Molecules

In this subsection we will take a closer look at the TOF signal close to the trapped molecules arrival time region to get a better view of the evolution of the molecular beam shape.

Figure 7.19: Density plots representing time-of-flight profiles in the regions where molecules are trapped in minima for a): guiding at 190 m/s and b): decelerating from 190 to 150 m/s. Their corresponding source signals are respectively shown in Figure 7.11a and Figure 7.13a. The dashed line traces out the maxima of the signal at different neon flow rates.

Figure 7.20: Density plots representing time-of-flight profiles in the regions where molecules are trapped in minima for a): guiding at 190 m/s and b): decelerating from 190 to 150 m/s, while varying the cell temperature. Their corresponding source signals are respectively shown in Figure 7.15a and Figure 7.17a.

Figure 7.21: Density plots representing time-of-flight profiles in the regions where molecules are trapped in minima for guiding at 190 m/s, while varying the neon flow rate after Sr ablation. The dashed line traces out the maxima of the signal at different neon flow rates. The corresponding source signal is shown in Figure 7.7a.

Figure 7.19 to Figure 7.21 show the arrival time region of trapped molecules at different experimental conditions. Figure 7.21 shows the region in which the molecules are trapped after Sr ablation and guided at 190 m/s. What can be seen is that molecules in the trap region seem to be arriving later as the neon flow rate increases up to ~ 20 sccm, beyond this flow rate the arrival times start to stagnate and seemingly reduces. The stagnation/reduction is visible from the dashed lines in Figure 7.19a and Figure 7.21 tracing the arrival time of the signal maxima at different flow rates. As the flow rate increases further the signals becomes too small to obtain a reliable trace of their maxima. The reduction/stagnation of the arrival times could already be seen from the absorption signals of Figure 7.6 to Figure 7.11. This behaviour of the trapped molecules seems to be directly correlated with the cryogenic source behaviour. Changing the cell temperature has little effect on the arrival times.

7.4 Acceptance Matching

Ideally all the molecules produced from the source are available for use in the decelerator, or at least an optimized yield from the source should also mean an optimal yield for the decelerator. Ideally this would also hold for the molecules that can be trapped in the decelerator field minima. Through changing the cell temperature and the neon flow the influence on the yield and transfer efficiency from the source to the decelerator is studied in this section.

Figure 7.22: Comparison of total absorbed signal 5 mm after the source (blue) and the total fluorescence signal after the decelerator (black) as function of the neon flow rate a): when the decelerator is off and b): after guiding at 80 m/s.

When the decelerator is off we expect that the more molecules the source produces, the more molecules can be detected after the decelerator. Figure 7.22a shows the relation between the yields obtained from the two detected signals, before and after the decelerator. The absorption signal indicates that up to a neon flow rate of ~ 20 sccm, both signals are increasing. Beyond ~ 20 sccm, the source signal is still increasing while fluorescence after the decelerator starts decreasing. Since the decelerator is off, the difference in the behaviour between the source signal and the signal after the decelerator might be explained by effects of gravity, beam divergence and obstacles along the beam path. Gravity causes the molecules to lose altitude, obstacles on the beam path might be the decelerator rings, while higher beam divergences might be the result of increasing beam temperatures. This result could also indicate a misalignment between the source and the fluorescence detection zone or a misalignment between the two detection

zones. After the decelerator was switched on, guiding at 80 m/s was performed and the results are shown in Figure 7.22b. Comparing the situation where the decelerator is switched off with 80 m/s guiding shows that at guiding the decelerator signal already drops after 10 sccm, while the absorption signal still increases and reaches its maximum at ~ 20 sccm. The difference in behaviour between the signals of Figure 7.22a and Figure 7.22b, might be related to the fact that Figure 7.22a was obtained with an Sr target (high yield) at a cell temperature of 20 K, while Figure 7.22b was obtained with an SrF_2 target (lower yield) at a cell temperature of 17 K.

Figure 7.23: Comparison of the total absorbed signal 5 mm after the source (blue) and the total fluorescence signal after the decelerator (black) as function of the neon flow rate a): after guiding at 190 m/s and b): after decelerating from 190 to 150 m/s.

Deceleration and guiding at higher velocities show the same behaviour between the absorption signal and fluorescence as indicated by Figure 7.23. The difference between the source signals of Figure 7.23a and Figure 7.23b is most probably due to target degradation, leading to lower yields when the measurement of Figure 7.23b was performed.

Figure 7.24: Comparison of total absorbed signal 5 mm after the source (source) and the total fluorescence signal after the decelerator (decel) as function of the cell temperature a): after guiding at 190 m/s and b): after decelerating from 190 to 150 m/s.

When the temperature is varied, a high proportionality between the fluorescence and the absorption signal is obtained. Figure 7.24 shows this behaviour for both guiding and deceleration. The neon flow rate used here is 9 sccm.

One can estimate the fraction of trapped molecules by defining a trap region and a signal region and taking the ratio between the integrals under the curve in these regions. Estimates of the fraction of trapped molecules guided by the decelerator are shown in Figure 7.25 for guiding at 190 m/s, while varying the neon flow or the cell temperature. The trap region here is set to time $\in [23.7, 24.4]$ ms and the signal region to time $\in [10, 40]$ ms.

Figure 7.25: The ratio of the total count in the trapped region and the total count in the signal region when guiding at 190 m/s as function of a) the neon flow and b) the cell temperature.

For the yield in the trap region, Figure 7.25a shows that as the flow rate increases, the fraction of trapped molecules decreases almost linearly. Figure 7.25b shows that the optimal cell temperature for the trapped fraction is between 15 and 20 K. Comparing this to Figure 7.23 and Figure 7.24, shows that, except at 17 K, these cell temperatures do not correspond to the conditions for optimum source and/or decelerator yield. Even though a fraction close to 18% can be trapped, the total number of molecules is limited by the phase space acceptance of the decelerator. For example: for the best obtained molecular signal from the source a 3% absorption 5 mm after the cell corresponded to a total PMT count close to 10^6 , while for measurement leading to the trapped fraction of 18% a 2% absorption corresponded to a total PMT count of $\sim 10^2$.

7.5 Conclusion

The cryogenic source was coupled to a 4 meter travelling-wave Stark decelerator. With the decelerator off it was possible to detect molecules 4.538 m away from the cell exit. With the decelerator on, the molecular beam was guided at 190 m/s. At this velocity the maximum molecular fluence was detected after the decelerator. A small deceleration from 190 to 150 m/s was also achieved. The results suggest that guiding and/or deceleration suppresses the fluence through the decelerator at high buffer gas flow rates. Compared to having the decelerator off—if the decelerator is off, the yield increases with the flow rate while the inverse is true when guiding or decelerating. The origin of the latter behaviour has to be investigated further in order to increase the molecular fluence through the decelerator. From the TOF profile modulation of the molecular beams is observed when the decelerator is in operation, to understand this a study of the molecular dynamics in the decelerator might be useful [25]. From the simultaneous TOF measurements from absorption and fluorescence detection we observed that at conditions where the source has the maximal yield, the yield through the decelerator becomes small under cer-

tain conditions. This mismatch between the phase space of the decelerator and the molecular beam from the source might be solved using an electrostatic guide [127, 128, 129, 63, 130].

If one assumes that a significant part of the molecules coming from the cryogenic source are lost through transverse expansion before reaching the decelerator, then it might be worth considering realignment or redesigning the cell exit or using an electrostatic guide. Constructing the cell exit in the shape of a Bell nozzle, has proven to be effective in reducing the transverse temperature/spread of buffer gas beams. This has been shown for both neon and helium buffer gas sources [131]. An electrostatic guide after the source has been shown to increase the yield transfer [127, 128, 129, 63, 130]. Another remarkable result is that when guiding or decelerating, increasing the buffer gas flow rate seems to expand the trapped molecules distribution towards later arriving time and eventually back to earlier arriving times, as could be seen in Figure 7.21 and Figure 7.19a. The latter behaviour seems to have its origin in processes inside the cryogenic source —the signal detected 5 mm after the cell exit shows a similar behaviour (see Figure 7.7a and Figure 7.6a). With Figure 7.7a and Figure 7.21 in mind, a possible explanation for the latter behaviour could be as follows:

1. Just after ablation, the molecules have high kinetic energy. At low buffer gas density the molecules leave the cell without fully thermalizing and thus arrive early at the detection
2. As the cold neon flow increases, its density in the cell increases, resulting in better cooling and slower molecules. The arrival time of the molecules increases.
3. Beyond a certain neon flow rate the molecules are fully thermalized with the neon before leaving the cell. For the measurements in this chapter this flow rate is around 20 sccm for both Sr and SrF_2 ablation, but it is cell temperature dependent and most probably also depends on the ablation fluence. Increasing the neon flow rate further does not cool the molecules further, but adds to their kinetic energy and the molecular beam arrival time decreases.
4. The stages mentioned before have a significant effect on the position-velocity phase-space of the molecular beam, and thus when coupled to the decelerator, will determine the arrival times of the molecules depending on their guiding or deceleration velocity.

The same reasoning can be used for Figure 7.11a and Figure 7.19a. Later measurements performed by colleagues in our lab, have shown that the voltage V_0 supplied to the decelerator rings determines the properties of the modulations seen in the detected molecular signals after the decelerator.

Source	Sr ablation		SrF ₂ ablation		
	O ⁻	Guiding 80 m/s	Guiding 80 m/s	Guiding 190 m/s	Deceleration 190 -150 m/s
	T _{cell} (K)	-	17	17	17
Decelerator	Ne °o w (sccm)	~ 37	~ 37	~ 20	~ 20
	T _{cell} (K)	-	17	17	17
	Ne °o w (sccm)	~ 20	14-16	7-11	9-15

Figure 7.26: The optimal cryogenic source parameters for producing the highest yields just after the cryogenic source (source) and just after the decelerator for different decelerator operational states: off, guiding at 80 m/s, guiding at 190 m/s and deceleration from 190 to 150 m/s. Some of the results are obtained from Sr ablation and others from SrF₂ ablation.

A summary of the parameters that resulted in the optimal yield for both the yields just after the cryogenic source and after the decelerator is given in Figure 7.26. Not only do the optimal experimental parameters differ for the decelerator and the source, but also for the source yield obtained before and after the combining the source with the decelerator. The latter might be due a change in the source conditions after it was coupled to the decelerator. There might also be a change in the detection laser properties or setup. Finding out what caused the difference in its behaviour might be useful for future use of the source. For the source using a SrF₂ target it is expected that the optimal ablation energy and spot sizes are the same as those summarized in Section 5.4: 24 mJ at 1 and 0.5 mm spot size.

Summary

The main subject of this thesis is the building and characterisation of a cryogenic source for heavy diatomic molecules. The ultimate motivation of this work is to perform a very sensitive test of the fundamental symmetries in the Standard Model (SM). This theory is the most successful theoretical description of the physics of fundamental particles and their interactions. Despite this success, it can not account for the matter-antimatter imbalance in the universe and the missing matter in the universe, which is usually referred to as 'dark matter'. An extended theoretical description of physics is therefore needed to include the physics that is currently beyond the Standard Model (BSM), for example by . This extended theory can include new particles and interactions. As it turns out, slow and intense beams of heavy molecules can play an important role in exploring the limits of the Standard Model [57, 55, 53].

Typically, new particles are searched for at high-energy colliders. A totally different approach to study the same fundamental physics is to conduct precision experiments at low energy, which probes fundamental discrete symmetries, i.e. C,P and T, in nature. Of particular interest is the combination of charge conjugation C and parity P, the so called CP symmetry. Assuming the invariance of observation to the combined symmetry CPT, where T stands for time-reversal, CP violation is equivalent to T violation. A permanent electric dipole moment (eEDM) on the electron would violate CP symmetry. Thus performing measurements of the eEDM is a way to probe CP violation. In theoretical work by Leonard Schiff (in 1963) and Patrick Sandars (in 1965) on the eEDM it was shown that by performing measurements on molecules (or atoms) one could be very sensitive to the eEDM. Currently there are several groups working on such measurements of an eEDM using molecules. In 2018, the most sensitive upper limit for the eEDM has been set to $1.1 \cdot 10^{-29}$ ecm at 90% confidence level by the ACME collaboration [13, 132].

In 2017 a collaborative research program was started at the VSI in Groningen in collaboration with the VU in Amsterdam, within the organisation of Nikhef, to measure a possible eEDM with a new approach using an intense, slow and cold beam of molecules. The work presented here is part of this research program. The motivation to produce a slow and intense beam of molecules comes from the requirement of a large number of molecules for a low statistical uncertainty of an eEDM measurement (Subsection 2.2.1). Therefore an intense beam of slow molecules is

needed. In this thesis I report on the design of this molecular beam source, the measurements that were performed to characterize the molecular beam, and I present data on the first combination with the travelling-wave decelerator in our lab [21, 24, 25].

From the analysis of experimental requirements for an eEDM measurement, the development of a well characterized intense and slow beam source of heavy diatomic molecules is indeed beneficial. Because cryogenic sources can produce molecular beams with these properties, it was decided to construct such a source for the experiment. In Chapter 3, the design choices and construction approach of the cryogenic source is presented. In a cryogenic source, molecules are produced and thermalized by a cold buffer gas inside a cold cell at cryogenic temperatures. Figure 9.1 illustrates the cryogenic buffer-gas source.

Figure 8.1: Schematic setup of the cryogenic source. A two stage cryostat is cooling a cell to a constant temperature. An ablation laser ablates a rotating Sr or SrF_2 target in the cell. In case of a SrF_2 target, the ablation products contain SrF. In case of a Sr target, the ablation products are mixed with SF_6 gas in the cell to create SrF. A continuous flow of neon gas thermalizes and carries the SrF, together with other products, out of the cell in the form of a beam. The figure is not to scale.

The buffer gas flows out of the cell together with the molecules, resulting in a cold molecular beam that travels ~ 200 m/s. For the eEDM measurement, barium fluoride (BaF) molecules will be used. Because of previous experience with strontium fluoride (SrF) in the group and the available detection lasers in the laboratory, the cryogenic source has been developed and characterized using SrF . This molecule is lighter than BaF , but very similar in its energy level structure and chemical properties. The cryogenic source produced pulsed molecular beams with a frequency of 10 Hz. Every pulse starts by laser ablating a rotating target inside a copper cell. Two different targets have been tested: an SrF_2 target and a Sr target in the presence of SF_6 gas. The copper cell is kept at around 20 K by a two stage pulse tube cryostat, while neon gas is flushed into the cell continuously to thermalize the SrF molecules and to form a molecular beam containing the SrF molecules.

To detect and characterize the molecular beam, two detection methods are used: laser-induced fluorescence (LIF) and laser absorption. The detection setup and results from its application are

discussed in Chapter 4. An important part of the laser-based detection is the laser frequency stability, for which we have built an automated system based on a scanning Fabry-Perot cavity and a stable reference laser (Section 4.3).

The average velocity in the molecular beam of 140 - 270 m/s depends on the operation conditions of the source. In this thesis a systematic study of the effects of the neon flow, cell temperature and the ablation energy on the molecular beam properties is presented. In Chapter 5 the study on a SrF_2 target is presented, while in Chapter 6 the Sr target is evaluated. The signal from the Sr target was found to be of order 10^3 more intense than the signal from the SrF_2 target.

The maximum number of produced molecules with this source has been estimated to be around $\sim 10^9$ molecules per pulse, occupying a single rotational state ($N = 1$) (Section 4.5). This performance is comparable to similar sources described in literature [73, 93, 88]. Besides the intensity, an important property is the stability of the molecular yield. The rotation of the target is crucial to maintain a high molecular yield after every ablation pulse. It was found that the molecular yield has some remaining regular fluctuations, caused by the target rotation mechanism and target inhomogeneities.

One of the main findings in these characterizing measurements is that depending on the laser ablation intensity, multi-modal distributions (both spatial and in velocity) are observed in a single molecular beam pulse. The higher the ablation laser intensity the larger the number of modes is. The conditions for stable beam formation, the variation of the intensity, and the occurrence of these multi-modal distributions is studied in Chapter 5.

The multimode nature of the signal complicates the analysis of the molecular beam properties. To distinguish between spatial and velocity modulation, we have used a molecule decelerator to select molecules based on their velocities. The travelling wave Stark decelerator [25, 24, 21] in our lab has been employed in these measurements. It has been designed to produce even slower beams of heavy diatomic molecules, for increased precision in the spectroscopy. In the NL-eEDM program, it will decelerate part of the molecules to a velocity around 30 m/s. A schematic depiction of how the cryogenic source molecular beam is being loaded into the decelerator is shown in Figure 9.2. The first measurements of the combined source and the decelerator are reported in Chapter 7.

Figure 8.2: Schematic experimental setup: molecules from the cryogenic source travel into the decelerator, where a fraction of them are captured by travelling traps consisting of electric field minima. The velocity of these travelling traps is computer controlled, leading to deceleration or guiding of the trapped molecules. The molecules are detected 5 mm after the cell using absorption detection. Fluorescence is collected from the molecules 18.1 cm after the last ring of the decelerator. The figure is not to scale.

The decelerator consists of a series of rings with different voltages on them, to create an electric field pattern along the decelerator length that attracts molecules in field minima. The velocity of the field minima can be adjusted to guide or decelerate molecules with a computer-controlled velocity. After they have left the decelerator, the molecules can be detected using a fluorescence detection system.

Light absorption and fluorescence measurements, before and after the decelerator respectively, have been used to reveal the optimal source conditions to load molecules into the decelerator. A surprising result that we report on in this thesis is that the optimum source conditions based on the fluorescence signal were found to be different from the optimum source conditions based on the absorption measurements. At conditions where the source has the maximal yield, the yield through the decelerator was significantly reduced. This can be seen in Figure 7.11 in Chapter 7 for example and is further discussed in Section 7.4. Further investigation is needed to determine the reasons behind these results. A possible reason is a geometric misalignment between the source and the decelerator. Potentially also the transverse motion of the molecules in the decelerator, which is known to be strongly dependent on the voltage applied to the decelerator rings, plays a role.

The molecular beam that has been created by the cryogenic source will be used to perform a sensitive measurement of the electron-EDM. The optimal sensitivity in this measurement is reached with a molecular beam that combines a low velocity with a high intensity. We have demonstrated in this thesis that we can produce intense beams of suitable molecules with a velocity of on average around 200 m/s and an intensity of order 10^9 molecules per pulse, which matches the design goal of the NL-eEDM experiment.

Outlook

With the successful completion of the source, it is time to look further downstream the experiment. As the molecular beam leaves the source, it spreads out in space due to the transverse velocity of the molecules. This means that for a practical experiment not the full intensity of the beam is available. In the measurements presented here, the distance between the source and the decelerator was such that only with a transverse velocity below ~ 1 m/s the decelerator could be reached. Since the velocity acceptance of the decelerator is ± 5 m/s (or even ± 10 m/s for an increased voltage on the electrodes), the coupling of the source and decelerator can be strongly improved. Since the distance can not be significantly reduced (heat shields are blocking the way), we have chosen an electrostatic guide, which is being installed into the machine as these conclusions are being written. With the aid of this guide, the phase-space acceptance of the decelerator can be fully used. And since the position of the electrostatic guide is adjustable, possible misalignments between the source and decelerator can also be fixed.

Even though the cryogenic source is currently producing pulses at 10 Hz with the design intensity, ways might still be found to increase that intensity further, which would directly benefit any downstream measurement. For this purpose, a dedicated cryogenic source has been built within our consortium at the VU Amsterdam. Here, using combined detection of both the molecules and the carrier gas, optimized ways of BaF molecule production might be found. An interesting option is also to tune the exit hole of the cell such that the transverse spreading of the beam is reduced. The transverse velocity spread can in some cases be even tuned with the buffer gas flow rate [131]. Another option that we advice to explore is the use of different cell geometries to reduce turbulences and therefore provide better thermalization, leading potentially to lower average velocities. Another method to increase the molecule number is to do optical pumping of the molecules into the desired rotational state before they enter the decelerator.

In this thesis an intense source of slow molecules to study the violation of fundamental symmetries in the Standard Model of particle physics has been presented. This step marks the beginning of an exciting project. The source has been employed in the deceleration and trapping of SrF [133, 134].

9

Nederlandse Samenvatting

Het hoofdonderwerp van dit proefschrift is het bouwen en karakteriseren van een cryogene bron voor zware diatomische moleculen. Het uiteindelijke doel van dit werk is het uitvoeren van een zeer gevoelige test van fundamentele symmetrieën in het standaardmodel (SM) van de deeltjesfysica. Deze theorie is de meest succesvolle beschrijving van de fysica achter fundamentele deeltjes en hun onderlinge wisselwerkingen. Ondanks haar succes kan deze theorie de dominante aanwezigheid van materie ten opzichte van antimaterie in het universum niet verklaren. Ook voor de ontbrekende hoeveelheid materie, aangeduid als ‘donkere materie’, heeft deze theorie geen verklaring. Er is dus een uitbreiding van de huidige theoretische beschrijving nodig om de fysica buiten het standaardmodel (BSM) te accommoderen, bijvoorbeeld door het toevoegen van ontbrekende (nieuwe) deeltjes of wisselwerkingen. Het blijkt dat intense, langzame, koude bundels van zware moleculen een belangrijke rol spelen bij het verkennen van de grenzen van het huidige standaardmodel [57, 55, 53].

Traditioneel vindt de zoektocht naar nieuwe deeltjes plaats middels botsingen tussen hoogenergetische deeltjes. Een totaal andere benadering om dezelfde fundamentele natuurkunde te bestuderen is het uitvoeren van precisie experimenten bij lage energieën, welke gevoelig zijn voor discrete symmetrieën. Met name de combinatie van ladingsconjugatie (C) en pariteit (P), de zogenaamde CP symmetrie, is interessant. Onder de aanname dat de gecombineerde CPT symmetrie invariant is, waarin T staat voor tijdsomkering, is CP schending equivalent aan T schending. Mocht het elektron een permanent elektrisch dipool moment (eEDM) hebben, dan zou dat CP schending betekenen. Precisie metingen van een eEDM zijn dus een manier om CP schending te onderzoeken. In eerder theoretisch werk gedaan door Leonard Schiff (in 1963) en Patrick Sandars (in 1965) aan het eEDM is gebleken dat metingen aan atomen en moleculen zeer gevoelig kunnen zijn voor het eEDM. Tegenwoordig zijn er een aantal onderzoeksgroepen die werken aan metingen van een eEDM met behulp van moleculen. De meest nauwkeurige bovengrens van een eEDM is in 2018 gemeten door het ACME samenwerkingsverband [13, 132] en staat op $1.1 \cdot 10^{-29}$ ecm.

Sinds 2017 bestaat er een gezamenlijk onderzoeksprogramma tussen het VSI van de universiteit Groningen en VU Amsterdam binnen het kader van het Nikhef om een eEDM meting te verrichten met een nieuwe benadering die gebruik maakt van intense, langzame, koude molecuulbundels. Dit samenwerkingsverband draagt de naam “NL-eEDM”. Het onderzoek gepre-

senteerd in dit proefschrift is onderdeel van dit onderzoeksprogramma. De motivatie voor het produceren van langzame, intense molecuulbundels is de noodzaak van een zo laag mogelijke statistische onzekerheid in de eEDM meting (paragraaf 2.2.1). In dit proefschrift presenteer ik het ontwerp van de bron van de molecuulbundels, de karakterisatie van de molecuulbundels en data verkregen uit de eerste combinatie van de bron en de lopendegolf-Starkafremmer in ons laboratorium [21, 24, 25].

Uit de analyse van de experimentele voorwaarden voor een eEDM meting blijkt dat het ontwikkelen van een goed gekarakteriseerde bron van intense, langzame molecuulbundels voordelig is. Omdat cryogene buffergas bronnen in staat zijn molecuulbundels te produceren met de vereiste eigenschappen, is besloten om dit type bron te bouwen voor het experiment. In hoofdstuk 3 zijn de ontwerpkeuzes en de bouwmethode voor de cryogene bron beschreven. In een cryogene bron worden moleculen geproduceerd in een koude cel gekoeld tot cryogene temperaturen. Binnen de cel worden de moleculen gethermaliseerd door een koud buffergas. Figuur 9.1 illustreert de werking van de cryogene bron.

Figuur 9.1: Een schematische weergave van de opstelling van de cryogene bron. Een tweetraps cryostaat koelt de cel af tot een constante lage temperatuur. Een ablatielaser verhit een roterende SrF_2 of Sr doelwit in de cel. In het geval van SrF_2 bevatten de ontstane producten SrF moleculen en bij Sr worden de ablatie producten gemengd met SF_6 om SrF te vormen. Door een continue stroming van het buffergas neon worden de SrF moleculen gekoeld en uit de cel geleid in de vorm van een bundel. De figuur is niet op schaal.

Het buffergas stroomt samen met de moleculen de cel uit, resulterend in een koude molecuul bundel met een snelheid van ongeveer 200 m/s. Voor de uiteindelijke eEDM meting zullen barium fluo ide (BaF) moleculen gebruikt worden. Vanwege de beschikbare kennis omtrent strontium fluo ide (SrF) molecuulbundels in onze groep en de beschikbaarheid van detectielasers met hiervoor relevante golflengtes in ons laboratorium, is de cryogene bron ontwikkeld en gekarakteriseerd door gebruik te maken van SrF moleculen. Dit molecuul is lichter dan BaF, maar heeft vergelijkbare energieniveaus en chemische eigenschappen. Met de gebouwde bron kunnen molecuulbundels geproduceerd worden met een frequentie van 10 Hz. Elke bundel begint met de ablatie van een roterend doelwit binnen een koperen cel. Twee verschillende doelwitten zijn getest: een SrF_2 doelwit en een Sr doelwit in de aanwezigheid van SF_6 gas. De koperen cel wordt gekoeld tot 20 K door een tweetraps cryostaat, daarna stroomt neon gas

continu door de cel om de SrF moleculen eerst te koelen en daarna aan de cel te onttrekken in de vorm van een molecuulbundel.

Om de molecuulbundel te detecteren worden twee methoden gebruikt: lasergeïnduceerde fluo escentie- en absorptiedetectie. De opstelling en de resultaten verkregen met de twee detectiemethoden worden besproken in hoofdstuk 4. Een belangrijk onderdeel van deze laser gebaseerde detectiemethoden is de golflengte stabilisatie. Hiervoor hebben wij een geautomatiseerd stabilisatiesysteem gebouwd (paragraaf 4.3). De gemiddelde snelheden van de molecuulbundels zijn geschat tussen 140 en 270 m/s, afhankelijk van de operatiecondities van de bron. In dit proefschrift worden de uitkomsten van een systematische studie naar de invloeden van de neon stroming, de cel temperatuur en de ablatie energie op de eigenschappen van de molecuulbundel gepresenteerd. In hoofdstuk 5 wordt de studie naar het gebruik van een SrF₂ doelwit gepresenteerd, terwijl in hoofdstuk 6 het gebruik van een Sr doelwit wordt geëvalueerd. Het signaal verkregen met Sr bleek ongeveer 1000 keer hoger te zijn dan dat verkregen met SrF₂ ablatie.

Het meest intense signaal verkregen met de bron correspondeert met ongeveer 10^9 moleculen per ablatiepuls in één rotationele toestand ($N = 1$) (paragraaf 4.5). Deze prestatie is vergelijkbaar met soortgelijke bronnen beschreven in de literatuur [73, 88, 93]. Naast de intensiteit van de bundel, is de stabiliteit ook belangrijk. De rotatie van het doelwit is cruciaal voor het behouden van een hoge bundelintensiteit na elke ablatiepuls. Het is gebleken dat er reguliere fluctuaties voorkomen in de bundelintensiteit, veroorzaakt door het rotatiemechanisme van het doelwit en door inhomogeniteit in de doelwiten. Een belangrijke bevinding uit de metingen is dat afhankelijk van de ablatie-energie, meerdere molecuul distributies waargenomen kunnen worden in individuele molecuulbundels. Hoe hoger de ablatie-energie, hoe hoger het aantal distributies. De omstandigheden voor een stabiele bundelformatie, de variatie van de bundelintensiteit en de manifestatie van deze distributies wordt bestudeerd in hoofdstuk 5. Het multimodale karakter van het gedetecteerde bundelsignaal compliceert de analyse van de bundelsnelheid. Om onderscheid te maken tussen ruimtelijke en temporele bundelmodulatie, maken we gebruik van de lopendegolf-Starkafremmer in ons laboratorium om moleculen te selecteren gebaseerd op hun snelheid. De afremmer is ontworpen om de geproduceerde molecuulbundels af te remmen en daardoor spectroscopische metingen met hoge precisie mogelijk te maken. Voor het NL-eEDM programma zal de afremmer de moleculen tot een snelheid van 30 m/s afremmen. Een schematische weergave van de koppeling van de afremmer met de cryogene bron is weergegeven in Figuur 9.2. De eerste metingen aan de bron-afremmer combinatie worden gepresenteerd in hoofdstuk 7.

Figuur 9.2: Schematische weergave van de experimentele opstelling: een gedeelte van moleculen uit de cryogene bron wordt in de afremmer opgevangen in lopende vallen bestaande uit elektrisch veldminima. De snelheid van deze lopende vallen kan computergestuurd aangepast worden om te zorgen voor de begeleiding of afremming van moleculen. Met behulp van absorptiedetectie worden moleculen 5 mm achter de cel gedetecteerd. Fluorescentiedetectie vindt plaats 18.1 cm achter de afremmer. De figuur is niet op schaal.

De afremmer bestaat uit een reeks ringen waarover verschillende spanningen staan om een repeterend elektrisch veldpatroon, met minima die moleculen aantrekken, te creëren in de afremmer. Nadat de moleculen de afremmer uit zijn worden ze middels laser geïnduceerde fluorescentie gedetecteerd. Middels absorptie- en fluorescentiedetectie vóór en achter de afremmer respectievelijk, was het mogelijk om de optimale condities voor de overdracht van moleculen van de bron naar de afremmer te achterhalen. Een opmerkelijk resultaat uit de detectie metingen is dat de optimale broncondities om zoveel mogelijk moleculen te produceren niet overeenkomen met de optimale afremmercondities om zoveel mogelijk moleculen door te laten. Bij optimale broncondities bleek dat het aantal moleculen dat door de afremmer ging in sommige vallen juist veel lager was vergeleken met suboptimale broncondities. Dit is bijvoorbeeld zichtbaar in Figuur 7.11 in hoofdstuk 7 en wordt verder besproken in paragraaf 7.4. Voor het verklaren van dit resultaat is meer onderzoek nodig. Een mogelijke verklaring is een suboptimale uitlijning tussen de bron en afremmer. Mogelijk speelt de transversale beweging van moleculen in de afremmer, welke sterk afhankelijk is van de spanning over de ringen, ook een rol.

De molecuulbundels gecreëerd met de bron zullen gebruikt worden om een gevoelige meting te doen aan het eEDM. De optimale gevoeligheid in deze meting wordt bereikt met een molecuulbundel dat een lage snelheid combineert met een hoge intensiteit. In dit proefschrift

hebben wij laten zien dat dat we intense bundels van geschikte moleculen kunnen produceren met een gemiddelde snelheid rond 200 m/s en een intensiteit van de orde 10^9 moleculen per bundel, wat overeenkomt met de ontwerpdoelen van het NL-eEDM experiment.

Vooruitzicht

Met de succesvolle constructie van de bron is het tijd om verder in de toekomst van het experiment te kijken. Tijdens het verlaten van de bron, verspreid de molecuulbundel zich transversaal in de ruimte door de transversale snelheid van de moleculen. Dit betekent dat een experiment geen gebruik kan maken van de volledige intensiteit van de gecreëerde bundels. In de metingen gepresenteerd in dit proefschrift konden alleen moleculen met een transversale snelheid lager dan ongeveer ± 1 m/s de afremmer bereiken. Aangezien de snelheidsacceptatie van de afremmer ± 5 m/s is (of zelfs 10 m/s is bij een verhoogde spanning op de ringen), kan de koppeling tussen de bron en afremmer sterk verbeterd worden. Gegeven dat de afstand tussen de bron en de afremmer niet heel klein gemaakt kan worden (hitteschilden staan in de weg), hebben wij gekozen voor een elektrostatische begeleider, welke op het moment van schrijven wordt geïnstalleerd in de experimentele opstelling. Met behulp van deze begeleider kan de volledige faseruimte-acceptatie van de afremmer gebruikt worden. Daarnaast kan de positie van de begeleider aangepast worden zodat mogelijke uitlijningsfouten tussen bron en afremmer ook gecorrigeerd kunnen worden.

Ondanks dat de cryogene bron op dit moment molecuulbundels produceert met een frequentie van 10 Hz en met de beoogde intensiteit, kunnen er nog altijd manieren gevonden worden om de intensiteit te verhogen. Dit zou voordelig zijn voor elk experiment na de bron. Voor dit doeleinde is er aan de VU Amsterdam een toegewijde bron gebouwd binnen het NL-eEDM programma. Met de laatstgenoemde bron kunnen er nieuwe manieren gevonden worden voor de optimale productie van BaF middels de detectie van zowel moleculen als buffergas atomen. Een interessante optie is het aanpassen van de celuitgang zodat de transversale spreiding van de bundels gereduceerd wordt. Een andere mogelijkheid die onderzocht zou kunnen worden is het aanpassen van de celgeometrie om turbulentie in de cel te reduceren, dit leidt tot betere thermalisatie en daardoor lagere gemiddelde snelheden van de moleculen. Een andere methode om de molecuulbundelintensiteit te verhogen is het optisch pompen van moleculen naar de gewenste rotationele toestand voordat ze de afremmer bereiken.

In dit proefschrift is een bron van intense, langzame, koude molecuulbundels voor het bestuderen van fundamentele symmetrieën in het standaardmodel van de deeltjesfysica gepresenteerd. Deze stap is het begin van een veelbelovend project. De bron is al gebruikt voor het afremmen en invangen van SrF [133, 134].

A

Hard Sphere Collisions

In a simple hard-sphere approach, one can picture the collision between a molecule of mass m_x and a buffer gas atom of mass m_b to be as illustrated in Figure A.1, a similar model is used in [63, 135, 136, 73]. All velocities are defined in the rest frame of the buffer gas. Assuming elastic collisions (ignoring energy dissipation to rotational and vibrational degrees of freedom), the following conservations apply:

$$m_x \mathbf{u} = m_x \mathbf{v} + m_b \mathbf{v}_{bg} \quad (\text{A.1a})$$

$$m_x \mathbf{u}^2 = m_x \mathbf{v}^2 + m_b \mathbf{v}_{bg}^2 \quad (\text{A.1b})$$

Figure A.1: Hard sphere collision diagram between a molecule with mass m_x (blue/large) and a colder atom of mass m_b (grey/small). $\mathbf{u}$, $\mathbf{v}$ and $\mathbf{v}_{bg}$ are their corresponding velocities before and after the collision. The angles ϕ and θ of the particles with a reference axis are also shown.

The velocities of the particles can be decomposed into two perpendicular directions with (A.1) still applicable to each direction.

$$\mathbf{u} = |\mathbf{u}| \hat{\mathbf{x}} \quad (\text{A.2a})$$

$$\mathbf{v} = |\mathbf{v}| \cos(\theta) \hat{\mathbf{x}} + |\mathbf{v}| \sin(\theta) \hat{\mathbf{y}} \quad (\text{A.2b})$$

$$\mathbf{v}_{bg} = |\mathbf{v}_{bg}| \cos(\phi) \hat{\mathbf{x}} - |\mathbf{v}_{bg}| \sin(\phi) \hat{\mathbf{y}} \quad (\text{A.2c})$$

Definin $\alpha = m_x/m_b$ and rewriting (A.1) for all directions results in:

$$\alpha (|\mathbf{u}| - |\mathbf{v}| \cos(\theta)) = |\mathbf{v}_{bg}| \cos(\phi) \quad (\text{A.3a})$$

$$\alpha |\mathbf{v}| \sin(\theta) = |\mathbf{v}_{bg}| \sin(\phi) \quad (\text{A.3b})$$

$$\alpha (|\mathbf{u}|^2 - |\mathbf{v}|^2) = |\mathbf{v}_{bg}|^2 \quad (\text{A.3c})$$

Rewriting (A.3a) to:

$$\alpha |\mathbf{v}| \cos(\theta) = \alpha |\mathbf{u}| - |\mathbf{v}_{bg}| \cos(\phi) \quad (\text{A.4})$$

Summing the squares of (A.3b) and (A.4), and rewriting yields:

$$\alpha^2 (|\mathbf{v}|^2 - |\mathbf{u}|^2) = 2\alpha |\mathbf{u}| |\mathbf{v}_{bg}|^2 \cos(\phi) - |\mathbf{v}_{bg}|^2 \quad (\text{A.5})$$

Equating (A.5) to (A.3c) multiplied by $-\alpha$ results in:

$$|\mathbf{v}_{bg}| = \frac{2\alpha}{\alpha + 1} |\mathbf{u}| \cos(\phi) \quad (\text{A.6})$$

Immediately after ablation, before any collisions with the buffer gas atoms occur the velocity of the buffer gas atom is considered to be negligible compared to that of the molecules. Even though both velocities become of the same order as the molecules are being cooled, the molecule are sufficiently thermalized when that condition is reached. With this approximation the amount of kinetic energy gained by an atom after collision with a molecule is:

$$\begin{aligned} \Delta E &= \frac{1}{2} m_b |\mathbf{v}_{bg}|^2 \\ &= \left[\frac{4\alpha^2}{(\alpha + 1)^2} \cos^2(\phi) \right] \frac{1}{2} m_b |\mathbf{u}|^2 \\ &= \left[\frac{4\alpha}{(\alpha + 1)^2} \cos^2(\phi) \right] \frac{1}{2} m_x |\mathbf{u}|^2, \end{aligned} \quad (\text{A.7})$$

corresponding to a fraction:

$$\epsilon = \frac{4\alpha}{(\alpha + 1)^2} \cos^2(\phi) \quad (\text{A.8})$$

removed from the initial kinetic energy E_0 of the molecule.

Scattering of the atom after a collision can occur at all angles $\phi \in [-\pi/2, \pi/2]$ relative the molecule's initial direction axis. Knowing that $\langle \cos^2(\phi) \rangle_{[-\pi/2, \pi/2]} = \frac{1}{2}$, one can derive that the average energy fraction lost per collision is:

$$\epsilon = \frac{2\alpha}{(\alpha + 1)^2} = \frac{2m_x m_b}{(m_x + m_b)^2} \quad (\text{A.9})$$

From (A.9) it can be concluded that after every n^{th} collision, a fraction, ϵ , of the total kinetic energy E is transferred to the colder atoms, or in equation form:

$$E(n+1) - E(n) = -\epsilon E(n) \quad (\text{A.10})$$

The net transfer of energy halts when the kinetic energy of the molecules equals that of the atoms. The atoms are assumed to be cooled continuously due to their collisions with the cold cell wall and other buffer gas atoms.

Casting (A.10) into differential form yields:

$$\frac{dE}{dn} = -\epsilon E(n) \quad (\text{A.11})$$

The solution to (A.11) is given by:

$$E(n) = (E_0 - E_{bg}) e^{-\epsilon n} + E_{bg} \quad (\text{A.12})$$

Where E_0 is the initial kinetic energy of the molecule and E_{bg} the kinetic energy of the buffer gas atoms. Since the kinetic energy of an atom or molecule at temperature T can be written as $E = 3/2 k_B T$ [137], one can rewrite (A.12) as:

$$T(n) = (T_0 - T_{bg}) e^{-\epsilon n} + T_{bg} \quad (\text{A.13})$$

Turning (A.13) into:

$$T(n) = (T_0 - T_{bg}) \exp \left[-\frac{2m_b^2}{(m_x + m_b)^2} n \right] + T_{bg} \quad (\text{A.14})$$

This shows that the temperature of the molecules exponentially decays towards the buffer gas temperature as function of the number of collisions with the buffer gas molecules.

B

Counting Molecules

In this chapter, methods will be derived and applied to determine the number of molecules, based on the absorption detection and fluorescence detection. This quantitative evaluation is used for the characterisation of the performance of the source. The evaluation requires the detailed description of the absorption and emission process of the $\Sigma \rightarrow \Pi$ transition. Furthermore the detection solid angle, the overlap with the molecular beam, possible optical cycling in the transition and properties of the light collection are taken into account.

Figure B.1: Relevant energy structure of SrF for extracting the number of molecules from the counted photons, together with the accessible molecular transitions for the used laser light in this work. The molecular energy transitions are grouped into 4 transitions here.

At this stage it is useful to represent part of the molecular energy structure of SrF for the $\Sigma \rightarrow \Pi_{1/2}$ transition, this is done in Figure B.1. In the figure, the accessible molecular transitions for the used laser are also shown. The $m_F = \pm 2$ states are shown as dark states for the following reason: the only allowed transitions are those where $\Delta F = 0, \pm 1$ and if $F = F_g$ in the ground state is larger than $F = F_e$ in the excited state, then two of these transitions are not allowed—and only those obeying $F_g \rightarrow F_e = F_g - 1 \rightarrow F_g$ are allowed [138]. Although not shown here the $v > 0$ states are also dark for the laser used in this work.

B.1 Number of Photons Scattered per Molecule

A single molecule can be excited maximally once every $2 \times \text{excited state lifetime}$. If the molecules spent more time in the laser beam, there is a probability that more than one photon is scattered per molecule. The expected number of scattered photons per molecule has to be calculated. For that, one has to calculate how often a molecule can be transferred to the excited state during the laser-molecule interaction time, until it moves into an inaccessible state or out of the laser beam. The upper limit of the number of emitted photons is set by the time the molecule spent interacting with laser photons. In other words, one has to keep track of the population of the excited states ($\Pi_{1/2}$) while the molecule interacts with the laser. The recipe used here for photon counting is summarized in two steps:

1. Keep track of the population in excited state(s).
2. Sum the number of photons scattered from the excited states, during the laser-molecule interaction time.

Step 1: Keep Track of the Population in Excited State(s)

To keep track of the population in the excited states, the semi-classical master equation known as the Gorini–Kossakowski–Sudarshan–Lindblad equation will be used [139]. This latter equation will be noted as the master equation in this work. This master equation describes the time evolution of the state operator (a.k.a. density matrix).

Figure B.2: 3-level energy system based on the energy structure of SrF and the available laser in the current experimental setup. The respective probabilities for the decay channel to occur are also shown for each channel.

For a quantum system interacting with a driving electro-magnetic field the so called Lindblad form of this equation is given by:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] + R \quad (\text{B.1})$$

Where ρ is the state operator and R , is the relaxation operator given by:

$$R = L_\mu \rho L_\mu^\dagger - \frac{1}{2} L_\mu^\dagger L_\mu \rho - \frac{1}{2} \rho L_\mu^\dagger L_\mu, \quad (\text{B.2})$$

where Einstein summation rules apply. If there are other sources of relaxation other than the vacuum field, e.g collisions, they can be added in the form of an additional element L_μ of L . H is the Hamiltonian of the system. L_μ is a so called jump operator, representing a transition rate, induced by a relaxation mechanism.

For this work only spontaneous emission will be considered as the relaxation mechanism, although other mechanisms such as stray electric and magnetic field in the lab are also present, but estimated to be negligible. To solve the master equation, one would have to consider all the states involved and the possible transitions. Since one is only interested in whether a molecule is in an excited state, laser accessible state or none of both, this system can be reduced to an effective three-level system.

Figure B.2 illustrates the effective three-level energy structure for SrF in combination with available laser light in the experimental setup. The excited state contains all the excited states possible for the experiment namely: $A^2\Pi_{1/2}(v=0, J=1/2)$. While the inaccessible state consists of all the states where $v > 0$ and the $m_F = -2$ and 2 states shown in Figure B.1. The accessible states consists of all other sub-states of $X^2\Sigma^+(v=0, N=1)$, except the $m_F = -2$ and 2 states. The probability for the different decay channels of this reduced system are calculated from the branching ratios and Franck-Condon factors of the individual transitions [75]. The probability for the excited state population to decay into the ground state is 0.98 as given by the Franck-Condon factor. From the 0.98, a fraction 0.08335 (~ 0.08 of the total) decays into the inaccessible $m_F = -2$ and 2 states and 0.91665 (~ 0.9 of the total) to the accessible states [75]. For decay from the excited state to the inaccessible $v > 0$, the probability is 0.02. From the above it can be concluded that from the excited state a fraction of 0.9 decays to the accessible state and $0.08 + 0.02 = 0.1$ to the inaccessible state, these are the numbers shown in Figure B.2.

The Hamiltonian of this reduced driven system is given by:

$$H = H_0 + V_{int}(t) \quad (B.3)$$

Where H_0 is the Hamiltonian of the particle, only subjected to the vacuum electro-magnetic field, and $V_{int}(t)$ is the Hamiltonian attributed to the particle's interaction with a non-vacuum external electro-magnetic field (the laser). To describe the three level system further, a Hilbert space for the energy states is chosen to be consisting of the following basis states:

$$|g\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, |l\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, |e\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

The notation of these states corresponds to the state notation used in Figure B.2.

H_0 then becomes:

$$H_0 = \hbar\omega_g |g\rangle \langle g| + \hbar\omega_l |l\rangle \langle l| + \hbar\omega_e |e\rangle \langle e|, \quad (B.4)$$

with $\hbar\omega_x$ representing the energy a particle would have, if it occupied state $|x\rangle$. Without loss of generality, the energy of state $|g\rangle$ can be taken as the zero energy level, converting (B.4) into:

$$H_0 = \hbar\omega_{gl} |l\rangle \langle l| + \hbar\omega_{ge} |e\rangle \langle e|, \quad (B.5)$$

where ω_l is subtracted from all energies and ω_{gl} and ω_{ge} represent energies associated with the transitions $|g\rangle \leftrightarrow |l\rangle$ and $|g\rangle \leftrightarrow |e\rangle$. For the interaction Hamiltonian $V_{int}(t)$ it holds that there is only a direct interaction between states $|g\rangle$ and $|e\rangle$. In the electric dipole approximation it holds that:

$$V_{int}(t) = \mu_{ge} \tilde{E}(t) |e\rangle \langle g| + \mu_{ge}^* \tilde{E}(t) |g\rangle \langle e|, \quad (B.6)$$

with $\tilde{E}(t)$ as the electric component of the driving field and μ_{ge} the electric transition dipole moment between $|e\rangle$ and $|g\rangle$. if the transition $|g\rangle \leftrightarrow |e\rangle$ is driven by a monochromatic field of amplitude E and frequency ω , $\tilde{E}(t)$ can be written as:

$$\tilde{E}(t) = |E| (e^{-i\omega t} + e^{i\omega t}) \quad (B.7)$$

Another assumption made in (B.6) is that the states $|g\rangle$ and $|e\rangle$ have a definite parity so that $\mu_{gg} = \mu_{ee} = 0$. The Hamiltonian now becomes:

$$H = \hbar\omega_{gl} |l\rangle \langle l| + \hbar\omega_{ge} |e\rangle \langle e| + \mu_{ge} \tilde{E}(t) |e\rangle \langle g| + \mu_{ge}^* \tilde{E}(t) |g\rangle \langle e| \quad (B.8)$$

The driving field introduces a time dependence into the Hamiltonian of the system and the master equation cannot be solved exactly. An approximate solution can be obtained by means of the rotating wave approximation (RWA) [140]. The RWA corresponds to solving the master

equation in a frame rotating with the same frequency as the driving field frequency ω and neglect the fast oscillating terms in the master equation as they average to zero on the time scales of the driving field oscillations. To introduce this rotation to (B.1), a unitary rotational operation on the system's state is performed. The unitary operator is given by:

$$U_R = e^{-i\omega t |e\rangle\langle e|} \\ = e^{i\omega t} |e\rangle\langle e| + |l\rangle\langle l| + |g\rangle\langle g| \quad (\text{B.9})$$

It can be shown that after the unitary operation, the transformed master equation becomes:

$$\frac{d\tilde{\rho}}{dt} = -\frac{i}{\hbar} [\tilde{H}, \tilde{\rho}] + R\tilde{\rho}, \quad (\text{B.10})$$

where the transformed objects $\tilde{\rho}$ and $\tilde{H}$ are given by [141, 142]:

$$\tilde{\rho} = U_R^\dagger \rho U_R \quad (\text{B.11})$$

and

$$\begin{aligned} \tilde{H}(t) &= U_R^\dagger H(t) U_R - i\hbar U_R^\dagger \frac{\partial U_R}{\partial t} \\ &= e^{i\omega |e\rangle\langle e|} H e^{-i\omega t |e\rangle\langle e|} - i\hbar \left[e^{i\omega |e\rangle\langle e|} \cdot (-i\omega) |e\rangle\langle e| \cdot e^{-i\omega t |e\rangle\langle e|} \right] \\ &= \hbar\omega_{ge} |e\rangle\langle e| + \mu_{ge} \tilde{E}(t) e^{-i\omega t} |g\rangle\langle e| + \hbar\omega_{gl} |l\rangle\langle l| + \mu_{ge}^* \tilde{E}(t) |e\rangle\langle g| - \hbar\omega |e\rangle\langle e| \end{aligned} \quad (\text{B.12})$$

or in matrix notation:

$$\tilde{H}(t) = \hbar \begin{pmatrix} \omega_{ge} - \omega & 0 & \frac{\mu_{ge}|E|}{\hbar} (1 + e^{-2i\omega t}) \\ 0 & \omega_{gl} & 0 \\ \frac{\mu_{ge}|E|}{\hbar} (1 + e^{2i\omega t}) & 0 & 0 \end{pmatrix}, \quad (\text{B.13})$$

where (B.7) was used and that $\mu_{ge} = \mu_{ge}^*$ [143]. In the rotating wave approximation the fast oscillating terms are discarded and one ends up with.

$$\tilde{H}(t) = \hbar \begin{pmatrix} \omega_{ge} - \omega & 0 & \Omega_{ge} \\ 0 & \omega_{gl} & 0 \\ \Omega_{ge} & 0 & 0 \end{pmatrix}, \quad (\text{B.14})$$

where Ω_{ge} is called the Rabi frequency and define as:

$$\Omega_{ge} = \frac{|\mu_{ge}| |E|}{\hbar} \quad (\text{B.15})$$

Knowing the laser intensity I , the electric field strength $|E|$ can be calculated from:

$$I = 2\epsilon_0 c |E|^2 \quad (\text{B.16})$$

For spontaneous emission the jump operator L is governed by:

1. Emission of a photon combined with the transition $|e\rangle \rightarrow |g\rangle$
2. Photon emission during the transition $|e\rangle \rightarrow |l\rangle$

The emission rates for the above processes are respectively Γ_{eg} and Γ_{el} . The jump operator elements describing the two process above will be noted as L_{eg} and L_{el} and are given by:

$$L_{eg} = \sqrt{\Gamma_{eg}} |g\rangle \langle e| \quad (\text{B.17})$$

and

$$L_{el} = \sqrt{\Gamma_{el}} |l\rangle \langle e| \quad (\text{B.18})$$

Equation (B.10) can be rewritten using Einstein notation:

$$\frac{d}{dt} \tilde{\rho}_{\alpha\beta} = -\frac{i}{\hbar} (\tilde{H}_{\alpha\gamma} \tilde{\rho}_{\gamma\beta} - \tilde{\rho}_{\alpha\gamma} \tilde{H}_{\gamma\beta}) + R_{\alpha\beta} \quad (\text{B.19})$$

With:

$$R_{\alpha\beta} = L_{\mu\alpha\gamma} \tilde{\rho}_{\gamma\delta} L_{\mu\beta\delta} - \frac{1}{2} L_{\mu\gamma\alpha} L_{\mu\gamma\delta} \tilde{\rho}_{\delta\beta} - \frac{1}{2} \tilde{\rho}_{\alpha\gamma} L_{\mu\delta\gamma} L_{\mu\delta\beta} \quad (\text{B.20})$$

Where L the relaxation jump operator and μ marks the summation over all its elements, in this case L_{eg} and L_{el} so that:

$$\mu \in \{eg, el\} \quad (\text{B.21})$$

Rewriting equations (B.17) and (B.18) in matrix form results in:

$$L_{el} = \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{\Gamma_{el}} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (\text{B.22})$$

$$L_{eg} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \sqrt{\Gamma_{eg}} & 0 & 0 \end{pmatrix} \quad (\text{B.23})$$

And $\tilde{\rho}$ is given by:

$$\tilde{\rho} = \begin{pmatrix} \tilde{\rho}_{ee} & \tilde{\rho}_{el} & \tilde{\rho}_{eg} \\ \tilde{\rho}_{le} & \tilde{\rho}_{ll} & \tilde{\rho}_{lg} \\ \tilde{\rho}_{ge} & \tilde{\rho}_{gl} & \tilde{\rho}_{gg} \end{pmatrix} = \begin{pmatrix} \tilde{\rho}_{00} & \tilde{\rho}_{01} & \tilde{\rho}_{02} \\ \tilde{\rho}_{10} & \tilde{\rho}_{11} & \tilde{\rho}_{12} \\ \tilde{\rho}_{20} & \tilde{\rho}_{21} & \tilde{\rho}_{22} \end{pmatrix} \quad (\text{B.24})$$

Explicitly writing the differential equation governing ρ_{00} from (B.19), (B.20) results in:

$$\frac{d}{dt}\tilde{\rho}_{00} = -i\Omega(\tilde{\rho}_{20} - \tilde{\rho}_{02}) - (\Gamma_{eg} + \Gamma_{el})\tilde{\rho}_{00} \quad (\text{B.25})$$

and for the ground state

$$\frac{d}{dt}\tilde{\rho}_{22} = -i\Omega(\tilde{\rho}_{02} - \tilde{\rho}_{20}) + \Gamma_{eg}\tilde{\rho}_{00} \quad (\text{B.26})$$

In the same way the other differential equations for the populations and coherences (off diagonal terms) can be explicitly written. Finally, one can write (B.19) in the form of a Liouville equation:

$$\frac{d}{dt}\tilde{\rho} = \mathcal{L}\tilde{\rho}, \quad (\text{B.27})$$

with

$$\mathcal{L} = \begin{pmatrix} -\gamma & 0 & i\Omega & 0 & 0 & 0 & -i\Omega & 0 & 0 \\ 0 & i\omega_{gl} - i\Delta - \gamma & 0 & 0 & 0 & 0 & 0 & -i\Omega & 0 \\ i\Omega & 0 & -i\Delta - \gamma & 0 & 0 & 0 & 0 & 0 & -i\Omega \\ 0 & 0 & 0 & -i\omega_{gl} + i\Delta - \gamma & 0 & i\Omega & 0 & 0 & 0 \\ \Gamma_{el} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & i\Omega & 0 & -i\omega_{gl} & 0 & 0 & 0 \\ -i\Omega & 0 & 0 & 0 & 0 & 0 & i\Delta - \gamma & 0 & i\Omega \\ 0 & -i\Omega & 0 & 0 & 0 & 0 & 0 & i\omega_{gl} & 0 \\ \Gamma_{eg} & 0 & -i\Omega & 0 & 0 & 0 & i\Omega & 0 & 0 \end{pmatrix}, \quad (\text{B.28})$$

Where $\Delta = \omega_{ge} - \omega$ is the laser detuning away from the transition frequency between $|g\rangle$ and $|e\rangle$ and $\gamma = 1/2(\Gamma_{el} + \Gamma_{eg})$ is the decoherence rate. Furthermore $\tilde{\rho}$ is a rewritten version of (B.24):

$$\tilde{\rho} = \begin{pmatrix} \tilde{\rho}_{00} & \tilde{\rho}_{01} & \tilde{\rho}_{02} & \tilde{\rho}_{10} & \tilde{\rho}_{11} & \tilde{\rho}_{12} & \tilde{\rho}_{20} & \tilde{\rho}_{21} & \tilde{\rho}_{22} \end{pmatrix}^T \quad (\text{B.29})$$

The lifetime τ_0 of the $A^2\Pi_{1/2}(v=0, J=1/2)$ state is 24 ns [144], resulting in $\Gamma_{eg} = 0.9 \cdot 1/24 \cdot 10^9 = 37.5$ MHz and $\Gamma_{el} \approx 4.2$ MHz. The wavelength λ of the transition between $|g\rangle$ and $|e\rangle$ is 663.3 nm. The beam intensity I is 239 ± 3 W/m². The molecules spent around $t_{int} = 10$ μ s interacting with the laser light, based on the typical molecular beam velocity and the used laser beam diameters.

The transition dipole moment, μ_{eg} , can be calculated from the following equation [100]:

$$\mu_{eg} = \sqrt{\Gamma_{eg}\lambda^3 \frac{3\epsilon_0\hbar}{8\pi^2}}, \quad (\text{B.30})$$

resulting in $\mu_{eg} = 5.89$ Debye.

Figure B.3: Population in the different states of the reduced system. The system is driven from the accessible state to the excited state, while spontaneously decaying from the excited state to the accessible and inaccessible state. After 2.5 μs the molecule has practically stopped emitting photons and is inaccessible for the laser.

The population in the different states are obtained from solving the Liouville equation (B.27). On-resonance detection was performed resulting in $\Delta \approx 0$.

For the conditions described earlier, the evolution of the population in the different states of the reduced system is illustrated in Figure B.3.

Step 2: Sum the Number of Photons Scattered From the Excited States During the Laser-Molecule Interaction Time.

To calculate how often a single molecule emits a photon on average before it enters the inaccessible state $|I\rangle$ or escapes from the laser beam, the population in the excited state must be integrated in time, since it is the last state occupied before the molecule makes a fluorescent transition. This population corresponds to the state operator element $\tilde{\rho}_{ee}$ or equivalently $\tilde{\rho}_{00}$. Whatever the population is in $\tilde{\rho}_{00}$ will decay with rate Γ_{eg} back to the accessible state, meaning that this fraction will be re-excited. This decay and excitation process will continue for the duration of the laser-molecule interaction τ or until the total population is in the inaccessible state. The number of scattered photons from this process is then given by:

$$N_s = \int_0^\tau \tilde{\rho}_{00}(t) \Gamma_{eg} dt + \mathcal{P}_{el} \int_0^\tau \tilde{\rho}_{00}(t) \Gamma_{el} dt \quad (\text{B.31})$$

The first term in (B.31) accounts for the photons scattered from transitions between the excited and the accessible state, while the last term accounts for the fact that a fraction $\mathcal{P}_{el}$ of

the molecules decaying into the inaccessible state, decay to hyperfine states of rotational state $N = 1$. These latter transitions emit photons in the detectable range, which are detected by the PMT. For the detection system at hand the fluorescent transitions to $|I\rangle$ are those to $m_F = \pm 2$. 80 % of the molecules decaying from $|e\rangle$ to $|I\rangle$ end up in these hyperfine states [75], resulting in $\mathcal{P}_{el} = 0.8$.

The result is that there are $N_s = 9.8$ photons emitted (scattered) on average by a single molecule before it becomes inaccessible. If one would manage to effectively mix the inaccessible m_F states with the accessible states (e.g. by using a magnetic field) ~ 50 photons would be emitted before the molecule becomes inaccessible. If the hyperfine structure would not be addressed (not using the EOM described in Chapter 4), only 1.3 photons would be scattered before a molecule decays to an inaccessible state—one thus gains a factor of 7.5 more signal when the sidebands are used. Comparing the latter to the experimental result shown in Figure 4.16, where ~ 8 times more signal was obtained with the EOM, shows that the EOM is very effective in addressing the hyperfine structure.

B.2 Counting Molecules

Figure B.4: Illustration of the intersection between a detection laser of circular cross section $\varnothing$ (diameter is $d_\varnothing$) and molecular beam of diameter $\mathcal{D}$ a distance L away from the cell exit. The cell exit has diameter d , while the divergence angle of the beam is noted as θ .

Only a fraction of the total molecules produced, interacts with the laser beam. Figure B.4 illustrates how a detection laser beam of circular cross section $\varnothing$ (diameter is $d_\varnothing$) and the molecular beam interact. A distance L away from the cell exit of diameter d , the molecular beam Full width at half maximum (FWHM) diameter is $\mathcal{D}$. θ is the divergence angle of the molecular beam.

B.2.1 Counting Molecules from Molecular Fluorescence

The focus will now be on the laser induced fluorescence (LIF) detection scheme. The light collection geometry and the PMT quantum efficiency determine what fraction of the scattered photons will be registered and counted. The PMT quantum detection efficiency will for now be noted as η_{dev} . Furthermore in the LIF process photons scatter at all angles in an indiscriminate way, but only those scattered at certain angles, as one can see from the LIF chamber shown in Figure 4.3, are detected. The detected fraction is represented via the total solid angle Θ_{sol} , from which photons are focused onto the PMT. The mirrors, lenses and other optics used for collecting the scattered photons also dissipate energy, reducing the fraction of detected photons by η_{opt} .

Only a fraction η_{cross} of the produced molecules interact with the laser beam. If N_{ph} is the number of photons detected, then total number of produced molecules M_{mols} is then given by:

$$M_{\text{mols}} = \frac{N_{ph}}{N_s} \frac{1}{\eta_{\text{cross}}} \frac{1}{\eta_{\text{dev}}} \frac{1}{\eta_{\text{opt}}} \frac{4\pi}{\Theta_{\text{sol}}} = \frac{N_{ph}}{\eta}, \quad (\text{B.32})$$

where $1/\eta$ is the overall detected fraction of the total number of produced molecules. The fraction η_{cross} , will be estimated from the molecular beam divergence angle θ and the distance L . Although θ was not measured in this work, measurements performed in [75] show that θ is reasonably constant over the flow range utilized in this work and is given by $\theta \approx 35^\circ$. considering the geometry in Figure B.4, one can calculate that:

$$\mathcal{D} = d + 2 \tan(\theta/2)L \quad (\text{B.33})$$

The molecular beam density is symmetric in the transverse directions and decreases as a Gaussian away from the beam centre [145].

The number of molecules M_{mols} in the beam, can be calculated from the molecular flu Φ through a circular surface S of diameter $\mathcal{D}$, as illustrated in figure B.5 and can be written as:

$$M_{\text{mols}} = \iint \Phi dS dt \quad (\text{B.34})$$

The relation between the molecular signal density number s and the flu is given by:

$$\Phi = s v_z, \quad (\text{B.35})$$

Figure B.5: molecular beam through a surface of diameter $\mathcal{D}$.

where v_z is the molecular beam velocity at position L along the beam line. Just like the molecular number, Φ decreases like a Gaussian away from the centre of S .

Under the condition that $\pi \mathcal{D}^2 \gg \varnothing$, the measured molecular signal density s can be approximated to be the maximum of a 2D Gaussian distribution living on S , with $\mathcal{D}$ its full width at half maximum (FWHM). From the above it follows that:

$$\begin{aligned} M_{\text{mols}} &= \iint s(t) v_z(t) dt dS \\ &= 2\pi \sigma_{\mathcal{D}}^2 \int s(t) v_z(t) dt, \end{aligned} \quad (\text{B.36})$$

where the time dependency of s is explicitly written and it was used that the surface under a 2D Gaussian with amplitude $s(t) v_z(t)$ and standard deviation $\sigma_{\mathcal{D}}$, is $2\pi \sigma_{\mathcal{D}}^2 \cdot s(t) v_z(t)$.

To find an expression for $s(t)$, the detection geometry is considered [146]. The approximate overlap between the field of view of the PMT sensitive surface, the detection laser beam and

the molecular beam will be noted as the collection volume V_c . The width and length (z and x) are determined by the approximate magnification of the sides of the PMT sensitive surface. The magnification is around 1/3, leading to a $x = z = 5/3$ mm. The height of V_c , y , is given by the diameter of the detection laser: $y = 3$ mm, resulting in a volume $V_c = 25/3$ mm³.

The solid angle of this volume viewed from the molecular beam origin at the cell exit is estimated by

$$\Omega_c = \frac{A}{L^2} = 8.6 \cdot 10^{-5} \text{ sr} \quad (\text{B.37})$$

where A is the detection area defined as an area of $x \cdot y$ and $L = 31.1$ cm is the distance between V_c and the cell exit. For comparison with other sources, the number of molecules per steradian per shot $\mathcal{B}$ of the molecular beam is given by:

$$\mathcal{B} = \frac{M_{\text{mols}}(\eta_{\text{cross}} = 1)}{\Omega_c}, \quad (\text{B.38})$$

where M_{mols} is given by (B.32) and setting $\eta_{\text{cross}} = 1$.

To estimate the total number of produced molecules, the photon number density in V_c is estimated by:

$$s(t) = \frac{N_{ph}(t)}{\eta V_c} \quad (\text{B.39})$$

using $\sigma_{\mathcal{D}} = \mathcal{D} / (2\sqrt{2\ln(2)})$ and (B.36):

$$\begin{aligned} M_{\text{mols}} &= \frac{D^2 \pi}{4 \ln(2) \eta V_c} \int N_{ph}(t) v_z(t) dt \\ &\approx \frac{3 \cdot 10^9}{25 \eta} \frac{D^2 \pi}{e} \int N_{ph}(t) v_z(t) dt \end{aligned} \quad (\text{B.40})$$

Using that $d = 4.5$ mm and $\theta \approx 35$ [75, 22] and $L = 31.1$ cm, (B.33) results in $\mathcal{D} = 20.1$ cm and finally leading to:

$$\bullet \quad \eta_{\text{cross}} = \frac{2\pi \sigma_{\mathcal{D}}^2}{A} = 1/9156$$

all the factors in (B.32) are given in Table B.2:

,

resulting in $\eta = 2860$.

The experimental results from the fluorescence detection with a typical highest fluorescence signal for Sr and SrF₂ ablation, are shown in Figure B.6. From the data of Figure B.6, the number of molecules per steradian per shot and the estimated number of produced molecules per shot M_{mols} in the state $X^2\Sigma^+(v=0, N=1)$ are given in Table B.2.

Table B.1: Typical values for the parameters in equation (B.32)

parameter	value
η_{dev}	0.33
Θ_{sol}	1.095 sr
η_{opt}	0.9
N_s	9.8
η_{cross}	$1.1 \cdot 10^{-4}$

Figure B.6: Number of (PMT) counted photons versus ablation shots for two molecule production methods, obtained from fluorescence detection.**Table B.2:** The estimated number of molecules per steradian per shot $\mathcal{B}$ and number of produced molecules per shot M_{mols} in the state $X^2\Sigma^+ (v=0, N=1)$ for both SrF_2 and Sr ablation.

	SrF_2	Sr
$M_{mols} \left(\text{shot}^{-1} \right)$	$\sim 10^6$	$\sim 10^9$
$\mathcal{B} \left(\text{sr}^{-1} \text{shot}^{-1} \right)$	$\sim 10^7$	$\sim 10^{10}$

B.2.2 Counting Molecules from Molecular Absorption of Photons

For the same molecular beam used for the calculation of the molecular number from fluorescence, labelled as $Sr + SF_6$ in Figure B.6, absorption spectroscopy have been performed at 5 mm after the cell exit. In the method that follows in this subsection, the use of sidebands to addresses the SrF hyperfin structure was not accounted for even though the data was taken using sidebands.

The number of molecules derived from the amount of absorbed light, is based on Lambert-Beer's law:

$$\frac{1}{1 - \alpha} = e^{-n\sigma_0 l_x}, \quad (\text{B.41})$$

where α is the absorbed fraction of the light, n is the number density of the molecules, σ_0 the

absorption cross section and l_x the absorption path length. For the molecular number one is interested in the number density n .

Rewriting (B.41):

$$n = \frac{\ln(1 - \alpha)}{\sigma_0 l_x} \quad (\text{B.42})$$

The molecular number dM in an infinitesimally small volume dV is given by:

$$dM = n dV = n \cdot v_z dt \cdot \pi \frac{\mathcal{D}^2}{4}, \quad (\text{B.43})$$

where $\mathcal{D}$ is the molecular beam diameter at the laser position L along the beam line, v_z is the longitudinal molecular beam velocity and dt an infinitesimal change in time.

For the calculation of dV an infinitesimally small cylindrical volume along the beam line was taken, with its length given by $v_z dt$, as shown in Figure B.7. Taking $l_x = \mathcal{D}$ and adding time dependency where appropriate, the total number of molecules is given by:

$$M_{mols} = \frac{\pi \mathcal{D}}{4 \sigma_0} \int \ln(1 - \alpha(t)) v_z(t) dt, \quad (\text{B.44})$$

Figure B.7: Infinitesimally small volume dV .

where (B.42) has been used. The analysis that follows, is based on [143]. The absorption cross section σ_0 is related to the molecule polarisability $\mathcal{P}$ via:

$$\sigma_0 = \Im\{\mathcal{P}\} \frac{\omega}{c}, \quad (\text{B.45})$$

where ω is the laser frequency in angular frequency units. $\mathcal{P}$ is given by:

$$\mathcal{P} = \frac{1}{\epsilon_0 \hbar} |\mu_{ge}|^2 \left[\frac{1}{(\omega_{ge} - \omega) - i\gamma_{ph}} + \frac{1}{(\omega_{ge} + \omega) + i\gamma_{ph}} \right], \quad (\text{B.46})$$

with γ_{ph} the dipole dephasing rate.

$$\gamma_{ph} = \frac{\Gamma_e + \Gamma_g}{2} + \gamma_{ge}^{col} \quad (\text{B.47})$$

Γ_e and Γ_g are the decay rates of the excited and ground state respectively and γ_{ge}^{col} is the decay rate of the excited state to the ground states due to collisions. The last two terms are zero, as the ground state does not decay further. For this approximation collisions are not taken into account due to the low molecular density. The dephasing rate becomes $\gamma_{ph} = \Gamma_e/2 = \gamma$.

At resonance $\omega = \omega_{ge}$. Substituting into (B.46) and removing the non-resonant terms leads to:

$$\mathcal{P} = \frac{i}{\epsilon_0 \hbar} \frac{|\mu_{ge}|^2}{\gamma} \quad (\text{B.48})$$

From (B.45), (B.46) and (B.30) it follows that:

$$\sigma_0 = \frac{3\lambda^2}{2\pi} \frac{\Gamma_{eg}}{2\gamma} \quad (\text{B.49})$$

This is the maximum absorption cross section. The molecules typically have non-zero transverse velocity $v_\perp$, in that case laser light is not in resonance with the molecular transition ($\omega_{ge} \neq \omega$) and the absorption cross section σ_0 is altered. The Doppler shifted laser frequency in the frame of a molecule is given by:

$$\Delta = \omega \frac{v_\perp}{c} \quad (\text{B.50})$$

Replacing ω in (B.46) with $\omega \pm \Delta$ and taking its imaginary part turns (B.45) into:

$$\sigma_{0\pm} = \frac{|\mu_{ge}|^2}{\epsilon_0 \hbar} \frac{\gamma}{\Delta^2 + \gamma^2} \left(\frac{\omega_{ge}}{c} \pm \frac{\Delta}{c} \right) \quad (\text{B.51})$$

It is reasonable to approximate that one half of observed molecules will experience light of frequency $\omega + \Delta$ and the other half $\omega - \Delta$, resulting in an average Doppler corrected absorption cross section:

$$\begin{aligned} \sigma_0 &= \frac{|\mu_{ge}|^2}{\epsilon_0 \hbar} \frac{\gamma}{\Delta^2 + \gamma^2} \frac{\omega_{ge}}{c} \\ &= \frac{3\lambda^2}{2\pi} \frac{\Gamma_{ge}\gamma}{2(\Delta^2 + \gamma^2)} \end{aligned} \quad (\text{B.52})$$

Equation (B.53) can then be rewritten as:

$$M_{mols} = -\frac{\mathcal{D}\pi^2 (\Delta^2 + \gamma^2)}{3\lambda^2 \Gamma_{eg} \gamma} \int \ln(1 - \alpha(t)) v_z(t) dt \quad (\text{B.53})$$

Using (B.33) with $x = 5$ mm, results in $\mathcal{D} = 7.7$ mm (FWHM). Furthermore, $\lambda = 663$ nm, $\Gamma_{eg} = 37.5$ Mhz, $\gamma = 41.7$ Mhz. Typical translational temperatures obtained for single mode TOF's, and rotational temperatures obtained in this work are both around 10 K. To estimate the transverse velocity, it will be assumed that the molecules were in thermal equilibrium before they expanded out of the cell, in that case the average thermal velocity of the molecules $\bar{v}_x$ is given by (3.19). Both [22] and [75] have estimated the transverse velocity of the molecules close to the cell exit to be $\sim 20\%$ higher than the thermal velocity in the cell for the flow regime used here (Reynolds number ≈ 25) and for cell aperture sizes of 3 and 4.5 cm. Eventhough they used different molecular species and buffer gasses, the transverse velocities are similar. The temperature in the cell is set to 17 K. The result is that $\bar{v}_x \approx 62$ m/s and $v_\perp \approx 76$ m/s (FWHM) (with $v_{||} \approx 200$ m/s, $\alpha \approx 40^\circ$ in Figure B.4). Using half of the FWHM transverse speed, Δ is then estimated to be 360 MHz. For the molecular beam used to obtain the Sr + SF₆ yields in Figure B.6, the yield obtained through light absorption is shown in Figure B.8b.

Figure B.8: a): A measured time-of-flight profile averaged over ~ 3000 shots, obtained from absorption detection. b): The corresponding estimation of the number of molecules versus ablation shot plot. The same molecular beam was used to obtain the Sr + SF₆ molecular yields shown in Figure B.6.

The results for another measurement is shown in Figure B.9. Although the absorbed fraction is higher, there is no significant difference in the molecular yield between this data and the data in Figure B.8.

Figure B.9: a): Another measured time-of-flight profile averaged over ~ 3000 shots, obtained from absorption detection. b): The corresponding estimation of the number of molecules versus ablation shot plot. The same molecular beam was used to obtain the Sr + SF₆ molecular yields shown in Figure B.6. The yield stability is higher compared to the data of Figure B.8.

Technical drawing of the cell

The adapter for the cell exit and the extension of the ablation window are not included here.

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