Femtosecond laser detection of xenon and Stark decelerated polyatomic molecules

VRIJE UNIVERSITEIT

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ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan de Vrije Universiteit Amsterdam, op gezag van de rector magnificus prof. dr. F.A. van der Duyn Schouten, in het openbaar te verdedigen ten overstaan van de promotiecommissie van de Faculteit der Exacte Wetenschappen op dinsdag 30 juni 2015 om 13.45 uur in het auditorium van de universiteit, De Boelelaan 1105

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Congsen Meng

geboren te Jiangsu, China

promotor: prof.dr. W. M. G. Ubachs copromotor: dr. H. L. Bethlem If we knew what we were doing, it wouldn't be called research, would it?
Albert Einstein

This thesis was approved by the members of the reviewing committee:

Prof.dr. K.S.E. Eikema (Vrije Universiteit Amsterdam)
Dr. S. Hoekstra (University of Groningen)
Prof.dr. L. Visscher (Vrije Universiteit Amsterdam)
Prof.dr. S. Stolte (Vrije Universiteit Amsterdam and Jilin University)
Dr. G. Santambrogio (LENS and University of Florence)





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Chapter 1

Introduction

Nowadays, commercial table top femtosecond laser systems can produce short pulses with typical peak intensity on the order of 10^{14} W/cm² at its focus. These high intensities are sufficient to ionize virtually any atom or molecule, thus potentially providing a very general and sensitive detection method for atoms and molecules. Inherently, femtosecond lasers do not provide any state-specificity; due to the uncertainly principle a short pulse duration is accompanied by an extremely broad bandwidth. For instance, pulses of 100 fs have bandwidths on the order of 10 THz, which cover a large range of rovibrational energy levels in molecules. This lack of specificity results in a large background from unwanted states. Until now, this background problem was the main obstacle that limited the use of fs lasers as a detection method in molecular beam experiments.

In this thesis, I present a number of experiments that demonstrate the great potential of femtosecond lasers in molecular beam experiments – particularly its use for detecting polyatomic molecules which lack suitable transitions for conventional detection schemes such as resonance-enhanced multiphoton ionization (REMPI) or laser induced fluorescence (LIF), and as a means to measure absolute densities in molecular beams.

In the first experiment, the absolute densities of pure and seeded xenon beams are determined by comparing the signal strengths obtained in the beam to those from a thermal distribution of xenon gas in the apparatus. If one uses a narrow-band laser to probe a resonant transition via LIF or REMPI then the Doppler broadened signal obtained in a thermal gas is very different from the signal obtained from a supersonic molecular beam. In the case of a gas, the Doppler width will be much broader than the laser bandwidth, while in the beam case the Doppler width will be narrower than the laser bandwidth. By using a non-resonant approach this problem is circumvented. This method is used to characterise a novel cantilever piezovalve for making molecular beams that was developed at VU LaserLaB [1].

In the second experiment, the possibility for performing high-resolution

spectroscopy on methanol in a Stark-deflected molecular beam is explored. Methanol is one of the simplest molecules that exhibits internal rotation; the methyl (CH_3) group rotates with respect to the alcohol (OH) group. In addition, the molecule rotates as a whole. It was shown that microwave transitions that convert the internal rotation to overall rotation – and vice versa – are very sensitive to the proton-to-electron mass ratio [2]. By comparing the transition frequencies measured in very distant astrophysical objects with those measured in the lab, a very stringent bound could be set on a possible time-variation of fundamental constants [3; 4]. The precision of these tests is currently limited by the precision of the astrophysical observations, but for future tests more accurate lab data will be needed. A major obstacle for performing microwave spectroscopy in a molecular beam – currently the most precise method – is the lack of suitable excited states that could be used for state-selective methods such as LIF or REMPI. Some kind of state-selection is required to be able to tell if a microwave transition has been induced. We investigate the possibility to use an inhomogeneous electric field to deflect specific quantum states and detect these by multiphoton ionization using a fs laser.

In the third experiment, a fs laser is used to detect methyl fluoride molecules that are decelerated and trapped using time-varying electric fields. Deceleration by time-varying electric fields is inherently state-specific; it only works for molecules in states that have a sufficiently large Stark effect. However, a state-selective method is still advantageous as it helps to reduce the background from thermal gas in the vacuum chamber. This thermal gas will be distributed over many states and hence does not pose a problem when a stateselective method is employed. When a fs laser detection scheme is used, all thermal background will be ionized giving a background that is comparable to or larger than the signal from the decelerated molecules. It is demonstrated that this background can be reduced effectively by using velocity map imaging; the decelerated molecular beam has a much narrower velocity spread than the background resulting from the thermal gas in the chamber. By the selective detection of ions which have a low velocity the background is eliminated. Methyl fluoride is so far the heaviest and most complex molecule that has been decelerated to rest. This proof-of-principle experiment opens up the study of cold large polyatomic molecules.

In the fourth experiment, the fs laser scheme is used to detect Stark decelerated ammonia molecules and compared to the conventional detection method that employs (2+1) REMPI around 322 nm using tunable light from a ns dyelaser. The main motivation for this work was the hope to increase the number of molecules that are being detected to increase the precision of spectroscopic studies on cold molecules.

In addition, as many photons are required to ionize molecules, ions are only produced in the central part of the focus. This results in a well defined detection volume that is crucial to determine absolute densities of molecules. The size of this volume can be calibrated by simultaneously recording the signal from a well studied gas such as xenon. This method is applied to determine the density of trapped methyl fluoride and ammonia molecules.

The remainder of this chapter is organized as follows: In the first part a brief survey of techniques to produce and detect cold molecules and applications of cold molecules are discussed. Emphasis is put on high resolution spectroscopy, which is the main objective of the molecular fountain currently developed at VU LaserLaB. The principle of Stark deceleration is discussed in detail. In Sec. 1.3 techniques for generating femtosecond pulses are reviewed and the femtosecond laser systems employed in my experiments are introduced. Finally, it ends with an outline of the main body of this thesis.

1.1 Creation, detection and applications of cold molecules

Inspired by the great success of laser cooling techniques to create ultracold atoms and associated exciting discoveries, a large effort has been spent over the last few decades to develop techniques for producing molecules at cold (1 mK - 1 K) or ultra cold (<1 mK) temperatures. The rich structures and properties of cold molecules provide unique possibilities in a variety of research fields, ranging from fundamental physics to cold chemistry, molecular physics, and quantum physics (see recent reviews and references therein [5–8]). Nowadays, the quest for cold molecules at high densities [9] and the search of their applications [10; 11] are marching side by side.

1.1.1 Creation of cold molecules

The target features to achieve in experiments with cold molecules are fourfold: (i) dense clouds, (ii) containing a large number of molecules, (iii) that have a low translational temperature, and (iv) are all in a single, preferably the lowest, rovibrational state. The ideal cooling method should be able to meet these characteristics simultaneously and be amenable to any type of molecules. To date, no such universal technique has been found, but a number of techniques have been developed that each addresses a different class of molecules and has its own particular strengths and weaknesses. In general, methods for cooling molecules can be broadly classified into two types: indirect and direct.

As mentioned before, molecules have a more complex structure than atoms. The additional degrees of freedom, particularly the vibration of the molecule, precludes an effective extension of laser cooling techniques, although it has been applied to a few specific molecules [12–14]. This disqualification has led to the development of a range of alternative techniques. Rather than applying laser cooling to molecules directly, laser cooling can be used to obtain cold molecules in an indirect fashion by assembling two laser-cooled atoms into a bound molecule via photoassociation [15] or magneto-association [16]. Typically, these molecules are formed in a highly excited vibrational state, which

are subsequently transferred to the rovibrational ground state using STIRAP. This method was first demonstrated by Ni *et al.* to produce KRb molecules near Fermi degeneracy [17]. The application of this technique is limited to molecules whose constituent atoms can be laser cooled and trapped.

In contrast to the indirect method, direct methods can be applied to a somewhat larger group of molecules, including polyatomic molecules and molecules that are relevant for chemical studies. These methods include buffer-gas cooling, velocity filtering and Stark (Zeeman, optical) deceleration.

A powerful and versatile method for producing cold, state-selected molecules is buffer-gas cooling, pioneered by the group of Doyle [18]. This cooling process is realized by thermalizing the species of interest via elastic collisions with cryogenically cooled inert gas atoms (like He or Ne atoms). Since this cooling mechanism does not depend on the internal structure of the species, buffer gas cooling can be applied to nearly any atom or small molecule. An additional advantage of this technique is that cooling of the translational degrees of freedom in the buffer gas is accompanied by efficient rotational cooing. The main disadvantage of this technique lies in the complexity of the apparatus, which grows rapidly as the temperature decreases.

Another direct method, velocity filtering, exploits a velocity filter to separate slow moving molecules from fast moving molecules. At room temperature, velocities in a gas of molecules are described by a Maxwell-Boltzmann distribution. Although typically only 0.1% of the molecules have a speed below 10%of the mean velocity, the total number of slowly moving molecules can still be high. These slow molecules can be selected by using a curved electric or magnetic guide that only transports molecules below a certain threshold velocity, as first demonstrated by Rangwala *et al.* [19]. The main disadvantage of this technique is its poor quantum state selectivity. This problem can be solved by combining this method with cryogenically cooled beams [20; 21].

In contrast to the passive way of selecting out the slow moving molecules, Stark deceleration, exploits the interaction of dipolar molecules with timevarying inhomogeneous electric fields to actively slow down the molecules in the laboratory frame. By applying appropriate time-varying electric fields an effective or genuine 3D trap is created that moves along with the molecules. By lowering the velocity of the moving trap the molecules can be decelerated to any desired velocity. This technique was first demonstrated by Bethlem *et al.* in 1999 [22]. A more detailed discussion of Stark deceleration is presented in the next section. The arguments and principles presented here also apply to Zeeman and optical deceleration. Zeeman deceleration results from the interaction between the magnetic moment of a molecule and an external magnetic field while optical deceleration arises from the polarizability interaction between molecules and an applied optical field.

1.1.2 Detection of cold molecules

With the advance of techniques to produce cold molecules, the family of cold molecules is rapidly expanding. Meanwhile, the lack of universality of conventional detection methods has become an obstacle to add new members. Most experiments on cold molecules have employed either LIF or REMPI for detection. LIF techniques use tunable narrow-band lasers to drive transitions to an excited state, from which after a certain time the molecule decays and emits a photon. This photon is collected using a photo-multiplier tube and is used as signal. If the used transition is closed, i.e., if the molecule decays to its initial state, each molecule can be excited multiple times and a high signal-to-noise ratio can be obtained. For molecules closed transitions are typically nonexistent and only one or a few photons will be emitted per molecule. As only a small fraction of these photons is collected the signal-to-noise ratio is limited. LIF has been used in most experiments on Stark decelerated molecules and in all experiments on buffer gas cooling. In experiments on magneto-association the molecules are detected indirectly by converting the molecules back to atoms and detecting those [16].

The REMPI technique involves a resonant single or multiple photon absorption to an electronically excited intermediate state, followed by another photon which ionizes the molecule. As the produced ions can be detected with near unity efficiency, this detection method is very sensitive. However, for light molecules, usually the excitation step requires more than one photon which means that the laser needs to be focused rather tightly. This implies a strong restriction on the size of the detection volume. REMPI has been used in experiments with Stark decelerated beams of ammonia and with experiments on molecules that are formed by photo-association of laser cooled atoms.

LIF and REMPI require a suitable transition to an electronic state. This excludes many polyatomic molecules that have excited states that are either repulsive or that are strongly coupled to repulsive excited states, severely limiting the scope of molecules that can be cooled. In this thesis, I will present measurements of fs laser-detected Stark-decelerated methyl fluoride molecules.

For the sake of completeness, it should also be mentioned that other detection methods have been used in cold molecule research. For instance, molecules in an electronically excited metastable state (e.g., CO in the $a^{3}\Pi$ state) can be detected via the ejection of electrons from a surface (Auger de-excitation process) when the metastable molecules strike the metal [23]. Experiments with velocity filtered slow beams [19] and experiments on Zeeman deceleration of oxygen molecules [24] have employed quadrupole mass spectrometers for detection. The downside of these methods is that they cannot be used to detect molecules inside the trap.

1.1.3 Precision measurement

Cold molecules play an important role in many physics and chemistry experiments, ranging from studying collisions and reactions at low temperatures, investigating the influence of dipole-dipole interactions in quantum degenerate gases, testing fundamental physics theories and developing quantum computers (for recent review papers see [5–8]). I will focus here on the use of cold molecules for precision spectroscopy. Ultimately the resolution of a spectroscopic measurement is limited by the time that an atom or molecule interacts with the radiation field. In a typical molecular beam experiment the interaction time is limited to about 1 ms, resulting in a measured linewidth on the order of a kHz. The use of cold and hence slow molecules promises a significant increase in the interaction time. The accuracy of a spectroscopic test depends not only on the resolution but also on the obtained signal-to-noise ratio. This is expressed in the Allan deviation:

$$\sigma_y(\tau) = \frac{1}{Q} \sqrt{\frac{\tau_c}{\tau N_c}},\tag{1.1}$$

where $Q = f/\Delta f$ is the quality factor of the resonance, τ is the measuring time, τ_c is the duration of one cycle, i.e., one over the repetition frequency and N_c is the number of molecules that are detected per cycle. If the width of the transition is limited by the finite interaction time, Δt (i.e., $\Delta f \propto 1/\Delta t$), then the Allan deviation is proportional to $(\Delta t \sqrt{N_c})^{-1}$. From this equation it follows that if the number of molecules drops more rapidly than $(\Delta t)^2$, the cooling is of limited use (Note that the systematic error is normally proportional to the resolution (i.e., to Q), so increasing the interaction time may still help). Recently, Quintero-Pérez et al. [25] demonstrated that by performing adiabatic cooling of trapped ammonia molecules, they were able to observe molecules even after more than 10 ms of free expansion. Moreover they showed that a coherent measurement performed during this time would have a statistical uncertainty that decreases approximately as the inverse of the square root of the expansion time (i.e., interaction time). This offers interesting prospects for high-resolution spectroscopy and precision tests of fundamental physics theories.

1.2 Stark deceleration of polar molecules

As mentioned briefly in Sec. 1.1.1, the trajectories of neutral molecular beam molecules can be manipulated with inhomogeneous electric or magnetic fields. The use of static fields to deflect or focus beams in the transverse direction has played an important role in the field of atomic and molecular beams. In their famous experiment from 1922, Stern and Gerlach demonstrated space quantization via deflection of silver atoms in inhomogeneous magnetic field [26]. Later, hexapole focusers have been used extensively to perform collision studies between state-selected and oriented beams of polar molecules [27; 28]. The

longitudinal motion of polar molecules in a beam can also be controlled via time-varying fields, as demonstrated in the Stark decelerator.

1.2.1 Principle of Stark deceleration

The Stark decelerator for neutral polar molecules is analogous to a linear accelerator for charged particles [29]. The quantum-state specific force that a polar molecule experiences in an electric field is given by

$$F_{\text{Stark}} = -\frac{dW_{\text{Stark}}}{dr} = \mu_{\text{eff}} \frac{\partial |\vec{E}|}{\partial r} \quad \text{with } \mu_{\text{eff}} = -\frac{\partial W_{\text{Stark}}}{\partial |\vec{E}|}, \qquad (1.2)$$

where W_{Stark} is the Stark shift and $|\vec{E}|$ is the electric field strength. Molecules in quantum states with a negative Stark shift experience a force towards a region of higher electric field and are referred to as high-field seekers, while molecules in states with positive Stark energy are called low-field seekers.

When a polar molecule in a low-field seeking state (e.g., CH_3F in the $|J,MK\rangle = |1,-1\rangle$ state) approaches a region of high electric field as illustrated in Fig. 1.1, its potential energy will be increased, and correspondingly, part of its kinetic energy will be lost while it climbs upward on the slope of the potential hill. The molecules will regain their lost kinetic energy when they leave the region of high electric field. This acceleration process can be avoided if the electric field is abruptly switched off before the molecules reach the top of hill.

Since the maximum electric field that is obtained in the laboratory is limited to about $200 \,\mathrm{kV/cm}$, the kinetic energy that is taken out per stage is only about 1% of the initial kinetic energy of molecules in a supersonic beam. In order to have a significant change in velocity, this deceleration process needs to be repeated many times. In a Stark decelerator this is realised by an array of electric field stages as shown in Fig. 1.1. The electric fields in the various sections are switched on and off synchronously with the motion of the molecules through the array. By switching the field off when the average of the beam has not yet reached the maximum electric field, molecules that are in front of the packet will be decelerated more, while molecules that are behind the average will be decelerated less. In this way, molecules are kept together in a tight bunch. This principle forms the basis for synchrotron-like charged particle accelerators and can be viewed as trapping of the particles in a traveling potential well formed by the accelerating fields. In order to achieve an effective trap in the transverse direction, the electric stages are alternately positioned horizontally and vertically. Note that in Fig. 1.1 the electrodes are depicted with the same orientation for clarity.



Figure 1.1 – Schematic representation of the operation principle of a Stark decelerator. The molecules lose kinetic energy while moving from a region of low electric field to a region of high electric field. By switching between two high-voltage configurations shown in panel (a) and (b) many times, molecules are slowed down in a stepwise fashion.

1.2.2 Traveling wave decelerator

In the decelerator formed by planar electrodes as discussed in the previous section, the principle of phase stability is employed, which ensures that molecules experience an effective 3D potential well that keeps them in a compact bunch during the deceleration process. The approximations used to derive this effective well are only valid at high velocity, and the model becomes unreliable at low velocity when the oscillation period of the molecules becomes comparable to the time it takes for them to travel from one stage to the next. As a result of this breakdown, the number of molecules in the packet as well as its phase-space density (the number of molecules per position and velocity interval) decrease at low velocities. This issue is solved by using a so-called traveling wave decelerator [30–32]. This traveling wave decelerator, schematically depicted in Fig. 1.2, consists of a series of ring electrodes to which voltages of up to ± 5 kV are applied. At any moment in time, the voltages applied to consecutive rings follow a sinusoidal pattern in z, where z is the position along the beam axis, resulting



Figure 1.2 – Schematic view of a traveling wave decelerator consisting of a series of rings to which 8 different voltages are applied.

in an array of electric field minima. These electric field minima represent a true 3D trap for low-field seeking molecules. By modulating these voltages sinusoidally in time the traps can be moved along the decelerator. The resulting velocity of the traveling potential wells is given by $v_z(t) = f(t)L$, with f the modulation frequency and L the periodic length. Thus the molecules that are trapped at the electric field minima, can be either decelerated or accelerated according to the modulation frequency. In particular, f = 0 corresponds to the situation that molecules are brought to standstill and trapped in the laboratory frame. Furthermore, as the molecules are always close to the zero point of the electric field, they can be decelerated in states that switch from low-field seeking to high-field seeking at relatively low electric fields. This makes it possible to decelerate heavy molecules such as YbF [33], SrF [34] and molecules composed out of many light atoms.

1.2.3 Supersonic expansion and phase-space density

The success of the Stark-deceleration technique strongly relies on the properties of the molecular packet that is sent into the decelerator. From the previous discussion, it can be seen that the role of Stark decelerator is only to select a part of the molecules and to slow them down in the laboratory frame. The real cooling occurs in the expansion process of the source, and therefore parameters as the rotational temperature, flow velocity and velocity distribution of the molecular beam are crucial to the performance of the Stark decelerator.

Typically, the molecules of interest are seeded in a supersonic beam of rare gas atoms at a concentration of a few percent. When the molecules flow from a region with high pressure (the container) to a region with low pressure (the vacuum chamber), many collisions occur. As a consequence of these collisions the molecules are accelerated up to several hundreds of meters per second, while their velocity spread is narrowed. As the velocity spread is connected to the temperature, this implies that the translational temperature, and also the rotational and vibrational temperatures, are lowered. Typically, the obtained translational temperature is below 1 Kelvin while the rotational and vibrational temperatures are around 5 and 50 Kelvin, respectively. For Stark deceleration experiments, it is favorable to have a large population in the desired state and to have a small flow velocity in the laboratory frame. This is helped by cooling the valve and seeding the molecules of interest in a heavy carrier gas such as xenon. The minimum temperature is limited by the formation of clusters in the beam. To reduce the gas load and lower the required pumping capacity we employ pulsed valves with opening times of typically $10-100 \,\mu s$. In Chapter 2, I will present measurements of the absolute density obtained using a home-built cantilever piezovalve.

Let us now turn to the concept of phase space density. As discussed, it is crucial to keep the decelerated packet of molecules together throughout the deceleration process. This feature is guaranteed by the fact that conservative forces are used to manipulate the molecules and no collisions occur over the time scales necessary to bring the molecules to a standstill. In this case Liouville's theorem dictates that the phase-space density defined as

$$D = n\Lambda^3 \quad \text{with} \Lambda = \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2},$$
 (1.3)

where *n* is the number density, *m* is the mass of a molecule and *k* is the Boltzmann's constant, stays constant. The phase-space density of Stark decelerated beams is typically 10^{-14} – 10^{-10} \hbar^3 , which is sufficient to perform high-resolution spectroscopy and collision measurements. To increase the phase-space density, dissipative forces, such as laser cooling [12–14], evaporative cooling [9] or sympathetic cooling [35] are required.

1.2.4 Stark effect in methyl fluoride

Stark deceleration is based on the interaction of polar molecules with timevarying electric fields. The length of the decelerator required to bring a molecule in a given rotational level to rest is inversely proportional to the ratio of the (positive) Stark shift of this level divided by the mass of the molecule. In this thesis, I present measurements on three molecules, namely methanol, methyl fluoride and ammonia. The Stark effect of methanol is discussed in Chapter 3, while the Stark effect of ammonia is discussed in detail in the theses of Jansen [36] and Quintero-Pérez [37]. In this section I will discuss the Stark effect in methyl fluoride. For a general discussion of the Stark effect in molecules see van de Meerakker *et al.* [7] and references therein.

Methyl fluoride, CH_3F , is a prototypical symmetric top molecule of C_{3v} symmetry. The rotational levels of methyl fluoride are labelled by J, the total angular momentum, K, the projection of J on the molecular symmetry axis, and M the projection of J on the space fixed axis. In the presence of an electric field, there are 2J + 1 possible orientations with respect to the static field direction, where M = J, J - 1, ..., -J. States with the same $|K| \neq 0$ are doubly degenerate and eigenfunctions with a definite parity are built from linear combinations of |JKM > and |J - KM >.

The Hamiltonian describing the interaction of a dipole $\vec{\mu}_{\rm el}$ in an electric field \vec{E} is expressed as

$$\hat{H}' = -\vec{\mu}_{\rm el}\vec{E},\tag{1.4}$$

where $\vec{\mu}_{\rm el}$ is the permanent electric dipole moment and \vec{E} the electric field vector. For a symmetric top molecule, the Stark effect will only occur for matrix elements of the form

$$\langle JKM|\hat{H}'|JKM\rangle = -\mu_{\rm el}|\vec{E}|\frac{MK}{J(J+1)},\tag{1.5}$$

$$\langle JKM|\hat{H}'|J+1KM\rangle = -\frac{\mu_{\rm el}|\vec{E}|}{J+1}\sqrt{\frac{((J+1)^2 - K^2)((J+1)^2 - M^2)}{(2J+1)(2J+3)}}.$$
 (1.6)

Levels with K > 0 exhibit a linear Stark shift and the M degeneracy is completely lifted, while levels with K = 0 only exhibit a quadratic Stark shift, and all levels with $M \neq 0$ are doubly degenerate. For low electric fields the secondorder Stark shift can be neglected and the Stark shift takes the approximate form

$$W_{\rm Stark} = \pm \sqrt{\left(\frac{W_{\rm inv}}{2}\right)^2 + \left(\mu_{\rm el} |\vec{E}| \frac{MK}{J(J+1)}\right)^2} \mp \frac{W_{\rm inv}}{2}, \qquad (1.7)$$

with the plus and minus sign denoting the low-field and high-field seeking states, respectively. W_{inv} is the inversion splitting. For CH₃F the barrier is



Figure 1.3 – Stark shift of the lowest rotational levels of the vibrational ground state of methyl fluoride. The energies are calculated using PGOPHER [38] with the parameters taken from Ref. [39].

almost equal to the dissociation energy and the inversion splitting is below 10 Hz. As a result, the energy shifts linearly with the applied field. Fig. 1.3 shows the Stark energies of the lowest rotational levels of the vibrational ground state of methyl fluoride calculated with PGOPHER [38] using as input the molecular constants given by Ref. [39]. In a cold molecular beam, the only populated state that has a significant positive Stark shift is the J = 1, MK = 1 level. As seen in Fig. 1.3 this level has a linear Stark shift in low (< 20 kV/cm) electric fields. At higher electric fields this level mixes with the J = 2, MK = -1 level and it Stark shift levels off and (above 130 kV/cm) the Stark shift reverses sign.

Let us now take into account the hyperfine structure due to the nuclear spins of the hydrogen nuclei. The wavefunction of the three identical hydrogen nuclei must be antisymmetric under simultaneous exchange of the nuclear coordinates and the projection of the spin. This implies that rotational levels with K = 0, 3, 6, ... combine only with nuclear spin wave function of A_1 symmetry (ortho-CH₃F), while rotational levels with K = 1, 2, 4, 5, ... combine only with nuclear spin wave function of E symmetry (para-CH₃F). In binary collisions the symmetry of the nuclear spin is preserved, implying that the ratio of the para to ortho-methyl fluoride in the molecular beam is the same as in the con-



Figure 1.4 – Stark shift for the various hyperfine levels of the $|J, K\rangle = |1, 1\rangle$ level of CH₃F in extremely weak electric fields. The curves are labeled by the M_F value. Adapted from Bulthuis *et al.* [40] with permission.

tainer. As a result, all para molecules will ultimately end up in the J=1, K=1 levels in a cold supersonic beam.

Fig. 1.4 shows the Stark shift of the various hyperfine levels of the $|J, K\rangle =$ $|1, 1\rangle$ level of CH₃F in very weak electric fields calculated by Bulthuis *et al.* [40]. The hyperfine interaction leads to a splitting on the order of tens of kHz, much larger than the inversion splitting which is predicted to be below 10 Hz. As a result of these small splittings an electric field of 100 mV/cm is sufficient to completely mix the hyperfine structure, making CH₃F extremely polarizable. Interestingly, the splitting between different hyperfine levels is nearly independent of the electric field, hence suggesting that hyperfine levels of electrically trapped CH₃F molecules may be used as 'quantum' bits.

1.3 Femtosecond laser pulses

Chirped-pulse amplification is nowadays widely used in bulk amplifier systems for generating femtosecond pulses with milli-Joule (single-stage amplifier) [41] or even Joule-level pulse energies (multi-stage amplifiers) [42]. The unique characteristics of these pulses open up new frontiers in fundamental physics and chemistry research and applications. Ultrashort pulses allow the investigation of light-matter interaction on a femtosecond timescale. By using pumpprobe techniques complex reaction dynamics have been revealed in real time, which was rewarded with the Nobel prize in Chemistry for Ahmed Zewail in 1999 [43]. More recently, the broad spectral width of femtosecond pulses has been exploited in high precision optical frequency metrology [44]. A series of discrete spectral lines serve as a frequency comb to measure the optical frequencies with sub-Hz uncertainties. The invention of the frequency comb was rewarded with the one half of the 2005 Nobel prize in Physics for John Hall and Theodor Hänsch.

1.3.1 Generation of femtosecond laser pulses

The introduction of titanium-doped sapphire (Ti:sapphire) as a broadband gain medium was crucial for the generation and amplification of ultrashort pulses. The first broad-bandwidth solid-state laser was constructed by Moulton in 1986 [45]. The gain medium determines the bandwidth over which the laser may operate. Ti:sapphire has a gain bandwidth of 128 THz (a 300 nm wavelength range centered around 800 nm), which can potentially support approximately 250,000 longitudinal modes (frequencies) for a $30\,\mathrm{cm}$ cavity. The frequency separation is given by c/2L, with c the speed of light and L the length of the cavity. The temporal intensity distribution of the laser pulses relies on the phase relations between the different modes. If the phase difference between the modes are random, that is, if these modes oscillate independently, the resultant intensity shows a near-constant distribution. In contrast, if modes have a fixed phase relationship they will constructively interfere with each other periodically, resulting in the emission of intense laser pulses at regular intervals. In this case, the laser is said to be phase or mode-locked. The duration of each pulse in the train is equal to $\tau_N = 2L/cN$. Thus, if the number of modes that are phase-locked is increased, the duration of the pulses will be decreased (resulting in a higher intensity).

Techniques to achieve mode-locking can be divided into two classes: passive mode-locking and active mode-locking. Active methods typically involve the use of an external clock signal (e.g. an acousto-optical modulator (AOM) [46] or an electro-optical modulator (EOM) [47]) to induce a modulation of the intracavity radiation. AOM modulation, which is the most commonly used technique, creates sidebands on a specific mode ν at frequencies $\nu + f$ and $\nu - f$, with f the modulation frequency. If the modulator is driven at the same frequency as the cavity-mode spacing, the cavity modes adjacent to the original

mode will be phase locked. As the modulator will also produce side bands on the adjacent mode at $\nu + 2f$, this mode will also be locked. This process eventually leads to all cavity modes being phase-locked together. Our Ti:sapphire oscillator (Spectra-Physics, Tsunami) uses this technique to initialize modelocking, as will be described in Sec. 1.3.2. Alternatively, mode-locking may result from self-amplitude modulation when the laser pulses travel inside the laser cavity. This can be achieved through the use of a saturable absorber, i.e., a material that exhibits an intensity-dependent transmission; if the intensity is low the absorber causes a relatively high loss. While if the intensity is high the light is hardly absorbed, resulting in the generation of short, intense pulses [48]. Another successful technique is called Kerr-lens mode-locking (KLM). This technique exploits the fact that the focusing properties of a medium depend on the intensity of the incoming light. This will cause nonlinearity in the gain medium which translates to intensity dependent losses. This modulation results in mode-locking in a similar fashion as for a saturable absorber. Kerr-lens mode-locking was first demonstrated by Sibbett and co-workers in 1991 [49].

A Ti:sapphire oscillator typically generates pulse energies at the nano-Joule level. For many experiments it is desirable to have pulse energies at a milli-Joule level or above, thus further amplification is required. The peak power of the pulses is lowered before entering the gain medium to make sure that it is below the damage threshold of the gain medium and to avoid possible nonlinear effects that may distort the shape of the beam. This is achieved by a technique called chirped pulse amplification (CPA), introduced by Strickland and Mourou [50]. In this scheme the duration of the laser pulses is stretched by a factor of 10^3-10^5 prior to amplification with the aid of gratings or prims. The stretched pulses can be safely amplified by a factor 10^6 or more. After amplification, another set of gratings or prisms is used to recompress the pulses to their original duration.

In order to extract the energy stored in the Ti:sapphire gain medium, the laser pulses need to pass the medium many times. The most widely used techniques for achieving this are multipass [51] and regenerative amplification [52]. In a regenerative amplifier, pulses are trapped in the cavity until their energy reach a maximum. At this point a Pockels cell switches the polarization of the light such that it leaves the cavity by reflecting off a broad-band polarizer. Rather than using an optical switch, a multipass amplifier controls the number of passes inside the cavity by the geometry of the configuration. Typically, the light passes the gain medium 4–8 times, limited by the difficulties associated with alignment of the beam through the medium.

1.3.2 Femtosecond laser system

In the experiments, we have used a standard commercial (Spectra Physics) chirped pulse amplification (CPA) titanium sapphire system, schematically depicted in Fig. 1.5. The seed light is generated by an actively mode-locked Titanium-Sapphire oscillator (Tsunami) pumped by a cw Nd:YVO4 laser (Mil-



Figure 1.5 – Schematic layout of the femtosecond laser system used in the experiments.

lennia). The layout of the Tsunami is shown in Fig. 1.6. The Tsunami generates pulses of 800 nm light with an energy of 5 nJ/pulse, a duration of about 100 fs and a repetition rate of 82 MHz. These pulses are amplified in a chirped regenerative (regen) amplifier (Spitfire-pro) which is schematically depicted in Fig. 1.7. The Regen is pumped by pulses from a Q-switched diode-pumped Nd:YLF laser (Empower) with a wavelength of 527 nm and a pulse energy of ~15 mJ. To avoid damage to the amplifier the oscillator pulses are stretched to several hundreds of picoseconds (corresponding to 10^4 in time domain) using a grating. The energy of the stretched pulses is subsequently amplified 10^6 times and re-compressed using a second grating compressor to provide pulses with a duration of 150 fs, and an energy of 2.5 mJ/pulse at a repetition rate of 1 kHz. The spectral profile of the output is monitored by a fiber spectrometer (Ocean Optics, USB4000).

The beam size and pulse duration are key features of the laser pulses which are characterized in the following way. (i) The beam size is determined by the so-called knife-edge technique [53]. In this technique the laser beam is progressively covered by a knife edge (blade) while the transmitted power is recorded. The beam profile is derived by differentiating the transmitted power. The beam shape is measured to be an ellipse with (full) axes of 6 mm and 4 mm (FWHM), respectively. (ii) The pulse duration is measured by a homebuilt single-shot autocorrelator [54]. In the autocorrelator the laser beams are split into two beams that are aligned with a relative angle of about 20 degrees through a nonlinear crystal. One of the two beams is sent though a variable delay line. A camera records the spatial profile of the blue light produced in the nonlinear crystal. The obtained spatial shape S(x) is proportional to the second-order autocorrelation function $G^{(2)}(t_d)$ of the incident pulses:

$$S(x) \propto \int_{-\infty}^{+\infty} I(t)I(t-t_d)dt = G^{(2)}(t_d),$$
 (1.8)

where t_d is the relative time delay between two incident beams. The full width



Figure 1.6 – Beam path and optical components in the Tsunami. The pulse width is modified by using two prism pairs, which produce a net negative group velocity dispersion. The central wavelength and bandwidth of the output is tuned by adjusting the position and width of the slit, respectively. The AOM, driven by a regeneratively–derived rf signal, is used for mode-locking. Adapted from the Tsunami user manual.



Figure 1.7 – Beam path and optical components in the Spitfire pro. The duration of the seed pulses are stretched by a factor of 10^4 using a grating and subsequently amplified and re-compressed using a second grating. Adapted from the Spitfire user manual.

at half maximum (FWHM) x_s of the spatial function S(x) is related to the temporal incident pulse FWHM τ by

$$\tau = K x_s \frac{\Delta t}{\Delta x},\tag{1.9}$$

where Δx is the relative spatial shift for a temporal delay Δt and K = 1.414 for a Gaussian pulse. The pulse duration τ is measured to be about 150 fs.

1.4 This thesis

In this thesis, I present a number of experiments that demonstrate the great potential of femtosecond lasers in molecular beam experiments. The thesis is structured as follows. In Chapter 2, the absolute densities of pure and seeded molecular beams are determined by the femtosecond ion imaging. In Chapter 3, the feasibility of performing high resolution microwave spectroscopy on selected transitions in methanol using a Rabi-type molecular beam setup in combination with a fs laser is estimated. In Chapter 4, the deceleration and trapping of methyl fluoride molecules in the low field seeking component of the J=1, K=1 state are demonstrated using a combination of a conventional Stark decelerator and a traveling wave decelerator. Methyl fluoride is so far the heaviest and most complex molecule that has been decelerated to rest. The methyl fluoride molecules are detected by non-resonant multiphoton ionization using a fs laser. It is demonstrated that in combination with ion imaging techniques to eliminate background signals, this detection method is extremely useful for experiments with Stark decelerated molecules. The well defined detection volume allows an accurate determination of the number of trapped molecules. In Chapter 5, the fs laser scheme is used to detect Stark decelerated ammonia molecules and compared to the conventional detection method based on (2+1) REMPI using UV light from a ns dye-laser.

Chapter 2

Measurement of the density profile of pure and seeded molecular beams by femtosecond ion imaging¹

In this chapter, we report on femtosecond ion imaging experiments to measure the density profile of a pulsed supersonic molecular beam. Ion images are measured for both a molecular beam and bulk gas under identical experimental conditions via femtosecond multiphoton ionization (MPI) of Xe atoms. We report the density profile of the molecular beam and the measured absolute density is compared with theoretical calculations of the centre line beam density. Subsequently, we discuss reasons accounting for the differences between measurements and calculations and propose that strong skimmer interference is the most probable cause for the differences. Furthermore, we report on experiments measuring the centre line density of seeded supersonic beams. The femtoseond ion images show that seeding the heavy Xe atom at low relative seed fractions (1-10%) in a light carrier gas like Ne results in strong relative enhancements of up to two orders of magnitude.

2.1 Introduction

Supersonic atomic and molecular beams [55; 56] have played an important role in various fields of physics and chemistry such as high harmonic generation [57], particle acceleration [58] and laser-induced fluorescence spectroscopy [59]. During the last decade great efforts have been made to generate and characterize ultracold high-density pulsed molecular beams [1; 60–64]. Very recently, Even and coworkers [62; 65] have extensively studied, both experimentally and with

 $^{^1\}mathrm{Based}$ on Congsen Meng and Maurice H.M. Janssen, Rev. Sci. Instrum. **86**, 023110 (2015).

computer simulations, the influence of the nozzle shape, and the skimmer geometry and position on the production and propagation of high-density supersonic beams. They reported that the center line beam density produced by a conical nozzle can be an order of magnitude larger than the density of a sonic nozzle. In the case of a conical nozzle the optimal compromise between maximal density and low clustering is found for a nozzle with a full opening angle in between $40^{\circ}-60^{\circ}$ [61; 62; 65]. Furthermore, they reported that the skimmer plays an important role in high density beams. Even for a skimmer with a large entrance diameter of 2–4 mm, skimmer interference [66] may still greatly degrade the beam performance (temperature and transmission) especially in high density beams when these skimmers are positioned too close to the nozzle exit [62; 65].

In general, it is not an easy task to measure the absolute density profile of a pulsed molecular beam. In the field of plasma diagnostics, there are several diagnostic techniques employed for the determination of the plasma density, mainly consisting of Langmuir probe [67], laser interferometry [68], Thomson scattering [69] and laser-induced-fluorescence [70]. As to Thomson scattering, the electron density can be determined from the intensity of the scattered light. However, these experiments are not easy to undertake due to the presence of low cross section of the underlying process and a careful absolute calibration is required afterwards. The laser interferometric method is based on the fact that the plasma index of refraction is proportional to the density of free electrons in plasmas. The resultant phase shift caused by the variation of the refractive index can be determined by the fringe amplitude of combined probe and reference beams. Laser-induced-fluorescence technique is also used to measure beam density, where the fluorescence intensity scales linearly with the number density of species. The fluorescence emission will decrease due to the occurrence of temperature-dependent thermal processes such as vibrational relaxation and collisional quenching. Typically, the absolute density is obtained by comparison with signal acquired at a known static pressure with the same temperature. However, it is extremely difficult to produce a static gas at such low temperature (typically with translational temperature of a few Kelvin or less) in a cell without condensation, which precludes us to implement this method directly.

Recently, Schofield *et al.* reported absolute density measurements of a molecular beam via multiphoton ionization [71]. In this chapter, we extent this method by combining nonresonant femtosecond multiphoton ionization with ion imaging. This enables us to image the molecular beam profile on a CCD imaging detector. The absolute density is acquired by comparison of the ion intensity of a pulsed molecular beam and a static gas. The chapter is structured as follows. In Sec. 2.2 we describe our experimental setup. Particular attention is paid to a discussion of ion counting by using the present CCD camera and a centroiding routine. In Sec. 2.3 we present and discuss our experimental results together with a comparison with theoretical prediction and modelling. The conclusions are summarized in Sec. 2.4.

2.2 Experimental

2.2.1 Laser apparatus and molecular beam

Here we present a brief description of the laser equipment that was used and the production of the molecular beam. A regeneratively amplified mode-locked Ti:Sapphire laser operating at 1 kHz produces linearly polarized laser pulses. The femtosecond pulse (centered at 800 nm, pulse duration with Full-Width at Half-Maximum about 120 fs) is frequency doubled in BBO. Using a lens with a 50 cm focal length the 400 nm laser beam ($\sim 5 \,\mu J/pulse$) is focused to a $\sim 64 \,\mu m$ spot on the molecular beam. The supersonic molecular beam is generated by a homebuilt cantilever piezovalve [1] and is operated at a repetition rate of 1 kHz in the present experiment. Typically, pure Xe is used at a pressure of 1 Bar behind the conical nozzle (40° full angular width, 200 μ m diameter). The generated Xe beam is collimated by a first skimmer (Beam Dynamics, diameter 1.5 mm) located at a distance of 3 cm from the nozzle. The second skimmer (diameter 1 mm) separates the buffer chamber from the imaging chamber and is located 2 cm downstream of the first skimmer. The skimmers are aligned to the center line of the molecular beam machine using a telescope. Half way between the repeller and extractor plates, the molecular beam is intersected by a linearly polarized laser beam at right angle. The total distance between the nozzle and the laser interaction region is about 16 cm.

2.2.2 Ion imaging apparatus and real-time ion count technique

The photofragment imaging system, schematically shown in Fig. 2.1, has been described in detail previously [72; 73]. The ions that are created are accelerated into a 40 cm long time-of-flight (TOF) tube and hit the position sensitive detector at the end of the TOF tube. The position sensitive detector consists of a micro-channel-plate (MCP) assembly coupled to a fast phosphor screen (Burle, P47). The light from the screen is collected on a high-resolution large frame $(2048 \times 2048 \text{ pixels})$ CCD camera (PCO2000). Simultaneously part of the light is monitored by a photomultiplier (Hamamatsu, R1527), which detects the total TOF mass spectrum. All through our experiments, the MCP is gated for Xe^+ by applying a fast rising (15 ns rise time) negative voltage pulse. The detection efficiency of ions is largely determined by the characteristics of MCPs, phosphor screen and CCD system employed. The two MCPs are placed in a so-called chevron configuration, and have a channel pore diameter of $D = 5 \,\mu m$, and a channel length (L) to channel diameter ratio of L:D = 60:1. The effective area of the MCP is about 40 mm in diameter. Both MCPs are operated with around 1000 volt/MCP to ensure sufficiently high gain. Under the present experimental conditions, a single ion results in a spot with a typical diameter of $110 \,\mu m$, corresponding to about 6 pixels on the CCD chip. The accumulation of events covering several pixels blurs the intensity

distribution to such large extent that it degrades the spatial resolution significantly. Experimentally the ultimate spatial resolution is limited by the channel size and channel spacing using the real-time ion-counting technique with event centroiding [74; 75]. Normally, the peak intensity varies from ion spot to ion spot because of detector inhomogeneity and statistical variation in MCP gain. Therefore, instead of adding ion signal intensity of the CCD chip over many exposed frames, we locate the position of the maximum intensity of a single ion event (with a predefined area of at least 2×2 pixels) within each frame of the image by a computer algorithm. The local maximum pixel within an observed ion event is then used for the location of the ion. A predefined pixel intensity threshold is carefully set to distinguish the signal from the background noise, which is mostly dark noise even though the camera is thermoelectrically cooled down to -30 °C. The present frame rate is 2 frames-per-second (FPS), which is limited by the current centroiding routine and not the camera itself that has a maximum FPS of 14.7. The exposure time per frame is set to 500 ms. A general problem for single ion counting is how to count all the ions without losses when many ions are produced per laser shot. This issue will be severe when bunches of ions are created in a relatively small volume, where part of these ion spots overlap on the CCD and will not be recognized by the computer routine as individual ion spots. This will inevitably lead to counting losses. In reality, this spatial congestion can be avoided by reducing either the molecular beam intensity or the laser beam intensity to reduce the signal level. In the present experiment the laser intensity at 400 nm is about $0.8 \times 10^{12} \,\mathrm{W/cm^2}$. At this laser intensity, each laser shot produces much less than one ion statistically. With such a low count rate, space charge effects are negligible. We checked that there is a linear relationship between the number of detected ion events and the exposure time of the CCD camera, and this confirms that all the ions are detected without counting losses. This laser intensity is the upper limit where the linear relationship between ion count and exposure time holds. To further prevent the occurrence of spatial overlapping of ion events on the CCD, the product ions are diverged in space with the help of the static electric field applied on the ion lenses. In the present experiment the following voltages were applied, V-repeller = 1700 V and V-extractor = 1350 V. Care is taken that all the ions coming from the laser interaction region impact on the detector. This was also checked by accurate SIMION trajectory simulations of our ion optics. Furthermore, by using a different electric field configuration, with the same laser intensity, it was confirmed that expansion of the ion cloud is beneficial to preventing overlapping events. The focus position of the CCD camera was carefully adjusted to minimize the ion spot on the image, which also helps to decrease the chance of neighbor events overlapping. Finally, the number of ion counts reported by the centroiding routine were also compared with the counts of a raw image per frame during our experiments, and both results show a good agreement.



Figure 2.1 – Panel (a) Schematic diagram of the experimental setup. R=repreller, E=extractor, G=ground electrode, PMT=photomultiplier. The electrodes are 70 mm in diameter with spacing 15 mm. The holes in R and E plates are 20 mm in diameter. The TOF tube is set perpendicular to the molecular path, which helps to suppress undesired collisions between produced ions and initial molecules in the case of the molecular beam. The bulk gas pressure inside the chamber is finely controlled by a needle valve at the gas inlet. Panel (b) Schematic illustration of the interaction region in two situations: for the molecular beam, the interaction volume is determined by the intersection region between laser and molecular beam, while for the bulk the interaction region is represented by the shape of the laser beam. Recorded images for both cases are shown at the top.

2.3 Results and discussion

2.3.1 Bulk gas density profile

The bulk gas is directly sent into the imaging chamber by a gas inlet and then diffuses freely in the large vacuum chamber. To achieve homogeneous and stable pressure in the chamber, the gas inlet is placed far away from the turbo molecular pump. Two Bayard-Alpert nude-type ionization gauges (BAGs) (Granville Phillips, series 274) located at two different positions are used to measure the gas pressure. The reproducible readings given by the two ion gauges confirm the good pressure homogeneity and stability. In this work, the real pressure is taken to be the average of both pressure readings. An ion gauge sensitivity correction factor for Xe (2.87 relative to N₂ = 1) is taken into account. Li and Jousten [76] did a systematic investigation of the



Figure 2.2 – The bulk density distribution along the laser beam path. The curve shows a plateau characteristic with length of 1600 pixels. MB labels the position of the molecular beam.

properties of this sensitivity factor and they found that this factor has small changes over a wide pressure range. For Argon, they found the relative factor for two BAGs is 1.306 and 1.304 respectively, which is very similar to the value of 1.29 that manufactures use [77]. So, we apply the reported relative sensitivity factor of 2.87 for Xe in our pressure measurements. Fig. 2.2 shows the bulk ion count distribution along the laser path. We observe quite a long plateau along the laser beam. It almost covers the whole window of the detector except the two ends of the image which are clipped by the edges of the detection system. SIMION simulations show that the interaction length seen by the detector is about $7.5 \,\mathrm{mm}$, which is first limited by the aperture (20 mm diameter) in the extractor plate, and subsequently further limited by the size of the MCP-detector (40 mm diameter). Within this limited interaction length, the magnification factor of the electric field can be considered to be approximately constant, regardless of the birthplace of ions. The amplification factor of the CCD camera is calibrated by taking an image of graphing paper that is put on the top of phosphor screen. From this test image the derived conversion factor of the camera lens is about 52.5 pixels/mm. Together with the measured total conversion factor of 192 pixels/mm (image to source see below), we can estimate the magnification factor contributed by static electric field to be 192 (pixels/mm)/52.5 (pixels/mm) = 3.7.

The observed TOF of Xe⁺ equals $10.5 \,\mu$ s in our experiments, and taking into account a mean speed of about $217 \,\mathrm{m/s}$ at room temperature, we calcu-

late the thermal spread in position at the MCPs to be $10.5 \,\mu s \times 217 \,\text{m/s} = 2.3 \,\text{mm}$. This value can be reproducible in the SIMION simulation (2.5 mm). Before impinging on the detector, the ion cloud expands due to two independent mechanisms: divergence induced by the electric field and spread caused by thermal motion. As is shown in Fig. 2.2, the length of the plateau is about 1200 pixels, which corresponds to 1200 pixels/52.5 (pixels/mm) = 22.8 mm. Tracing the length of plateau back to an interaction length in the source region, we find that this plateau originates from a source with a length of (22.8–2.3) mm/3.7 = 5.5 mm. This interaction length along the laser path covers only a small fraction of the Rayleigh length (32 mm) of the focused laser beam. Thus the intensity variation of the laser over this small source length of 5.5 mm is negligible. Consequently, the number of ions created at each position along the laser path can be considered to be constant. This argument is further experimentally confirmed by comparison bulk profile with molecular beam profile, see Sec. 2.3.2.

In the case of bulk gas measurement the whole imaging chamber is filled with Xe gas, so undesired contributions to the ion signal like ion scattering, charge-exchange processes and especially secondary ion emission generated by electron-atom collisions could come into play [78]. All these effects would exhibit a nonlinear dependence on the Xe gas pressure. Fig. 2.3 shows the measured ion count as a function of the bulk gas pressure, ranging between 3.2×10^{-5} mbar and 1.6×10^{-4} mbar (uncorrected pressure readings). The linear relationship that is observed means that those secondary influences can be ignored under the working pressure of 3.3×10^{-5} mbar that we used in the bulk imaging experiment. It is further worth mentioning that we never observed any highly charged Xe ions or cluster ions in TOF mass spectra.

2.3.2 Transverse density profile of molecular beam

In our experimental apparatus the piezovalve runs at the repetition rate of 1 kHz, which is synchronized with the laser beam at the crossing point by adjusting the delay between the drive pulse of the piezovalve and the Q-switched pulse of the regen laser system. The position of the nozzle is first coarsely aligned in front of the skimmer by optimizing the gas load in the imaging chamber, and is further optimized according to the ion signal level measured on the detector. Due to the cylindrical symmetry of the ion lens, the resultant electric field exhibits the same symmetry. The same influence on the ion trajectory is exerted by the field over ions having the same initial distance from the ion lens axis. To obtain the total conversion factor between mm (source) and CCD-pixel (image), we perform a scan of the laser focusing lens along the molecular beam propagation direction of 3 mm with respect to the ion lens axis. The position of the ion image changed by 576 pixels, resulting in a conversion factor of 192 pixels/mm. This conversion factor is also valid along the dimension of the laser beam path. In Fig. 2.4, we show the transverse profile of beam density along both the laser beam propagation direction and the TOF



Figure 2.3 – The variation of the ion signal intensity as a function of the bulk pressure.

direction. Both are derived from the histogram of single ion events in images with 3600 frames with each frame having an exposure time of 500 ms. The histogram along the laser beam path is obtained with the laser beam going exactly through the middle of molecular beam. The histogram along the TOF direction is acquired by moving the focusing lens vertically over the beam jet. In effect, this is equivalent to taking a series of slices through the molecular beam by the laser beam due to the fact that the laser beam waist is much smaller than the molecular beam radius. As can be seen in Fig. 2.4, a Gaussian function fits both distributions very well. Considering the known conversion factor 192 pixels/mm, the FWHM of the distribution along the molecular beam is 3.2 mm (608 pixels), which is similar to the FWHM of the distribution along the TOF direction (3.1 mm). Considering the cylindrical symmetry of nozzle and skimmers, these two equal widths of the molecular beam in both directions at the laser interaction region are as expected. We can also estimate the molecular beam diameter from the geometry, that is, the location of the nozzle and the two skimmers, and the diameters of the skimmers. In our case this is mainly determined by the diameter of the second skimmer (1 mm diameter). The estimated molecular beam diameter at the interaction point is $3.2 \,\mathrm{mm}$, which matches the measured beam diameters from the ion images very well. As illustrated in Fig. 2.5, along the molecular beam propagation direction, the ion count distribution of bulk images has much broader spread than that of beam image. Considering the same interaction area (determined by laser beam size)



Figure 2.4 – The beam density profile along both TOF axis (left-hand and bottom axes) and laser beam path (right-hand and top axes). For comparison, the length of top axis (pixel) is set equivalent to the length of bottom axis (mm). The two curves have exactly the same form. By fitting with a Gaussian function, we obtain the molecular beam spot size of 3 mm (FWHM) at the interaction point.

in the plane transverse to laser propagation direction, we conclude that the difference in width in the images results from the thermal velocity expansion. For the molecular beam gas the FWHM equals 13 pixels. This corresponds to 13 pixels/192 (pixels/mm) = $69 \,\mu \text{m}$ at the source region. This value is close to the calculated minimum waist (~ $64 \,\mu m$) of the focused laser beam. Taking into account the Maxwell-Boltzmann speed distribution we calculate with SIMION an extra spread of FWHM = 1.2 mm at the detector. According to the previous discussion, the bulk image width equals the thermal spread added to the beam image width, that is, 13.2 pixels + (2.3+1.2) mm \times 52.5 (pixels/mm) = 197 pixels. This value matches the measured FWHM of 201 pixels, see Fig. 2.5. Therefore, we conclude that the estimate of the interaction length that contributes to the plateau of constant intensity is justified and that neither the thermal velocity spread of the bulk sample nor the spread due to the electric field influence the shape of the ion distribution profile. The plateau shape in Fig. 2.2 means that the ion intensity measured by the detector has a uniform distribution along the laser path at the source region.



Figure 2.5 – The beam density distribution along the molecular beam propagation direction, where only a central segment of both images with equal length of 100 pixels along laser beam path are selected for a study. Both distributions are normalized and fitted to a Gaussian function.

2.3.3 Centre line density of pure molecular beam

The ion imaging measurements of the molecular beam and the bulk gas were performed under identical experimental conditions with respect to laser position, laser pulse intensity, ion electric field and ion detection efficiency. The gas pressure in the imaging chamber for the bulk experiment on Xenon was 3.3×10^{-5} mbar, with background pressure subtracted. This pressure corresponds to a bulk gas density of $n_0(bulk) = P/kT = 8.1 \times 10^{11} \,\mathrm{cm}^{-3}$, where k is the Boltzmann constant and $T = 295 \,\mathrm{K}$. We can now calculate the molecular beam peak density $n_0(beam)$, using the ion counts of the images of the bulk gas $N_i(bulk)$, and the molecular beam $N_i(beam)$, and scaling as follows $n_0(beam) = n_0(bulk) \times N_i(beam)/N_i(bulk)$. The peak ion count of the beam, $N_i(beam)$, is extracted by Gaussian fitting of the ion count histogram distribution along the laser beam propagation direction. The ion count in the bulk image, $N_i(bulk)$, was extracted from the bulk measurement taken under identical experimental conditions. With these two ion count values from the images and the measured bulk density we obtain the measured beam peak density, at a distance of 16 cm after passing two skimmers, $n_0(beam) = 5.5 \times 10^{11} \text{ cm}^{-3}$.

We will now compare the measured centre line beam intensity with other estimates and theoretical calculations. First we will compare this value with an estimate based on the gas load in the imaging chamber when the molec-
ular beam is on. The turbo molecular pump in the imaging chamber has a nominal pumping speed of 510 Ls^{-1} . When the molecular beam is on the pressure increment is 0.99×10^{-7} mbar which represents an average gas load of 0.5×10^{-7} bar L s⁻¹ in the imaging chamber. The repetition rate of the pulsed valve is 1 kHz, so this average load means that a single gas pulse provides a gas load of 0.5×10^{-10} bar L per pulse. This corresponds to 2.2×10^{-12} mol/pulse or $N_0 = 1.3 \times 10^{12}$ particles/pulse. As was shown in Fig. 2.4 the molecular beam distribution has a Gaussian shape in the plane transverse to the flow direction, referred here as the xy plane. By scanning the delay between the laser and the valve trigger, we also measured the temporal shape of the pulsed molecular beam. Even though the temporal shape has a faster rise and a somewhat longer tail, for simplicity we assume now that the temporal shape can also be represented by a Gaussian shape. The molecular beam density can then be represented by a Gaussian density function in three spatial coordinates as $n(x, y, z) = n_0 \times \exp[-(x^2/2\sigma_x^2 + y^2/2\sigma_y^2 + z^2/2\sigma_z^2)]$, with n_0 the centre line beam intensity at x = y = z = 0, where z = 0 represents the peak temporal position, and $\sigma_x, \sigma_y, \sigma_z$ are the usual widths in a Gaussian function and $\sigma_i = \text{FWHM}_i/2.355$ for each dimension i = x, y, z. The relationship between peak density and total number of atoms is given by $n_0 = N_0 / [(\sqrt{2\pi})^3 \sigma_x \sigma_y \sigma_z]$. From a Gaussian fit to the temporal pulse profile we find $\sigma_t \approx 110 \, \mu s$. We calculate the final most probable beam velocity of the molecular beam using, $v = \sqrt{2kT/m} \times \sqrt{\gamma/(\gamma - 1)} = 309 \,\mathrm{m/s}$, with T=295 K the temperature of the nozzle, m the mass of Xenon and $\gamma = 5/3$. Then we obtain $\sigma_z = \sigma_t v = 3.4$ cm. Furthermore, from the ion images (Fig. 2.4) we find $\sigma_x = \sigma_y = 3.12 \text{ mm}/2.355$ $= 0.132 \,\mathrm{cm}$. The centre line beam density can now be estimated as follows, $n_0 = N_0 / [(\sqrt{2\pi})^3 \sigma_x \sigma_y \sigma_z] = 1.4 \times 10^{12} \,\mathrm{cm}^{-3}$. This estimated value from the gas load is a factor of 2.5 larger than the value measured from the ion images. The reason for this difference may be due to the fact that the actual temporal distribution is not a Gaussian function but has a temporal shape with a relatively fast early rise and a tail at longer times. Furthermore, the real pump speed in the imaging chamber is probably somewhat lower than the specified nominal pump speed of the turbo pump due to the experimental geometry. Nevertheless, it is quite encouraging that the measured absolute beam density is within a factor of 2.5 from the density based on the gas load and the pump speed in the imaging chamber.

We can also make a comparison with the expected centre line beam density using the theoretical formalism developed by Beijerinck and coworkers [79] for rare gas supersonic beams. The centre line beam density at a distance z from the nozzle is given by [79]

$$n(z) = n_0 (z/z_{\rm ref})^{-2},$$
 (2.1)

with n_0 the number density of the gas in the reservoir and $z_{\text{ref}} = a(\gamma)R_{\text{nozzle}}$ a reference distance that depends on the nozzle diameter and a constant a that is found from numerical simulations for a given value of $\gamma = c_P/c_V$, the ratio

of specific heats of the gas. In our case, with $a(\gamma = 5/3) = 0.802$ and $R_{\text{nozzle}} = 100 \,\mu\text{m}$, we obtain $z_{\text{ref}} = 8.0 \times 10^{-3} \,\text{cm}$. Furthermore, with a nozzle source pressure of 1 bar Xe at T = 295 K, the nozzle density, n_0 , is $2.46 \times 10^{19} \,\text{cm}^{-3}$. Thus, we calculate the ideal centre line density for an unskimmed expansion of Xe at a distance of 16 cm to be $n(z = 16 \,\text{cm}) = 6.2 \times 10^{12} \,\text{cm}^{-3}$. This is about a factor of ten higher than the experimentally measured density. Furthermore, the theoretically calculated centre line intensity is for a sonic nozzle, and in our experiment we use a conical nozzle with an opening angle of about 40° . It was shown by Even and coworkers [61] that such a conically shaped nozzle increases the centre line intensity by an order of magnitude relative to a sonic nozzle shape.

There are two potential causes accounting for the large difference in the measured beam density and the calculated theoretical density. The first cause may be that the effective nozzle diameter of the pulsed expansion is not the nominal (optical) diameter of $200 \,\mu$ m. Due to the finite dynamical response of the piezo the effective diameter may be lower. To estimate the effective nozzle diameter we have calculated the flow rate using the pump speed and the pressure in the source chamber which contains the nozzle. The source chamber is pumped by a 5000 L/s diffusion pump with a water cooled baffle. The (corrected) pressure increase in the source chamber when the pulsed valve is running at 1 kHz is about 2.7×10^{-6} mbar. With the (nominal) pump speed it means that the flow rate is about 1.35×10^{-5} bar L/s = 3.4×10^{17} atoms/s. The duty cycle of the pulsed valve is about $2.355 \times 110 \times 10^{-6} \times 10^{3}$ = 3.37×10^{-3} . The flow rate is given by [79]

$$N = f(\gamma) n_0 \alpha_0 \pi R_{\text{nozzle}}^2, \qquad (2.2)$$

with $\alpha_0 = (2kT_0/m)^{1/2}$ is the characteristic velocity in the reservoir at a certain temperature T and $f(\gamma = 5/3) = 0.513$ a constant that is found from numerical simulations [79]. This means that the calculated flow rate through the nozzle with nominal diameter of 200 μ m, with a duty cycle of 3.37×10^{-3} , is 2.6 × 10^{17} atoms/s. This is somewhat smaller than the measured flow rate of 3.4×10^{17} atoms/s. However, taking into account the uncertainty in the measured pressure, and the fact that the temporal pulse shape is not Gaussian, the difference in measured and estimated gas load is not that large. From this comparison it seems that the effective nozzle diameter may be close to the nominal diameter and is probably not the dominant reason for the difference between the measured centre beam density and the theoretical beam density.

A second cause may be the effect of the two skimmers on the throughput of the molecular beam. It has been reported before [62; 65; 79] that skimmers may substantially reduce the intensity of a molecular beam. In the present experiment we used two skimmers, the first one with a diameter of 1.5 mm located about 3 cm from the nozzle exit, and a second skimmer with a 1 mm diameter located at 5 cm from the nozzle. According to Luria *et al.* [62], skimmers with diameters of 1–1.5 mm can have transmissions as low as 1-10% depending on

the molecular beam density at the skimmer entrance. Even at modest densities of about $3 \times 10^{15} \,\mathrm{cm}^{-3}$ calculations show that a 1.5 mm diameter skimmer has a throughput of only 15% (for Argon) [65]. If we take our theoretical beam density of an unskimmed beam at 16 cm of $6.2 \times 10^{12} \text{ cm}^{-3}$ and scale this to a distance of 3 cm (where our first skimmer is positioned), we obtain a density of $1.8 \times 10^{14} \,\mathrm{cm}^{-3}$. Furthermore, we have a conical nozzle shape with an angle of 40° and it was observed that the forward intensity is about an order of magnitude higher than a sonic nozzle [65]. This means that we estimate that the beam density of Xe at our first skimmer of 1.5 mm diameter is about 2 $\times 10^{15} \,\mathrm{cm}^{-3}$. The calculations in Even *et al.* [65] show that such a skimmer may have a throughput of only 15–20% for Argon at these modest beam densities, and perhaps even worse for Xenon. Furthermore, in our machine we have a second skimmer (with 1 mm diameter) located only a few cm downstream of the first skimmer. Therefore, it seems very plausible that the rather small skimmer diameters that were used at rather short distances from the nozzle exit, have a very strong effect on the throughput of the pulsed molecular beam, even at our modest backing pressure of 1 Bar. From the large difference between the measured beam density and the calculated ideal beam density, using the theoretical formalism of Beijerinck and co-workers [79], we estimate that the total reduction in throughput by the two small skimmers in our machine, using a conical nozzle expansion of 1 Bar Xe, is about two orders of magnitude (1%). If we take our measured density of 5.5×10^{11} cm⁻³ and multiply this with a factor of 100, we estimate an unskimmed centre line beam intensity of about $6 \times 10^{13} \,\mathrm{cm}^{-3}$ at 16 cm from the nozzle.

2.3.4 Centre line beam density of seeded molecular beams

From experiments with seeded beams it is known that heavy species have the tendency to be concentrated on the beam axis [55; 56]. We measured the relative enhancement of the centre line beam density of the heavy Xe atom seeded in the relatively light Ne carrier gas. The results reported here were measured for seeded beams with a backing pressure of 3.4 Bar. In the same way as reported above we measured the centre line intensity by averaging the Xe ion counts as obtained from the ion images. The molecular beams had the following composition: pure 100% Xe (MB100), 50% Xe in Ne (MB50), 10% Xe in Ne (MB10) and 1% Xe in Ne (MB1). When we normalize the measured Xe signal of the particular molecular beam to the signal as measured for the pure molecular beam we find: 1 (MB100), 2.4 (MB50), 4.7 (MB10) and 1.1 (MB1). This means that for instance the 10% Xe in Ne (MB10) seeded beam is almost a factor of five (4.7) stronger in intensity than a pure Xe beam (MB100). If one would take into account the 10% seeding ratio it appears as if the MB10 is almost a factor of fifty stronger than a pure beam of Xe. These results show that there is a large centre beam line enhancement of the seeded Xe molecular beam in the light carrier gas Ne. These results further demonstrate that besides the cooling that is obtained in a seeded molecular beam, also the

strong centre line (kinematic) enhancement of a heavy atom/molecule seeded in a light carrier gas (like Ne), make these cold seeded molecular beams very attractive for subsequent experiments.

2.4 Conclusion

In this chapter, we reported on a technique to measure the beam intensity of (seeded) molecular beams by femtosecond ion imaging. By using a nonresonant detection scheme, we could compare the ion intensity of a pulsed beam of Xe atoms relative to the ion intensity of bulk Xe gas recorded under the same experimental conditions which is not possible for resonant schemes as the Doppler profiles are very different. The experimentally measured peak density is lower than the theoretically predicted value and the difference is attributed to a significant reduction in beam intensity due to skimmer interference. Furthermore, we presented experimental data of seeded beams of Xe in Ne and measured a very strong centre beam line enhancement of the density relative to the seeding fraction of Xe. The universal method demonstrated in this chapter can be used, for instance, to measure the densities in crossed molecular beam experiments to determine absolute cross sections.

Appendix A

Skimmer effects

As stated in the previous chapter, the discrepancy between the measured density and the one expected from a theoretical calculation, might be explained by skimmer interference. After the publication of our paper, prof. Uzi Even of Tel Aviv University kindly performed simulations that support this hypothesis. These simulations will be presented here.

The measured centre line beam density of the doubly skimmed beam at 16 cm downstream of the nozzle, was simulated using the freely available DSMC program [80]. From eq. (2.1) with $z_s = 3$ cm, the estimated xenon density before the first skimmer is 2×10^{15} cm⁻³. From the simulations, shown in Fig. A.1, the transmission of this skimmer with diameter of 1.5 mm at this density is only 2%. It is evident from the simulation that at this large incoming beam



Figure A.1 – Simulated density map (left-hand side) and centre line beam density (right-hand side) at the first skimmer (diameter of 1.5 mm) assuming an initial xenon beam density of 2×10^{15} cm⁻³.

densities, skimmer clogging is a severe problem for skimmers with an entrance diameter of 1-1.5 mm. The reason for this, is the high temperature region at the skimmer entrance that causes the beam to heat up and to spread out, even when the mean free path is several mm. To reduce this clogging effects, it is necessary to use a large diameter entrance aperture (3–4 mm) and to move the skimmer by as much as 1000 nozzle diameters downstream from the nozzle (100–200 mm) [65]. In our setup two skimmers are employed. The second skim-



Figure A.2 – Simulated temperature map at the first skimmer assuming an initial beam density of 2×10^{15} cm⁻³.

mer has a diameter of 1 mm and is placed 50 mm downstream from the nozzle. Taking into account a 2% transmission, the estimated axial beam density, n_1 , at the exit of the first skimmer is ~ 4×10^{13} cm⁻³. The incoming beam density at the second skimmer is estimated to be $n_2 = (3/5)^2 n_1 = 1.4 \times 10^{13}$ cm⁻³. The simulations presented in Even [65] suggest that the transmission at this density is about 50%, So, combined, the transmission of the doubly skimmed xenon beam is ~ 1%. This agrees well with the measured density and confirms our hypothesis that skimmer effects are the main cause for the measured density being two orders of magnitude lower than expected.

We gratefully acknowledge Prof. Uzi Even for performing the presented simulations that are unpublished.

Chapter 3

Prospects for high-resolution microwave spectroscopy of methanol in a Stark-deflected molecular beam¹

Recently, the extremely sensitive torsion-rotation transitions in methanol have been used to set a tight constraint on a possible variation of the proton-toelectron mass ratio over cosmological time scales. In order to improve this constraint, laboratory data of increased accuracy will be required. In this chapter, we explore the possibility for performing high-resolution spectroscopy on methanol in a Stark-deflected molecular beam. We have calculated the Stark shift of the lower rotational levels in the ground torsion-vibrational state of CH_3OH and CD_3OH molecules, and have used this to simulate trajectories through a typical molecular beam resonance setup. Furthermore, we have determined the efficiency of non-resonant multiphoton ionization of methanol molecules using a femtosecond laser pulse. The described setup is in principle suited to measure microwave transitions in CH_3OH at an accuracy below 10^{-8} .

3.1 Introduction

Theories that extend the Standard Model of particle physics have presented scenarios that allow for, or even predict, spatial-temporal variations of the constants of nature [81]. Possible variations of the fine structure constant, α , representing the strength of the electromagnetic force, or the proton-to-electron mass ratio, μ , a measure of the strength of the strong force, lead to shifts in the spectra of atoms and molecules. Many studies have been devoted to observe these shifts. By comparing metal absorptions in the spectra from distant

¹Based on Paul Jansen, Isabelle Kleiner, Congsen Meng, Ronald M. Lees, Maurice H.M. Janssen, Wim Ubachs and Hendrick L. Bethlem, Mol. Phys. **111**, 1923 (2013).

quasars with the corresponding transitions measured in the laboratory, Webb et al. [82] found evidence that suggests that the fine structure constant, α , has a smaller value at high redshift. In later work, this variation was interpreted as a spatial variation of α [83]. In parallel, laboratory experiments on earth are used to probe possible variations in the current epoch. Compared to their astrophysical counterpart, their advantage is their great accuracy, reproducibility and unequivocal interpretation. By comparing transitions in different isotopes of dysprosium, a possible variation of the fine structure constant was found to be $< 2.6 \times 10^{-15}/\text{yr}$ [84]. Whereas atomic spectra are mostly sensitive to variations in α , molecular spectra can be used to detect a possible variation of μ . The most stringent independent test of the time variation of μ in the current epoch is set by comparing vibrational transitions in SF_6 with a cesium fountain, which has resulted in a limit for the variation of $\Delta \mu/\mu$ of $5.6 \times 10^{-14}/\text{yr}$ [85]. Tests of μ -variation on cosmological time scales have been performed by comparing spectra of molecular hydrogen measured in the laboratory with those observed at redshifts z = 2-3, corresponding to a look-back time of 10-12 Gyr, constraining $\Delta \mu/\mu < 10^{-5}$ [86]. The most stringent limit on a variation of μ in the early universe are set by Bagdonaite et al. [3] from comparing absorptions by methanol in objects at a redshift of 0.89, corresponding to a look-back time of 7 Gyr, with laboratory data. The uncertainty in the constraint derived by Bagdonaite *et al.* is dominated by the precision of the astrophysical data. However, when more accurate astrophysical data become available, the error in the laboratory data will become significant. In this chapter, we investigate the possibilities to increase the precision of selected microwave transitions in methanol. We focus on the four transitions in CH₃OH observed by Bagdonaite et al., and two transitions in CD_3OH that – provided that the precision is significantly enhanced – might be used for a laboratory test of the time variation of μ .

Line centers of methanol transitions in the microwave region are typically obtained from absorption measurements in a gas cell, resulting in (Dopplerlimited) measurement uncertainties around 50 kHz corresponding to a relative uncertainty of $\sim 10^{-7}$ [87]. For a limited number of lines higher resolution data was obtained by a pulsed molecular beam Fabry-Perot Fourier-transform microwave spectrometer of the Balle-Flygare type [88], reaching accuracies around 20 kHz [89]. Using a beam-maser setup, two single methanol transitions were recorded with relative accuracies of $\sim 10^{-8}$ [90]. So far, this is the only study that was able to (partly) resolve hyper-fine structure in methanol. All these studies are based on detecting absorption or emission of the microwave field. A significantly higher precision seems feasible in a Rabi-type setup using lasers to state-selectively detect the methanol molecules. Unfortunately, so far no suitable state-selective detection scheme for methanol has been demonstrated. The only study that reports the detection of methanol by resonance-enhanced multiphoton ionization (REMPI), involved either the repulsive 3s Rydberg state or one of the 3p Rydberg state; both resulting in broad unresolved bands [91].

Here, we explore the possibility for detecting methanol molecules using a

femtosecond laser, while relying on inhomogeneous electric fields to separate the different quantum states present in the beam. This seems a fitting subject for this Festschrift, given that Bretislav Friedrich wrote several seminal papers that helped to understand the physics of molecules in external fields. This chapter is organized as follows: In Sec. 3.2 we discuss the energy level structure of methanol, and review the origin of the large sensitivity coefficients that are found in this molecule. Furthermore, we outline the procedure that was adopted to calculate the Stark interaction for methanol. In Sec. 3.3 we simulate trajectories of methanol molecules through a typical beam resonance setup, using the derived Stark shifts as input. In Sec. 3.4, we present measurements that determine the efficiency of ionizing methanol molecules using femtosecond laser pulses. Finally, in Sec. 3.5, we use the simulations and measured ion yield to estimate the expected accuracy of the described beam resonance setup.

3.2 Theory

3.2.1 Torsion-rotation levels in methanol

Methanol is the simplest representative of the class of alcohol molecules and consists of a hydroxyl (OH) group attached to a methyl group (CH₃). The CO bond that connects the two parts of the molecule is flexible, allowing the methyl group to rotate with respect to the hydroxyl group. This rotation is hindered by a threefold potential barrier with minima and maxima that correspond to a staggered and eclipsed configuration of the two groups, respectively. For the lowest energy levels, the internal rotation or torsion is classically forbidden and only occurs due to quantum mechanical tunneling of the hydrogen atoms. In order to account for this additional degree of freedom, the normal asymmetric top Hamiltonian has to be augmented with a term that describe the torsion motion. To simplify the calculation, the coupling between overall and internal rotation is partly eliminated by applying an axis transformation to the coordinates of the Hamiltonian (the so-called "Rho-Axis Method" or RAM). In the rho-axis method, the full torsion-rotation Hamiltonian for methanol becomes [92]:

$$H_{\rm RAM} = H_{\rm tors} + H_{\rm rot} + H_{\rm cd} + H_{\rm int}.$$
(3.1)

where H_{tors} , H_{rot} , H_{cd} and H_{int} represent the torsion, overall rotation, centrifugal distortion, and higher-order torsion-rotation interaction terms, respectively. This Hamiltonian is implemented in the BELGI code [92] that we have used to calculate the level energies of methanol. The current version of the code was modified and improved by Xu *et al.* [87] in a number of ways useful for treating the large datasets available for the methanol molecule. Furthermore, the code has been optimized to make it faster and a substantial number of higher order parameters has been added. Using a set of 119 molecular constants for CH₃OH from Ref. [87] and 54 constants for CD₃OH from Ref. [93], the lower energy levels are found with an accuracy < 100 kHz. The Hamiltonian of Eq. (3.1) is diagonalized in a two-step process to obtain the torsion-rotation energy levels [94]. In the first step, the torsional Hamiltonian (H_{tors}) is diagonalized:

$$H_{\text{tors}} = F \left(p_{\alpha} - \rho J_z \right)^2 + V \left(\alpha \right), \qquad (3.2)$$

where F is the internal rotation constant, ρ is the ratio of the moment of inertia of the methyl top relative to the moments of inertia of the molecule as a whole, and $V(\alpha)$ is the internal rotation potential barrier, p_{α} is the internal rotation angular momentum, J_z is the projection of the global rotation on the zmolecular axis and α is the torsional angle. The eigenvalues obtained after this first step are the torsional energies for each torsional level that are characterized by the quantum numbers K, ν_t and $\sigma = 0$ (A species) or ± 1 (E species). The A and E symmetry species can be considered as two different molecular species in the same sense as ortho- and para ammonia. The torsional eigenfunctions can be written as linear combinations of the basis wave functions [94]:

$$|K\nu_t\sigma\rangle = \frac{1}{\sqrt{2\pi}}|K\rangle \sum_{k=-10}^{10} A^{K,\nu_t}_{3k+\sigma} \exp\left(i\left[3k+\sigma\right]\alpha\right),\tag{3.3}$$

where k is an integer. In the second step, the rotational factor $|K\rangle$ in the eigenfunctions from Eq. (3.3) is replaced by the full symmetric top wave function $|JKM\rangle$ to generate the basis set used to diagonalize the remaining terms of the Hamiltonian from Eq. (3.1), i.e. $H_{\rm rot}$, $H_{\rm cd}$, and $H_{\rm int}$.

The lowest energy levels of CH_3OH and CD_3OH are calculated at zero electric field using the molecular constants from Refs. [87; 93], and are shown in the upper and lower panels of Fig. 3.1, respectively. The arrangement of energy levels within a symmetry state resembles that of a prolate symmetric top, with the difference being that every K ladder obtains an additional energy offset due to the K dependent tunneling splitting. As a consequence, certain states in neighboring K ladders may become nearly degenerate. It was shown by Jansen *et al.* [95] and Levshakov *et al.* [96] that transitions between these nearly degenerate states are very sensitive to possible variations of the protonto-electron mass ratio, μ . The sensitivity of a transition with a frequency ν is defined as

$$\frac{\Delta\nu}{\nu} = K_{\mu} \frac{\Delta\mu}{\mu}.$$
(3.4)

The overall rotational energy of the molecule scales with its rotational constants and is thus inversely proportional to the reduced mass of the system. Therefore, pure rotational transitions have a sensitivity coefficient, $K_{\mu} = -1$. The torsional energy arises from the tunneling effect and – similar to the inversion splitting in ammonia – depends exponentially on the effective mass that tunnels. For the normal isotopologue of methanol, the sensitivity coefficient of a purely torsional transition has a value of $K_{\mu} = -2.5$. Note that, due to



Figure 3.1 – Level scheme of the lowest torsion-rotation states in the torsionvibrational ground state ($\nu_t = 0$) of CH₃OH (upper panel) and CD₃OH (lower panel). The energies are calculated at zero electric-field strength using the molecular constants from Refs. [87; 93] and are given with respect to the zero point of the torsional well. The levels are labeled by J_K (indicated on the left-hand side of each level). For the *A* levels the so-called parity quantum number (+/-) is also indicated. Arrows in the upper panel mark transitions that were used in Bagdonaite *et al.* [3] to constrain $\Delta \mu/\mu$. The shaded area in the lower panel highlights the near degeneracies between the 2₀ *E*, 1₁ *E*, and 2₂ *E* levels in CD₃OH.

symmetry, such transitions are not allowed in methanol. An interesting effect occurs for transitions between different K ladders. In this case, part of the



Figure 3.2 – Calculated level energies and effective dipole moments of the $3_{-1}E$ and 2_0E levels in CH₃OH (left panel) and 2_0E , 1_1E , and 2_2E levels in CD₃OH (right panel) as function of the applied electric field.

overall rotational energy is converted into internal rotation energy or vice versa. When the energies involved are rather similar – i.e., when the levels are nearly degenerate – this results in enhanced sensitivity coefficients. These enhancements occur generally in every internal rotor molecule, but because of a number of favorable properties, the effect is exceptionally large in methanol [95].

The arrows in the upper panel of Fig. 3.1 mark transitions that have been observed in the study of Bagdonaite *et al.* [3]. The two transitions in the K = 0 ladder are pure rotational transitions and have a sensitivity coefficient of $K_{\mu} = -1$. The transitions between the K = 0 and |K| = 1 ladder have sensitivities of $K_{\mu} = -7.4$ and -33. The shaded area in the lower panel of Fig. 3.1 highlights the near degeneracies present between the $2_0 E$, $1_1 E$, and $2_2 E$ levels in CD₃OH. The $2_2 \leftrightarrow 1_1 E$ transition and the $1_1 \leftrightarrow 2_0 E$ have sensitivity coefficients of 330 and -42, respectively. Thus, if μ increases, the frequency of the $2_2 \leftrightarrow 1_1 E$ transition becomes larger while the frequency of the $1_1 \leftrightarrow 2_0 E$ transition becomes smaller. By comparing these two transitions over a number of years, a possible variation of μ can be constrained or measured.

3.2.2 Stark effect in methanol

In order to calculate the Stark shift on the energy levels of methanol for different values of the electric field, we have included the Stark Hamiltonian H_{Stark} in the second diagonalization step of the BELGI code. The Stark term is given by

$$H_{\text{Stark}} = -\vec{\mu}_e \vec{E},\tag{3.5}$$

where $\vec{\mu}_e$ is the body-fixed electric dipole moment vector and \vec{E} the electric field. In our calculation, $\vec{\mu}_e$ is represented by the body-fixed dipole moments μ_a and μ_b along the *a* and *b* axes of the RAM frame, respectively. For CH₃OH, $\mu_a = 0.889$ D and $\mu_b = -1.44$ D [87], while for CD₃OH, $\mu_a = 0.8340$ D and $\mu_b = -1.439$ D [97]. The matrix elements of H_{Stark} are taken from Eqs. (1)–(4) of Kleiner *et al.* [98]. Since the Stark effect induces nonzero matrix elements $\langle J|H_{\text{Stark}}|J \pm 1 \rangle$, the Hamiltonian matrix was extended to include those interactions. For a given J value, the Hamiltonian matrix only has off-diagonal blocks involving the nearby $J \pm 1$ states. Each J, K energy level is split into 2J + 1 components, characterized by M_J , the projection of the total angular momentum J along the laboratory axis Z. M_J is the only good quantum number in the presence of the electric field, hence the basis used for calculating the Stark effect for a certain M_J level includes all states with this specific M_J .

Our approach was tested by comparing the Stark shifts calculated by the modified version of BELGI with the results of a perturbation-like calculation using a code written by Lees and coauthors [99]. For J levels up to J = 2, the ratios of the Stark shifts obtained by these two methods are close to unity at 10 kV/cm and range from 0.7 to 1 at 50 kV/cm.

In the left and right-hand side of Fig. 3.2, energies of the near-degenerate $3_{-1}E$ and 2_0E levels of CH₃OH and 2_0E , 1_1E , and 2_2E levels of CD₃OH, respectively, are plotted as function of the applied electric-field strength. The lower panels of Fig. 3.2 show the corresponding effective dipole moments μ_{eff} , defined as

$$\mu_{\rm eff} = -\frac{\partial W_{\rm Stark}}{\partial |\vec{E}|},\tag{3.6}$$

where W_{Stark} is the Stark shift of the quantum state in an electric field of magnitude $|\vec{E}|$. The effective dipole moment is a measure for the orientation of the molecule in a specific state, i.e., the expectation value of the dipole moment in a space-fixed axes system. Note that in the Hamiltonian used, $|J, +K, -M_J\rangle$, E levels are degenerate with $|J, -K, +M_J\rangle$, E levels (if $K \neq 0$ and $M_J \neq 0$) and, as these levels have different parity, this degeneracy results in a effective dipole moment that is non-zero at 0 kV/cm. This non-physical result disappears when high-order couplings are incorporated [100]. In Table 3.1 the effective dipole moments of a selection of levels are listed.

3.3 Trajectory simulations

In this section, we use the obtained effective dipole moments to simulate molecular trajectories through a typical beam resonance setup [101]. We consider a molecular beam apparatus that consists of (i) a collimation section; (ii) an electric deflection field for state preparation; (iii) a microwave cavity; (iv) a

Table 3.1 – Effective dipole moments of selected torsion-rotation states of $\rm CH_3OH$ and $\rm CD_3OH.$

	S	State)	Energy (cm^{-1})	Energy (cm^{-1})	$u_{\rm eff} ({\rm cm}^{-1}/[{\rm kV/cm}])$	N_i/N
J	K	M_J	Sym	at $0\mathrm{kV/cm}$	at $60\mathrm{kV/cm}$	at $60\mathrm{kV/cm}$	at $5\mathrm{K}$
C	H_3O	Η					
0	0	0	A^+	127.683	127.475	6.54×10^{-3}	1.03×10^{-1}
2	-1	-2	E	136.400	135.995	8.34×10^{-3}	2.08×10^{-2}
2	-1	-1	E	136.400	136.140	6.09×10^{-3}	2.08×10^{-2}
2	-1	0	E	136.400	136.292	3.65×10^{-3}	2.08×10^{-2}
2	-1	1	E	136.400	136.455	4.14×10^{-4}	2.08×10^{-2}
2	$^{-1}$	2	E	136.400	136.586	-1.10×10^{-3}	2.08×10^{-2}
0	0	0	E	136.805	136.701	3.00×10^{-3}	3.70×10^{-2}
1	0	$^{-1}$	E	138.419	138.425	-3.45×10^{-5}	2.33×10^{-2}
1	0	0	E	138.419	138.575	-4.66×10^{-3}	2.33×10^{-2}
1	0	1	E	138.419	138.427	-1.94×10^{-4}	2.33×10^{-2}
1	1	-1	A^+	139.388	138.932	$8.11 imes 10^{-3}$	1.77×10^{-3}
1	1	0	A^+	139.388	139.392	-1.25×10^{-4}	1.77×10^{-3}
1	1	1	A^+	139.388	138.932	8.11×10^{-3}	1.77×10^{-3}
3	-1	-3	E	141.240	140.908	7.20×10^{-3}	5.16×10^{-3}
3	-1	-2	E	141.240	140.899	$7.65 imes 10^{-3}$	5.16×10^{-3}
3	-1	-1	E	141.240	140.927	7.18×10^{-3}	5.16×10^{-3}
3	-1	0	E	141.240	140.978	6.32×10^{-3}	5.16×10^{-3}
3	-1	1	E	141.240	141.051	5.28×10^{-3}	5.16×10^{-3}
3	-1	2	E	141.240	141.154	$3.87 imes 10^{-3}$	5.16×10^{-3}
3	-1	3	E	141.240	141.354	$1.52 imes 10^{-5}$	5.16×10^{-3}
2	0	-2	E	141.646	141.752	-2.28×10^{-3}	9.19×10^{-3}
2	0	-1	E	141.646	141.845	-4.57×10^{-3}	9.19×10^{-3}
2	0	0	E	141.646	141.884	$-5.53 imes10^{-3}$	9.19×10^{-3}
2	0	1	E	141.646	141.872	-5.21×10^{-3}	9.19×10^{-3}
2	0	2	E	141.646	141.801	-3.68×10^{-3}	9.19×10^{-3}
C	D_3O	Η					
2	0	-2	E	133.587	133.557	1.43×10^{-3}	9.96×10^{-3}
2	0	$^{-1}$	E	133.587	133.362	4.76×10^{-3}	9.96×10^{-3}
2	0	0	E	133.587	132.989	1.05×10^{-2}	9.96×10^{-3}
2	0	1	E	133.587	132.766	1.32×10^{-2}	9.96×10^{-3}
2	0	2	E	133.587	132.961	1.34×10^{-2}	9.96×10^{-3}
1	1	-1	E	133.635	133.730	-2.34×10^{-3}	4.91×10^{-3}
1	1	0	E	133.635	133.713	-3.03×10^{-3}	$4.91{\times}10^{-3}$
1	1	1	E	133.635	133.586	1.02×10^{-3}	$4.91{\times}10^{-3}$
2	2	-2	E	133.675	134.156	-6.13×10^{-3}	$4.86{ imes}10^{-3}$
2	2	-1	E	133.675	134.600	-1.60×10^{-2}	$4.86{\times}10^{-3}$
2	2	0	E	133.675	134.266	-9.64×10^{-3}	$4.86{\times}10^{-3}$
2	2	1	E	133.675	133.837	-3.24×10^{-3}	$4.86{\times}10^{-3}$
2	2	2	E	133.675	133.557	1.05×10^{-3}	4.86×10^{-3}

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second electric deflector for state-selection and (v) a detector. In the calculations, we assume a methanol beam with a mean velocity of 800 m/s. This beam is collimated by two 0.6 mm diameter skimmers that are separated by 500 mm. The deflection fields used for pre and post state selection consist of a cylindrical electrode and a parabolically shaped electrode to which a voltage difference is applied. The electric field inside such a deflector was analyzed by de Nijs and Bethlem in terms of a multipole expansion [102]. It was shown that the most optimal deflection field is created by choosing a field that only contains a dipole and quadrupole term, the strength of which is represented by a_1 and a_3 , respectively. In our calculations, we take $a_1=18$ kV and $a_3=3.6$ kV while all other expansion terms are set to 0. Furthermore, r_0 that characterizes the size of the electrodes is taken as $3 \,\mathrm{mm}$ (i.e., the distance between the electrodes is $2r_0 = 6$ mm). This results in an electric field magnitude of 60 kV/cm on the molecular beam axis. For CH₃OH the deflectors are assumed to be $200 \,\mathrm{mm}$ long, while for $\mathrm{CD}_3\mathrm{OH}$ a length of $150 \,\mathrm{mm}$ is used. Both deflectors are oriented in the same direction, i.e., a molecule that is deflected upwards in the first electric field, will again be deflected upwards in the second electric field, if it has not undergone a microwave transition. The force on a molecule inside one of the deflection fields is found from:

$$\vec{F} = -\mu_{\text{eff}} \nabla |\vec{E}|, \qquad (3.7)$$

where the gradient of the electric field is calculated from an analytical expression derived in de Nijs and Bethlem [102]. The two deflection fields are separated by 200 mm. After the last deflection field, the molecules travel 200 mm further before being ionized in the focus of a femtosecond laser. The total flight path adds up to 1350 mm for CH_3OH and 1250 mm for CD_3OH . The 200 mm free flight between the deflection fields can be used to drive a microwave transition.

In our simulations, the trajectories of typically 5×10^6 molecules are calculated. The position and velocity spread are sampled randomly from a Gaussian distribution. The initial quantum state is sampled from a Boltzmann distribution that assumes a temperature of either 5 or 10 K. As mentioned earlier, Aand E type methanol should be considered as two different molecular species. In A-type methanol, the total spin is $I = \frac{3}{2}$, whereas in E-type methanol $I = \frac{1}{2}$, hence, the nuclear spin degeneracy for A-type methanol is twice that of E-type methanol. However, this is matched by the presence of both K > 0 and K < 0levels of E symmetry [103]. In our calculations, we assume equal numbers of molecules of A and E species for CH₃OH, whereas the A/E ratio in CD₃OH is taken to be 11/16 [104].

Fig. 3.3 shows the distribution of the effective dipole moment of the molecules. The black curve (a) shows the distribution when the deflection fields are off and the laser focus is situated at the molecular beam axis. The red (b) curve shows this distribution when the deflection fields are on and the laser focus is situated 2.2 mm above the molecular beam axis. It is observed that only



Figure 3.3 – Distribution of the effective dipole moments of the methanol molecules in a molecular beam with a temperature of 5 K. The black curve (a) shows the distribution when the deflection fields are off and the laser focus is situated at the molecular beam axis. The red (b) and blue (c) curve show this distribution when the deflection fields are on and the laser focus is situated 2.2 mm above the molecular beam axis. For the red curve, M_J is assumed to be preserved in the field-free region, whereas for the blue curve complete M_J scrambling is assumed. The curves are given an offset for clarity.

molecules are detected in states that have an effective dipole moment of $-0.5 \times 10^{-2} \,\mathrm{cm}^{-1}/(\mathrm{kV/cm})$. With these settings, the resolution of the selector, $\Delta \mu_{\mathrm{eff}}$, is $0.2 \times 10^{-2} \,\mathrm{cm}^{-1}/(\mathrm{kV/cm})$. In these simulations, the M_J state of the molecule is assumed to be preserved – i.e., it is assumed that a homogeneous electric field



Figure 3.4 – Upper panel: simulated spatial distribution of the methanol beam along the y axis when the microwave field is off resonance (black curve) and on resonance with the $3_{-1} \rightarrow 2_0 E$ transition (red curve), assuming a rotational temperature of 5 K. Both curves are normalized to the number of molecules that are detected at y = 0when the deflection fields are turned off. Lower panel: difference between the count rate on and off resonance.

is applied between the deflectors to keep the molecules oriented. However, in our experiment the region where the microwave excitation takes place should be completely shielded from external magnetic or electric fields. In this case the different M_J levels are degenerate and, in the worst case scenario, the M_J distribution after the interaction zone is randomized completely. The results of a simulation that assumes complete de-orientation is shown as the blue curve (c) in Fig. 3.3. Clearly, M_J scrambling greatly reduces the effectiveness of the state selection. Note that due to hyperfine splittings, the degeneracy of the different levels at zero electric field is lifted. The hyperfine structure has not been taken into account in our simulations as it is largely unknown, in fact, resolving the hyperfine splittings is an important motivation for this study.

Fig. 3.4 shows a simulation of what would be observed if the vertical (y) position of the laser focus is scanned, i.e., the spatial distribution of the methanol

beam in the direction of field-gradient. The red curve shows the distribution that is observed when the microwave field drives 50% of the molecules from the $J_K = 3_{-1} E$ to $J_K = 2_0 E$ level, and vice versa. We assume that the microwave field only drives $\Delta M_J = 0$ transitions. The black curve shows the distribution when no micro-wave field is present. In both cases the M_J distribution after the interaction zone is assumed to be randomized completely. Both curves are normalized to the number of molecules that are detected at y = 0 when the deflection fields are turned off. We define the count rate with the microwave field being on or off resonance as $R_{\rm on}$ and $R_{\rm off},$ respectively. The count rate of the undeflected beam is defined as R_0 . In order to observe if a transition has occurred, we look for a difference between R_{off} and R_{on} , i.e., the difference between the black and red curves in Fig. 3.4. This difference is shown in the lower panel of Fig. 3.4. If we choose the vertical position of the laser focus to be 2.3 mm above the molecular beam axis, $R_{\text{off}}/R_0 = 0.062$ and $R_{\text{on}}/R_0 = 0.048$. This results in a normalized averaged count rate, $\bar{R} = \frac{1}{2}(R_{\text{off}} + R_{\text{on}})/R_0 = 0.06$, and a difference in count rate, $\Delta R = (R_{\text{off}} - R_{\text{on}})/R_0 = 0.013$. In Sec. 3.5, it is shown that the accuracy scales with $|\Delta R|/\sqrt{R}$. For the $3_{-1} \rightarrow 2_0 E$ transition, this number is equal to 0.056. Table 3.2 lists ΔR and $|\Delta R|/\sqrt{R}$ for the selected transitions assuming a rotational temperature of 5 and 10 K. The errors in ΔR and $|\Delta R|/\sqrt{R}$ are estimated to be 10 - 20% for CH₃OH and 20 - 40% for CD₃OH. For the selected transitions in CH₃OH $|\Delta R|/\sqrt{R}$ is 0.03 - 0.08 at 5 K and slightly less at 10 K. For the two considered transitions in CD_3OH , these numbers are even less favorable, which is slightly surprising given that the effective dipole moments of the levels involved are rather different; the different M_J states of the $J_K = 2_2 E$ level all have a positive Stark shift, the M_J states of the $J_K = 2_0 E$ level have a negative Stark effect, whereas the M_J states of the $J_K = 1_1 E$ level have virtually no Stark shift. However, the fact that the effective dipoles of the different M_J states within the levels varies considerably, combined with M_{I} scrambling in the interrogation zone, complicates state-selection. Furthermore, the population of the levels involved is rather small.

3.4 Non-resonant ionization of methanol using femtosecond laser pulses

In order to estimate the efficiency of non-resonant multiphoton ionization of methanol by a femtosecond laser, we have performed test measurements in an existing molecular beam machine described elsewhere [72]. A supersonic molecular beam is prepared by expanding a mixture of ~0.5% CH₃OH in argon through a 200 μ m diameter pulsed piezo nozzle [1] operating at a repetition frequency of 10–1000 Hz. The pressure behind the nozzle was kept below 1 Bar in order to prevent cluster formation. The molecular beam passes a 1.5 mm and a 1.0 mm skimmer, before entering the detection region where it is intersected at right angle with a focused (f = 500 mm) femtosecond laser beam. The total

3.5 Non-resonant ionization of methanol using femtosecond laser pulses 47

Table 3.2 – Simulated normalized difference in count rate, $\Delta R = (R_{\text{off}} - R_{\text{on}})/R_0$, and $|\Delta R|/\sqrt{\bar{R}}$ with $\bar{R} = \frac{1}{2}(R_{\text{off}} + R_{\text{on}})/R_0$, for selected transitions in methanol at a temperature of 5 and 10 K. The fourth and seventh columns indicate the *y* position of the focused laser beam used that results in the maximum ratio of $\Delta R/\sqrt{\bar{R}}$. The third column lists the sensitivity of the transition for a variation of the proton-toelectron-mass ratio, K_{μ} .

Transition, J_K	ν (MHz)	K_{μ}		T = 5	K		T = 10	K
			$y(\mathrm{mm})$	ΔR	$ \Delta R /\sqrt{\bar{R}}$	$y(\mathrm{mm})$	ΔR	$ \Delta R /\sqrt{\bar{R}}$
CH_3OH								
$3_{-1} \rightarrow 2_0 E$	12178.587	-33	2.3	0.013	0.056	2.5	0.017	0.063
$0_0 \to 1_1 A^+$	48372.460	-1.00	-3.5	0.028	0.078	-3.7	0.012	0.045
$0_0 \rightarrow 1_0 E$	48376.887	-1.00	2.1	0.008	0.028	-1.7	0.012	0.026
$2_{-1} \to 1_0 E$	60531.477	-7.4	1.6	0.012	0.041	-1.2	-0.016	0.029
$\mathrm{CD}_3\mathrm{OH}$								
$1_1 \rightarrow 2_2 E$	1202.296	330	2.1	-0.003	0.018	-4.2	-0.002	0.017
$2_0 \to 1_1 E$	1424.219	-42	-1.7	0.018	0.033	-3.4	0.004	0.023

flight path from the nozzle to the detection zone adds up to 160 mm. The produced ions are accelerated towards a position sensitive microchannel-plate detector mounted in front of a fast phosphor screen where they are counted. The femtosecond pulses are generated by a commercial amplified regen laser system (Spectra Physics Spitfire) that produces a 1 kHz pulse train and is tunable around 800 nm with an output energy of about $800 \,\mu\text{J}$ and a duration of 120 fs. The fundamental 800 nm light is doubled in a BBO crystal to obtain a 400 nm laser pulse with an energy of about 100 μ J. As the ionization potential of methanol is 10.84 eV [105], at least four photons of 3.10 eV are required to ionize it. Table 3.3 lists the number of detected parent ions per second using an intensity of 20 or $100 \,\mu\text{J}$ per pulse at a 1kHz repetition rate. Although the ion yield can probably be increased by further optimization of the molecular beam parameters and focal properties of the laser beam, it seems unlikely that this changes the obtained results by more than a factor of 2. The fact that the nonresonant multiphoton ionization rate does not follow a I^n dependence, with I the laser intensity and n the number of photons absorbed, can be understood by considering the intensity profile of the laser focus. At a certain laser intensity, $I_{\rm sat}$, the ionization rate at the beam waist reaches unity, and the signal increases due to the increase in volume for which $I > I_{sat}$. For comparison, the ion yield for methyl fluoride CH_3F is also listed in Table 3.3. Note that the ionization potential of methyl fluoride is 12.50 eV [105] and at least five photons are required to ionize it.

Table 3.3 – Number of methanol and methyl fluoride parent ions resulting from a 400 nm 120 fs laser pulse at a repetition rate of 1 kHz. For this measurement, methanol and methyl fluoride molecules were seeded in argon with relative concentrations of 0.5 and 5%, respectively.

molecule	$IE^a (eV)$	R (ion	R (ions/sec)	
		$20\mu J/pulse$	$100\mu\mathrm{J/pulse}$	
CH ₃ OH	10.84	1200	20000	
CH_3F	12.50	3500	25000	

3.5 Estimated accuracy

From the measured ion yield and the results from the simulations, we can now estimate the accuracy that can be obtained in the described beam machine. In general, the accuracy of a frequency measurement depends on the Q factor of the system and the signal to noise ratio, S/N. In an experiment that relies on counting individual ions the accuracy is expressed by the Allan deviation [106]

$$\sigma_y(T) = \frac{1}{Q} \frac{1}{S/N} \sqrt{\frac{T_c}{T}} \quad \text{with } Q = \frac{\nu}{\Delta\nu}, \tag{3.8}$$

where T_c defines the duration of one measurement cycle, T is the total measurement time, ν is the frequency of the measured transition and $\Delta\nu$ the width of the spectral line. In our simulations, we assume that the microwave cavity (or microwave cavities, if we use a Ramsey type setup) has a length of 160 mm while the molecular beam has a velocity of 800 m/s. This implies that the total interrogation time for the measurement is $200 \,\mu s$, corresponding to a spectral width of $\sim 4 \,\mathrm{kHz}$. For the $3_{-1} E$ to $2_0 E$ transition at 12 GHz, this results in a Q-factor of 3×10^6 . The S/N depends on the number of ions that are detected per cycle. If we spend half the duration of a measurement cycle on and off resonance, the number of ions that contribute to the signal is given by $S = T_c |R_{\mathrm{off}} - R_{\mathrm{on}}|/2$. Assuming Poissonian statistics, the noise on the total number of detected ions is given by $N = \sqrt{T_c (R_{\mathrm{off}} + R_{\mathrm{on}})/2}$. Thus the Allan deviation becomes

$$\sigma_y(T) = \frac{1}{Q} \frac{\sqrt{R_{\text{off}} + R_{\text{on}}}}{|R_{\text{off}} - R_{\text{on}}|} \sqrt{\frac{2}{T}} = \frac{1}{Q} \frac{\sqrt{\bar{R}}}{|\Delta R|} \frac{2}{\sqrt{R_0 T}},$$
(3.9)

As expected, the Allan deviation becomes infinite when the count rates on and off resonance are equal, while it scales with $1/\sqrt{R_{\text{off}}}$ when R_{on} is zero (background free). The extra factor of $\sqrt{2}$ arises because we spend half of the time on signal and half of the time off signal. The values for $|\Delta R|/\sqrt{R}$ are given in Table 3.2. R_0 , the count rate when the deflection fields are turned off, can be estimated from the test measurements. Assuming that the density in the molecular beam decreases quadratically with the distance from the nozzle, the expected signal at a distance of 1350 mm behind the nozzle is about a

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factor of 64 smaller than that obtained in the test setup, hence $R_0 = 3.1 \times 10^2$ ions/sec. For the $3_{-1} E$ to $2_0 E$ transition at 12 GHz, the Allan deviation is $7.0 \times 10^{-7} / \sqrt{T}$. In order to achieve a fractional accuracy of 10^{-8} a measurement time of about 80 minutes would be required. Similar results are found for the other transition in CH₃OH listed in Table 3.2. The expected accuracy for CD₃OH is less favorable.

3.6 Conclusion

In this chapter, we estimate the feasibility of performing high resolution microwave spectroscopy on selected transitions in methanol using a Rabi-type molecular beam setup in combination with a femtosecond laser. We have adapted the BELGI programme to calculate the Stark effect for the different isotopologues of methanol. The calculated Stark shifts are reasonably large, typically between -1 and $1 \,\mathrm{cm}^{-1}$ in a field of $100 \,\mathrm{kV/cm}$ for the different rotational states. Thus, the molecules can be easily manipulated using modest sized deflection fields. Due to the small rotational constants of methanol, many states are populated even at the low temperatures that can be obtained in supersonic beams. With the resolution obtained in a typical molecular beam deflection setup, it is not possible to select individual quantum states. Typically, 5 or more states are present within the laser focus. Furthermore, in the field free region used for inducing the microwave transition, the M_{I} quantum number is not preserved, leading to a reduction of the state purity. Note that, M_J -scrambling is both a blessing and a cure, on one hand it reduces the observed difference between $R_{\rm on}$ and $R_{\rm off}$, on the other hand it ensures that all hyperfine levels are addressed without he need to change the position of the laser focus. M_J -scrambling can be enforced by rapidly switching the second deflection field on entrance of the molecules [107]. From simulations, we find that the differences in signal on or off resonance, ΔR , are in the range of 0.01 - 0.02for the selected transitions in CH₃OH, and slightly less for the two considered transitions in CD_3OH . In order to estimate the detection efficiency of methanol molecules using a femtosecond laser, we have performed test measurements in an existing molecular beam machine. Using a laser power of $100 \,\mu\text{J}$ per pulse at 1 kHz repetition rate, 2×10^4 ions per second were detected at a distance of 160 mm behind the nozzle. From these numbers, the described molecular beam deflection setup seems suited to measure microwave transitions in CH₃OH at an accuracy below 10^{-8} , although the required measurement times are rather long. Currently the laser system is being upgraded to provide peak intensities that are 5 times higher than used in this study. This should result in an increase of the ion yield of at least a factor of 25, making this experiment perfectly feasible². Due to the small differences in count rate, however, it might

 $^{^2 \}rm For a more accurate estimate of the expected increase in signal, we should measure the signal as a function of the laser power, such as is done for <math display="inline">\rm CH_3F$ and $\rm NH_3$ in Chapters 4 and 5.

be tedious to find the optimal position of the laser focus. For a laboratory test using CD_3OH an accuracy well below 10^{-10} would be required. This seems unlikely to be achieved in a beam machine as considered here.

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Chapter 4

Femtosecond laser detection of Stark decelerated and trapped methyl fluoride molecules¹

In this chapter, we demonstrate deceleration and trapping of methyl fluoride (CH_3F) molecules in the low field seeking component of the J=1, K=1 state using a combination of a conventional Stark decelerator and a traveling wave decelerator. The methyl fluoride molecules are detected by non-resonant multiphoton ionization using a femtosecond laser. Subsequent mass and velocity selection of the produced ions enable us to eliminate most background signal resulting from thermal gas in our vacuum chamber. This detection method can be applied to virtually any molecule, thereby enhancing the scope of molecules that can be Stark decelerated. Methyl fluoride is so far the heaviest and most complex molecule that has been decelerated to rest. Typically we trap 2×10^4 CH₃F molecules at a peak density of 4.5×10^7 cm⁻³ and a temperature of 40 mK.

4.1 Introduction

Cold molecules offer unique prospects for precision tests of fundamental physics theories, cold chemistry and quantum computation (see for instance [5–8]). One of the techniques that has been successful in producing samples of cold and trapped molecules is Stark deceleration. This technique uses a series of electrodes at high voltage to generate an effective [108–110] or genuine [30–32] traveling potential well that moves along with molecules in a beam. By gradually lowering the velocity of the moving potential, molecules are decelerated and ultimately brought to a standstill. Stark deceleration has been applied to many molecules, including CO(a³II), ND₃, NH₃, OH, OD, NH(a¹ Δ), H₂CO, SO₂, CaF, YbF, C₇H₅N, and SrF [7]. So far (isotopomers of) four of these

 $^{^1 \}mathrm{Based}$ on Congsen Meng, Aernout P.P. van der Poel, Cunfeng Cheng and Hendrick L. Bethlem, Submitted.

molecules, NH₃, OH, CO and NH have been brought to a standstill and subsequently confined in an electrostatic trap. For the success of Stark deceleration it is important that techniques are developed to increase the density and decrease the temperature of the trapped molecules, but also that the techniques become more general and can be applied to larger and heavier molecules. Here, we demonstrate deceleration and trapping of methyl fluoride (CH_3F) molecules, the largest and heaviest molecule that has been trapped using Stark deceleration so far. Methyl fluoride is of interest for a number of reasons: (i) it is highly polarizable [40] and hence serves as a benchmark for studying steric effects in chemical reactions [111], (ii) it is a model system for ortho-para conversion [112], (iii) its structure makes it suitable for use in quantum computation and simulation schemes [113; 114], and (iv) it can be further cooled by electrical-optical cooling [12]. Methyl fluoride, as most polyatomic molecules, has no suitable transitions for detection via laser induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI) schemes that have been used in previous experiments on Stark deceleration. In this work, we detect methyl fluoride molecules by non-resonant multiphoton ionization using a femto second laser. Subsequent mass and velocity selection of the produced ions enables us to eliminate most background signal resulting from thermal gas in our vacuum chamber. This detection scheme can be applied to virtually any molecule, thereby greatly enhancing the scope of molecules that can be Stark decelerated. Furthermore, the well defined detection volume allows an accurate determination of the density of trapped molecules.

4.2 Theory

Methyl fluoride, CH₃F, schematically depicted on the right-hand side of Fig. 4.1, is a prototypical symmetric top molecule. The barrier for inversion in CH_3F is very large, hence the inversion splitting is predicted to be much smaller than the hyperfine splittings [115]. Consequently, hyperfine levels with opposite parity are completely mixed in electric fields as small as $1 \,\mathrm{V/cm}$ [40] resulting in a linear Stark shift. In a supersonic expansion, molecules are adiabatically cooled, and only the lowest rotational levels in the vibrational and electronic ground state are populated. In this cooling process, the symmetry of the nuclear spin wave function is preserved. Therefore, the ratio of ortho and para-methyl fluoride is the same in the beam as it is in the reservoir. Fig. 4.1 shows the distribution over different rotational levels in a molecular beam with a temperature of 5 K as a function of the Stark shift at $90 \, \text{kV/cm}$ (the maximum electric field on the molecular beam axis in our Stark decelerator). For the settings used in our experiment, molecules in states that have a Stark shift larger than $0.8 \,\mathrm{cm}^{-1}$ are decelerated in a phase-stable fashion. This implies that only molecules in the $|J, MK\rangle = |1, -1\rangle$ state, the ground state of para-methyl fluoride that is populated by 11% of the beam, are decelerated.



Figure 4.1 – Distribution of CH_3F molecules over different Stark states in a molecular beam with a rotational temperature of 5 K. The Stark shift at 90 kV/cm is calculated using the molecular constants given in Papousek *et al.* [39]. Levels are (non-uniquely) labelled by J_{MK} . The inset shows the Stark shift of the J=1, |K|=1 state as a function of the applied electric field.

4.3 Experimental

The experiments described here are performed in a vertical molecular beam machine (see Fig. 4.2) that was used earlier to decelerate and trap ammonia molecules [25; 32; 116]. A mixture of 5% methyl fluoride molecules in xenon is released into vacuum using a pulsed valve (General Valve Series 9) that is cooled to $173 \,\mathrm{K}$ resulting in a beam with an average velocity of around $315 \,\mathrm{m/s}$ and a velocity spread of 60 m/s. Methyl fluoride molecules in the $|J, MK\rangle = |1, -1\rangle$ state are decelerated to 90–150 m/s using a conventional Stark decelerator consisting of 101 pairs of electrodes to which voltages of $+10 \,\text{kV}$ and $-10 \,\text{kV}$ are applied. The traveling-wave decelerator, which is mounted 24 mm above the last electrode pair of the first decelerator, consists of a series of 336 rings, each of which is attached to one of eight stainless steel rods to which voltages of up to ± 5 kV are applied. At any moment in time, the voltages applied to successive ring electrodes follow a sinusoidal pattern in z, where z is the position along the beam axis. These voltages create minima of electric field every 6 mm that act as 3D traps for weak-field seeking molecules. By modulating the voltages sinusoidally in time, the traps are moved along the decelerator; a constant modulation frequency results in a trap that moves with a constant



Figure 4.2 – Schematic view of the vertical molecular beam machine. A beam of methyl fluoride molecules is decelerated and trapped using a combination of a Stark decelerator and a traveling-wave decelerator. The inset shows the electric field magnitude inside the traveling-wave decelerator (in steps of $2.5 \,\mathrm{kV/cm}$) with the voltages as indicated.

positive velocity along the molecular beam axis, while a constant acceleration can be achieved by applying a linear chirp to the frequency [30; 31].

The molecules are ionized 20 mm above the traveling-wave decelerator using pulses of light from a commercial laser system consisting of a Titanium-Sapphire oscillator (Spectra-Physics, Tsunami) and a chirped regenerative amplifier (Spectra-Physics, Spitfire Pro). Using a 300 mm lens, the fundamental laser output at 800 nm (2 mJ per pulse, $\tau = 150$ fs) is focused to a (1/e) spot size of $25 \times 15 \,\mu \text{m}^2$, giving a peak intensity of above $10^{14} \,\text{W/cm}^2$. This intensity is sufficient to ionize virtually any molecule in the laser focus. Using an ion lens, the produced ions are focused onto a double Micro Channel Plate (MCP) mounted in front of a fast response (1/e time ~ 10 ns) Phosphor Screen (Photonis P-47 MgO). The light of the phosphor screen is imaged onto a CCD camera and monitored by a Photo Multiplier Tube (PMT). By applying voltages of 2 kV and 1.1 kV to the first and second extraction plate, respectively, ions with the same initial velocity are focused at the same position on the detector (Velocity Map Imaging (VMI) [117]). A mask on the back side of the phosphor screen is used to pass light from the central part of the image onto a photomultiplier only, thereby collecting light originating from molecules with a small transverse velocity [118]. In this way we can discriminate signal from the (decelerated) beam from signal originating from thermal gas in the chamber [119]. Note that in our experimental setup, a very short TOF tube with limited mass and velocity resolution is used and it is believed that with a more elaborated design, background can be completely removed. The signal from the PMT is digitized and ions with an arrival time that corresponds to mass 34 (CH_3F^+) and 15 (CH_3^+) are monitored.

4.4 Stark deceleration and trapping methyl fluoride

Fig. 4.3 shows experimental time-of-flight (TOF) profiles for decelerated methyl-fluoride molecules when different waveforms are applied to the traveling wave decelerator. The position of the electric field minimum with respect to the beginning of the traveling wave decelerator as a function of time is shown in the inset. The horizontal axis is always centered around the expected arrival time of the molecules. The blue, red and green curves correspond to the situation where molecules are decelerated using the conventional Stark decelerator from 282 to 150 m/s, 266 to 120 m/s, and 257 to 90 m/s, respectively. For the measurements shown in the upper graph, the traveling wave decelerator is used to guide the molecules at a constant speed. The observed decrease in signal from 150 to 90 m/s is mainly attributed to the lower intensity at the starting velocity in the Stark decelerator.

The middle panel of Fig. 4.3 shows similar measurements when waveforms are applied to the traveling wave decelerator that decelerate molecules with a rate of 48, 30 and $17 \times 10^3 \text{ m/s}^2$, respectively, bring them to a standstill in the middle of the decelerator, trap them for 50 ms, and subsequently accelerate them to their original velocity with an opposite acceleration. The signal for trapped molecules starting from 90 m/s is virtually the same as that of



Figure 4.3 – Observed time-of-flight (TOF) profiles for methyl fluoride when waveforms are applied to the traveling wave decelerator to guide the molecules at a constant speed (upper panel), bring the decelerator to a standstill in the middle of the decelerator, trap the molecules for 50 ms and accelerate them to their initial velocity (middle panel), and to bring the molecules to a standstill near the end of the traveling wave decelerator, move them back to the beginning of the decelerator and accelerate them to their original velocity (lower panel). The inset shows the position of the electric field minimum with respect to the beginning of the traveling wave decelerator as a function of time for molecules that are decelerated to 90 m/s.

guided molecules at this velocity, which again demonstrates that, at a sufficiently low acceleration, a traveling wave decelerator can decelerate and trap molecules without losses [25]. For 120 m/s the required acceleration is close to

the maximal acceleration that can be exerted on methyl fluoride molecules in our decelerator and the trapped signal is about a factor of 2 smaller than that of the guided molecules. For 150 m/s no trapped signal is observed.

The lower panel of Fig. 4.3 shows measurements when a waveform is applied to bring methyl fluoride molecules to a standstill near the end of the traveling wave decelerator, move them back to the beginning of the decelerator and accelerate them to their original velocity. Effectively, this doubles the decelerator and halves the required acceleration, thus making it possible to trap molecules that are injected with a large velocity. As observed, however, this 'slingshot' sequence introduces some additional losses. For molecules that are injected with 90 m/s, the intensity of molecules that were decelerated with the 'slingshot' waveform is 50% smaller than the guided or trapped molecules. For molecules that are injected with 120 m/s the intensity is 55% smaller than the guided molecules, but 2 times larger than the trapped signal. For molecules that are injected with 150 m/s the intensity is 5 times smaller than the guided molecules².

4.5 Temperature and density of trapped methyl fluoride

We determine the temperature of the trapped molecules by lowering the depth of the trap and monitor which fraction of the molecules remains. If the temperature of the cloud is much lower than the trap depth, the voltages can be lowered without substantial losses. If on the other hand the temperature of the cloud is essentially the same as the trap depth, large losses will occur when the voltages are lowered only slightly. Note that if the voltages are lowered slowly, the molecules are also cooled adiabatically; the velocity spread of the trapped molecules are lowered at the expense of an increased position spread [25; 32; 116]. Fig. 4.4(a) shows the result of such an experiment. The solid lines results from simulations assuming (initial) temperature of 30, 40, and 60 mK. From this we conclude that the temperature of the trapped methyl fluoride molecules is around 40 mK.

In order to translate the number of detected ions into the density and the total number of trapped methyl fluoride molecules, we need to know the detection volume. For a highly non-linear process this turns out to be remarkably simple. As at least 8 photons are required to ionize methyl fluoride, we expect that if the laser light is of low intensity the ion signal scales with the 8th power of the intensity. At higher intensities, however, virtually all molecules within a certain distance from the laser focus will be ionized. If the laser intensity is increased further, the increase in signal only reflects the increase of the detection volume. For a laser beam with a Gaussian intensity profile of peak intensity I_0 and intensity I_0/e at radius R, the ion signal becomes equal to [120]

²Although methyl fluoride molecules in the J = 1, MK = -1 state are strongly oriented (P₁ = 0.5) and modestly aligned (P₂ ~ 0.1) by the electric field used to extract the ions, we did not observe a dependence of the ion signal on the polarisation of the laser beam.



Figure 4.4 – (a) Trapped methyl fluoride signal (background subtracted) as a function of the amplitude of the waveform when the trap is slowly (squares) or abruptly (triangles) reduced. The solid lines are simulations that assume an initial temperature of 30, 40, and 60 mK. (b) Ion signal for methyl fluoride (sum of CH_3F^+ and CH_3^+) and xenon (sum of Xe⁺, Xe²⁺ and Xe³⁺) as a function of the pulse energy. The solid lines show fits to the data assuming a sudden onset model.

$$S = \alpha c l \pi R^2 \ln \left(I_0 / I_{\text{sat}} \right), \tag{4.1}$$

with α the detector efficiency, c the density of molecules, l the length over which ions are collected along the direction of laser propagation and I_{sat} a characteristic intensity that indicates the relative ease of ionization for a certain molecule.

Fig. 4.4(b) shows the ion signal for methyl fluoride and xenon recorded in

the undecelerated molecular beam as a function of the pulse energy. The solid lines show fits to the data using Eq. 5.6, where the peak intensity, I_0 is related to the pulse energy, P via $I_0 \approx P/\pi R^2 \tau$, with τ the pulse duration. By scaling our data to the saturation intensity for xenon, $I_{sat} = 63 \text{ TW/cm}^2$ [121], we find a beam radius $R = 41 \,\mu\text{m}$. This is somewhat larger than the one inferred from measurements of the spatial extent of the beam at the lens, which is attributed to the fact that the spatial profile of our laser beam is not perfectly Gaussian. The saturation intensity of CH₃F is then found to be 95 TW/cm², in reasonable agreement with Tanaka *et al.* [122]. Taking the efficiency of our MCP detector, α , to be 0.6 [123] and l to be 2.8 mm, we finally find the CH₃F density in the beam to be $2.6 \times 10^7 \text{ cm}^{-3}$, and the xenon density to be $5.5 \times 10^8 \text{ cm}^{-3}$. Typically, the signal for trapped CH₃F molecules is ~14 times less than that of the beam. Taking into account that the cloud expands slightly from the decelerator to the detection region, this implies that our trap contains about 2×10^4 molecules at a peak density of $4.5 \times 10^7 \text{ cm}^{-3}$.

4.6 Conclusion

In this chapter, we have decelerated and trapped methyl fluoride (CH_3F) molecules using a combination of a Stark decelerator and a traveling wave decelerator. Because of its favourable Stark shift over mass ratio, methyl fluoride is an ideal candidate for Stark deceleration experiments [7; 124]. Here, we detect methyl fluoride molecules by non-resonant multiphoton ionization using a femtosecond laser. This detection method can be applied to virtually any molecule, thereby enhancing the scope of molecules that can be Stark decelerated. Furthermore, we show that this detection scheme can be used to accurately determine the density of trapped molecules. A disadvantage of nonresonant multiphoton ionization is that it is not state-selective, however, we show that rotational cooling in the supersonic expansion combined with state selection in the Stark decelerator provides us with a pure sample of para-methyl fluoride in the rotational ground state. Furthermore, we show that by using velocity map imaging and mass selection, we can suppress signals from thermal gas in our chamber. With a more elaborate VMI setup, the background can be suppressed further. Methyl fluoride is so far the heaviest and most complex molecule that has been decelerated to rest. By increasing the length of the traveling wave decelerator [34] or starting from a buffer gas beam [21; 33], even heavier molecules could be trapped, opening up the study of cold large polyatomic molecules.

Appendix B

Density of trapped CH₃F

In this appendix, we elaborate on the process of determining the trapped density of CH_3F from our measurements. We start with a description of the basic feature of femtosecond pulses. The intensity profile of a Gaussian laser beam is given by

$$I(r,z,t) = I_0 \left(\frac{w_0}{w(z)}\right)^2 \exp\left(\frac{-2r^2}{w^2(z)}\right) \exp\left(\frac{-t^2}{2\sigma^2}\right)$$
(B.1)

where I_0 the peak intensity, w_0 the beam waist, σ the standard deviation of the temporal profile [125]. At the focus, $w(z) = w_0$, and the intensity becomes

$$I(r,t) = I_0 \exp\left(\frac{-2r^2}{w_0^2}\right) \exp\left(\frac{-t^2}{2\sigma^2}\right)$$
(B.2)

The pulse energy is obtained by integrating over the duration and spatial spread of the pulse

$$P = \int_{r} \int_{t} I(r,t) 2\pi r dr dt$$

= $I_0 \int_0^{\infty} \exp\left(\frac{-2r^2}{w_0^2}\right) 2\pi r dr \int_{-\infty}^{\infty} \exp\left(\frac{-t^2}{2\sigma^2}\right) dt$ (B.3)
= $I_0 \frac{\pi w_0^2}{2} \sqrt{2\pi}\sigma$

The peak intensity is related to the pulse energy as follows

$$I_0 = \frac{2P}{\pi w_0^2} \frac{1}{\sqrt{2\pi\sigma}} \tag{B.4}$$

Taking the definition $I(R) = I_0/e$ used in the paper by Hankin *et al.* [120], we have $R = w_0/\sqrt{2}$. Further considering that $\tau = 2\sqrt{2 \ln 2\sigma}$ with τ the full-width

at half-maximum (FWHM), we obtain

$$I_{0} = \frac{2P}{\pi w_{0}^{2}} \frac{1}{\sqrt{2\pi}\sigma},$$

= $\frac{2P}{\pi (\sqrt{2}R)^{2}} \frac{1}{\sqrt{2\pi}} \frac{2\sqrt{2\ln 2}}{\tau}$
 $\approx \frac{P}{\pi R^{2}\tau}$ (B.5)

The beam radius R is given by

$$R = \left(\frac{2P\sqrt{\ln 2}}{\pi\sqrt{\pi}\tau I_0}\right)^{\frac{1}{2}} \approx \left(\frac{P}{\pi\tau I_0}\right)^{\frac{1}{2}}$$
(B.6)

In order to determine the density determination it is necessary to convert the measured current through the micro-channel plate (MCP) into the number of ions that are being detected. To do this, we have performed measurements at very low signal by either reducing the laser power or the molecular beam density. Fig. B.1 shows a histogram that plots how often a certain ion signal (in units of the measuring program) is observed when the MCP voltage is set at 1800 V. The lower peak is is attributed to electronic noise on our oscilloscope, the peak at 0.7 units corresponds to the detection of a single ion. The inset shows the ions signal (on a logarithmic scale) as a function of the voltage applied to the MCP. The signal is approximately doubled when the MCP voltage is increased by 100 V.

In order to determine the density we have recorded the CH_3F and xenon signal in the undecelerated beam as a function of the pulse energy as shown in Fig. 4.4(b). According to the model by Hankin *et al.* [120], the increase in signal is given by

$$S = \alpha c l \pi R^2 \ln \left(I_0 / I_{\text{sat}} \right) \tag{B.7}$$

with α the detector efficiency, c the density of molecules, l the length over which ions are collected along the direction of laser propagation and I_{sat} a characteristic intensity that indicates the relative ease of ionization for a certain molecule. Experimentally, we determine the saturation power which is related to the saturation intensity via Eq. B.5. A fit to the data presented in Fig. 4.4(b) yields

Slope(Xe) = 4900
$$P_{sat}(Xe) = 0.53 \times 10^{-3} \text{ J/pulse}$$

Slope(CH₃F) = 230 $P_{sat}(CH_3F) = 0.80 \times 10^{-3} \text{ J/pulse}$ (B.8)

with the Slope being equal to $\alpha c l \pi R^2$. Taking the saturation intensity for xenon, $I_{\rm sat}({\rm Xe}) = 63 \times 10^{12} \text{ W/cm}^2$ [121], and measured pulse duration, $\tau = 150 \times 10^{-15}$ s, and the help of Eq. (B.6) we find $R = 41 \,\mu$ m. This is about

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Figure B.1 – A histogram showing how often a certain signal is observed. The inset shows the ion signal (on a logarithmic scale) as a function of the MCP voltage.

twice as big as expected from the measured beam size on the lens, which is attributed to a nonideal Gaussian spatial profile of the laser beam. The saturation intensity for methyl fluoride can be derived as follows

$$I_{\rm sat}({\rm CH}_3{\rm F}) = I_{\rm sat}({\rm Xe}) \frac{P_{\rm sat}({\rm CH}_3{\rm F})}{P_{\rm sat}({\rm Xe})} = 95 \times 10^{12} \,{\rm W/cm}^2$$
 (B.9)

which is consistent with the value found by Tanaka *et al.* [122]. By mechanically scanning the laser beam perpendicular to the molecular beam axis (i.e., our ion optics are cylindrically symmetric, hence we expect the detection volume to be the same in both transverse directions), we find the length of the detection volume to be l = 2.8 mm. Furthermore, taking the efficiency of the MCP, α to be 0.6, we obtain that the density *c* of xenon in the beam to be

$$c(\text{Xe}) = \frac{\text{Slope}(\text{Xe})}{\alpha \pi R^2 l} = 5.5 \times 10^8 \,\text{cm}^{-3}$$
 (B.10)

Similarly, the density of CH₃F in the undecelerated beam is found to be

$$c(CH_3F) = \frac{Slope(CH_3F)}{\alpha\pi R^2 l} = 2.6 \times 10^7 cm^{-3}$$
 (B.11)

From the measurements shown in Fig. 4.4(a), the temperature of the trapped molecules is found to be 40 mK, implying that the trapped molecules typically have a velocity spread with a FWHM of about 7 m/s and a spatial spread with

a FWHM of $1 \times 1 \times 0.6 \text{ mm}^{-3}$. Typically, the signal for trapped CH₃F molecules is ~ 14 times less than that of the beam. Taking into account that the cloud expands from the decelerator to the detection region, we find that our trap contains about 2×10^4 molecules at a peak density of $4.5 \times 10^7 \text{ cm}^{-3}$.
Chapter 5

Comparing detection schemes for Stark decelerated ammonia molecules based on femtosecond and nanosecond lasers¹

In this chapter, decelerated and trapped ammonia molecules (NH₃) are detected using two different schemes; (i) non-resonant multiphoton ionization using intense femtosecond pulses in the near infrared and (ii) resonance-enhanced multiphoton ionization using nanosecond pulses from a tunable UV laser. The observed number of ions per shot for both schemes are similar, however the fs laser detection scheme suffers from an increased background. By recording the signal as a function of the power of the fs laser, we could accurately determine the detection volume and the density of the ammonia molecules in the beam. In order to determine the detection volume of the ns laser detection scheme we have performed measurements where the decelerated ammonia molecules are bunched to a packet with a longitudinal spread well below $\sim 100 \,\mu$ m. From these measurements it is concluded that the detection volume for the ns laser detection scheme.

5.1 Introduction

Owing to the rapid development in laser technology during the last decades, amplified femtosecond laser systems produce focused laser intensities well over 10^{14} W/cm², corresponding to electric fields that are comparable to, or larger than, the atomic Coulomb fields that binds matter together (see e.g. [126–129]). This implies that virtually any atom or molecule will be ionized in the laser focus, thus potentially providing a very general and sensitive detection

¹Based on Congsen Meng, Cunfeng Cheng and Hendrick L. Bethlem, In preparation

method for atoms and molecules. The obvious downside of this method is that it lacks state specificity which has thus far limited its use in molecular beam experiments. We have recently used a fs laser to detect Stark decelerated and trapped methyl fluoride molecules (see Chapter 4). In these experiments, rotational cooling in the supersonic expansion combined with state selection in the Stark decelerator provides a pure sample of para–methyl fluoride in the rotational ground state. The use of velocity map imaging and mass selection suppressed unwanted signals from thermal gas in the vacuum chamber. This proof-of-principle experiment opens up the study of cold and trapped poly-atomic molecules, which lack suitable transitions for detection via more conventional methods such as REMPI and LIF.

A major advantage of fs-laser detection is that the well defined detection volume allows an accurate determination of the density of the molecules in the beam. If only ions are collected from the central portion of the laser focus where the laser beam is effectively parallel, the ion yield varies as a function of the peak intensity in a rather simple way. This allows a direct measurement of ionization efficiencies, and can lead with few assumptions to absolute densities [120]. We have used this technique to determine the number of trapped methyl fluoride molecules (see Chapter 4).

In this chapter, we use a fs laser to detect Stark decelerated ammonia molecules and compare it to the conventional detection method that employs resonant multiphoton ionization by UV laser light from a ns dye-laser [130; 131]. The main motivation of our work was the hope to increase the number of molecules that are being detected to increase the precision of spectroscopic studies on cold molecules [132; 133]. With the maximum intensity of the fs laser that is used in our experiments, the ion yield is comparable to the maximum signal obtained with the ns laser. However, from previous experiments, and from inspection of the profile of the multi-mode ns laser beam, we suspected that the detection volume of the ns scheme was substantially larger than that of the fs scheme. Since in the planned spectroscopic experiments we use very cold samples that are focused to a very small volume, the fs laser might still be advantageous [25; 133]. In order to investigate this we have performed experiments where ammonia molecules are focused to a packet with a longitudinal spread below 100 μ m.

This chapter is organized as follows; In Sec. 5.2 we review models that are developed to describe the MPI process and calculate how the detection volume in MPI depends on the laser intensity. In Sec. 5.3 we describe our molecular beam deceleration setup and the lasers that are used in the experiments. In Sec. 5.4, we use MPI to determine the number of ammonia molecules in the beam and compare the ion signals obtained with the fs and ns laser. In Sec. 5.5, we present experiments where we use the decelerator to bunch the molecules. Conclusions and future prospects are given in Sec. 5.6.

5.2 Nonresonant multiphoton ionization

A variety of processes may occur when atoms or molecules are exposed to intense ultra short laser pulses, such as MPI, tunnel ionization and high harmonic generation [134; 135]. In an MPI process multiple photons are simultaneously absorbed, with their energy exceeding the ionization potential. At very high intensity, when the electric field of the laser light becomes comparable to the Coulomb field that binds the molecule, electrons may tunnel through the distorted potential barrier and escape the molecule. This quantum phenomenon is called tunnel ionization. The two processes mentioned above are associated with the Keldysh parameter $\gamma = \omega \sqrt{2I_P}/F$ [136], where ω is the laser frequency, I_P is the ionization potential, and F is the peak electric-field strength. When $\gamma < 1$ tunneling dominates and when $\gamma > 1$ multiphoton ionization dominates. In our experiments the Keldysh parameter is around 1.3 and we expect that multiphoton ionization is the dominant process [120].

MPI of atoms and molecules from a focused intense beam has been thoroughly investigated both theoretically and experimentally [137; 138]. We review the essential features of MPI following the description given by Hankin *et al.* [120]. Let us consider an ionization process with rate W(I),

$$A \xrightarrow{W(I)} A^+ + e^-. \tag{5.1}$$

In the case of a multiphoton ionization the ionization rate is given by

$$W(I) = \sigma_n I^n, \tag{5.2}$$

where σ_n is the *n*-photon cross section with *n* being the number of photons required to ionize the molecule. It is instructive to look at the variation of the ionization probability as a function of the position in the focal volume. For a Gaussian laser beam the radial intensity profile is give by

$$I_r = I_0 \exp(-r^2/R^2), \tag{5.3}$$

with the peak intensity I_0 and beam waist at the focus R. Fig. 5.1 shows the ionization probability as a function of the transverse and longitudinal position for different *n*-photon ionization processes (note the vastly different scales on the horizontal axes). The intensity and beam waist are chosen to be identical to the ones in our experiment. For the 1-photon transition the cross section is chosen such that 50% of the molecules are ionized at the origin. As the saturation intensity is defined to be the intensity at which 43% of the molecules are ionized [120], this implies that the peak intensity is slightly (1.16 times) larger than the saturation intensity. For the calculation of the *n*-photon processes the cross section is adjusted in such a way that this ratio is the same, i.e., the saturation intensity is always reached at the same distance from the origin. For a 1-photon transition the ionization probability follows the laser intensity directly. When *n* is increased, however, the ionization probability becomes more



Figure 5.1 – The variation of the ionization probability as a function of the position in the focal volume for different *n*-photon ionization processes. x is the transverse direction (upper panel) and z the propagation direction of the laser beam (lower panel).

peaked. For ionization processes that involve many photons, the ionization probability becomes essentially unity when the intensity is above I_{sat} and zero if below I_{sat} . This implies that the detection volume for a multiphoton process is extremely well defined which is crucial for determining the density.

Let us now study the dependence of the ion yield on the laser intensity. We assume that ions are only collected from the central portion of the laser focus along the z direction. Experimentally this is achieved by introducing a slit in the ion optics with a width that is small compared to the Rayleigh length of the focused laser beam. At low intensities the ion yield S is proportional to



Figure 5.2 – Monte Carlo simulation of the ion yields for multiphoton processes that require *n* photons. The ionization rate is given by $W(I) = \sigma_n I^n$.

 I^n . However, as we have just seen, if the laser intensity is increased above the saturation intensity all molecules within a certain range are ionized and the increase in signal when the laser intensity is increased further merely reflects the increased detection volume along the radial direction. The ion yield dS from a volume element, $dV = 2\pi r l dr$ with radius r and length l, is given by [120]

$$dS = \alpha 2\pi rcl \left(1 - e^{-\int_{-\infty}^{+\infty} W(I_r f(t))dt} \right) dr, \tag{5.4}$$

where α is the instrument sensitivity, c is the density of neutral species, l is the length of the cylinder projected on the detector and f(t) denotes the temporal pulse profile. The total ion yield is given by [120]

$$S = \alpha \pi R^2 c l \int_0^{I_0} \left(\frac{1 - e^{-\int_{-\infty}^{+\infty} W(I_r f(t)) dt}}{I_r} \right) dI_r.$$
(5.5)

At high intensities, i.e., $e^{-\int_{-\infty}^{+\infty} W(I_r f(t))dt} \ll 1$, it is found that the ion signal scales with the logarithm of the intensity, that is [120]

$$S = \alpha \pi R^2 c \ln \left(I_0 / I_{sat} \right). \tag{5.6}$$

Fig. 5.2 shows a Monte Carlo simulation of the ion-yield for multiphoton processes that require 1, 2, 3, 5 and 10 photons. As can be observed, for processes that require many photons, the ion yield is well described by a 'sudden onset' model, i.e., if the intensity is below the saturation intensity, no ions are observed, while if the intensity is above the saturation intensity, the ion yield grows as predicted by Eq. 5.6. Experimentally, the density can be determined by measuring the ion yield as a function of the laser power and fitting Eq. 5.6 to it. The intensity scale can be calibrated by recording the ion yield of a well characterized gas such as xenon under the same conditions.

5.3 Experimental setup

The experiments described in this chapter are performed in a vertical molecular beam machine (see Fig. 5.3) that was used earlier to decelerate and trap ammonia [25; 32; 116] and methyl fluoride molecules (see Chapter 4). A mixture of 5% ammonia (NH₃) molecules in xenon is released into vacuum using a pulsed valve (Jordan valve). Ammonia molecules in the $|J, MK\rangle = |1, -1\rangle$ state are decelerated to 90–150 m/s using a conventional Stark decelerator consisting of 101 pairs of electrodes to which voltages of $+10 \,\mathrm{kV}$ and $-10 \,\mathrm{kV}$ are applied. A traveling-wave decelerator, mounted 24 mm above the last electrode pair of the first decelerator, consists of a series of 336 rings, each of which is attached to one of eight stainless steel rods to which voltages of up to $\pm 5 \,\mathrm{kV}$ are applied. At any moment in time, the voltages applied to successive ring electrodes follow a sinusoidal pattern in z, where z is the position along the beam axis. These voltages create the minima of electric field every 6 mm that act as 3D traps for weak-field seeking molecules. By modulating the voltages sinusoidally in time, the traps are moved along the decelerator; a constant modulation frequency results in a trap that moves with a constant positive velocity along the molecular beam axis, while a constant acceleration or deceleration can be achieved by applying a linear chirp to the frequency [30; 31]. For the bunching experiments described in Sec 5.5, we initially apply constant voltages with reduced amplitude to guide the molecules transversely while allowing them to spread along the longitudinal direction. Subsequently, when the molecules are near the end of the decelerator, voltages are applied to deliver a traveling potential that moves along with the molecules over a short distance (indicated by the blue box).

The molecules are ionized 40 mm above the traveling-wave decelerator using light from either a fs or ns laser. The fs laser system consists of a Titanium-Sapphire oscillator (Spectra-Physics, Tsunami) and a chirped regenerative amplifier (Spectra-Physics, Spitfire Pro). The fundamental laser output at 800 nm (2 mJ per pulse, 1 kHz repetition rate, $\tau = 150$ fs) is focused using a lens with a 300 or 500 mm focal length giving a peak intensity of above 10^{14} W/cm². The ns laser system consists of a dye laser (Sirah) pumped by a Nd:YAG laser (Spectra Physics, Quanta-Ray). The output of the dye laser is doubled in a KD*P crystal yielding ~10 mJ in a 5 ns pulse, which is focused using a lens with a focal length of 500 mm. The frequency of the laser is resonant



Figure 5.3 – Schematic view of the vertical molecular beam machine. A beam of ammonia molecules is decelerated and/or trapped using a combination of a Stark decelerator and a traveling-wave decelerator. For the bunching experiments voltages are applied to deliver a travelling potential that moves along with the molecules over a short distance (~15 mm) when the molecules are near the end of the traveling wave decelerator. This distance is indicated with the blue box. The inset shows the electric field magnitude inside the traveling-wave decelerator (in steps of 2.5 kV/cm) with the voltages as indicated.

with the $\tilde{X}(1) \to \tilde{B}(3)$, ${}^{r}S1_{1}^{-}$ transition around 161 nm. From previous studies [37; 130; 131], it was found that (2+1) REMPI via the \tilde{B} -state is the most efficient detection scheme for ammonia using ns lasers. While going to higher vibrational levels of the \tilde{B} -state, NH₃ predissociates more rapidly, but the



Figure 5.4 – Observed time-of-flight (TOF) profiles for ammonia molecules when waveforms are applied to the traveling wave decelerator to guide them at 90 m/s (upper panel) or to bring the molecules to a standstill in the middle of the decelerator, trap the molecules for 50 ms, and then accelerate them back to 90 m/s (lower panel). The black curves show the signal obtained using the fs laser (left axes) while the red curves show the signal obtained using the ns laser (right axes).

dyes used in generating the tunable light become more efficient at the necessary wavelengths. We choose the $\nu_2 = 3$ as a compromise between the two. With the used laser power, a 500 mm lens gives us optimal signal; focusing the laser more tightly results only in broadening the spectral lines to several wavenumbers. The lenses used to focus the fs and ns laser pulses are mounted on motorized translation stages that allow optimizing the position of the laser foci in three directions. The laser–produced ions are mass-selectively detected using a micro channel plate detector (Photonis).

5.4 fs and ns laser detection of trapped ammonia molecules

Fig. 5.4 shows the observed time of flight (TOF) profiles for ammonia (NH_3) molecules when waveforms are applied to the traveling wave decelerator to guide molecules at a constant velocity of $90 \,\mathrm{m/s}$ (upper panel) or to bring the molecules to a standstill in the middle of the decelerator, trap the molecules for 50 ms, and then accelerate them back to their initial velocity and finally detect them (lower panel). The black and red curves correspond to the ion signal obtained using the fs and ns laser, respectively. In both cases the measured currents are converted to the number of detected ions per shot. As observed, the number of detected ions using the fs laser (left axis) is comparable to that obtained with the ns laser (right axis), however, the background for the signal of the fs laser is much larger. This background arises from the thermalized ammonia molecules in the vacuum chamber. As only a small part of these thermalized molecules are in the J=1, K=1 state, the observed background for the resonant detection scheme is much smaller. In previous experiments we have shown that background can be effectively suppressed using velocity map imaging [119]. Note that the signal for the guided NH_3 molecules is a factor of 8 smaller than obtained in earlier experiments with ND_3 , this is attributed to the smaller Stark shift of NH_3 and to the increased distance to the detection zone in these experiments. We observe a significant decrease in signal from guiding to trapping, mostly due to poor phase-space matching for NH_3 between the Stark decelerator and the traveling wave decelerator. We expect to improve this by appropriately adjusting the voltages when the molecules enter the traveling decelerator or once they are trapped.

In order to translate the number of detected ions into the density and the total number of trapped molecules, we use the method outlined in Sec. 5.2. Fig. 5.5 shows the ion signal for ammonia and xenon recorded in the undecelerated molecular beam as a function of the pulse energy of the fs laser. The solid lines show fits to the data using Eq. 5.6, where the peak intensity, I_0 is related to the pulse energy, P via $I_0 = 2\sqrt{(\ln 2/\pi)P/\pi R^2\tau} \approx P/\pi R^2\tau$, with τ the pulse duration. By scaling our data to the saturation intensity for xenon, $I_{sat} = 63 \text{ TW/cm}^2$ [121], we find a beam radius $R = 41 \,\mu\text{m}$. This is somewhat larger than the one inferred from measurements of the spatial extent of the beam at the lens, which is attributed to the fact that the spatial profile of our laser beam is not perfectly Gaussian. The saturation intensity of NH_3 is then found to be 57 TW/cm². Taking the efficiency of our MCP detector, α , to be 0.6 [123] and l to be 2.8 mm, we finally find the NH₃ density in the beam to be 1×10^7 cm⁻³, and the xenon density to be 5×10^8 cm⁻³. Note that the observed ammonia/xenon ratio is 1/50, which is different from the expected 1/20 for the gas mixture. This may be explained by mass focusing in the supersonic molecular beam [55; 56]. Typically, the signal for guided NH₃ molecules is ~ 3 times less than that of the beam. Taking into account that the cloud expands



Figure 5.5 – Ion signal for ammonia molecules (NH_3^+) and xenon (sum of Xe⁺, Xe²⁺ and Xe³⁺) recorded in the undecelerated molecular beam as a function of the pulse energy of the fs laser. The solid lines show fits to the data assuming a sudden onset model.

from the decelerator to the detection region, this implies that the peak density of the guided beam is 2×10^7 cm⁻³.

5.5 Tomography of a laser beam

In the previous section we have seen that with the available intensities the observed number of ions is comparable for the fs and ns detection schemes. Since the detection scheme based on a fs laser suffers from a much larger background it seems advantageous to use the ns laser for experiments with ammonia. However, we expected that the detection volume of the (multiple transverse modes) ns laser is substantially larger than that of the fs laser. Since we plan to perform spectroscopic experiments using adiabatically cooled samples that are focused to a very small volume [25; 133], the fs laser might still be advantageous. In order to investigate this, we have performed experiments where we focus the ammonia molecules to a very small bunch - so small that it becomes comparable to the size of the laser focus. The applied bunching scheme is similar to that used by Crompvoets *et al.* [139] and Heiner *et al.* [140].

In the bunching experiments, we use the conventional Stark decelerator to decelerate molecules to 150 m/s, but now, rather than switching on the traveling potential immediately, we let the molecules expand in the longitudinal direction for most of the length of the traveling wave decelerator before applying



Figure 5.6 – Ion signal for the ns detection scheme as a function of the voltage used for transversely guiding ammonia molecules through the traveling wave decelerator. In this measurement, the molecules travel at a speed of 150 m/s and the bunching pulse is applied over a length of 13 mm.

the traveling potential. With the used settings², the molecules leaving the Stark decelerator have a spatial and velocity spread, of about $\Delta z = 1 \text{ mm}$ and $\Delta v_z = 5 \text{ m/s}$, respectively. In free flight, the molecules will disperse; the fast molecules will be ahead of the average while the slow molecules will be behind the average. In phase space this corresponds to an elongated distribution that is tilted with respect to the axes. The applied voltage pulse will accelerate molecules that are behind, while decelerating molecules that are ahead of the packet. In phase space this corresponds to a rotation of the distribution. When the bunching voltages are applied for exactly the right duration, the packet is refocused at the detection zone. In this process the spatial extent is decreased by a factor of L_1/L_2 , where L_1 and L_2 are the distances before and after the position of the molecules when the bunching voltages are applied. In our case this corresponds to a factor of about 10, hence the spatial distribution at the detection zone is reduced to below 100 μ m.

To avoid loss in the transverse direction, we apply constant voltages to the traveling wave decelerator at a reduced amplitude. These voltages focus the molecules in the transverse direction but do not alter the velocity in the longitudinal direction. Fig. 5.6 shows the ion signal measured with the ns

 $^{^2 {\}rm In}$ the experiments the voltages applied to the conventional Stark decelerator are reduced to $8.8\,{\rm kV}$ to decrease the spatial spread of the molecules.



Figure 5.7 – (a) Observed time-of-flight (TOF) profiles when waveforms are applied to the traveling wave decelerator to longitudinally focus ammonia molecules in the detection zone. The black curves shows the signal obtained using the fs laser (left axis) while the red curves shows the signal obtained using the ns laser (right axis). The traveling wave is applied for 9 mm, 13 mm and 16 mm, for the upper, middle and lower curves, respectively. (b) FWHM widths of the observed TOF profiles as a function of the bunching length that the traveling wave decelerator is applied for molecules traveling with a velocity of 150 m/s.

detection scheme as a function of this voltage. We observe a clear maximum when a voltage of around $1.4 \,\mathrm{kV}$ is applied.

Fig. 5.7(a) shows a number of observed time-of-flight profiles when the traveling wave decelerator is used to longitudinally focus molecules at the detection zone. The black curves shows the signal obtained using the fs laser (left axis) while the red curves shows the signal obtained using the ns laser (right axis). The duration of the pulse that is applied to the traveling wave decelerator is expressed in terms of a length. The upper, middle and lower curves are measured with $L_{bunch} = 9 \,\mathrm{mm}$, 13 mm and 16 mm, respectively. In order to obtain a measure for the width of the observed TOF profiles, we have subtracted a baseline, integrated and normalized the profiles, and obtained the time difference between the times at which 0.25 and 0.75 of the ions are detected. The obtained widths are plotted in Fig. 5.7(b). The black open squares, red open and solid circles correspond to the measurements using the fs laser, and the ns laser with the laser beam in two orientations denoted by 'ns-x' and 'nsy', respectively. The minimum width of the TOF profiles are obtained when the bunching pulse is applied over a length of 13 mm. The minimum FWHM obtained with the fs detection scheme is $0.56 \,\mu s$, corresponding to a spatial spread of $84 \,\mu\text{m}$. From the data presented in Fig. 5.5, we infer that the detection volume has a width of about 80 μ m, which suggests that the observed width mainly reflects the size of the laser beam. Note that it was necessary to reduce acoustic noise in the lab to obtain the smallest widths. As observed in Fig. 5.7(b) the minimum FWHM obtained with the ns laser are slightly, but significantly, larger than measured with the fs laser. From this we conclude that the detection volume for the ns laser has a diameter of 140 and 120 μ m in the x and y direction, respectively. This conclusion is consistent with the fact that the fs and ns signals for guided and trapped molecules shown in Fig. 5.4 are similar, while for bunched molecules the signal obtained with the fs laser is almost 2 times larger.

5.6 Conclusion

In this chapter, we use MPI with a fs laser to detect Stark-decelerated ammonia molecules and compare it to the conventional detection method that employs resonant multiphoton ionization by UV laser light from a ns dye-laser. At the intensities of the fs and ns lasers available to us, the observed number of ions per shot for both schemes are similar, however the fs laser detection scheme suffers from an increased background. By measuring the ion yield as a function of the energy of the fs pulses, we found that molecules within a diameter of about $80 \,\mu\text{m}$, are ionized. From measurements where the ammonia molecules are bunched to a very small bunch we found that the detection volume of the ns laser detection scheme is only 1.5 to 2 times larger. This was slightly surprising to us as from previous measurements we suspected that the radius of the detection volume of the ns would be significantly larger. From this

measurements it is concluded that for the planned spectroscopy experiments on ammonia the fs laser scheme offers no advantages. It should be noted, however, that in the current experiments we use only 1 out of every 100 pulses from the fs laser system, i.e., the experiment runs at 10 Hz while the fs laser runs at 1 kHz. The signal can be increased by amplifying the fs pulses at a 10 Hz rate using an external amplifier similar to that of Witte *et al.* [129] (increasing the intensity of the ns laser with a similar factor is unfeasible). Another option would be to detect the molecules inside the trap (as was done in previous experiments [130; 141]), by lowering the voltages applied to the trap for a short (< 20 μ s) duration of time. Under these conditions, the fs laser scheme potentially gives 100 times more signal than the currently used detection scheme.

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Publications

- Measurement of the density profile of pure and seeded molecular beams by femtosecond ion imaging.
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- Prospects for high-resolution microwave spectroscopy of methanol in a Starkdeflected molecular beam.
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- Femtosecond laser detection of Stark decelerated and trapped methyl fluoride molecules.
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- Comparing detection schemes for Stark decelerated ammonia molecules based on femtosecond and nanosecond lasers.
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 In preparation (2015).

Summary

The structure and properties of molecules make them invaluable test beds for exploring physics beyond the Standard Model. Precision measurements in molecules are used, for instance, to look for a possible time variation of fundamental constants such as the fine-structure constant and the proton-toelectron mass ratio, to test if fundamental laws obey time-inversion symmetry and to measure the energy difference between the two enantiomers of chiral molecules. Ultimately the resolution of any precision measurement is limited by the time a molecule spends in the measuring device. At VU LaserLab, we exploit the interaction of polar molecules with time-varying electric fields to produce beams of slow and cold molecules which can be used to test fundamental physics theories with unprecedented precision. For the success of this technique it is imperative that sensitive detection methods are developed that can also be applied to larger and heavier molecules.

In this thesis, a fs laser is employed for the first time to detect Stark decelerated and trapped molecules by non-resonant multiphoton ionization. The advantages of this detection scheme is twofold: (i) is laser pulses have peak powers on the order of $10^{14} \,\mathrm{W/cm^2}$ at its focus. These high intensities are sufficient to ionize virtually any atom or molecule, thus potentially providing a very general and sensitive detection method for atoms and molecules. In particular, this method can be applied to polyatomic molecules, which in general lack suitable transitions for commonly used detection schemes such as resonance-enhanced multiphoton ionization (REMPI) or laser induced fluorescence (LIF), thus greatly enhancing the scope of molecules that can be Stark decelerated. (ii) as many (infrared) photons are required to ionize these molecules, the interaction volume is inherently restricted to the central part of the laser focus. This implies a small and well defined detection volume which allows for an accurate determination of the absolute densities of molecules. Moreover, this volume can be calibrated by simultaneously measuring the ion yield of a well-studied atom such as xenon.

Compared to resonant detection schemes, the obvious disadvantage of the fs-laser detection scheme is that it does not provide any state-specificity, which complicates the interpretation of the experiment and gives an increased background. However, in typical Stark-deceleration experiments, rotational cooling in the supersonic expansion combined with state selection in the Stark decelerator ensure that only one or a few states are populated in the decelerated beam. Furthermore, in this thesis we demonstrate that background signals from thermal gas in our chamber can be effectively suppressed by using velocity map imaging (VMI) and mass selection, hence this non-resonant detection scheme using a fs laser can be quite useful for the detection of Stark-decelerated molecules.

This thesis consists of four chapters, which describe four different experiments. Chapter 2 adopts the fs ion imaging technique to characterize the density profile of pure and seeded molecular beams generated from the homebuilt cantilever piezovalve. The measured xenon beam density is two orders of magnitude lower than expected which is attributed to the severe skimmer clogging. Chapter 3 explores the feasibility of performing high resolution microwave spectroscopy on methanol in a Stark-deflected molecular beam. The motivation behind this work is that microwave transitions in methanol are demonstrated to be very sensitive to a possible variation of the proton-to-electron mass ratio. Unfortunately, no suitable resonant transitions are available for state-selective detection of methanol. We investigate if non-resonant detection using a fs laser in combination with an electric deflection field will be sufficiently sensitive and specific. In Chapter 4, non-resonant multiphoton ionization with a fs laser is used to detect Stark decelerated and trapped methyl fluoride molecules. Methyl fluoride is so far the heaviest and most complex molecule that has been decelerated to rest. It is demonstrated that the background resulting from thermal gas in the chamber can be effectively suppressed by the VMI technique. In addition, owing to the highly non-linear process, it turned out to be straight forward to accurately determine the density and the total number of trapped methyl fluoride molecules. Finally, in Chapter 5, the fs laser is used to detect Stark decelerated ammonia molecules and compare it to the conventional detection method that employs resonant multiphoton ionization by UV laser light from a ns dye-laser. The motivation for this work was the hope to increase the number of detected molecules, thereby increasing the precision of spectroscopic studies on cold ammonia. It is found that a fs laser shows no apparent advantage for the planned spectroscopy experiments on ammonia, partly because the experiment runs at a 10 Hz repetition rate while the femtosecond laser runs at 1 kHz. If all intensity of the fs laser could be used for the detection, the signal obtained with the fs detection scheme would be 100 times more than that of the ns detection scheme.

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