Manipulation and Control of Molecular Beams

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1. INTRODUCTION

“Born in leaks, the original sin of vacuum technology, molecular beams are collimated wisps of molecules traversing the chambered void that is their theater [...]. On stage for only milliseconds between their entrances and exits, they have captivated an ever growing audience by the variety and range of their repertoire.” This is how John B. Fenn affectionately phrased it about 20 years ago, when he reflected on the long and rich history of molecular beams in his foreword to one of the classic books on this subject.1 He could not have foreseen the spectacular leap forward that the level of control over molecular beams would take, in particular, methods that have been developed since then to slow down and store molecular beams, thereby stretching the duration of their performance on stage by orders of magnitude, that have made whole new classes of experiments possible.

The motion of neutral molecules in a beam can be manipulated and controlled with inhomogeneous electric and magnetic fields. Static fields can be used to deflect or focus molecules, whereas time-varying fields can be used to decelerate or accelerate beams of molecules to any desired velocity. In this Review, we reflect on the deflection, focusing, and deceleration of molecular beams, and we discuss how this has been, and can be, applied in a variety of experiments. Other reviews, covering part of the material presented here, have appeared during the past decade.2–7 The importance and impact of these methods in the wider field of Cold Molecules has been documented in two recently published books8,9 as well as in the several topical issues of scientific journals on cold and ultracold molecules.10–14 In this Review, we start with an historical overview, in which the important role of molecular beam deflection and focusing experiments in the development and testing of quantum mechanics is emphasized. After this, the interaction of molecules with electric and magnetic fields is treated. The underlying design principles for deflection and focusing elements are then discussed, and their use in state-of-the-art experiments is highlighted. In the central part of this Review, we outline how the forward velocity of a molecular beam can be controlled, and we describe in detail how a three-dimensional packet of molecules can be kept together, both in position space and in velocity space, while traversing an array of electric or magnetic fields, as in a Stark decelerator or in a Zeeman decelerator, respectively. We then describe the operation principle of traps and storage rings for neutral molecules and discuss how all of the elements in the beamline have to be combined to efficiently inject molecules from the source into stationary traps, storage rings, and synchrotrons. An overview of the various applications that this new molecular beam technology has led to, together with the respective future directions, concludes this Review. The applications range from novel crossed-beam scattering studies at low collision energies and high-resolution spectroscopy to the measurement of the radiative lifetime of molecules trapped above the surface of a chip. Last but not least, the samples of cold molecules that are produced via this molecular beam technology provide good starting conditions for the application and testing of various cooling schemes.

In this Review, we restrict ourselves to the manipulation of molecular beams with electric and magnetic fields. We will not go into detail concerning the molecular beam production itself; here, the sources merely provide us with a fast moving beam of internally cold molecules. In many of the experiments that are discussed, seeded pulsed supersonic expansions are employed. True cooling, in the sense of phase-space compression and accumulation of population in the desired low lying internal energy levels of the molecules, takes place via collisions in the expansion region of the beam. The conservative forces exerted further downstream by the electric and magnetic fields enable us to manipulate and control the shape and the position of the distribution in the six-dimensional phase-space, but no further compression is possible with these forces alone. We do not discuss deflection, focusing, deceleration, and trapping with electro-magnetic radiation and alignment of molecules with laser fields, nor “mechanical” methods to influence the velocity of molecules in a beam, for example, via elastic scattering from rapidly spinning or retracting surfaces or via collisions with other molecules, nor methods that rely on imparting velocity changes on molecular fragments by photodissociation or reactions. For all of these topics, the reader is referred to the extensive specialized literature.2–7
aimed at proving space quantization via measuring the deflection of a beam of atoms with a magnetic moment when moving through an inhomogeneous magnetic field.\(^\text{17}\) No further account on the early electric deflection experiment in Berlin is to be found in the literature, while Stern and Gerlach performed their famous experiment within one year,\(^\text{18}\) in February of 1922, as indicated on the memorial plaque in Frankfurt, shown in Figure 1. Electric deflection of a beam of polar molecules was first demonstrated by Erwin Wrede, a graduate student of Stern, several years later in Hamburg.\(^\text{19}\)

All of the original experimental geometries were devised to create strong magnetic or electric field gradients to efficiently deflect particles from the beam axis. In 1939, Isidor Rabi introduced the molecular beam magnetic resonance method by using two magnets in succession to produce inhomogeneous magnetic fields of oppositely directed gradients. In this setup, the deflection of particles caused by the first magnet is compensated by the second magnet, such that the particles are directed on a sigmoid path to the detector. A transition to “other states of space quantization” induced between the magnet sections can be detected via the resulting reduction of the detected signal. This provided a new method to accurately measure nuclear or other magnetic moments.\(^\text{20}\) Later, both magnetic\(^\text{21,22}\) and electric\(^\text{23}\) field geometries were designed to focus particles in selected quantum states onto the detector. An electrostatic quadrupole focuser, that is, an arrangement of four cylindrical electrodes with alternating positive and negative voltages, was used to couple a beam of ammonia molecules into a microwave cavity. Such an electrostatic quadrupole lens focuses ammonia molecules that are in the so-called low-field seeking, upper level of the inversion doublet, while it simultaneously defocuses those that are in the lower, high-field seeking, level. The inverted population distribution of the ammonia molecules that is thus produced in the microwave cavity led to the invention of the maser by Gordon, Zeiger, and Townes in 1954–1955.\(^\text{24,25}\) In Figure 2, Gordon and Townes are shown next to their experimental apparatus, with a schematic drawing of the experimental setup, taken from their original publication, underneath. Apart from the spectacular observation of the amplification of the microwaves by stimulated emission, these focusing elements more generally enabled the recording, with high resolution and good sensitivity, of microwave spectra in a molecular beam. By using several multipole focusers in succession, with interaction regions with electro-magnetic radiation in between, versatile setups to unravel the quantum structure of atoms and molecules were developed. In scattering experiments, multipole focusers were exploited to study steric effects, that is, to study how the orientation of an attacking molecule affects its reactivity.\(^\text{26}\) Variants of the molecular beam resonance methods as well as scattering machines that employed state-selectors were implemented in many laboratories and have yielded a wealth of detailed information on stable molecules, radicals, and molecular complexes, thereby contributing enormously to our present understanding of intra- and intermolecular forces.

The manipulation of beams of atoms and molecules with electric and magnetic fields is thus about as old as the field of atomic and molecular beams itself, and it actually has been crucial for the success of the latter field. In his autobiography, Norman Ramsey, who himself later invented the separated...
oscillatory fields method and wrote a very influential book on molecular beam methods,27 recalls that Rabi was rather discouraged about the future of molecular beam research when he arrived in Rabi’s lab in 1937, and that this discouragement only vanished when Rabi invented the molecular beam magnetic resonance method.28 The manipulation of beams of molecules with external fields that has been used extensively and with great success in the past exclusively involved the transverse motion of the molecules. It was only in 1999 that it was experimentally demonstrated that appropriately designed arrays of electric fields in a so-called “Stark decelerator” can also be used to influence and control the longitudinal (forward) velocity of the molecules in a beam, for example, to decelerate a beam of neutral polar molecules.29 Since then, the ability to produce focused packets of state-selected accelerated or decelerated molecules has made a whole variety of new experiments possible.

In the first experimental demonstration of Stark deceleration, a beam of metastable CO(a^1Π,J = 1) molecules was slowed from 225 to 98 m/s.29 Experiments of this kind had been considered and tried before. Electric field deceleration of neutral molecules was first attempted by John King at MIT in 1958. He intended to produce a slow ammonia beam to obtain a maser with an ultranarrow line width. However, in the physical chemistry community, the experimental efforts of Lennard Wharton, to demonstrate electric field acceleration of a molecular beam, are much better known. In the 1960s, at the University of Chicago, he constructed an 11 m long molecular beam machine for the acceleration of LiF molecules in high-field seeking states from 0.2 to 2.0 eV, aiming to use these high energy beams for reactive scattering studies.30 An excellent paper, in which the focusing of beams of polar molecules in high-field seeking states was theoretically analyzed, resulted from this work.31 Both of these experiments were unsuccessful, however, and were not continued after the Ph.D. students completed their theses.32,33 Whereas interest in slow molecules as a maser medium declined due to the invention of the laser, the molecular beam accelerator was made obsolete by the seminal demonstration of John Fenn and co-workers of gas dynamic acceleration of heavy species in seeded supersonic He and H2 beams.34

One of the main motivations to develop the Stark deceleration technique was to be able to slow molecules to a standstill and to confine them in a trap. “If one extends the rules of two-dimensional focusing to three dimensions, one possesses all ingredients for particle trapping.” This is literally how Wolfgang Paul stated it in his Nobel lecture,35 and as far as the underlying physical principles of particle traps are concerned, it is indeed as simple as that. To experimentally realize the trapping of neutral particles, however, the main challenge is to produce sufficiently slow particles that they can be trapped in the relatively shallow traps that can be made. When the particles are confined along a line, rather than around a point, the requirements on the kinetic energy of the particles are more relaxed, and storage of neutrons in a 1 m diameter magnetic hexapole torus constituted the first example of such a trapping experiment.36 Trapping of atoms in a 3D trap only became feasible when Na atoms were laser cooled to sufficiently low temperatures that they could be confined in a quadrupole magnetic trap.57 The Stark decelerator enabled the first demonstration of 3D trapping of neutral ammonia molecules in a quadrupole electrostatic trap38 even before it was used in the demonstration of an electrostatic storage ring for neutral molecules.39

It is clear, that there are large similarities between the manipulation of polar molecules and the manipulation of charged particles, and concepts used in the field of charged particle physics can be applied to neutral polar molecules and vice versa. Both Hartmut Kallmann and Wolfgang Paul first worked on the deflection and focusing of beams of neutral molecules before they turned their attention to controlling the motion of charged particles; it is interesting to realize that multipole fields were actually first used in molecular beam physics. However, there are also important differences. The force on a charged particle is given by the product of the charge with the gradient of the electric potential. The force on a polar molecule can be expressed analogously as the product of an effective dipole moment with the gradient of the electric field strength. Contrary to the charge, however, the effective dipole moment depends on the quantum state of the molecule and is a function of the electric field strength. Moreover, as the electric potential can not have a minimum nor a maximum in free space, trapping of neither positive nor negative ions is possible with static electric potentials. In contrast, the electric field strength can have a minimum in free space (note that the Earnshaw theorem does not allow for a maximum), and molecules in low-field seeking quantum states, that is, in quantum states with a negative effective dipole moment, can thus be trapped with static electric fields.40,41

3. STARK AND ZEEMAN EFFECT

3.1. Introduction

For the manipulation of molecules with electric or magnetic fields, a detailed understanding of the influence of the external field on the energy level structure of the molecules is required. Space quantization dictates that in an electric or magnetic field, the total angular momentum vector \( \vec{J} \) of the molecule can only have certain discrete orientations in space. The magnitude of the vector \( \vec{J} \) is given by \( h((J + 1))^{1/2} \), and the component of \( \vec{J} \) in the field direction is given by \( hM \), with \( M = J(−1,...,−J) \); a precession of the vector \( \vec{J} \) takes place around the direction of the external field at an angle whose cosine is given by \( M/(J(−1,...,−J))^{1/2} \). The states with different quantum numbers \( M \) have different energies, and it is these \( M \)-dependent energies that need to be calculated.

The change in energy of a certain quantum level due to the presence of an electric field \( \vec{E} \) or a magnetic field \( \vec{B} \) is given by \( -\mu^E \vec{E} \) or \( -\mu^B \vec{B} \), respectively, where \( E(B) \) is the magnitude of the electric (magnetic) field, and \( \mu^E(\mu^B) \) is the mean value of the component of the electric (magnetic) dipole moment along the direction of the field. The basic features of the dependence of the Stark and Zeeman effect on the quantum numbers of the molecule can be understood by deducing the mean value for \( \mu^E \) (\( \mu^B \)) from a simple, yet instructive, vector diagram.

Let us first consider a heteronuclear, diatomic molecule with a permanent electric dipole moment with magnitude \( \mu^E \). Note that lower case letters refer to vectors that are defined with respect to the molecular frame, while upper case letters refer to vectors that are defined with respect to the laboratory frame. This dipole moment is necessarily directed along the internuclear axis and is thus perpendicular to the angular momentum of end-over-end rotation, \( \vec{N} \). In a \( ^1\Sigma \) state, the vector \( \vec{J} \) is identical to \( \vec{N} \) and the mean value of the dipole moment along \( \vec{J} \) is zero, and thus \( \mu^E \) is zero as well. In first
order, therefore, a polar diatomic molecule in a \( ^1\Sigma \)-state does not experience a Stark shift of the rotational levels. If the molecule is in a \( \Pi \) or \( \Delta \) state, on the other hand, a nonzero component of the dipole moment along \( J \) arises, the magnitude of which depends on the exact coupling of the rotational and electronic motion. In the Hund’s case (a) coupling scheme depicted in Figure 3, for instance, the electron orbital and electron spin angular momenta are each separately strongly coupled to the internuclear axis. Therefore, the projection of the orbital angular momentum of the electrons (\( \vec{L} \)) on the internuclear axis, denoted as \( \Lambda \), couples with the projection of the total electron spin (\( \vec{S} \)) on the internuclear axis, denoted as \( \Sigma \), to the further good quantum number \( \Omega = \Lambda + \Sigma \). The corresponding vector \( \vec{\Omega} \) combines with \( \vec{N} \) to the total angular momentum \( \vec{J} = \vec{N} + \vec{\Omega} \). Nutation of the internuclear axis around the total angular momentum vector \( \vec{J} \) leads to a mean value of the dipole moment along \( \vec{J} \) given by \( \mu^2 \Omega / [J(J + 1)]^{1/2} \) and thus to a value of \( \mu^R \) given by \( \mu^R \Omega / [J(J + 1)] \). In this case, therefore, a Stark shift of the energy levels already occurs in first order.

The dominant contribution to the magnitude of the magnetic dipole moment \( \mu^M \) of a diatomic molecule originates from the orbital and spin angular momenta of the electrons. When the latter are different from zero, which is the case for all molecules that are used in the magnetic manipulation experiments described in this Review, the much smaller contributions due to the rotational motion of the molecule and the spins of the nuclei can be neglected. The magnetic moment due to the orbital angular momentum of the electrons is equal to the Bohr magneton, \( \mu_B \), times the magnitude of the angular momentum; the contribution due to the electron spin is twice as large. The value of \( \mu^S \) depends again on the way in which the rotational and electronic motion couple in the molecule. Following the same argumentation as given above for the electric field case, it is seen that in the Hund’s case (a) coupling scheme, in which \( \mu^* \) is along the internuclear axis and has a magnitude of \( (\Lambda + 2\Sigma)\mu_B \), the value of \( \mu^S \) is given by \( \mu^2 \Omega / [J(J + 1)] \).

This pictorial presentation correctly yields the first-order expressions for the Stark- and Zeeman-shift of a single, isolated rotational level. Interactions between different rotational or (hyper-) fine structure levels, or, in the case of Rydberg states, interactions between different electronic states, perturb this simple picture. To calculate the shifting and splitting of the energy levels in the presence of electric or magnetic fields in more detail, one normally starts with the levels in the absence of an external field. These are most times experimentally known with high precision, and a Hamiltonian accurately reproducing all these levels is available. When the interaction with the external field is added as a perturbation to the field-free Hamiltonian, one particularly needs to know the matrix elements between the various quantum levels that can be coupled by the external field. These matrix elements can be found in various advanced textbooks as well as in specialized journals, although it is unfortunately true that these often contain typographical errors and that the specific conventions that have been used are not always clear. It is for this reason that the most important matrix elements, for example, those that are needed in the calculation of the Stark- and Zeeman-effect for the example molecules listed at the end of this section, together with some fundamental aspects of their derivation are given in the following.

3.2. General Formalism

In general, the interactions in a molecule are described by the molecular Hamiltonian \( H \) and the molecular energy levels can be derived by diagonalizing the Hamiltonian matrix using a complete set of basis wave functions. The interaction of a molecule with an applied electric or magnetic field is represented by adding the appropriate Stark Hamiltonian \( H_{\text{Stark}} \) or Zeeman Hamiltonian \( H_{\text{Zeeman}} \) to \( H \). Diagonalization of this new matrix yields the energy levels of the molecule in an electric or magnetic field. In this section, we will restrict ourselves to those cases where the interaction between the molecule and the applied field is small as compared to the electronic and vibrational energy level splittings of the molecule. In this case, we only have to consider the rotational part \( H_B \) of the Hamiltonian, and the rotational wave functions of the molecule.

The rigid rotor functions \( |JKM\rangle \) (see eq 2) form a complete basis set of rotational wave functions.\(^{42}\) We can now distinguish two different situations: If we know the rotational energy levels and the corresponding rotational wave functions (i.e., the expansion coefficients of the wave function on the basis set \( |JKM\rangle \)) of the molecule, we can set up the matrix using these rotational wave functions as a basis set. The rotational energies of the molecule will then appear on the diagonal of the matrix, and only \( H_{\text{Stark}} \) will give off-diagonal elements. This approach is often convenient for diatomic molecules like OH. If, however, the rotational wave functions are not known, we have to set up the matrix using the basis set \( |JKM\rangle \) that are not the eigenfunctions of the molecule; that is, the matrix will contain off-diagonal elements for both the rotational part and the part that describes the interaction with the electric or magnetic field. This approach is necessary for asymmetric tops like \( \text{H}_2\text{CO} \). In either case, we need to calculate matrix elements of the type \( \langle JKM|H_{\text{Stark/Zeeman}}|JKM\rangle \).

These matrix elements can be found in the literature and in several textbooks (see, for instance, Gordy and Cook\(^{43}\)). Recently, based on the derivation given in ref 43, the methods to calculate the Stark effect in (a)symmetric tops were summarized by Hain et al.\(^{44}\) The methods to calculate the Zeeman effect for diatomic molecules are described by Takazawa and Abe\(^{45}\) and Friedrich et al.\(^{46}\) Here, we present a compact form of the matrix elements for \( H_{\text{Stark}} \) and \( H_{\text{Zeeman}} \) which are very useful for the calculation of the Stark and

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**Figure 3.** Vector diagram of a Hund’s case (a) (left) and a Hund’s case (b) (right) molecule in an external field.
Zeeman effect in a wide variety of molecules. We will first describe the procedure to calculate the Stark effect for polar molecules; a similar analysis for the Zeeman effect is then given in section 3.4. In these sections, we will only treat the rotational energy levels, excluding hyperfine structure.

3.3. Stark Effect

3.3.1. Matrix Elements of $H_{\text{Stark}}$. The dipole moment of a molecule in a given rovibrational state is the vibronic expectation value of the first moment of the charge. The interaction energy of a dipole $\vec{p}$ in an electric field $\vec{E}$ is expressed as $H_{\text{Stark}} = -\vec{p} \cdot \vec{E}$. The dipole moment vector $\vec{p}$ has a well-defined orientation in the (rotating) body-fixed frame of the molecule, while the electric field vector $\vec{E}$ is usually defined in the (static) laboratory frame of reference. We define the space-fixed frame of coordinates as ($X,Y,Z$), while the molecular coordinate frame is given by ($\hat{x},\hat{y},\hat{z}$). We choose the quantization axis in the space-fixed frame to be directed along the electric field vector.

The calculation of the Stark effect requires the evaluation of matrix elements of the type:

$$\langle J'K'M'|H_{\text{Stark}}|JKM \rangle$$

where $|JKM\rangle$ are the symmetric top wave functions:

$$|JKM\rangle = \frac{2J+1}{8\pi^2} D_{JKM}^{\Phi\theta\chi}(\phi, \theta, \chi)$$

where $K$ and $M$ are the projections of $J$ on the molecule-fixed $\hat{z}$-axis and the space-fixed $\hat{Z}$-axis, respectively, and run from $-J$ to $J$. $\phi$, $\theta$, and $\chi$ denote the Euler angles, which define the orientation of the $(\hat{x},\hat{y})$ and $\hat{z}$ axes with respect to the $X$, $Y$, and $Z$ axes. Here, we use the commonly accepted convention of the Euler angles given, for example, in Zare.\textsuperscript{42}

After integration over the Euler angles, this yields:

$$\langle J'K'M'|H_{\text{Stark}}|JKM \rangle = -E\sqrt{(2J+1)(2J'+1)} \sum_q (-1)^{K-K'} \mu_q^e$$

$$\times \left( \begin{array}{cc} J & 1 \\ M & 0 \\ -M' & K \end{array} \right) \left( \begin{array}{cc} J & 1 \\ 1 & J' \end{array} \right)$$

where $\mu_q^e$ are the spherical components of the dipole moment vector $\vec{p}$ in the molecular frame. They relate to the Cartesian components in the molecular frame as follows:

$$\mu_{-1}^e = \frac{1}{\sqrt{2}}(\mu_x - i\mu_y)$$

$$\mu_0^e = \mu_z$$

$$\mu_1^e = -\frac{1}{\sqrt{2}}(\mu_x + i\mu_y)$$

The selection rules follow from the 3-$J$ symbols:

$$J = J'$$

or

$$J = J' \pm 1, \quad M = M', \quad K' = K = 0, \pm 1$$

Equation 3 represents the matrix elements for $H_{\text{Stark}}$ in a compact form and is equivalent (when evaluating the 3-$J$ symbols) to Table 4 in ref 44 and Table 2.1 in ref 43. Unfortunately, the matrix elements in ref 44 contain a few errors.

3.3.2. Matrix Elements in a Basis of Symmetrized Wave Functions. Because the rotational Hamiltonian is invariant under inversion through the origin of the spatial coordinates (space-fixed inversion), it is convenient to set up the rotational matrix using wave functions of well-defined parity. For nonlinear molecules, symmetrized rotational wave functions $|JKM\rangle$ and $|JKM-\rangle$ are defined as

$$|JKM\rangle = \frac{1}{\sqrt{2}}[|JKM\rangle + (-1)^{J-K}|JM\rangle]$$

$$|JKM-\rangle = \frac{1}{\sqrt{2}}[|JKM\rangle - (-1)^{J-K}|JM\rangle]$$

where $K$ runs now from 1 to $J$, and $M$ runs from $-J$ to $J$. For $K = 0$, the symmetric top wave function has already a defined parity of $(-1)^J$. The parity of the wave function $|JKM\rangle$ relates to the parity of the total wave function of the molecule, and in nonlinear molecules this relation is fixed within a given rovibrational state.

From eq 3, it follows that the nonvanishing Stark matrix elements in this parity basis are given by:

$$\langle J'K'M'|H_{\text{Stark}}|JKM\rangle = \langle J'K'M'|H_{\text{Stark}}|JKM\rangle$$

Within a rovibrational state, the Stark effect therefore connects rotational wave functions with opposite parity, and consequently only molecular states with opposite parity.

3.3.3. Diatomic Molecules and (A)symmetric Tops. In diatomic molecules, the dipole moment vector lies along the molecular axis. In addition, the quantum number $K$ is replaced by $\Omega$, which is the projection of the total electron angular momentum on the molecular axis. As a consequence, the nonvanishing matrix elements of $H_{\text{Stark}}$ in the parity basis defined by section 3.3.2 read:

$$\langle J'\Omega'M'|H_{\text{Stark}}|J\Omega M\rangle = \delta_{\Omega\Omega'} \delta_{J'J} \langle J'\Omega'M'|H_{\text{Stark}}|J\Omega M\rangle$$

and the additional selection rule $\Omega = \Omega'$ follows. Depending on the electronic state of the molecule, and the occurrence of fine-structure effects like $\Lambda$-doubling, the Stark effect is most easily calculated by setting up the rotational matrix using either the basis $|JKM\rangle$ or the parity basis defined above.

For (a)symmetric tops, the rotational Hamiltonian in the absence of an applied field is given by:\textsuperscript{42}

$$H_\text{R} = A J_x^2 + B J_y^2 + C J_z^2$$

where $J_x$, $J_y$, and $J_z$ are the projections of $J$ on the three principal axes of inertia $(\hat{a},\hat{b},\hat{c})$ of the molecule, and $A$, $B$, and $C$ are the rotational constants that are inversely proportional to the principal moments of inertia (with the convention that $A \geq B \geq C$). In the case of a symmetric top, two of the moments of inertia are equal, while in a spherical top all three are equal. The Hamiltonian $H_\text{R}$ is defined with respect to the principal axes of inertia of the molecule, whereas the functions $|JKM\rangle$ are defined in the molecule-fixed frame $(\hat{x},\hat{y},\hat{z})$. A proper choice of identification of the natural coordinate system of the molecule $(\hat{a},\hat{b},\hat{c})$ to the molecule-fixed reference frame $(\hat{x},\hat{y},\hat{z})$ is very useful when calculating the rotational energies because it can simplify the energy matrix considerably. The chosen identifications are hereafter labeled according to Zare’s representations,\textsuperscript{42} and the matrix elements of $H_\text{R}$ in all of these representations can be found in refs 42 and 44. When the Stark effect is incorporated in the calculation, the situation is different. In many cases, the dipole moment of a (a)symmetric top is directed along one of the principal axes of inertia. It is
very convenient to choose a representation that identifies the \( \hat{z} \)-axis with the direction of the dipole moment. It then follows that \( q = 0 \) in eq 3, simplifying the matrix elements of \( H_{\text{stark}} \). A further simplification of the matrix can be obtained by exploiting group theory. 43

The procedure to calculate the Stark shifts is illustrated in detail below for cases that are representative for a wide variety of molecules. The diatomic molecules HCl, OH, and YbF, the symmetric top ND\(_3\), and the asymmetric tops H\(_2\)CO and HDO are discussed. The Stark energies of the rotational states that are most relevant for Stark deceleration experiments are calculated as a function of the applied field strength. From this collection of molecules, the species OH and ND\(_3\) have been used most extensively in Stark deceleration and trapping experiments.

3.3.4. HCl, OH, and YbF. The molecule HCl has an electric dipole moment of 1.1 D,\(^47\) and one might expect this molecule to be an interesting candidate for Stark deceleration and trapping experiments. The electronic ground state of the molecule, however, is of \( \Sigma' \) character. Consequently, there are no orbital and spin angular momenta, and the rigid rotor functions \( |J\Omega = 0,M\rangle \) are the eigenfunctions of the rotational Hamiltonian.\(^48\) The only nonzero Stark matrix elements occur between rotational states with \( \Delta J \neq 0 \) that have a large energy spacing, rendering small Stark energies. This is illustrated in Figure 4a in which the Stark shifts for the \( J = 1 \) level are shown. The largest interaction occurs with the \( J = 0 \) rotational ground state that is nearest in energy. Because this level only has one component in an electric field characterized by \( M = 0 \), the \( M = 0 \) component of the \( J = 1 \) level gains energy in an electric field.

The calculation is more difficult for open-shell radical species like the OH radical. The OH radical has a dipole moment of 1.67 D.\(^49,50\) The electronic ground state is of \( \Sigma^+ \) character, and two spin–orbit manifolds exist with \( |\Omega| = 3/2 \) and \( |\Omega| = 1/2 \), respectively. In addition, each rotational level is split into two \( \Lambda \)-doublet components of opposite parity. Hence, the Stark matrix is most conveniently set up using the symmetrized wave functions of section 3.3.2, such that the \( \Lambda \)-doublet splitting energies can be incorporated in the diagonal matrix elements.

As can be seen from eq 11, the Stark effect is quadratic for low electric field strengths. For higher electric fields, the wave functions of the two \( \Lambda \)-doublet components are completely mixed, and the Stark shift becomes linear.

The molecule YbF has an electric dipole moment of 3.91 D.\(^52\) There is a current interest in the Stark deceleration of YbF molecules because of its suitability to measure the value of a possible electric dipole moment of the electron.\(^53\) The electronic ground state is of \( \Sigma'^- \) character, and the projection of the orbital angular momentum on the molecular axis is zero. The rotational states are labeled by the Hund’s case (b) quantum number \( N \) with \( N = J \pm \Omega = J \pm 1/2 \). There are only Stark matrix elements between neighboring rotational states with a different value for \( N \), which have an energy separation that scales with the rotational constant \( B \). The Stark energy curves for the first four rotational levels are shown in Figure 4c. Because the rotational constant of YbF is relatively small, the
zero field rotational energy splittings are relatively small. Consequently, the Stark energy curves result from the interaction between multiple rotational states, and levels that initially gain Stark energy as a function of the electric field show the opposite behavior at higher field strengths.

3.3.5. ND₃, H₂CO, and HDO. The symmetric top molecule ND₃ has its dipole moment of 1.50 D directed along the c-axis of the molecule and is therefore called a c-type rotor. Hence, representation III of ref 42 is the most natural way to set up the energy matrix. In addition to the rotational degree of freedom, the ND₃ molecule has a pyramidal structure that allows a vibrational umbrella motion, and the complete symmetry classification of the molecular rovibronic wave functions therefore requires the D₃h molecular symmetry group.55,56 As a result, the rotational levels that are calculated using the formalism of section 3.3.3 are split by the tunnelling effect along the umbrella motion. This inversion splitting Eᵦᵦᵦᵦᵦ gives rise to two inversion components within a rotational level, which have a definite, but opposite, parity. The inversion splitting for the Jₓ = 1, rotational ground state of para-ND₃ amounts to 1.6 GHz, which is much smaller than the inversion splitting for the same state in the NH₃ molecule.57,58 This results in a more linear and larger Stark shift for ND₃, making the deuterated isotopomer more amenable for Stark deceleration experiments than the common isotope.

The Stark matrix is again set up most conveniently using the symmetrized wave functions of section 3.3.2, such that the inversion splitting energies can be incorporated in the diagonal matrix elements. The resulting Stark shift of the Jₓ = 1; level is shown in Figure 5a. The Stark effect in the ND₃ molecule can also be approximated by considering only the interaction between the two inversion components, such that the eigenvalues of the Stark energy matrix are given by eq 11, where Eᵦ is replaced by Eᵦᵦᵦᵦᵦ and Ω eff is replaced by K. Note that K is a good quantum number and takes integer values, whereas Ω eff is an effective quantum number that involves mixing of different spin–orbit states of a diatomic molecule. The resulting Stark curves for the Jₓ = 1; state in ND₃ are shown by the dashed lines for all values of M in Figure 5a. It is seen that for fields higher than 50 kV/cm, the interaction with rotational levels J > 1 becomes significant, and the two-level approximation deviates significantly from the exact result.

The asymmetric top H₂CO is almost a prolate symmetric top (A > B ≈ C), with its dipole moment of 2.34 D directed along the a-axis of the molecule.65,69 It is therefore most convenient to use representation I of ref 42 to set up the energy matrix using the basis wave functions J(K(Ω)K). The matrix is truncated at J = 7 and diagonalized for fields up to 200 kV/cm. The calculated Stark shifts for the lowest rotational states of ortho-H₂CO are presented in Figure 5b. Because of the asymmetry of the molecule, the rotational states JₓKₓCₓ = 11 and 11 are split by 0.16 cm⁻¹ in zero field (K-doubling).69 It is observed that the 11111 level interacts with the 11111 level and gains Stark energy in an increasing electric field. However, because of the symmetry of the wave functions involved, the 110 level also interacts with the 211 level. As a result, the 11111 level becomes high field seeking above a field of about 150 kV/cm.

The asymmetric top HDO has a dipole moment of 1.8 D however, the dipole moment is not directed along one of the principal axes of inertia. The dipole moment has a component of 0.7 D along the a-axis, and a component of 1.7 D along the b-axis. Because the largest component is directed along the b-axis, we choose representation II of ref 42 to set up the energy matrix. The full sum over q in eq 3 needs to be evaluated, resulting in a mixing of different values of the quantum number K.62,63 The resulting Stark shift for the 110 state is shown in Figure 5c. Unlike the situation for H₂CO, the interacting rotational states 110 and 111 have a rather large energy gap of 2.7 cm⁻¹ in zero field, resulting in a Stark shift that is rather small and nonlinear.

3.3.6. Candidate Molecules for Stark Deceleration. On the basis of the Stark shifts that are calculated using the formalism outlined above, a selection of polar molecules suited for deceleration is given in Table 1. Unless stated otherwise, the Stark shift in an electric field of 200 kV/cm is given. When the Stark shift reaches a maximum at lower values of the electric field, this maximum shift is given.

To date, Stark deceleration of the molecules CO,²⁹,⁶⁴ H₂CO,⁶⁵ LiH,⁶⁶ NH,⁶⁷ ND₃,⁶⁸,⁶⁹ NH₃,⁶⁸ OH,⁶⁹–⁷¹ OD,⁷² SO₂,⁷³ YbF,⁷⁴ CaF,⁷⁵ and benzonitrile⁷⁶ has been experimentally demonstrated; Stark deceleration of CH₂F,⁷⁷ CH₃,⁷⁸ and SrF⁷⁹ has been proposed.

Figure 5. The Stark energy level diagrams of the rotational states that are of interest for Stark deceleration experiments for the symmetric top ND₃ and the asymmetric tops H₂CO and HDO. The zero-field rotational energy of the lowest rotational level that is displayed in each panel is set to zero. In panel (a), the calculated Stark shifts based on a two-level approximation are shown as dashed lines.
Table 1. A Selection of Polar Molecules Suiited for Deceleration and Trapping Experiments, With Their Relevant Properties

<table>
<thead>
<tr>
<th>molecule</th>
<th>state</th>
<th>Stark shift at 200 kV/cm (cm⁻¹)</th>
<th>dipole moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td></td>
<td>1/2, Ω = -1/4</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3/2, Ω = -9/4</td>
<td>1.88</td>
</tr>
<tr>
<td>CH₃F</td>
<td></td>
<td>(KМ) = 1000</td>
<td>0.54*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ω = 1 ± 1</td>
<td>1.05*</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>(KМ) = 1</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(KМ) = 2</td>
<td>2.87</td>
</tr>
<tr>
<td>H₂CO</td>
<td></td>
<td>(KМ) = 1</td>
<td>1.44*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(KМ) = 1</td>
<td>1.11*</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>(KМ) = 1</td>
<td>0.45</td>
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<tr>
<td></td>
<td></td>
<td>(KМ) = 1</td>
<td>0.72</td>
</tr>
<tr>
<td>D₂O</td>
<td></td>
<td>(KМ) = 1</td>
<td>0.73</td>
</tr>
<tr>
<td>HDO</td>
<td></td>
<td>(KМ) = 1</td>
<td>3.11</td>
</tr>
<tr>
<td>LiH</td>
<td></td>
<td>(KМ) = 1</td>
<td>2.67</td>
</tr>
<tr>
<td>LiD</td>
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<td>(KМ) = 1</td>
<td>3.34</td>
</tr>
<tr>
<td>NH</td>
<td></td>
<td>Ω = 2</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Ω = 2</td>
<td>2.11</td>
</tr>
<tr>
<td>N₂H₃</td>
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<td>(KМ) = 1</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(KМ) = 1</td>
<td>2.29</td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td>Ω = 2</td>
<td>0.17</td>
</tr>
<tr>
<td>N₂O</td>
<td></td>
<td>(KМ) = 1</td>
<td>0.26</td>
</tr>
<tr>
<td>OCS</td>
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<td>(KМ) = 1</td>
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<td></td>
<td>(KМ) = 1</td>
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<td></td>
<td></td>
<td>(KМ) = 1</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(KМ) = 1</td>
<td>1.49</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td>(KМ) = 1</td>
<td>1.47</td>
</tr>
<tr>
<td>YbF</td>
<td></td>
<td>Ω = 1</td>
<td>0.16*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ω = 0</td>
<td>-10.74</td>
</tr>
<tr>
<td>SrF</td>
<td></td>
<td>Ω = 1</td>
<td>0.16*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ω = 0</td>
<td>-9.47</td>
</tr>
</tbody>
</table>

“For some heavy molecules, the Stark shift of the high-field seeking state, relevant for alternate gradient deceleration, is also given. The Stark shift at 200 kV/cm is indicated. If the Stark energy reaches a maximum at smaller field strengths, indicated by the symbol “*”, the maximum Stark shift is given. Reprinted with permission from ref 68. Copyright 2002 American Physical Society.

3.4. Zeeman Effect

The Dirac equation formulates the relativistic quantum mechanics of a free electron in a magnetic field \( \mathbf{B} \). It constitutes the starting point to derive the standard electronic Zeeman Hamiltonian, which is usually employed in atomic and molecular physics. Here, we restrict ourselves to the terms of the molecular Zeeman Hamiltonian that are of relevance for the manipulation of neutral atoms and molecules with inhomogeneous magnetic fields. Therefore, the Zeeman Hamiltonian of interest here only involves the contributions of the angular momentum and the spin of the electrons and reads:

\[
H_{\text{Zeeman}} = -\mu_\mathbf{B} \cdot \mathbf{B} = \mu_B h^{-1} \hat{L} \cdot \mathbf{B} + \mu_B h^{-1} \hat{s} \cdot \mathbf{B} \tag{12}
\]

where \( \mu_B = e / 2m_e \) is the Bohr magneton with value 9.274 × 10⁻²⁴ J/T or 1.39 MHz/Gauss, and \( \mu_e \) is the free electron g-factor, with the value ~2.002₃₂, inferred from quantum electrodynamics. \( \hat{L} \) stands for the electronic orbital angular momentum operator and \( \hat{s} \) for the electronic spin operator. Throughout this section, we choose the quantization axis in the space-fixed frame \( \hat{Z} \) to be directed along the local magnetic field. In the following subsections, we derive the matrix elements of the Zeeman Hamiltonian of eq 12, first for atoms, and then for diatomic molecules described in Hund’s cases (a) and (b).

3.4.1. Matrix Elements of \( H_{\text{Zeeman}} \) In Atoms.

For atoms, the calculation of the matrix elements of both operators we retained in the Zeeman Hamiltonian of eq 12 is a straightforward application of the Wigner–Eckart theorem.\(^{32}\) We characterize the atomic basis by the spectral term, \( | J^S + 1 \rangle \), where \( S \) is the electronic spin, \( L \) is the orbital angular momentum, and \( J \) is the angular momentum resulting from the coupling of the former two vectors. \( M \) stands for the projection of the total angular momentum on the space-fixed quantization axis \( \hat{Z} \). Together with an additional label \( n \), which generically accounts for the rest of the atomic structure, these quantum numbers describe a complete basis set of atomic wave functions. In this basis, the matrix elements read:

\[
\langle n', J'^S + 1 \rangle \langle J M | n J' M' \rangle = \mu_B B_n \delta_{J M} \delta_{JJ'} \left\langle J M | (-1)^J \sqrt{(2J + 1)(2J' + 1)} \left( \begin{array}{c} J & 1 \\ M & 0 \\ \end{array} \right) \right\rangle \times \left( \begin{array}{c} J & 1 \\ M & -M' \end{array} \right) \times \left( \begin{array}{c} J' & 1 \\ M' & 0 \end{array} \right) + \left( -1 \right)^J \sqrt{S(S + 1)(2S + 1)} \times \left( \begin{array}{c} J & 1 \\ M & 0 \end{array} \right) \times \left( \begin{array}{c} J' & 1 \\ M' & 0 \end{array} \right) \times \left( \begin{array}{c} L & S \\ J & J' \end{array} \right) \right\rangle \tag{13}
\]

The hyperfine structure can easily be taken into account in the calculation of the matrix elements of \( H_{\text{Zeeman}} \) by applying the Wigner–Eckart theorem in the atomic hyperfine basis.

3.4.2. Matrix Elements of \( H_{\text{Zeeman}} \) In Diatomic Molecules. Hund’s Case (a).

The Zeeman Hamiltonian of eq 12 involves spin operators and angular momentum operators of the electrons. Therefore, the internal electronic structure of the diatomic molecule of interest needs to be described in more detail for the calculation of the matrix elements of \( H_{\text{Zeeman}} \) than for the calculation of the Stark effect given above in section 3.3. To do so, one uses internal quantum numbers and labels, in addition to the quantum numbers describing the symmetric top wave functions. In the following, \( S \) stands for the electronic spin of the molecule under consideration, while \( hA \) is the projection of the electronic orbital angular momentum on the body-fixed axis \( \hat{z} \). In addition to these quantum numbers, \( n \) denotes the additional labels that are required to construct a complete basis set of molecular wave functions, such that

\[
| \Lambda_n S J M \rangle = | \Lambda_n S \rangle | J M \rangle \tag{14}
\]

Note that these wave functions are a priori not of definite parity. For all practical purposes in the framework of magnetic manipulation experiments, the Zeeman interaction will be very small with respect to the Stark shift at 200 kV/cm.
to the energy difference between different vibrational states and a fortiori between different electronic states. We therefore restrict ourselves to the calculation of the matrix elements of $H_{\text{Zeeman}}$ within a given rovibronic state. The calculation yields:

$$
\langle \Lambda n S' J' M' | H_{\text{Zeeman}} | \Lambda n S J M \rangle
$$

$$
= \mu_B g_S S \delta_{SS} \sqrt{(2J' + 1)(2J + 1)} \left[ \frac{1}{M} \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix} \right]
$$

$$
\times g_s \delta_{NN} \sqrt{S(S + 1)(2S + 1)} \left[ S \begin{pmatrix} 1 & J' \\ \Omega & \Omega' - \Omega & -\Omega' \end{pmatrix} \right]
$$

$$
\times \left( \Omega' + \Omega \right) + \Lambda (-1)^{\Omega - M} \left( J \begin{pmatrix} 1 & J' \end{pmatrix} \right)
$$

$$
= \frac{1}{\sqrt{2}} \left[ \langle \Lambda | n S J M | \Omega \rangle \pm (-1)^{S+1} \langle -\Lambda | n S J M | -\Omega \rangle \right]
$$

where $\Sigma$ is defined as $\Omega - \Lambda$. The selection rules set $S = S'$ and $M' = M$.

Exactly like in the treatment of the Stark effect, one can introduce a parity basis, that is, a basis of wave functions of well-defined parity:

$$
| \Lambda n S J M \pm \rangle = \frac{1}{\sqrt{2}} \left[ | \Lambda n S J M \rangle \pm (-1)^{J+S+1} | -\Lambda n S J M \rangle \right]
$$

From these Hund’s case (b) wave functions, we can set a parity basis set defined as:

$$
| \Lambda n S J M \pm \rangle = \frac{1}{\sqrt{2}} \left[ | \Lambda n S J M \rangle \pm (-1)^{N+1} | -\Lambda n S J M \rangle \right]
$$

for non-$\Sigma$ electronic states, where $\Lambda$ is now an unsigned quantity. For $\Sigma$ states, the Hund’s case (b) wave functions have already a well-defined parity. In this parity basis, the nonvanishing matrix elements of $H_{\text{Zeeman}}$ are:

$$
\langle \Lambda n S' J' M' | H_{\text{Zeeman}} | \Lambda n S J M \pm \rangle
$$

$$
= \langle \Lambda n S' J' M' | H_{\text{Zeeman}} | \Lambda n S J M \rangle
$$

As expected, the Zeeman Hamiltonian couples only molecular states of identical parity. The use of Hund’s case (b) is especially convenient to calculate the Zeeman effect in diatomic molecules in electronic states of $\Sigma$ symmetry, for example, for diatomic molecules such as $\text{O}_2$, $\text{NH}$, $\text{MnH}$, and $\text{CrH}$ in their electronic ground state.

### 3.4.3. The Zeeman Effect of $\text{OH}(X^2\Pi_i)$ and $^{16}\text{O}_2(X^3\Sigma_g^-)$

As already discussed, the electronic ground state of the OH radical is of $^2\Pi$ character and splits into two distinct spin–orbit manifolds, labeled by $|\Omega|=1/2$ and $|\Omega|=3/2$. The OH radical in its electronic ground state is best described in Hund’s coupling case (a). In a Hund’s case (a) basis set of definite-parity wave functions $|\Lambda n S J M \rangle$, as constructed in section 3.3.2, the diagonal matrix elements of the Zeeman Hamiltonian read:

$$
\mu_B \frac{M \Omega (\Lambda + g_s)}{J(J + 1)}
$$

where $\Sigma = \Omega - \Lambda$ is the projection of the electronic spin on the molecular axis. The spin–orbit constant of the electronic ground state of OH is negative and therefore yields an inverted $^2\Pi$ state; that is, the absolute ground state corresponds to $|\Omega|=3/2$. Consequently, the lowest spin–orbit manifold of the OH radical shows a linear Zeeman effect, as displayed in Figure 6a.

**Figure 6.** The Zeeman energy level diagram of OH$(X^2\Pi_i)$ (a) and $^{16}\text{O}_2(X^3\Sigma_g^-)$ (b).
The $A$-doubling structure is clearly visible in the Zeeman diagram of OH, which reveals that the Zeeman Hamiltonian does not couple wave functions of opposite parities. In the upper spin–orbit component, of character $\Omega \Sigma = 1/2$, the linear Zeeman effect reduces to $\mu_B BM(2 - g_e)/(4J(J + 1))$ and therefore vanishes.

Molecular oxygen is one of the few chemically stable molecules that are paramagnetic in the ground state. Nuclear spin statistics restrict the rotational quantum number $M$ to odd values. The electron spin $S$ couples to the rotation $N$, which splits each rotational level into three components of distinct total angular momentum $J = N - 1, N, N + 1$. In Figure 6b, we show the Zeeman effect of molecular oxygen $^{16}\text{O}_2$ in its rotational ground state $N = 1$, in a magnetic field up to 2 T. As expected, in the low-field region, the Zeeman shift changes linearly with the magnetic field strength. The Zeeman Hamiltonian couples states of different $J$ values, so at moderate field strengths, $J$ is no longer a good quantum number. States sharing the same magnetic quantum number $M$ repel each other, as can be seen in Figure 6b within the rotational manifold $N = 1$. At higher fields than displayed in Figure 6b, above 8 T, different rotational manifolds start overlapping in energy, which gives rise to numerous avoided crossings.

### 3.4.4. Candidate Molecules for Zeeman Deceleration.

The vast majority of atoms have an open shell and are therefore paramagnetic in the ground state. Many atomic species could thus potentially be manipulated with the Zeeman deceleration technique, as emphasized in the periodic table displayed in Figure 7. The atomic species are reported with the maximum effective magnetic dipole of their ground state (in Bohr magnetons) divided by their mass (in amu). Atoms highlighted in yellow could be decelerated to standstill within less than 100 stages of a decelerator beam machine similar to that used by Hogan et al. Atoms in red would require more than 400 stages to be brought to rest.

On the basis of the calculation of the Zeeman effect derived above, a selection of paramagnetic molecules that are good candidate molecules for Zeeman deceleration experiments is given in Table 2. The Zeeman shift of each selected molecule in the specified quantum state in a magnetic field of 2.0 T is indicated. As a reference, these values are given for H and D atoms as well.

To date, the Zeeman deceleration of H and D atoms, as well as Ne and Ar atoms in a metastable state, has been experimentally demonstrated. The only molecular species that has been experimentally addressed with the Zeeman deceleration technique is molecular oxygen $^{16}\text{O}_2$.

### 4. DEFORMATION AND FOCUSING OF MOLECULAR BEAMS.

A wide variety of electric and magnetic field geometries have been devised over the years to manipulate the transverse motion of polar molecules. To deflect or focus certain molecules, one would like the absolute magnitude of the field to follow a certain functional form. Unfortunately, in many cases, the ideal field cannot be created, not due to lack of ingenuity or resources, but because Maxwell’s equations do not

---

**Table 2. A Selection of Paramagnetic Molecules Suited for Deceleration and Trapping Experiments, With Their Relevant Properties, Together With The Corresponding Properties for H and D Atoms**

<table>
<thead>
<tr>
<th>molecule</th>
<th>state</th>
<th>Zeeman shift at 2.0 T (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$</td>
<td>\Sigma_{1/2}, F = 1, M = 1 \rangle$</td>
</tr>
<tr>
<td>D</td>
<td>$</td>
<td>\Sigma_{3/2}, F = 3/2, M = 3/2 \rangle$</td>
</tr>
<tr>
<td>CH</td>
<td>$</td>
<td>\Pi_{1/2}, J = 3/2, M = -3/2 \rangle$</td>
</tr>
<tr>
<td>CO</td>
<td>$</td>
<td>\Pi_{1/2}, J = 1, M = 1 \rangle$</td>
</tr>
<tr>
<td>NH</td>
<td>$</td>
<td>\Delta_{1/2}, J = 2, M = 2 \rangle$</td>
</tr>
<tr>
<td>NO</td>
<td>$</td>
<td>\Pi_{3/2}, J = 3/2, M = 3/2 \rangle$</td>
</tr>
<tr>
<td>OH</td>
<td>$</td>
<td>\Pi_{1/2}, J = 3/2, M = 3/2 \rangle$</td>
</tr>
<tr>
<td>OD</td>
<td>$</td>
<td>\Pi_{1/2}, J = 3/2, M = 3/2 \rangle$</td>
</tr>
<tr>
<td>SO</td>
<td>$</td>
<td>\Sigma^+_1, (N = 0, J = 1, M = 1) \rangle$</td>
</tr>
<tr>
<td>$^{16}\text{O}_2$</td>
<td>$</td>
<td>\Sigma^+_1, N = 1, J = 2, M = 2 \rangle$</td>
</tr>
<tr>
<td>CaH</td>
<td>$</td>
<td>\Sigma^+_1, N = 0, J = 1/2, M = 1/2 \rangle$</td>
</tr>
<tr>
<td>CH</td>
<td>$</td>
<td>\Sigma^+_1, N = 0, J = 5/2, M = 5/2 \rangle$</td>
</tr>
<tr>
<td>MnH</td>
<td>$</td>
<td>\Sigma^+_1, N = 0, J = 3, M = 3 \rangle$</td>
</tr>
</tbody>
</table>

**Note:** The Zeeman shift at 2.0 T in the specified quantum state is reported.

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dx.doi.org/10.1021/cr200349r
allow it, and one has to settle for an approximation to this ideal field. In this section, we will analyze deflection and focusing fields in terms of a multipole expansion, following an approach similar to the one used by Kalnins et al.\textsuperscript{91} and Bethlem et al.\textsuperscript{92} This multipole expansion makes it easy to see which electric fields can be realized and which cannot, and how one can best approximate a field that cannot be realized exactly. For ease of discussion, we restrict ourselves to electric manipulation fields, but the analysis also holds for magnetic manipulation fields. In this section, we will discuss 2D fields with translational symmetry; in section 6.1, we will treat 3D fields that have cylindrical symmetry.

### 4.1. Multipole Expansion of the Electric Field in Two Dimensions

In the absence of free charges, the electric potential $\Phi$ obeys the Laplace equation $\nabla^2 \Phi = 0$. In two dimensions, the general solution of the Laplace equation may be represented by a multipole expansion \textsuperscript{91,92} as:

$$\Phi(r, \theta) = \Phi_0 \left[ \sum_{n=1}^{\infty} a_n \left( \frac{r}{r_0} \right)^n \cos(n\theta) + \sum_{n=1}^{\infty} b_n \left( \frac{r}{r_0} \right)^n \sin(n\theta) \right]$$

(18)

Here, $r = (x^2 + y^2)^{1/2}$ and $\theta = \tan^{-1}(y/x)$ are the usual cylindrical coordinates, $a_n$ and $b_n$ are dimensionless constants, and $r_0$ and $\Phi_0$ are scaling parameters that characterize the size of the electrode structure and the applied voltages, respectively. The electric field magnitude at the center is given by $E(0) = E_0 = (\Phi_0/r_0)(a_1 + b_1)^{1/2}$. The $n = 1$ terms in eq 18 represent a homogeneous electric field, while the $n = 2$ and $n = 3$ terms represent quadrupole and hexapole fields, respectively.

Manipulation tools for polar molecules in low-field seeking and high-field seeking states can now be created by choosing suitable coefficients in eq 18.

### 4.2. Deflection Fields

One of the simplest manipulation tools is the electric or magnetic deflection field. The ideal electric deflection field for polar molecules exerts a strong, constant force in one direction, while the force in the perpendicular direction is zero. Deflection fields are extensively used to determine the magnetic and electric properties of atoms and molecules and clusters, ranging from alkali atoms,\textsuperscript{94} C$_{60}$ molecules\textsuperscript{95} to water\textsuperscript{96} and metal clusters\textsuperscript{97} (see, for instance, the review papers of Miller and Bederson\textsuperscript{98} and Bonin and Kresin\textsuperscript{99} and references therein). Recently, deflection fields have been used to prepare samples of molecules in the lowest rotational levels for subsequent laser-induced alignment and orientation studies\textsuperscript{100} as well as to separate individual conformers of large molecules.\textsuperscript{101}

In Figure 8a is shown the layout of a typical molecular beam deflection experiment. A well collimated beam of molecules is sent through an inhomogeneous electric field, and the displacement of the beam after a certain path length is measured. To measure polarizability-dependent shifts more accurately, Arndt and co-workers have used an interferometric technique, as shown in Figure 8b. A density modulation is imprinted on the beam through the action of two free-standing gratings. Tiny shifts of this pattern are then observable by recording the transmitted flux behind a third mask that is laterally shifted over the beam profile.\textsuperscript{102}

To obtain accurate values for the polarizability of atoms and molecules, it is necessary to know both the electric field magnitude and its gradient with high accuracy. In the early experiments, the two wire field geometry was used, as this field and gradient are directly calculable from the geometry, thus avoiding difficult and tedious measurements of these quantities.\textsuperscript{27} With the advent of numerical methods to calculate electric fields from arbitrary electrode geometries, an analytical expression of the electric field is no longer necessary. Recently, Stefanov et al.\textsuperscript{93} and de Nijs and Bethlem\textsuperscript{103} derived how more ideal deflection fields can be obtained by optimizing the shape of the electrodes. We will here follow the treatment by de Nijs and Bethlem.\textsuperscript{103}

As mentioned, finding the ideal deflection field comes down to choosing suitable coefficients for the different multipole terms of eq 18. If we choose the molecules to be deflected in the $x$-direction, we can create a deflection field by setting all $b_n = 0$, and setting $|a_1| \gg |a_3| \gg |a_2|$. This geometry is depicted on the left-hand side of Figure 9. We will refer to this geometry as an “AA-type” deflection field or “conventional” deflection field. Alternatively, we may create a deflection field by setting all $a_n = 0$, and setting $|b_1| \gg |b_3| \gg |b_2|$. This geometry is depicted on the right-hand side of Figure 9. We will refer to this geometry as a “BB-type” deflection field or wedge field. The solid curves in Figure 9 show the voltage in steps of 5 kV. At the center the voltage is 0 V. These fields can be created by placing an electrode at any of the potential lines.

Although the resulting potentials and electric fields for the AA and BB geometries are different, the magnitudes of the electric field and the forces are the same. Using eq 18, we can write the electrostatic potential for the AA field as:

---

\textsuperscript{4839} doi.org/10.1021/cr200349r Chem. Rev. 2012, 112, 4628–4678
\[ \Phi(x, y) = \Phi_0 \left( \frac{x}{r_0} + a_2 \frac{(x^2 - y^2)}{2r_0^2} + a_3 \frac{(x^3 - 3xy^2)}{3r_0^3} \right) \] (19)

From this potential, we can obtain the electric field magnitude, via:

\[ E(x, y) = \sqrt{\left( \frac{\partial \Phi}{\partial x} \right)^2 + \left( \frac{\partial \Phi}{\partial y} \right)^2} \] (20)

From the electric field magnitude, we can obtain the Stark shift and the force on the molecules, via:

\[ \vec{F} = -\nabla W(E) = \mu_{\text{eff}} \nabla E \] (21)

Here, we assume that the molecules experience a linear Stark shift, \( W = -\mu_{\text{eff}}(E_0)E \) in the applied field, with \( \mu_{\text{eff}}(E_0) \) being the effective dipole moment of the molecule in the electric field at the center of the deflector. \( \mu_{\text{eff}} \) is positive for molecules in high-field seeking states and negative for molecules in low-field seeking states. Note that the Stark shift is assumed to be linear only over a small range of electric fields; this is a rather good approximation even for molecules that have a quadratic Stark shift. Throughout the region \( r < r_{\text{cr}} \), we can expand the force resulting from eq 19 as:

\[ F_{\text{Stark},x}(x, y) = \mu_{\text{eff}} E \left[ \frac{a_2}{a_1} \frac{1}{r_0} + 2 \frac{a_3}{a_1} \frac{x}{r_0^2} - \frac{1}{2} \left( \frac{a_2}{a_1} \right)^3 \frac{y^2}{r_0^3} + \ldots \right] \] (22)

\[ F_{\text{Stark},y}(x, y) = \mu_{\text{eff}} E \left[ - \left( \frac{a_2}{a_1} \right)^3 \frac{y^2}{r_0^3} + \ldots \right] \] (23)

Ideally, the deflection force is constant and strong in the \( x \)-direction, while it is zero along the \( y \)-direction. Thus, we would like to keep only the first term of eq 22 and set all other terms in eqs 22 and 23 equal to zero. We see that the desired term scales as \( a_2/a_1 \), while the undesired terms scale as \( a_2/a_1 \) or as the second or third power of \( a_3/a_1 \). Thus, the undesired terms can be made arbitrary small, by choosing \( a_3 = 0 \) and \( a_2/a_1 \ll 1 \), but at the expense of the strength of the deflection force. In practice, one usually cannot afford to choose \( a_2/a_1 \) much smaller than 1/5. The dominant undesired term in this case is the first term of eq 23. From numerical simulations, it has been shown that \( a_3 \) should be slightly negative or zero.103

4.3. Focusing Low-Field Seekers

As discussed in the Introduction, the use of focusing elements for molecules in low-field seeking states has been pivotal in the development of the field of molecular beams. In molecular beam deceleration experiments, quadrupoles and hexapoles are used to map the phase-space volume from the orifice of the valve to the decelerator and from the decelerator to a ring or trap (see section 7).

To create a perfect lens, we require the force to be harmonic. For polar molecules in a low-field seeking state that have a quadratic Stark shift, this implies that the electric field magnitude should be zero at the center (the molecular beam axis) and should increase linearly with the distance \( r \) from the center. Such a field can be created by choosing all coefficients in eq 18 to be zero except for \( a_2 \):

\[ \Phi(x, y) = \Phi_0 \frac{a_2}{r_0} \cos(2\theta) = \Phi_0 \left( \frac{a_2}{2r_0^2} \left( \frac{x^2 - y^2}{r_0^2} \right) \right) \] (24)

which results in an electric field magnitude given by:

\[ E(r, \theta) = \Phi_0 \frac{a_2}{r_0^3} r \] (25)

which indeed has the required form. The same electric field can be created by choosing all coefficients to be zero except for \( a_3 \), which corresponds to rotating the geometry over 45°. This is referred to as a "skew" quadrupole.

Similarly, for polar molecules in a low-field seeking state that have a linear Stark shift, this implies that the electric field magnitude should be zero at the center (the molecular beam axis) and should increase quadratically with the distance \( r \) from the center. Such a field can be created by choosing all coefficients to be zero except for \( a_3 \):

\[ \Phi(x, y) = \Phi_0 \frac{a_3}{r_0} \cos(3\theta) = \Phi_0 \left( \frac{a_2}{3r_0^3} \left( x^3 - 3xy^2 \right) \right) \] (26)

as then

\[ E(r, \theta) = \Phi_0 \frac{a_3}{r_0^2} r \] (27)
Again, the same electric field can be created by choosing all coefficients to be zero except for $b_0$, which corresponds to rotating the geometry by $30^\circ$.

For an ideal hexapole, the hyperbolic surfaces of the electrodes would nearly touch at large radii, leading to electrical discharges when a high voltage difference is applied between adjacent electrodes. To prevent this, and for ease of manufacturing, cylindrical electrodes are commonly used. The electric field for the ideal hexapole composed of hyperbolic surfaces is shown in Figure 10a.\textsuperscript{104} The dashed circles show the contours of the rods used to approximate the hyperbolic surfaces. Figure 10b and c shows the field resulting from a hexapole composed of six cylindrical rods placed equidistantly on the outside of a circle with radius $R$. In Figure 10b, the rods have a radius of $R/2$, following Reuss.\textsuperscript{105} The contour lines of the electric field in this geometry show a hexagonal perturbation close to the electrodes. This deviation from the cylindrical symmetry has been experimentally observed in two-dimensional imaging experiments.\textsuperscript{106} A better approximation of the ideal hexapole field can be obtained for a rod radius of $0.565R$, as recommended by Anderson.\textsuperscript{107} The electric field resulting from this geometry is shown in Figure 10c. It can be seen that the contour lines of the electric field in this geometry remain more circular close to the electrodes.

As discussed in section 3, the Stark shift for molecules that are typically used in molecular beam manipulation experiments is on the order of 1 cm$^{-1}$ ($\approx$1.44 K) in an electric field of 100 kV/cm. As in a typical molecular beam experiment, the transverse velocity distribution is centered around 0 m/s with a full-width-at-half-maximum (fwhm) spread of several tens of m/s, corresponding to a transverse translational temperature below 1 K, fields can be made high enough to focus all molecules coming from the source. Normally, the multipole focusers are made just long enough to focus a beam of molecules at the interaction or detection point somewhere downstream, and inside the multipole the molecules move on a short part of a sinusoidal path. The position of the focus can be controlled by varying the voltage on the multipole electrodes, or, while using a fixed voltage, by changing the duration that these voltages are switched on.

In Figure 11 are shown the trajectories of polar molecules, all flying with the same velocity, through a hexapole focuser. In the left panel, the molecules are assumed to have a perfect linear Stark shift. In this case, the lens is perfectly harmonic, and all molecules are focused at the same point. In the right panel, the molecules are assumed to have a quadratic Stark shift at low electric field and a linear Stark shift at high electric field. In this case, the lens is not ideal, and the sharp point-like focus changes into a ring-shaped focus (cylindrically symmetric around the hexapole axis). This effect is similar to spherical aberrations in optical lenses that leads to caustics and has been experimentally observed in two-dimensional imaging experiments on beams of metastable CO molecules.\textsuperscript{108} To make a perfect lens for molecules with a nonzero inversion or A-doublet splitting, one would need to create an electric field that increases linearly with $r$ near the molecular beam axis and quadratically with $r$ further away from the molecular beam axis. Unfortunately, such a field cannot be created from any combination of expansion coefficients. A more ideal lens can however be made by a combination of a quadrupole, a hexapole, and again a quadrupole lens. By applying the appropriate voltages on the composite lens, the nonlinearities in the force are compensated.

\subsection*{4.4. Guiding Low-Field Seekers}

In a hexapole or quadrupole focuser, molecules are typically only focused during a time that is short as compared to their oscillation period. Longer hexapole or quadrupole focusers, in which molecules make multiple oscillations, are commonly referred to as “guides” or “2D-traps”. A curved guide will only transport molecules below a certain threshold velocity; faster molecules are unable to follow the curved trajectory, strike the electrodes of the guide, and are removed from the beam. Rangwala et al.\textsuperscript{111} used a linear electrostatic quadrupole with a curved section to select slow formaldehyde ($\text{H}_2\text{CO}$) and deuterated ammonia ($\text{ND}_3$) molecules from a room-temperature reservoir and guide them into an ultrahigh vacuum
in the molecular beam axis. However, there is no requirement of the electric source of lithium atoms. Figure 12a shows a schematic view of the curved guide used by Rieger et al. to create a slow beam of water molecules.

Figure 12. (a) Schematic of the setup used by Rieger et al. On the left is the effusive source, which injects thermal D2O molecules into the four-wire guide. Neighboring electrodes have opposite polarity, creating a quadrupolar electric field. Molecules that are slow enough are guided through the first and second (not shown) 90° bends and are finally detected by a mass spectrometer. Reprinted with permission from ref 109. Copyright 2003 American Physical Society. (b) Schematic view of the setup used by Van Buuren et al. Warm molecules are cooled by collisions with a cold helium gas. Behind the cell, an electric quadrupole extracts slow molecules in low-field-seeking states out of the cryogenic environment into the detection chamber, where they are detected by a quadrupole mass spectrometer (QMS). Depletion measurements are performed by counterpropagating an UV laser beam through the guide. Reprinted with permission from ref 110. Copyright 2009 American Physical Society.

More dense beams in predominantly one rovibrational state can be obtained by first cooling the warm molecules by collisions with a cryogenic helium buffer gas and then extracting the cold molecules by means of a magnetic or electrostatic multipole guide and transporting them to a remote location, for example, for trapping. This combines cryogenic buffer-gas cooling with Zeeman or Stark filtering. Figure 12b shows a schematic view of the setup used by Van Buuren et al. 4.5. Focusing High-Field Seekers

To focus polar molecules in high-field seeking states, one would require the electric field magnitude to have a maximum at the center (the molecular beam axis). However, there is no combination of multipole fields that has this property. On the other hand, it is possible to create a field that has a saddle point at the molecular beam axis. In such a field, molecules in high-field seeking states are focused in one direction while being defocused in the other. By alternating the orientation of these fields, molecules are alternately focused and defocused in both directions. As the particles are, on average, further away from the axis when the field is focusing and closer to the axis when the field is defocusing, the trajectories are stable. This scheme is called strong focusing or alternating-gradient (AG) focusing and was proposed by Courant, Livingstone, and Snyder as a means to stabilize the motion of charged particles in accelerators. The application of AG focusing to polar molecules was first considered by Auerbach et al. in a design study for a neutral particle accelerator at the University of Chicago, and was experimentally demonstrated by Kakati and Lainé.

Interest in AG-focusing of polar molecules has resurfaced over the past few years, as it provides a means to stabilize the motion of heavy molecules in a Stark decelerator (see section S.8). Nonlinear forces in the AG-lenses, however, turned out to be a severe obstacle. Here, we will follow the treatment of Bethlem et al. to outline how a suitable AG-lens can be created.

To make a good AG lens, we require the magnitude of the electric field to be nonzero at the origin, and symmetric under reflection in the $x$- and $y$-axes. To achieve this, we make $\Phi$ symmetric under reflection in the $x$-axis and antisymmetric under reflection in the $y$-axis by setting all $b_{n}$ to 0 and retaining only the $a_{n}$ terms of odd $n$. Anticipating the result that high-order terms introduce undesirable nonlinearities into the force, we choose to retain only $a_{1}$, $a_{3}$, and $a_{5}$. Hence:

$$
\Phi(x, y) = \Phi_{0}\left(\frac{x}{r_{0}} + a_{3}\frac{(x^{3} - 3x^{2}y^{2})}{3^{3}} + a_{5}\frac{(x^{5} - 10x^{3}y^{2} + 5xy^{4})}{5r_{0}^{5}}\right)
$$

(28)

From this potential, we obtain the electric field magnitude.

$$
E(x, y) = E_{0}\left(1 + \frac{a_{3}}{a_{1}}\frac{(x^{2} - y^{2})^{2}}{r_{0}^{2}} + 2\left(\frac{a_{5}}{a_{1}}\right)^{2} - 3\frac{a_{5}}{a_{1}}\right)\frac{x^{3}y^{2}}{r_{0}^{4}} + \frac{a_{5}}{a_{1}}\frac{x^{4} + y^{4}}{r_{0}^{4}} + \ldots
$$

(29)

The first two terms have the desired form and dominate the expansion. The other terms produce focusing aberrations. It might appear advantageous to set $a_{5}/a_{1} = (a_{3}/a_{1})^{2}/3$ so as to cancel the cross term. However, the best policy is to minimize $a_{3}/a_{1}$ because the $x^{4} + y^{4}$ term is also a damaging aberration.

To produce these fields, we need to choose electrodes whose surfaces map onto the equipotentials. We are free to choose $a_{3}/a_{1}$ either positive or negative.

Figure 13a shows equipotentials for $a_{3}/a_{1} = +1/7$ and $a_{5} = 0$. The choice of $a_{3}$ is constrained by the condition $a_{3} \ll a_{1}$, while remaining large enough to provide significant focusing. The solid white lines show electrodes, chosen to be circular for ease of construction, that match the equipotentials closely. They have radii of $R = 3r_{0}$ and are centered at $x = \pm 4r_{0}$, leaving a gap.
of $2r_0$. Because these electrodes do not match the equipotential exactly, higher-order terms appear in the field. From a fit to the numerically calculated electrostatic potential, we find for this geometry $a_3/a_1 = 0.143$ and $a_5/a_1 = 0.143$. This two-rod field has been used extensively in AG-decelerators for polar molecules as will be discussed in section 5.8. The rather large value of $a_5/a_3$ can be reduced by adding two grounded electrodes tangential to the $\Phi = 0$ equipotentials at $y = \pm 2.65r_0$. These are shown dashed in Figure 13a, where for simplicity we have given the new rods the same radius $R$. In this case, the coefficients become $a_3/a_1 = 0.157$ and $a_5/a_1 = 0.070$. At the expense of a slightly less ideal field and a smaller electric field on the molecular beam axis, one can position the four identical electrodes at the corners of a square. This has the advantage that one is free to choose in which plane the field focuses or defocuses by simply switching the voltages. This is a necessary condition for an ac guide; see section 4.6.

Figure 13b shows equipotentials for $a_3/a_1 = -1/7$ and $a_5 = 0$. This is well approximated by electrodes of radius $R = 2.35r_0$, with a minimum gap of $2r_0$ as shown by the solid white lines of Figure 13b. The precise field produced by these electrodes has $a_3/a_1 = -0.039$ and $a_5/a_1 = -0.014$. This geometry compares very favorably to the cases considered in Figure 13a with regard to minimizing $a_5$ and hence the lens aberrations. As this geometry is symmetric, the focusing and defocusing directions can again be easily reversed by interchanging the potentials on the top-right and bottom-left electrodes of Figure 13b. The field at the center is only 41% of the maximum field, which is unfavorable for the use of this design in a decelerator.

### 4.6. Guiding High-Field Seekers

In analogy to the guides for molecules in low-field seeking states discussed in section 4.4, guides for molecules in high-field seeking states can be created by extending the length of an AG-lens. In the case of an AG-guide, the voltages must be switched between configurations where the molecules are focused in one direction and defocused in the other, and vice versa. The acceptance of a guide for molecules in high-field seeking states is typically 100 times smaller than a comparable guide for molecules in low-field seeking states.\cite{92,120}

An ac-guide was first demonstrated by Junglen et al.\cite{121} In that work, a 50 cm long curved guide, with an electrode geometry as discussed in the context of Figure 13a, was used to select slow ND$_3$ molecules from a room-temperature reservoir and to guide them into an ultrahigh vacuum chamber. As the detection of the ND$_3$ was not state-specific, it was unclear which fraction of the beam is in high-field seeking states and which is in low-field seeking states. Later work on the stability of AG guides suggests that the fraction in high-field seeking states was probably rather small.

Filsinger et al.\cite{122} used a 100 cm long ac-guide, with an electrode geometry similar to the one shown in Figure 13b, to select and spatially separate the two conformers of 3-aminophenol (C$_6$H$_7$N O) present in a molecular beam. Analogous to the separation of ions based on their mass-to-charge ratios in a quadrupole mass filter, the neutral conformers are separated on the basis of their different mass-to-dipole-moment ratios. For a given ac frequency, the individual conformers experience different focusing forces, resulting in different transmissions through the selector. Just like in a quadrupole mass filter, the resolution of the device can be improved by adding a dc offset field to the ac field, or by using an asymmetric ac switching cycle.\cite{123} Putze et al.\cite{119} used a 164 cm long ac-guide to demonstrate the rotational-state specific guiding of benzonitrile molecules. The data in Figure 14 show that the guide can selectively transmit the quantum states with a large effective dipole moment, such as the ground state, or those with smaller effective dipole moments, by operating it at different ac frequencies and using different ac switching cycles. Wall et al.\cite{124} used an ac guide to transport CaF molecules in high-field seeking states.

### 5. DECELERATION OF NEUTRAL MOLECULES

In multipole focusers and in the deflection elements that have been discussed in the previous section, the velocity component of the particles along the beam axis is not changed. In this section, we describe how the longitudinal velocity of molecules in a beam can be changed using time-varying electric and magnetic fields in a Stark and Zeeman decelerator, respectively.

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**Figure 13.** Electrostatic equipotentials of eq 28 for the cases (a) $a_3/a_1 = +1/7$, $a_5 = 0$ and (b) $a_3/a_1 = -1/7$, $a_5 = 0$. Red and blue colorings correspond to positive and negative potentials, respectively. The white lines show electrode surfaces designed to follow these contours. Reprinted with permission from ref 92. Copyright 2006 IOP Publishing.

**Figure 14.** Rotationally resolved fluorescence excitation spectra of benzonitrile. Upper trace: Spectrum obtained without selection. The $J_{K,a} \leftrightarrow J_{K,c}$ assignment for each of the rotational lines is indicated. Middle trace: Spectrum obtained with the selector operating at an ac switching frequency of 2.7 kHz and employing a symmetric switching cycle (duty cycle equal to 0.5). Lower trace: Spectrum obtained with the selector operating at an ac switching frequency of 3.8 kHz and employing a switching cycle with a duty cycle equal to 0.565. Reprinted with permission from ref 119. Copyright 2011 RSC Publishing.
We will discuss the various types of decelerators that have been developed over the years and detail their operation principles. We also discuss several mechanisms that can lead to a loss of molecules during the deceleration process.

5.1. Operation Principle of Stark Deceleration

In a Stark decelerator, the longitudinal velocity of a beam of polar molecules is manipulated using longitudinally inhomogeneous electric fields. Let us consider an electric field stage composed of two opposing electrodes that are connected to power supplies of opposite polarity, as is shown in Figure 15.

![Figure 15](image15.png)

**Figure 15.** The Stark energy level diagram of the OH $X^2\Pi_{3/2}, J = 3/2$ radical, and the potential energy $W(z)$ of OH radicals as a function of position $z$ along the molecular beam axis. A high electric field is created by two high voltage electrodes at opposite polarity.

Stark deceleration was first demonstrated using metastable CO$_2$, and the technique was later applied to many other molecules. Throughout this section, to illustrate the deceleration process, we will use the Stark deceleration of OH radicals in the $X^2\Pi_{3/2}, J = 3/2$ state as an example. In the presence of an electric field, four levels exist that are labeled by the value of the product $M\Omega$, as discussed in section 3.3.4. Consider an OH radical in the low-field seeking $X^2\Pi_{3/2}, J = 3/2, M\Omega = -9/4$ state. This state is indicated with the bold line in Figure 15. When an OH radical in this state approaches the plane of the electrodes, work is done by the electric field to oppose the motion of the molecule, and the molecule slows down. When the molecule leaves the region of high field again, however, it will regain the same amount of kinetic energy. The acceleration on the downward slope of the hill can be avoided if time-varying inhomogeneous electric fields are used. When the electric field is abruptly switched off before the molecule has left the region of high electric field, the kinetic energy of the molecule is not regained.

The maximum electric field strength that can be obtained in the laboratory is typically limited to ~200 kV/cm. The potential energy of most molecular species in such an electric field is 1 or 2 orders of magnitude smaller than the kinetic energy these molecules possess in a molecular beam, and a Stark shift is effective. Only for atoms or molecules in Rydberg states, which exhibit very large electric dipole moments, can a Stark shift be achieved that is sufficient to significantly manipulate the atomic or molecular velocities using a single stage. Using inhomogeneous electric fields below the field ionization limit, hydrogen atoms in a supersonic beam have been decelerated, stopped, and even reflected while surviving in a selected Rydberg state. The Stark deceleration of Rydberg states is potentially very general and holds in principle for any atom or molecule. Nevertheless, several restrictions exist that may hamper the extension of this method. In non-hydrogenic atoms, the electric field should be kept below the Inglis–Teller limit, while, in addition to autoionization, molecular Rydberg states can experience predissociation, and the spectroscopic selection of the Rydberg state can be complicated. Some of these limitations can be circumvented by implementing an electric trap that is moving with the molecular beam. Recently, hydrogen molecules in a beam have been decelerated and brought to rest using this approach.

For ground-state molecules, where the effect of a single electric field stage on the forward velocity of the molecules in the beam is too small, the deceleration process needs to be repeated many times to obtain a significant change in the velocity. In a Stark decelerator, this can be achieved using an array of equidistant electric field stages, separated by a distance $L$, as shown in Figure 16. Each stage consists of two parallel cylindrical metal rods with radius $r$, centered a distance $2r + d$ apart. One of the rods is connected to a positive, and the other to a negative switchable power supply. The rods from every other electric field stage are connected to each other. At a given time, the rods at the even-numbered positions are switched to high voltage, and the rods at odd-numbered positions are grounded. The potential energy $W(z)$ of a molecule in a low-field seeking quantum state as a function of the position $z$ along the beam axis is shown in Figure 16 as well. The deceleration procedure is now straightforward: when the molecule has reached a position that is close to the top of the first potential hill, the stages that were at high voltage are switched to ground, and vice versa. After switching, the molecule will find itself again in front of a potential hill and will again lose kinetic energy when climbing this hill. When the molecule has reached the high electric field region, the voltages are switched back to...
the original configuration. By repeating this process many times, the velocity of the molecule can be reduced in a stepwise fashion.

The amount of kinetic energy that is lost per stage, and thus the velocity with which the molecule exits the decelerator, depends on the exact position of the molecule at the time that the fields are being switched. An important property of the Stark decelerator is that the deceleration process does not only work for one molecule in the beam, but that it works for all molecules that at the entrance of the decelerator have a position and velocity that are within the so-called acceptance of the decelerator. Together, these properties allow one to decelerate (or to accelerate) part of the beam to any desired velocity, while keeping the selected part of the beam together as a compact packet.\textsuperscript{68,137}

5.2. Phase Stability in the Stark Decelerator

Central to the understanding of the operation principle of a Stark decelerator are the concepts of the synchronous molecule and phase stability. Referring back to Figure 16, the position $z$ (with periodicity $2L$) of a molecule at the time that the fields are switched is called the “phase angle” $\phi = z\pi/L$ (with periodicity $2\pi$). We define the position with $\phi = 0$ as the position between two adjacent pairs of electrodes such that the electrodes at $\phi = \pi/2$ are grounded just after the fields are switched. By definition, a molecule with velocity $v_0$ is called synchronous if its phase $\phi_0$ on the potential is always the same at the time that the fields are switched; that is, $\phi_0$ remains constant, and the molecule will lose a constant amount of kinetic energy $\Delta K(\phi_0)$ per stage. The synchronous molecule achieves this by traveling exactly a distance $L$ in the time interval between two successive switch times. This means that the synchronous molecule is always “in phase” with the switching of the fields in the decelerator. A molecule that has a slightly different phase $\phi$ and/or velocity $v$ than the synchronous molecule will experience an automatic correction toward the equilibrium values $\phi_0$ and $v_0$. For instance, a molecule that has a phase that is slightly higher than $\phi_0$ at a certain switch time will lose more kinetic energy than the synchronous molecule, and the molecule will slow down with respect to the synchronous molecule. Its phase will get smaller, until it lags behind, after which the process reverses. Molecules within a certain region in phase-space, bound by the so-called separatrix, will undergo stable phase-space oscillations around the synchronous molecule. This phenomenon is referred to as phase stability and ensures that a packet of molecules is kept together in the Stark decelerator throughout the deceleration process.

To better understand phase stability, it is helpful to consider the trajectories of the molecules along the molecular beam axis and to derive the longitudinal equation of motion for these. The most important elements of the derivation are reproduced here; more details can be found elsewhere.\textsuperscript{68,137–139} A mathematically more rigorous derivation, based on a spatial and temporal Fourier representation of the potential, has also been given.\textsuperscript{140}

The Stark energy of a molecule $W(z\pi/L)$ is symmetric around the position of a pair of electrodes and can be conveniently written as a Fourier series:

$$W(z\pi/L) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos(n(z\pi/L + \pi/2))$$

where $a_0 = a_1 \sin \frac{2\pi}{L} - a_2 \cos \frac{2\pi}{L} + a_3 \sin \frac{3\pi}{L} + \ldots$

(30)

The change in kinetic energy per stage $\Delta K(\phi_0) = -\Delta W(\phi_0)$ for a synchronous molecule with phase $\phi_0$ and velocity $v_0$ at a certain switch time is then given by the difference in potential energy at the positions $\phi_0$ and $\phi_0 + \pi$:

$$\Delta W(\phi_0) = W(\phi_0 + \pi) - W(\phi_0) = 2a_1 \sin \phi_0$$

(31)

The average force $\bar{F}$ that acts on the synchronous molecule is then given by:

$$\bar{F}(\phi_0) = \frac{-\Delta W(\phi_0)}{L} = -\frac{2a_1}{L} \sin \phi_0$$

(32)

If we only take the leading terms up to $n = 2$ in eq 30 into account, the average force acting on a nonsynchronous molecule with phase $\phi = \phi_0 + \Delta \phi$ and with velocity $v_0$ is given by $-(2a_1/L) \sin(\phi_0 + \Delta \phi)$, and to a good approximation the equation of motion with respect to the synchronous molecule is

$$\frac{mL}{\pi} \frac{d^2 \Delta \phi}{dt^2} + \frac{2a_1}{L} (\sin(\phi_0 + \Delta \phi) - \sin(\phi_0)) = 0$$

(33)

where $m$ is the mass of the molecule. For small deviations from the synchronous molecule’s trajectory, that is, for $\Delta \phi \ll 1$, this results in a harmonic oscillation, both in position and in velocity, around the synchronous molecule.

In the phase stability diagrams of Figure 17, lines of constant energy are shown that result from a numerical integration of eq

Figure 17. Phase stability diagram for OH ($I = 3/2$, $M\Omega = -9/4$) radicals when the decelerator is operated at a phase angle of $\phi_0 = 0^\circ$ or $\phi_0 = 70^\circ$. Reprinted with permission from ref 141. Copyright 2006 Annual Reviews.
33 for OH radicals in the $J = 3/2$, $\Omega = -9/4$ state, using parameters for a decelerator that has a periodicity $2L = 22$ mm, an electrode radius of $r = 3$ mm, an electrode spacing of $d = 4$ mm, and that is operated using a potential difference of 40 kV between opposing electrodes.\textsuperscript{131} The equilibrium phase angles $\phi_0 = 0^\circ$ and $\phi_0 = 70^\circ$ for the synchronous molecule are used. The solid lines indicate the trajectories in phase-space that molecules will follow. Closed curves in the phase-space diagram correspond to bound orbits; molecules within the “bucket” bound by the thick contour, called the separatrix, will oscillate in phase-space around the phase and velocity of the synchronous molecule. Note that operation of the decelerator at $\phi_0 = 0^\circ$ corresponds to transporting (part of) the beam through the decelerator without deceleration, while acceleration or deceleration of the beam occurs for $-90^\circ < \phi_0 < 0$ and $0 < \phi_0 < 90^\circ$, respectively. The separatrix defines the longitudinal acceptance of the Stark decelerator and is shown for different phase angles $\phi_0$ in Figure 18. It is seen that the acceptance is larger for smaller values of $\phi_0$ while the deceleration per stage increases for higher values of $\phi_0$. Because for deceleration both are desirable, there is a trade-off between the two.

The molecular trajectories in the Stark decelerator depend on the quantum state of the molecule. Nevertheless, the simultaneous deceleration of bunches of molecules of different species, or molecules of the same species but with a different Stark shift, is possible. The requirement for the simultaneous deceleration of two distinct molecular packets for a given time sequence can be written as:\textsuperscript{68}

$$\frac{\Delta K'(\phi_0)}{m'} = \frac{\Delta K(\phi_0)}{m}$$

In this expression, the synchronous molecule for which the time sequence of the decelerator is calculated has mass $m$ and loses a kinetic energy $\Delta K(\phi_0)$ per electric field stage. The corresponding parameters for the additional synchronous molecule are indicated by primes. From eq 34, it can be seen that if the time-sequence is calculated for the molecule that can be least well decelerated, a synchronous molecule with a different Stark effect and/or different mass exists as well. Both molecules are then matched to the time-sequence and are simultaneously decelerated, although the acceptance of the decelerator will be different for both cases. The possibility to simultaneously decelerate different molecular species has first been demonstrated by decelerating a beam containing various isotopomers of ammonia.\textsuperscript{68} The simultaneous deceleration of OH radicals in the $X^2 \Pi_{1/2}, J = 3/2$, $\Omega = -9/4$ and the $X^2 \Pi_{3/2}, J = 3/2$, $\Omega = -3/4$ states, which possess a Stark shift that differs by a factor of 3, has been demonstrated as well. Recently, Lewandowski and co-workers studied the simultaneous deceleration of ammonia molecules in various rotational quantum states and discussed the implications of the state purity of the decelerated beam for collision experiments.\textsuperscript{142}

5.3. Higher-Order Resonances in a Stark Decelerator

In the conventional operation mode of a Stark decelerator, the fields are switched between the two voltage configurations with a “switching” velocity $v_{sw}$ that is equal to the velocity $v_0$ of the synchronous molecule. In a more extensive description of phase stability in a Stark decelerator including higher-order effects, it has been shown that additional phase-stable regions exist that originate from the spatial and temporal periodicity of the electric fields.\textsuperscript{130} These higher-order resonances are labeled with the index $s$, where $s = v_0/v_{sw}$. It was found that first-order resonances exist for $s = l/n$ (both $l$ and $n$ odd). The corresponding phase-stable regions have periodicity $2\pi/n$, and the size of the separatrices in velocity scales as $1/\sqrt{l}$. Weaker second-order resonances exist as well for which $s = 2l$ ($l$ integer) and $s = l/2$ ($l$ odd). A comprehensive and intuitive picture of the physical background of these higher-order resonances was presented by Van de Meerakker et al.\textsuperscript{138} These higher-order phase-stable regions can also be understood to result from interferences of partial waves in the Fourier expansion of the field.\textsuperscript{140,143}

The higher-order phase-stable regions have been visualized using numerical simulations. The time-averaged velocity of OH radicals that pass through a 300-stage Stark decelerator that is operated using $\phi_0 = 0^\circ$ and at a constant switching velocity $v_{sw} = 150$ m/s is shown in Figure 19. Resonances appear as regions in phase-space where all of the molecules have the same average velocity. Both the first- and the second-order resonances have been experimentally observed using a beam of OH ($^1\text{H}_2\text{O}^+\nu = 0, J = 3/2$) radicals passing through a Stark decelerator.\textsuperscript{138}

5.4. Transverse Stability in the Stark Decelerator

Phase stability only ensures that the packet of molecules is kept together in longitudinal phase-space. However, we also require that the molecules are kept together in the transverse direction. In the electrode geometry as shown in Figure 16, molecules in low-field seeking states stay transversely confined to the molecular beam axis as the electric field is always lower on this axis than on the electrodes. To focus the molecules in both transverse directions, the electrode pairs that make up a deceleration stage are alternately positioned horizontally and vertically.\textsuperscript{29,68}

The influence of the transverse motion of the molecules on longitudinal phase stability has been studied extensively.\textsuperscript{144} The longitudinal acceptance of the decelerator was calculated using numerical trajectory calculations, assuming that the molecules fly along the molecular beam axis (referred to as a 1D calculation), and taking the real trajectories of the molecules into account (3D calculation). The results of these simulations for OH radicals are shown in Figure 20. It was found that for high values of the phase angle $\phi_0$ the transverse motion enhances the region in phase-space for which phase-stable deceleration occurs. For low values of $\phi_0$, however, the transverse motion reduces the acceptance of a Stark decelerator, and unstable regions in phase-space appear. For $\phi_0 = 0^\circ$, for instance, the longitudinal phase-space distribution shows regions that are alternately empty and filled. Surrounding the empty center, a stable ring is found. Further away from the center, the stable ring suddenly changes into an empty ring.
referred to as a halo. Close to and on the separatrix, a thin outer stable ring appears. These effects have been quantitatively explained in terms of a coupling between the longitudinal and transverse motion. In the longitudinal direction, a molecule oscillates in position and velocity around the synchronous molecule, while in the transverse direction, a molecule oscillates around the molecular beam axis. The oscillation frequencies that are involved strongly depend on the phase angle $\phi_0$, but are in general similar in magnitude, as is shown in Figure 21. The transverse motion is driven by the longitudinal motion, and the transverse equations of motion have been derived. These equations are of the Mathieu type, whose solutions exhibit stable or unstable behavior. From this set of equations, the existence and position of the halo could be quantitatively understood. The low acceptance in the center of the phase-stable region, as well as the existence of the halo, was verified experimentally by passing a molecular beam of OH ($2^3\Pi_{3/2}, \nu = 0, J = 3/2$) radicals through a 1 m-long Stark decelerator. Ideally, the transverse focusing would be completely decoupled from the longitudinal motion. This would require spatially separated focusing and deceleration stages, and decelerators employing this idea have been proposed. However, there are large technical challenges associated with the construction of separate focusing and deceleration elements, and such decelerators have to date not been built. Using the existing electrode design, however, a similar effect can be obtained by operating the decelerator using a higher-order resonance. For instance, when the decelerator is operated using the $s = 3$ resonance, the synchronous molecule travels a distance that is equal to three electric field stages before the fields are switched. The synchronous molecule therefore always traverses a set of electrodes that is at high voltage during its path between successive switch times. The transverse focusing properties of the decelerator are therefore fundamentally different as well: the synchronous molecule is more strongly focused, and the transverse oscillation frequency of molecules that are close to the synchronous molecule will be higher. This is shown on the right-hand side of Figure 21, where the longitudinal and transverse oscillation frequencies are shown for OH radicals passing through a Stark decelerator that operates on the $s = 3$ higher-order resonance. The corresponding phase-space acceptance that results from three-dimensional trajectory simulations is shown as well. It is seen

Figure 19. Contour plot of the average velocity of OH ($J = 3/2, M\Omega = -9/4$) radicals as a function of their initial position and velocity, which results from a one-dimensional numerical simulation of their trajectories through a 300-stage decelerator. The decelerator is operated at a phase angle $\phi_0 = 0^\circ$ and a “switching velocity” $v_{sw} = 150$ m/s. Resonances appear as regions in phase-space where all of the molecules have the same average velocity. The structure inside the separatrices is a result of the finite number of stages used in the simulation. Reprinted with permission from ref 138. Copyright 2005 American Physical Society.

Figure 20. Longitudinal phase-space distributions of OH ($X^2\Pi_{3/2}, J = 3/2, M\Omega = -9/4$) radicals inside the decelerator that result from 1D and 3D trajectory simulations when the Stark decelerator is operated at $\phi_0 = 0^\circ, 20^\circ, 40^\circ, 60^\circ$, and $80^\circ$. In all simulations, the molecules spend approximately 8 ms in the decelerator. Reprinted with permission from ref 144. Copyright 2005 American Physical Society.
that the distribution is homogeneous, and no regions of instability or reduced acceptance are observed.\textsuperscript{144}

Recently, the analysis of the total longitudinal and transverse phase stability in a Stark decelerator was extended with a simple model to calculate the total 6D phase-space acceptance of a Stark decelerator.\textsuperscript{3,147} The total 6D phase-space acceptance was also calculated numerically via three-dimensional trajectory calculations, as shown in Figure 22. For a decelerator operating in the $s = 1$ mode, the loss of molecules due to the instabilities could be quantified. In the $s = 3$ mode, the acceptance of the decelerator approaches the optimum value, that is, the value that is obtained when all couplings are absent. “True” six-dimensional phase stability is obtained in this case. From these studies, a number of important design criteria for a Stark decelerator could be derived.\textsuperscript{147} For a decelerator that operates in the $s = 1$ mode, a strategy to optimize the number of decelerated molecules by using low phase angles and a large number of deceleration stages is of limited use. There is a maximum in the 6D acceptance for a phase-angle of around 50°, and the optimum number of molecules is obtained when the length of the decelerator (for a given initial and final velocity) is adjusted such that this phase-angle can be used. A decelerator that operates in the $s = 3$ mode outperforms a decelerator in the $s = 1$ mode in almost all cases. In the $s = 3$ mode, lower phase angles always result in a larger acceptance, and the length of the decelerator can be chosen at will.

It is noted here that at low longitudinal velocities the assumptions used in the analytical model of the longitudinal and transverse motion are no longer valid. In general, large losses can be expected due to transverse overfocusing. Scharfenberg et al.\textsuperscript{147} derived a simple model to calculate the velocity below which losses can be expected. In general, for a Stark decelerator operating in the $s = 1$ and $s = 3$ modes, losses are expected at velocities below about 50 and 150 m/s, respectively. A significant loss of molecules for velocities below this value has been observed experimentally,\textsuperscript{147,145} and schemes have been proposed and implemented to mitigate these effects.\textsuperscript{145,146,3,49}

5.5. Laboratory Implementation of Stark Deceleration

Over the years, a large variety of Stark decelerators, ranging in length from tens of centimeters to several meters, have been implemented in a number of laboratories. A typical experimental setup in which the Stark deceleration method is employed is shown in Figure 23. To exploit the improved performance of the $s = 3$ mode of operation, discussed in the previous section, a 2.6 m-long Stark decelerator has been constructed consisting of 316 electric field stages.\textsuperscript{147} This machine will be described here, using the Stark deceleration of a beam of OH radicals as an example.

A pulsed beam of OH radicals is produced via ArF-laser (193 nm) dissociation of HNO$_3$ seeded in an inert gas. The dissociation is carried out inside a quartz capillary that is mounted on the orifice of a pulsed valve (General Valve, Series 99). The experiment runs at a repetition frequency of 10 Hz. During the supersonic expansion, the majority of the OH radicals cool to the lowest rotational and vibrational level of the X$^3$Π$_{1/2}$ spin–orbit manifold of the electronic ground state. This population is equally distributed over the two $\Lambda$-doublet components of the $J = 3/2$ level. After passage through a skimmer with a 2 mm diameter opening, the molecular beam enters the differentially pumped decelerator chamber. The beam enters the Stark decelerator 60 mm from the nozzle orifice. The Stark decelerator consists of three modules that are mechanically and electrically decoupled...
OH radicals can be state-selectively detected using a laser induced fluorescence scheme at the end of the decelerator and in the region between the first two modules. In the top inset, a photograph of a decelerator module is shown. Reprinted with permission from ref 147. Copyright 2008 American Physical Society.

Figure 23. Scheme of the experimental setup. A pulsed beam of OH radicals is produced via photodissociation of HNO₃ seeded in Xe, Kr, or Ar. The beam of OH radicals passes through a 2.6 m long Stark decelerator that consists of three modules of ~100 stages each. The OH radicals can be state-selectively detected using a laser induced fluorescence scheme at the end of the decelerator and in the region between the first two modules. In the top inset, a photograph of a decelerator module is shown. Reprinted with permission from ref 147. Copyright 2008 American Physical Society.

Figure 24. Time-of-flight profiles of OH radicals, recorded at the exit of the 316 stage Stark decelerator. The Stark decelerator is operated at the s = 3 mode and accelerates (curve a), guides (curve b), or decelerates (curve c) a packet of OH radicals with an initial velocity of 350 m/s. The TOF profiles that result from simulations of the experiment are shown underneath the experimental profiles. Reprinted with permission from ref 147. Copyright 2008 American Physical Society.

from each other. The first two modules consist of 104 electrode pairs (i.e., 103 electric field stages) each, whereas the last module contains 109 electrode pairs. These electrode pairs consist of two parallel 4.5 mm diameter stainless steel electrodes that are placed symmetrically around the molecular beam axis, providing a 3 mm gap for the molecular beam to pass through. Adjacent electrode pairs are alternately horizontally and vertically oriented, such that a 3 mm² opening area remains for the molecular beam. The electrodes of all horizontal (vertical) pairs within each module are electrically connected and switched simultaneously to high voltage. The center-to-center distance (L) of electrodes of adjacent pairs is 8.25 mm, and the three modules are carefully aligned to also maintain this distance between the electrode pairs of adjacent modules. The first and last eight electrode pairs of each module are mounted on conically shaped rods, as shown enlarged in Figure 23. This design provides excellent optical access for fluorescence collection in between adjacent decelerator modules. It also allows the exit of the Stark decelerator to be brought close to the detection region.

The electric field in the decelerator is switched back and forth between two different configurations, as discussed in section 5.2. In each configuration, the opposing electrodes of every other electrode pair are at ±20 kV, while the remaining electrodes are grounded. Switching between the two configurations is performed using fast air-cooled high voltage switches (Behlke HTS 301-03-GSM). To minimize the power dissipation per switch, each module is connected to four separate high voltage switches. Each switch is connected to its power supply via a 0.5 μF capacitor bank, limiting the voltage drop during a deceleration cycle to less than 5%.

The OH radicals can be state-selectively detected using an off-resonant laser induced fluorescence (LIF) detection scheme at two different positions along the beamline. The first detection zone is located between the first two modules, and the second one is 18 mm downstream from the last module, enabling the detection of OH radicals after 103 or 316 electric field stages, respectively. The 282 nm radiation of a pulsed dye laser crosses the molecular beam in either one of the detection regions at right angles and saturates the (spectroscopically not resolved) Q₂₁(1) and Q₂₃(1) transitions of the A²Σ⁺, v = 1 ← X²Π, v = 0 band. The fluorescence occurs predominantly on the A²Σ⁺, v = 1 ← X²Π, v = 1 transition around 313 nm. Stray light from the laser is minimized by passing the laser beam through light baffles between the entrance and exit windows, and by optical filtering in front of the photomultiplier tube (PMT).

The performance of the Stark decelerator can be studied by recording the time-of-flight (TOF) profile of the OH radicals exiting the decelerator, that is, by scanning the timing of the detection laser relative to the dissociation laser. Alternatively, the phase-space distribution of the molecules can be studied inside the decelerator by propagating a laser beam along the molecular beam axis, and by performing spatially resolved LIF detection from there. The latter strategy has been implemented by Jun Ye and co-workers at JILA, also using the OH radical. In Figure 24 is shown the intensity of the LIF signal of a beam of OH (j = 3/2) radicals seeded in Xe as a function of time after firing the dissociation laser using different deceleration sequences. The OH radicals are detected using the second LIF detection unit, and the Stark decelerator is operated in the s = 3 mode. In curve b, the TOF profile is shown that is obtained when the decelerator is operated at a phase angle of φ₀ = 0°, corresponding to guiding a packet of OH radicals at a constant velocity. A packet of OH radicals with a mean velocity of 350 m/s is selected, transported through the 2.6 m long decelerator, and arrives in the detection region some 7.6 ms after its production, with a fwhm of the arrival time distribution of 25 μs. The measurements shown in curve a are obtained with the decelerator operating at a phase angle of φ₀ = −50°, accelerating a packet of OH radicals from an initial velocity of 350 m/s to a final velocity of 544 m/s. There is no signature of the part of the molecular beam that is not accelerated. This is also expected as the electrodes of the decelerator are switched to ground when the accelerated packet exits the decelerator, about 1.5 ms before the remainder of the beam pulse would
Figure 25. Time-of-flight profiles of OH radicals that exit the Stark decelerator using the $s = 1$ and $s = 3$ modes of operation. The OH radicals are detected after 103 and after 316 electric field stages for $s = 1$ and $s = 3$, respectively. The measurements are recorded under otherwise identical conditions and are shown on the same vertical scale. The beam of OH radicals has a mean initial velocity of 350 m/s. The mean final velocity of the molecules and the phase angle used are indicated for selected profiles. Reprinted with permission from ref 147. Copyright 2008 American Physical Society.

For many applications of Stark-decelerated beams, the density of the packets of molecules that can be obtained is a critical parameter. In this respect, it is important to realize that the Stark decelerator merely selects a subset of the molecules from a molecular beams pulse, and subsequently manipulates the velocity and velocity distribution of this packet. For the success of experiments employing Stark decelerators, the initial molecular beam parameters are therefore equally important as the appropriate implementation of the Stark deceleration technique itself. Depending on the molecular species and the final velocity of the packet of molecules, densities that are typically reached for decelerated packets of molecules range from $10^6$ to $10^9$ molecules cm$^{-3}$. From Stark deceleration and trapping experiments in our laboratory, we know that the highest densities can be obtained for the molecules ND$_3$ and CO (a$^3$II). The density of decelerated OH beams, although often used in deceleration and trapping experiments, is already 1–2 orders of magnitude less, while decelerated beams of NH (a$^3$Δ) radicals are yet somewhat less intense.

5.6. Nonadiabatic Transitions in a Stark Decelerator

It is essential that molecules remain in the same quantum state throughout the deceleration process. To achieve this, the orientation of a molecule needs to adiabatically follow the field. This effect has been studied theoretically by Schwettmann et al.$^{151}$ for (a)symmetric tops, focusing on traversals of avoided crossings that can turn a weak-field seeking state into a high-field seeking state. Adiabatic traversals of avoided crossings between the Stark states of Ar atoms in a Rydberg state have been studied experimentally by Vliegen et al.$^{132}$ Wall et al.$^{75}$ studied the effect of switching the field both theoretically and experimentally. When the decelerator is switched from one configuration to the other, the electric field changes in magnitude and direction, and this can drive the molecules to other M states, some of which are high field seeking. The transition probability depends on how the rotation rate of the field vector compares to the splitting between neighboring $M$ states of the molecule, and Wall et al. studied this effect quantitatively. To ensure adiabatic behavior, the electric field in
the decelator should always be large enough that the minimum splitting between states greatly exceeds the maximum rotation rate. This can be achieved by applying a bias electric field and choosing switching rise and fall times that are as slow as possible while still being compatible with efficient deceleration. For molecules that have degenerate quantum states in zero electric field, like diatomics in a $\Sigma$ electronic state, the loss due to nonadiabatic transitions can be significant. Wall et al. showed, however, that the transition probability is a strong function of the position in the decelator and that the decelerated bunch, in particular, tends to be immune to nonadiabatic transitions. This is because these molecules are always in a large field when the decelator switches, which is particularly true when the synchronous phase angle is large. This is illustrated in Figure 26 where time-of-flight profiles of LiH molecules are shown that are decelerated from an initial speed of 420 m/s to a final speed of 213 m/s using a phase angle $\phi_0 = 51^\circ$. (a) Lower trace, experimental data. (b) Middle trace, simulation including nonadiabatic loss. (c) Top trace, simulation for the adiabatic case. In all cases, the signal is normalized to that obtained in dc mode. The traces are offset for clarity. Reprinted with permission from ref 75. Copyright 2010 American Physical Society.

LiH molecules are shown that are decelerated from an initial speed of 420 m/s to a final speed of 213 m/s. The experimental time-of-flight profile is only reproduced well by numerical trajectory simulations if the probability for nonadiabatic transitions is appropriately taken into account. Similar results were obtained for CaF molecules that were guided ($\phi_0 = 0^\circ$) through the decelator.75

For molecules that are not in $\Sigma$ states, effects like $\Lambda$-doubling that lift the degeneracy of states at zero electric field can significantly suppress the probability of nonadiabatic transitions. For the molecules OH and ND$_3$, loss of molecules in the Stark decelator due to nonadiabatic transitions is therefore not expected.

5.7. A Stark Decelator with Traveling Potential Wells

In the Stark decelator discussed so far, switching between two static electric field configurations, synchronous with the motion of the molecules, provides effective traps in which the molecules are confined and decelerated. As discussed, molecules can be lost from these effective traps, either by parametric amplification of their transverse or longitudinal oscillations or by overfocusing of the beam. Operation of a Stark decelator on an overtone has been demonstrated to resolve the first problem, but it renders the second one, which is relevant only below a certain threshold velocity, more problematic. Alternative designs for a Stark decelator have therefore been considered, and recently a decelator in which the molecules are confined in real three-dimensional traps throughout the decelation process has been demonstrated, first on a chip$^{152}$ and then in a macroscopic ring-type decelator.153 In the following, we will discuss the electric field distribution in this macroscopic cylindrically symmetric decelator, and we will detail its actual design and operation characteristics.

As the distribution of molecules in a beam is normally cylindrically symmetric around its propagation direction, that is, the molecular beam axis, it is evident that a decelator design that produces a cylindrically symmetric electric field distribution around this beam axis is preferred. As a single electric field stage will, for most molecules, not be sufficient to significantly influence the forward velocity, an electric field structure that is periodic along the propagation direction (taken as the $z$-direction) is needed, just as for the Stark decelators discussed so far.

Let us first evaluate the electrical potential inside an infinitely long hollow conducting cylinder. The cylinder has an inner radius given by $r_0$ and its symmetry axis coincides with the $z$-axis. In the absence of free charges, the electric potential $\Phi(r,z)$ (in cylindrical coordinates) inside the cylinder has to obey the Laplace equation $V^2 \Phi(r,z) = 0$. This partial differential equation can be solved using separation of variables. Assuming $\Phi(r,z) = \Phi(r)\Phi(z)$ results in two ordinary differential equations:

$$\frac{d^2\Phi(z)}{dz^2} + k^2\Phi(z) = 0 \tag{35}$$

$$r^2 \frac{d^2\Phi(r)}{dr^2} + r \frac{d\Phi(r)}{dr} - k^2 r^2 \Phi(r) = 0 \tag{36}$$

where $k$ is a constant. If $k$ is nonzero and real, then $\Phi(z)$ is sinusoidal, with a period length given by $\lambda = 2\pi/k$. The corresponding solution for $\Phi(r)$, assuming that the potential does not diverge on the $z$-axis, is proportional to a modified Bessel function of the first kind of order zero, that is, $\Phi(r) \propto I_0(kr)$. This function exponentially grows with its (positive) argument and starts at $I_0(0) = 1$; for values of $kr \leq 1$, $I_0(kr)$ can be approximated by $1 + (kr)^2/4$. Because Laplace’s equation is linear, linear combinations of its solutions are also solutions. Under the conditions that the potential is cylindrically symmetric, finite along the $z$-axis, and periodic with a period length given by $\lambda = 2\pi/k$, the most general solution is given by a series expansion:

$$\Phi(r,z) = \sum_{n=0}^{\infty} A_n \cos(nkz + \delta_n) I_0(nkr) \tag{37}$$

When the electric potential on the cylinder (at $r = r_0$) is given by $V_0 \cos(kz)$, all terms except where $n = 1$ are zero, and the potential is given by $\Phi(r,z) = [V_0/I_0(kr_0)]I_0(kr) \cos(kz)$. In particular, the electric potential on the beam axis will follow the potential applied to the cylinder, but is reduced by a factor $I_0(kr_0)$. The magnitude of the electric field inside the cylinder, $E(r,z)$, is then given by:
The function $I_1(kr)$, which is obtained as the derivative of $I_0(kr)$, is the modified Bessel function of the first kind of order one; this function also grows exponentially but starts at $I_1(0) = 0$, and $I_1(kr)$ can be approximated by $kr/2$ when $kr \leq 1$. On the molecular beam axis, the magnitude of the electric field is given by:

$$E(r = 0, z) = \frac{V_0k}{I_0(kr_0)} |I_1(kr)|$$

implying that there will be two electric field minima per period of the potential that is applied to the cylinder. Note that these electric field minima are at positions where the potential applied to the cylinder is maximum. The $r$-dependence of the electric field strength at the position of the electric field minima ($z = 0$) is given by:

$$E(r, z = 0) = \frac{V_0k}{I_0(kr_0)} I_1(kr)$$

From these two expressions for the electric field strength, it is seen that near perfect quadrupole electric traps are created on the molecular beam axis. In these traps, the electric field gradient in the $z$-direction, which is twice as strong as the gradient in the radial direction, is given by $V_0k^2/I_0(kr_0)$. As an example, we consider a hollow cylinder with an inner radius of 2 mm to which a periodic voltage with a peak amplitude of 10 kV and with a period length of 12 mm is applied. In this case, $I_0(kr_0) \approx 1.25$, and an electric field gradient of about 220 (kV/cm)/cm is produced along the $z$-axis, near the center of the traps.

In the actual implementation of the traveling wave decelerator, a periodic ring-electrode structure is constructed to sample the sinusoidally varying electric potential along the $z$-axis. The numerically calculated electric fields in such a ring-electrode decelerator are shown in Figure 27. When $N$ ring-electrodes are used to sample a full sine-wave, the required potential on the individual electrodes can be expressed as

$$V_0(t) = V_0 \sin(-\phi_0(t) + 2\pi n/N)$$

where $n$ is an integer numbering the electrodes, and $\phi_0(t)$ is the time-dependent phase offset. When $\phi_0(t)$ is constant, there is a static array of electric field minima on the molecular beam axis. By synchronously modulating the voltage on each of the electrodes, the traps are continuously translated along the decelerator structure. A linear increase of $\phi_0(t)$ with time shifts the traps with a constant speed along the cylinder axis. The time-dependence of the phase offset can be expressed as

$$\phi_0(t) = 2\pi \int_0^t f(\tau) d\tau$$

where the frequency $f(\tau)$ is the modulation frequency of the voltage on each individual electrode. Because one oscillation of the waveform moves the trap over one period, the instantaneous velocity of the traps is given by $\lambda f(\tau)$. Chirping the frequency leads to acceleration or deceleration of the traps. For deceleration experiments, the molecules are picked up at their source, and they remain trapped in three dimensions the entire time, until they are released from the decelerator at the desired velocity. Both guiding of metastable CO molecules at a constant velocity through this ring-decelerator and decelerating them from 288 to 144 m/s has been demonstrated. Trapping the molecules in stationary electrostatic traps can be achieved by simply bringing the moving traps to a standstill.

Although the sinusoidally varying electric potential is sampled only at discrete points in this setup, the basic features of the electric field traps as discussed for the hollow cylinder are almost quantitatively reproduced. It is seen in Figure 27 that the hollow cylinder with $r_0 = 2$ mm and $\lambda = 12$ mm used as an example above can be well approximated when $N = 8$ ring-electrodes with a thickness of 0.6 mm are used to sample a full sine-wave; the value of about 110 (kV/cm)/cm for the gradient of the electric field strength in the radial direction near the trap center mentioned earlier can be read off from panels A and C.

The accuracy with which the arrangement of discrete electrodes can reproduce the ideal sinusoidal potential can be determined by expanding the numerically calculated potential in terms of eq 37. When the potential is sampled with $N$ discrete electrodes, the first nonzero term after $n = 1$ occurs for $n = N - 1$. In other words, larger numbers of electrodes push
the errors in the potential to higher orders. The field distribution produced by a larger number of electrodes per period alone is not necessarily better: in optimizing the number of electrodes, it was found that, while keeping all other parameters the same, a decelerator with 8 electrodes per period performs better than one with 12 and also one with 6, while a decelerator with 10 electrodes per period performs about the same. With constant electrode thickness, a higher periodicity leads to reduced gaps between the electrodes, and the distortions to the field at the wall of the cylinder caused by the $n = N - 1$ term actually increase, despite being of higher order. When going from 8 electrodes to 6, these distortions do not decrease further, but the strength of the $n = 1$ term decreases, resulting in weaker fields around the central axis.

The traveling wave decelerator compares favorably with the conventional Stark decelerator (operating in the $s = 1$ or $s = 3$ modes) in terms of phase-space acceptance and deceleration rates.\textsuperscript{153} It is important to note, however, that this larger acceptance refers to the total 6D acceptance, that is, the product of the longitudinal and transverse phase-space acceptances. This larger acceptance is obtained mainly in the transverse dimension; the longitudinal acceptance is actually significantly smaller than in a conventional Stark decelerator. The larger deceleration rates at reduced electric field strengths enable the deceleration of molecules that were not previously accessible: heavy diatomic molecules, of great interest in precision spectroscopy studies, possess a rotational structure that leads to avoided crossings between neighboring states even at moderate electric fields. In conventional decelerators, the field strengths need to be so high that all of the lowest rotational states of these molecules become high-field seeking. For high-field seeking states, deceleration is only possible using the alternating-gradient principle, which is very sensitive to the alignment of the electrodes. In the traveling wave decelerator, the electric field magnitude in the stable region of the traps does not exceed about 40 kV/cm, which is below the first avoided crossing for several of the low rotational states in many of these molecules. Despite the reduced electric field strengths, the deceleration is efficient due to the relatively strong field gradients in the traps and because the trapping and deceleration forces act continuously on the molecules in the comoving traps.\textsuperscript{79,153}

### 5.8. The Alternating Gradient Decelerator

In the decelerators discussed in the previous sections, polar molecules in low-field seeking states are decelerated by letting them fly from a region of low electric field into a region of high electric field. Transverse stability is achieved by using an electrode geometry that produces a minimum of the electric field on the molecular beam axis, thereby continuously focusing the beam. It might appear straightforward to apply the above method to molecules in high-field seeking states by simply letting the molecules fly out of, instead of into, the region of a high electric field. For the motion of the molecules in the forward direction, this is indeed true. However, Maxwell’s equations do not allow for a maximum of the electric field in free space,\textsuperscript{41} for example, on the molecular beam axis. Therefore, transverse stability cannot be maintained easily; molecules in high-field seeking states have a tendency to crash into the electrodes where the electric fields are the highest. This fundamental problem can be overcome by using alternating gradient (AG) focusers,\textsuperscript{37} as discussed in section 4.5.

In Figure 28a is shown the general form of an AG decelerator. The AG lenses are formed from a pair of cylindrical electrodes to which a voltage difference is applied. The electric field that is produced by this geometry is shown in Figure 13 of section 4. Molecules in high-field seeking states will be defocused in the plane containing the electrode center lines while being focused in the orthogonal plane. As the molecules move down the beamline, the orientation of the lenses, and thus the focusing and defocusing directions, alternate. In any transverse direction, the defocusing lenses have less effect than the focusing lenses, not because they are weaker (they are not), but because the molecules are closer to the axis inside a defocusing lens than inside a focusing lens.

Molecules in high-field seeking states are accelerated while entering the field of an AG lens and are decelerated while leaving the field. By simply switching the lenses on and off at the appropriate times, AG focusing and deceleration of polar molecules can be achieved simultaneously. In Figure 28b is...
shown the potential energy along the z-axis of a single lens for a metastable CO(a^1Π, v = 0, J = 1) molecule in the MΩ = +1 high-field seeking state. The molecules enter each lens with the electric fields turned off so that their speed is not influenced. The fields are then suddenly turned on, and the high-field seeking molecules are decelerated as they leave the lens and move from a region of high field to one of low field. This process is repeated until the molecules reach the desired speed.

A prototype machine of this type consisting of 12 AG lenses has been used to decelerate high-field seeking metastable CO molecules.64 In the group of Hinds at Imperial College London, ground-state YbF molecules74 were decelerated, as illustrated in Figure 29. The transverse acceptance of this AG decelerator was determined to be about a factor of 100 smaller than for a decelerator for molecules in low-field seeking states having the same aperture.92 The acceptance can be increased by using a more sophisticated lens design consisting of four electrodes rather than two.92,156 AG deceleration of bezonitrile76 and OH radicals151 has also been demonstrated.

In recent years, it has become clear that the AG decelerator is particularly sensitive to mechanical misalignments of the electrode array. In combination with the nonlinear focusing terms in the AG fields, this can result in high losses in the number of molecules that are transported through the decelerator. The groups that are working on the deceleration of molecules like YbF have redirected their research efforts in looking for alternatives to produce slow molecular beams of the species in which they are interested.156

5.9. The Zeeman Decelerator

Triggered by the desire to extend the range of species that can be manipulated and decelerated, the magnetic analogue of the Stark decelerator has been developed over the past few years. Using time-dependent, inhomogeneous magnetic fields, the Zeeman decelerator manipulates longitudinal and transverse motions of neutral atoms and molecules possessing a magnetic dipole moment. In particular, the Zeeman decelerator can control particles with unpaired electrons and is therefore of particular interest for studies of the spectroscopic and chemical properties of radicals at low temperature.57

5.9.1. Multistage Zeeman Decelerators. Vanhaecke and co-workers at the ETH Zürich first demonstrated Zeeman deceleration by decelerating ground-state hydrogen atoms.86 Their setup consisted of a seeded supersonic beam of atomic hydrogen, passing through a series of six solenoids, centered on the beam axis, as shown in Figure 30. Time-of-flight profiles were recorded using laser excitation into a Rydberg state and pulsed-field-ionization at the end of the decelerator. Each solenoid consisted of a 5 mm inner diameter coil, with a 7.8 mm extension along the beam axis, and the solenoids were arranged in a periodic structure of 11 mm period, as shown in Figure 30.
velocities, as well as for several currents, which confirmed the robustness of the operation of the Zeeman decelerator. In addition, Hogan et al.\textsuperscript{87} pointed out the importance of keeping the quantization axis of the magnetic quantum number \( M_F \) (\( F \) being the total angular momentum including the nuclear spin) well-defined throughout the Zeeman deceleration process. As the time delay between the switch-off time of one solenoid and the switch-on time of the next one increases, the magnetic field dropped more and more between the pulses, and eventually vanished. Therefore, the probability of a \( M_F \)-changing transition increased with this time delay, leading to a redistribution of the population among the magnetic sublevels. Hogan et al.\textsuperscript{87} found that with their setup, if the time delay exceeded 3 \( \mu s \), the redistribution became significant and blurred the experimental time-of-flight profiles. Consequently, subsequent magnetic field pulses should slightly overlap in time.

A similar setup has been developed independently by Narevicus et al. at the University of Texas at Austin, Texas.\textsuperscript{158,159} The Zeeman decelerator constructed in the Austin group consisted of a series of solenoids, located on the atomic beam axis, 14 mm from each other. These solenoids had a bore diameter of 3 mm and were encased in a steel shell between two Permendur disks. Permendur is a magnetic alloy, which possesses a high saturation point (2.3 T) that allowed the Austin group to produce a maximum magnetic field of 3.6 T at the center of a solenoid fed with a current of 400 A. After the switch-on of a coil, the current took about 35 \( \mu s \) to reach its nominal value. After the switch-off, the magnetic field decreased by only 65\% in 6 \( \mu s \) even though the current fell to zero within that time. This is a consequence of the presence of the metal shell and the Permendur disks. After this, the magnetic field falls off exponentially with a time constant of 11 \( \mu s \) due to eddy currents, or the rate of demagnetization of the permendur. With a decelerator using this type of coil, Narevicus et al.\textsuperscript{159} demonstrated the deceleration of metastable neon atoms. A supersonic beam of metastable neon atoms with a mean velocity of 470 m/s was produced by using a liquid-nitrogen cooled Even-Lavie nozzle\textsuperscript{160} in combination with an electric discharge at the exit of the nozzle. After passing through a skimmer, the beam passed a series of 18 solenoids as described above, which could all be fed with independent currents. Using currents of 400 A, the deceleration of metastable neon from an initial velocity of 461 m/s to a final velocity of 404 m/s was reported, thereby removing 23\% of the initial kinetic energy of the atoms. Note that the phase angle used in this experiment needed to be constrained below 30\(^\circ\), which was imposed by the long switch-off time of the magnetic field.

To further decelerate the same beam of metastable neon atoms, the Austin group has extended the decelerator from 18 to 64 magnetic stages.\textsuperscript{88} With increased currents of 750 A, a maximum magnetic field of about 5.2 T was produced at the center of the coils. By tuning the phase angle at which the decelerator was operated, Narevicus et al.\textsuperscript{88} could control the final velocity of the decelerated cloud, ranging from 447 to 55.8 m/s. With this setup, operation of the decelerator at a slightly higher phase angle would bring the same beam to rest in the laboratory frame.

The same Zeeman decelerator has been used by the Austin group to slow molecular oxygen.\textsuperscript{90} Nuclear spin statistics restricts the rotational quantum number \( N \) of \( ^{16}\text{O}_2 \) in its \( ^3\Sigma_g^- \) electronic ground state to odd values. The electron spin couples to the rotation \( N \), splitting each rotational level into three components of distinct total angular momentum \( J \) (see section 3.4.3). The time sequence of the Zeeman decelerator was adjusted for the deceleration of the \( N = 1, J = 2, M = 2 \) sublevel, which exhibits a rather constant effective magnetic dipole moment of about 1.8 \( \mu_B \) both in the low-field region and in the medium-field region, where the electron spin does not decouple yet from the rotation (see Figure 6). After passing through the 64 coils of the Zeeman decelerator, the oxygen beam was detected by electron impact ionization followed by mass selective ion detection, about 10 cm downstream from the last decelerator solenoid. On the basis of time-of-flight measurements, Narevicus et al.\textsuperscript{90} reported the deceleration of molecular oxygen from an initial velocity of 389 m/s to selected final velocities. Figure 31 shows the full experimental time-of-

![Figure 31. Full experimental time-of-flight profile of a decelerated beam of molecular oxygen. The nondecelerated part of the beam is visible at early arrival times, and a decelerated cloud of oxygen molecules moving at 114 m/s arrives around 6.1 ms. Reprinted with permission from ref 90. Copyright 2008 American Physical Society.](image_url)
the nonperiodic potential energy $W$, the equation of motion with respect to the synchronous particle reads:

$$\frac{mL}{\pi} \frac{d^2 \Delta \phi}{dt^2} + \frac{1}{L} \left( W(\phi_0 + \Delta \phi) - W(\phi_0) \right) = 0$$

(43)

where $W(\phi)$ approximately takes a Gaussian $\phi$-dependence, $L$ is the periodicity of the coil arrangement, and $\phi_0$ stands for the phase angle. Because of the nonperiodicity of the potential (see Figure 32), even the use of phase angle $\phi_0 = 0$ results in a deceleration. In addition, the resulting shape of the separatrix differs from that found in a periodic Stark decelerator and does not exhibit any inversion symmetry even for $\phi_0 = 0$.

Wiederkehr et al.\textsuperscript{161} numerically studied the effects of three-dimensional forces on the phase-space acceptance of the Zeeman decelerator. At low phase angles, an empty halo structure appears within the separatrix. The central region is found to be non stable because of the lack of sufficient focusing forces applied to the particles, similar to the effect found earlier in the Stark decelerator.\textsuperscript{144} In addition, particles that oscillate in phase-space close to the separatrix experience a strong focusing force inside the solenoids and were found to be overfocused and lost during the deceleration process. As the phase angle $\phi_0$ increases, the phase-stable region decreases and selects particles for which the focusing and defocusing transverse forces compensate, resulting in a progressive disappearance of the unstable regions within the separatrix. Moreover, exactly like in a Stark decelerator,\textsuperscript{144} because of the transverse curvature of the magnetic field, the effective phase angle for off-axis particles exceeds the nominal phase angle (that of the synchronous particle), yielding an enhanced phase-space acceptance as compared to the one-dimensional model for phase angles above $60^\circ$.

Including finite switch-on and switch-off times of the solenoids of $8 \mu s$ in particle-trajectory simulations reveal significant changes in the phase-stable region.\textsuperscript{161} Overall, it results in an effective phase angle experienced by the particles, which is slightly higher than the nominal phase angle, as was already mentioned above. Moreover, this effective phase angle depends on the forward velocity of the decelerated bunch of particles. For phase angles above $30^\circ$, the finite rise and fall times stabilize the transverse trajectories of particles oscillating in phase-space near the synchronous particle. According to Wiederkehr et al., the finite switch-off time allows particles located outside the solenoid at the time it is switched off to nevertheless enter the solenoid within the fall time of the magnetic field and therefore to experience a net focusing force.

**5.9.3. Zeeman Decelators with Continuously Moving Traps.** In a multistage Stark or Zeeman decelerator, phase stability occurs thanks to the dynamical stabilization of trajectories. As we discussed above, this gives rise to several issues, such as losses at low velocities and coupling between longitudinal and transverse motions (see section 5.4). Alternatively, real three-dimensional confinement throughout the deceleration can be achieved by providing the particles with a comoving (decelerating) trap. The realization of this concept in the framework of Stark deceleration has been detailed in section 5.7. In the case of Zeeman deceleration, two groups have developed distinct approaches to a continuous deceleration.

A moving, three-dimensional magnetic trap with tunable velocity, provided by a traveling wave of magnetic field, has been demonstrated by Trimeche et al. in Orsay, France.\textsuperscript{89} A periodic geometry of conducting wires creates a magnetic field on the molecular beam axis, which is directed along the $\hat{z}$-axis with a $z$-dependence proportional to $\sin(kz)$, where $k = 2\pi/\lambda$ is the $z$-period of the setup. A second, similar geometry of conducting wires produces the same magnetic field $\lambda/4$ further in the $\hat{z}$-direction. By applying appropriate, modulated currents in both wire geometries, Trimeche et al.\textsuperscript{89} generate a propagating wave of magnetic field, moving in the $\hat{z}$-direction at the desired velocity. In this way, an array of moving magnetic quadrupole traps for atoms or molecules in low-field seeking states is generated, centered at the nodes of the magnetic field. In addition, an adjustable radially confining magnetic field gradient is generated by a quadrupole-like geometry of wires parallel to the beam axis. Using 500 A peak-to-peak currents at a fixed frequency of 40.00 kHz (respectively, 37.07 kHz), metastable argon atoms of a supersonic beam are trapped around a node of the generated magnetic wave moving at 464 m/s (respectively, 430 m/s). The experimental time-of-flight profiles presented by Trimeche et al.\textsuperscript{89} match well with simulated ones, thereby demonstrating the proof-of-principle of trapping in the moving magnetic trap. Chirping the frequency of the current modulation to lower values would then reduce smoothly the velocity of the trap and result in the deceleration of the trapped cloud.

The Austin group has proposed to build a Zeeman decelerator using a series of quadrupole traps,\textsuperscript{158} in a design similar to the conveyor belt used for ultracold atoms.\textsuperscript{62} Following these proposals, Zeeman deceleration of metastable neon atoms has been reported by Lavert et al. at the Weizmann Institute, Israel.\textsuperscript{163,164} A series of anti-Helmholtz coil pairs is centered on the supersonic beam axis. Each coil pair gives rise to a magnetic trap, provided that a current is fed to these coils. Subsequent pulses of current peaking at 500 A are provided to the series of traps, resulting in a moving magnetic trap. The anti-Helmholtz coils used by Lavert et al.\textsuperscript{163,164} have a bore diameter of 10.2 mm and are asymmetric, such that the front coil has twice as many windings as the back coil. This produces an asymmetric trap in the laboratory frame, which becomes symmetric in the moving frame when it decelerates at a pace of
50,000 m/s², which therefore also corresponds to the optimal operation of this decelerator in terms of phase-space acceptance. Lavert et al. have reported the deceleration of metastable neon atoms to various velocities (as low as 4 m/s) and found a very good agreement between the recorded time-of-flight profiles and the trajectory simulation data.

6. TRAPS AND STORAGE RINGS

The molecules that have been decelerated using the different techniques discussed in the previous section can be loaded into traps in which they can be confined for times up to seconds. In this section, we review the various kinds of traps that have been developed, both for low-field seeking and for high-field seeking molecules. In section 6.1, we start with a discussion of the electric field geometries that are suitable for the trapping of molecules in three dimensions. In section 6.4, we will discuss magnetic trapping fields and discuss experiments with magnetically trapped molecules.

6.1. Multipole Expansion of the Electric Field in Cylindrical Coordinates

We will start again by writing the electric field in a multipole series. In a spherical coordinate system (ρ, φ, θ) (note that we here use ρ to denote the distance to the origin (x² + y² + z²)¹/₂ in xyz as we will reserve r for denoting the distance to the origin in the x-y-plane; r = (x² + y²)¹/₂), the electric potential, $\Phi$, may be represented by a sum over spherical harmonics:¹⁶⁵

$$\Phi(\rho, \theta, z) = \sum_{L, M} a_{L,M} \rho^{L} Y_{L,M}(\phi, \theta)$$  \hspace{1cm} (44)

This multipole expansion provides a useful means for classifying electrostatic trap configurations. We are mostly interested in terms with $M = 0$, which are independent of $\theta$, and in terms with $M = L$, which are independent of $z$. We recognize the latter ones as the planar multipole fields discussed in section 4.1. The terms with $M = 0$ can be written as:¹⁶⁵⁻¹⁶⁷

$$\Phi(r, z) = \Phi_{0} + \Phi_{1} \frac{z}{z_{0}} + \Phi_{2} \left(\frac{z^{2} - r^{2}/2}{z_{0}^{2}}\right) + \Phi_{3} \left(\frac{z^{3} - 3rz^{2}/2}{z_{0}^{3}}\right) + \ldots$$  \hspace{1cm} (45)

with $z_{0}$ being a scale parameter. Here, the first term represents a homogeneous voltage, the second a homogeneous electric field, the third a quadrupole electric field, and the fourth a hexapole electric field. In a quadrupole electric trapping field, the absolute electric field is zero at the center and increases linearly away from the center. Similarly, in a hexapole electric field, the absolute electric field is zero at the center and increases quadratically away from the center. Thus, similar to the situation in section 4, a molecule with a (positive) quadratic Stark shift will experience a harmonic trapping force in a quadrupole electric field, whereas a molecule with a (positive) linear Stark shift will experience a harmonic trapping force in a hexapole electric field. For most experiments, one is only interested in having a strong confinement force, irrespective of its functional form. It can be seen that the strongest confinement force is obtained by a quadrupole field; hence most trapping experiments reported so far have employed a quadrupole trap.

6.2. Electric Traps for Low-Field Seekers

The first electrostatic trap for polar molecules was demonstrated in 2000 by Bethlem et al. using decelerated ND₃ molecules.³⁸ The trap consists of a ring electrode and two hyperbolic end-caps in a quadrupole geometry.⁴⁰ The trap was mounted directly behind the decelerator, and, through holes in the end-caps, a slow packet of molecules was loaded into the trap using the procedure that is schematically shown in Figure 33. The specific parameters in this figure apply to the OH trapping experiments of Van de Meerakker et al.⁷⁰ In this case, the Stark decelerator is programmed to produce a packet of molecules with a velocity of approximately 20 m/s. The slow beam of OH radicals is loaded into the electrostatic trap with voltages of 7, 15, and −15 kV on the first end-cap, the ring electrode, and the second end-cap, respectively. This “loading geometry” of the trap is shown on the left in Figure 33. In the loading geometry, a potential hill is created in the trap that is higher than the remaining kinetic energy of the incoming molecules. At the time that the molecules come to a standstill in the center of the trap, the trap is switched into the “trapping geometry”. In this geometry, a (nearly) symmetric 500 mK deep potential well is created in which the molecules are confined. Reprinted with permission from ref 141. Copyright 2006 Annual Reviews.
OH radicals in the trap, indicating that the molecules are confined. In the inset, the signal of the trapped OH radicals is shown on a 10 s time scale, from which a 1/e trap lifetime of 1.6 s is deduced. The efficiency of the trap loading process was later increased by feedback control optimization using evolutionary strategies, as well as by using special designs for the trap electrodes.

Electrostatic traps with other electrode geometries have been developed and tested as well. Van Veldhoven et al. have demonstrated a trap consisting of four electrodes in a hexapole geometry. By suitably choosing the voltages applied to the four electrodes, a field can be generated that (mainly) consists of a dipolar, a quadrupolar, and a hexapolar term. By combining (either adding or subtracting) the dipolar and the hexapolar terms, a double-well or a donut trapping potential can be created.

Kleinert et al. have trapped NaCs molecules in a trap consisting of four thin wires, which create a quadrupolar trapping field. The thin wires that form the electrodes of the trap allowed them to superimpose the trap onto a magneto-optical trap (MOT). In the experiment, ultracold polar NaCs molecules in the electronic ground state are created in the MOT via photoassociation, achieving a continuous accumulation in the trap.

Rieger et al. have reported an electrostatic trap consisting of five ring-shaped electrodes and two spherical electrodes at both ends. This results in a box-like potential; that is, the electric field is very flat in the center and increases rapidly toward the electrodes. The central ring electrode is made such that two quadrupole segments can be adapted, one for filling and one for extraction of the trapped gas. This trap was continuously loaded from an electrostatic quadrupole guide. Equilibration of the filling and loss rates results in a steady-state population of trapped molecules.

The main disadvantage of quadrupole traps, and other traps based on a single multipole, is that near the center of the trap, where the electric field strength is zero, molecules may undergo nonadiabatic transitions to untrapped states. These transitions are known to be a major loss-channel for paramagnetic atoms confined in a magnetic trap, but were until recently not observed for molecules confined in an electrostatic trap. Kirste et al. have trapped ND$_3$ molecules in the electrostatic analogue of a Ioffe–Pritchard (IP) trap, widely used for trapping paramagnetic atoms. The IP-type electrostatic trap can be created by adding a cylindrical hexapole field to a linear quadrupole field. In the experiment of Kirste et al., this is done by simply adding end-caps to either side of a short quadrupole focusing field. Somewhat unexpectedly, it was found that nonadiabatic transitions can be a dominant loss channel in electrostatically trapped molecules even at temperatures of tens of millikelvins. Whether this is the case depends strongly on the hyperfine structure of the molecule, and will be different from one isotopologue to the other.

### 6.3. Electric Traps for High-Field Seekers

Trapping molecules in high-field seeking states is of particular interest for two reasons: (i) The ground state of a system is always lowered by an external perturbation. Therefore, the ground state of any molecule is high-field seeking. In the ground state, trap loss due to inelastic collisions is absent, making it possible to cool these molecules further using evaporative or sympathetic cooling. This is particularly relevant as the dipole–dipole interaction is predicted to lead to large cross sections for inelastic collisions for polar molecules in excited ro-vibrational states. (ii) Molecules composed of heavy atoms or many light atoms, such as polycyclic hydrocarbons, have small rotational constants. Consequently, all states of these molecules become high-field seeking in relatively small magnetic or electric fields.

The problem of trapping molecules in high-field seeking states is essentially the same as that of focusing molecules in high-field seeking states discussed in section 4.5. Although it is not possible to generate a maximum of the electric field in free space using a combination of multipole fields of eq 44, it is possible to generate an electric field that has a saddle point by superimposing a hexapolar field with a dipolar field. In such a field, molecules are focused along one direction, while being defocused along the other. By reversing the direction of the inhomogeneous electric field, the focusing and defocusing directions can be exchanged. If this is done periodically, molecules will be further away from the saddle point along the focusing direction and closer to the saddle point along the defocusing direction, leading to a net time-averaged focusing force in all directions. Such a trap works both for molecules in high-field seeking states and for molecules in low-field seeking states. There are three possible electrode geometries that can be used to create the desired electric 3D trapping field. (i) The first is a linear AC trap. This is essentially the neutral analogue of the linear Paul trap for ions and was demonstrated with ND$_3$ molecules by Schnell et al. (ii) The second is a cylindrical AC trap. This is the neutral analogue of the Paul trap for ions. It was first proposed for neutral molecules by Peik and demonstrated with ND$_3$ molecules by van Veldhoven et al. (iii) The third is the three-phase AC trap. This is the neutral analogue of the three-phase trap for ions. It was proposed for neutral atoms by Shimizu and Morinaga and demonstrated with Rb atoms by Rieger et al.

Figure 35a schematically shows the electrode geometry of the cylindrical AC trap that has been used to trap ND$_3$ molecules. The trap has hexapole symmetry. Consequently, when positive and negative voltages are applied alternately to the four electrodes of the trap, a perfect hexapole field is obtained (see section 6.2). To create a saddle point, the voltage applied to one of the end-caps is increased, while the voltage on the other end-cap is decreased. This adds a dipole term to the electric field. If the direction of the hexapole term is reversed, the focusing and defocusing directions are interchanged. Parts b and c of Figure 35 show the strength of the electric field along the symmetry axis (z-axis) and along an axis...
perpendicular to this, respectively, when the field is either focusing along $z$ or focusing radially.

ND$_3$ molecules are loaded into the AC trap by decelerating them to a standstill while in their low-field seeking state, and by then applying a microwave pulse that pumps a fraction (about 20%) of the molecules into the high-field seeking levels. Figure 36a shows the density of ND$_3$ molecules at the center of the AC trap as a function of the switching frequency. The measurements are performed 80 ms after the molecules are loaded into the trap. The signal of the high-field seekers is scaled up by a factor of 5 to compensate for the fact that the initial density of high-field seekers is only about 20% of that of the low-field seekers.

For clarity, the signal for molecules in low-field seekers is only about 20% of that of the low-field seekers. At low frequencies of the applied field, when the field is focusing in the $r$-direction and defocusing in the $z$-direction, the density at the center stays approximately constant. The dynamic behavior of a trapped cloud of particles in an AC electric trap has been visualized via 2D absorption imaging of Rb atoms.

6.4. Magnetic Traps

Magnetic trapping of neutral particles has been proposed several decades ago, and was first realized with cold sodium atoms in low-field seeking states by Migdall et al. after laser slowing of an atomic beam. Calcium monohydride molecules have been magnetically trapped after buffer-gas cooling by Weinstein et al. In these experiments, CaH molecules are produced by laser ablation of solid CaH$_2$, and then thermalized by collisions with a helium buffer gas in a cryogenic cell at $\sim$300 mK. In the cell, superconducting magnet coils are arranged in the anti-Helmholtz configuration that allows for the trapping of CaH in low-field seeking states at sub-Kelvin temperatures. Vanhaecke et al. have demonstrated magnetic trapping of ultracold cesium molecules. The dimers are created by

Figure 36. (a) Density of $^{15}$ND$_3$ molecules in low-field seeking (lfs) and high-field seeking levels (hfs) of the $J_J K_J = 1,1$ state at the center of the trap as a function of the switching frequency. The measurements are performed 80 ms after the molecules are loaded into the trap. The signal of the high-field seekers is scaled up by a factor of 5 to compensate for the fact that the initial density of high-field seekers is only about 20% of that of the low-field seekers. (b) Spatial distribution along $z$ of $^{15}$ND$_3$ molecules in high-field seeking states after 79 (lower) and 79 1/2 (upper) cycles of the applied field. The bold lines show Gaussian fits to the distributions. Reprinted with permission from ref 174. Copyright 2006 American Physical Society.
photoassociation of ultracold cesium atoms in a magnetooptical trap, followed by spontaneous emission. The Cs$_2$ dimers in low-field seeking states of the lowest electronic triplet state $a'$, which are accumulated in the quadrupole magnetic trap. Competition between accumulation and trap losses leads to a steady-state population in the trap.

Magnetic trapping after Zeeman deceleration has been demonstrated by Hogan et al.\textsuperscript{85} Hydrogen atoms in the low-field-seeking magnetic sublevels of the electronic ground state are slowed by a 12-stage decelerator and are subsequently loaded into a magnetic trap, mounted at the end of the decelerator. In the continuation of the decelerator, two additional solenoids are mounted, which are similar to the decelerator solenoids, but made out of copper tubing. This allows for heat exchange with flowing water, thereby enabling 200 A currents to be sustained in the trap solenoids for more than a millisecond at a 10 Hz repetition rate. The magnetic trap is loaded in a similar fashion as discussed in section 6.2.\textsuperscript{58,60,70} In addition, the trap loading time sequence has been shaped such that the quantization axis of the magnetic moment remains well-defined over time, that is, such that the magnetic field experienced by the atoms never vanishes. The first trap solenoid is used as the last deceleration stage, and then the second trap solenoid stops the bunch of hydrogen atoms close to the center of the trap. The first trap solenoid is subsequently switched on again, with reversed current, resulting in two trap solenoids in an anti-Helmholtz configuration. On the basis of a measurement of the atom cloud expansion after sudden release of the magnetic trap, Hogan et al.\textsuperscript{85} could estimate the temperature of the trapped hydrogen sample to be $\sim 100$ mK.

In a modified setup in which the number of deceleration stages has been increased to 24, Wiederkehr et al.\textsuperscript{184} demonstrated the deceleration and the subsequent trapping of deuterium atoms. By stopping the deuterium atoms as close as possible to the center of the trap, subsequent oscillations of the atomic cloud in the trap could be reduced, resulting in a colder trapped sample. A temperature of the trapped cloud of 100 mK and a density of $10^6 \text{cm}^{-3}$ have been estimated.\textsuperscript{184} The trap lifetime could not be determined, because the trapping could not be sustained longer than 4 ms.

A number of molecules, like the OH radical in its ground state, have both an appreciable Stark and Zeeman shift. Combining Stark and Zeeman devices offers enhanced possibilities to manipulate those species. Confinement of OH radicals in a magnetoelectrostatic trap,\textsuperscript{185} which consists of a pair of coils located on the beam axis combined with a electrostatic quadrupole, as well as magnetic reflection on an array of magnets,\textsuperscript{186} has been demonstrated after Stark deceleration of OH radicals. In the trapping experiments, the OH radicals are stopped near the center of the trap by a magnetic potential produced by operating the downstream coil at 2 kA. The coils are then switched to the anti-Helmholtz configuration to provide longitudinal magnetic confinement, while transverse confinement is ensured by the quadrupole electrode geometry. The use of permanent magnets greatly simplifies the operation of a magnetic trap after a Stark decelerator: The magnets themselves can be switched to high voltage, thereby providing a Stark potential that is used to stop the decelerated beam at the center of the magnetic trap.\textsuperscript{187} Recently, the adjustable electric field has been used in the study of low energy dipolar interactions.\textsuperscript{188}

Following the proposal by Van de Meerakker et al.,\textsuperscript{189} NH radicals have been Stark decelerated in the $a'$, optically pumped to the $X^3Σ^−$ ground state, and subsequently magnetically trapped.\textsuperscript{190} Several bunches of NH radicals have been accumulated in the magnetic trap, exploiting the irreversibility of the process.

6.5. Trapping Molecules on a Chip

The manipulation of atoms above a chip using magnetic fields produced by current carrying wires is a mature field of research.\textsuperscript{191} This field was inspired by the notion that miniaturization of magnetic field structures enables the creation of large gradients, that is, large forces and steep potential wells for atoms. For the success of the field, it has been crucial that present-day microelectronics technology makes it possible to integrate multiple tools and devices on a compact surface area. Such atom chips have been used to demonstrate rapid Bose–Einstein condensation\textsuperscript{192} and have found applications in inertial and gravitational field sensing.\textsuperscript{193} The setups can be made sufficiently robust that they can be used, for instance, in free-fall experiments.\textsuperscript{194}

Stark deceleration and trapping of molecules can also be performed using miniaturized electric field structures that are integrated on a chip. Recently, it has been demonstrated that one can trap molecules on a chip using direct loading from a pulsed supersonic beam.\textsuperscript{193,195} Upon arrival above the chip, the molecules are confined in miniaturized electric field traps that move along with the molecular beam at a velocity of several hundred meters per second.\textsuperscript{152,196} A whole array of these moving traps is subsequently brought to a complete standstill over a distance of only a few centimeters. After a certain holding time, for example, after the experiments with the trapped molecules on the chip are over, the molecules can be accelerated off the chip again.

The operation principle of the Stark decelerator on a chip, the main tool that is used to bring the molecules onto the chip as well as to bring them to the detector afterward, relies on the superposition of electric fields created by the electrodes on the chip.\textsuperscript{152,196} When two dipolar fields with different length scales and opposite directions are superimposed, a minimum of the electric field strength is created. This minimum is located at the point where the long-range dipole that dominates far from the surface is canceled by the short-range dipole that dominates close to the surface. Such a minimum of the electric field strength presents a trap for polar molecules that are in a low-field seeking quantum state. When an array of electrodes is used, an array of electric field minima can be created above the surface. The Stark decelerator on a chip that is shown in Figure 37 consists of an extended array of equidistant parallel electrodes with a length of 4 mm arranged on a flat support. The electrodes have a width of 10 μm with a center-to-center separation of neighboring electrodes of 40 μm. This structure is periodically extended over about 50 mm. Each electrode is electrically connected to the electrodes that are (multiples of) six positions further. By applying the appropriate potentials, tubular minima of electric field strength (indicated as the blue tubes in Figure 37) with a diameter of about 20 μm are generated every 120 μm. It is noted that the two ends of the 4 mm long tubular minima are closed in the present design by the fringe fields near the ends of the electrodes. These electric field minima can be continuously moved over the full 50 mm length at a constant height of about 25 μm. The temporal variation that is required for each of the six potentials to keep the electric field minima at a constant height, maintaining the shape of the minima while moving at a constant velocity, turns out to be
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...that of a magnetic conveyor belt for atoms. In the operation principle of this minimas at a speed given by 120 regime for these experiments, results in a movement of the chip, the molecules have to pass through another 50 travel closely above the chip over its full 5 cm length. At the end of the point, the molecules pass through a 50 μm high entrance slit and then travel closely above the chip over its full 5 cm length. At the end of the chip, the molecules have to pass through another 50 μm high exit slit to then fly freely to a gold surface that is positioned 6 cm further downstream. The arrival time distribution of the molecules on the gold surface is measured via recording of the Auger electrons that are emitted when the metastable CO molecules impact there. Reprinted with permission from ref 195. Copyright 2009 AAAS.

Figure 37. Schematic of the experimental setup with an enlarged view of the chip. A pulsed beam of ground-state CO molecules with a mean velocity of about 310 m/s is produced by expanding a mixture of 20% CO in krypton through a cooled valve in vacuum. Just before passing through the skimmer, CO molecules are prepared in the upper A-doublet level of the a3Π, (v′ = 0, J = 1) state by direct laser excitation from the electronic ground state. The pulsed laser is weakly focused onto the molecular beam, creating a well-defined packet of metastable CO molecules. About 19 cm downstream from the laser excitation point, the molecules pass through a 50 μm high entrance slit and then travel closely above the chip over its full 5 cm length. At the end of the chip, the molecules have to pass through another 50 μm high exit slit to then fly freely to a gold surface that is positioned 6 cm further downstream. The arrival time distribution of the molecules on the gold surface is measured via recording of the Auger electrons that are emitted when the metastable CO molecules impact there. Reprinted with permission from ref 195. Copyright 2009 AAAS.

The proof-of-principle experiments on the chip have been performed with CO molecules in the low-field seeking levels of the metastable a3Π, (v′ = 0, J = 1) state. For these molecules, the electric field minima correspond to traps with a depth of about 35 mK when a constant frequency f is applied. When the frequency f is changed linearly in time, that is, when a constant acceleration is applied, the diameter and the depth of the traps sinusoidal. Three of the potentials can always be positive, the other three always negative, and within each polarity set the potentials need to be phase-shifted by 120°. Time variation of the potentials with a fixed frequency f, which is in the MHz regime for these experiments, results in a movement of the minima at a speed given by 120 [MHz] × f [MHz]. The operation principle of this “supersonic electric conveyor belt” is similar to that of a magnetic conveyor belt for atoms. In the Stark decelerator on the chip, the molecules are confined in stable three-dimensional traps throughout the whole deceleration process. In a way, the ring-type traveling wave decelerator described in section 5.7 can be viewed as an enlarged and rolled-up version of this chip decelerator.

The proof-of-principle experiments on the chip have been performed with CO molecules in the low-field seeking levels of the metastable a3Π, (v′ = 0, J = 1) state. For these molecules, the electric field minima correspond to traps with a depth of about 35 mK when a constant frequency f is applied. When the frequency f is changed linearly in time, that is, when a constant acceleration is applied, the diameter and the depth of the traps decrease, but three-dimensional confinement is maintained up to an acceleration of about 1.5 × 10^6 m/s². Along the long axis of the trap, molecules can be lost due to nonadiabatic transitions to nontrappable degenerate states. In magnetic traps for atoms on a chip, this hole at the center of the trap is commonly plugged by adding a homogeneous magnetic field. Such an offset magnetic field, directed parallel to the long axis of the trap, can also be added in the present setup. For molecules in electric traps, however, there often exists the unique alternative solution to simply select an isotopologue with a favorable hyperfine level structure such that there is no degeneracy between trappable and nontrappable states in zero electric field. The most abundant carbon monoxide isotopologue, 12C16O, has no hyperfine structure, and the low-field seeking MΩ = −1 level of the a3Π, (v′ = 0, J = 1) state is degenerate with the M = 0 level in zero electric field, making this species susceptible to nonadiabatic transitions. In 13C16O, however, the coupling of the nuclear spin of the 13C nucleus with the orbital angular momentum results in a lifting of this degeneracy. The low-field seeking levels never come closer to the nontrappable level than about 50 MHz in any electric field, effectively preventing nonadiabatic transitions from occurring. The reduced losses for 13CO relative to 12CO in the Stark decelerator on the chip are evident from the integrated intensities of the corresponding arrival time distributions as shown in Figure 38.

Using 13CO, it has been demonstrated that a whole array of electric field minima containing polar molecules can be brought to a complete standstill on the chip. The time during which the molecules can be held on the chip is limited by the radiative

Figure 38. Arrival time distributions of 13CO (black curves) and 12CO (red curves) molecules on the detector. The time scale is relative to the time of laser excitation, and the vertical scale is in counts per microsecond and per pulse. The initial frequency of the waveforms is 2.6 MHz in all cases, capturing molecules that travel with an initial velocity of 312 m/s, and this frequency is either kept constant or ramped down linearly in time while the molecules are above the chip. Ramping down to a final frequency of 2.0, 1.4, and 0.8 MHz results in final velocities of 240, 168, and 96 m/s and corresponds to accelerations of 0.40 × 10^6, 0.70 × 10^6, and 0.89 × 10^6 m/s², respectively. In the inset, the levels of the a3Π, (v′ = 0, J = 1) state of 12CO and 13CO are shown in low electric fields. Reprinted with permission from ref 195. Copyright 2009 AAAS.

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lifetime of the metastable CO molecules, which can thus be measured directly. First experiments demonstrating that rotational transitions can be induced in the molecules trapped on the chip have recently also been performed. In all of these experiments, the density of molecules in the moving traps on the chip has been about $10^7 \text{ cm}^{-3}$. By placing the chip closer to the source or by using additional microstructured reflection and focusing elements, it is expected that this density can still be significantly increased.

6.6. Storage Rings and the Molecular Synchrotron

In its simplest form, a storage ring is a trap in which the particles, rather than having a minimum potential energy at a single location in space, have a minimum potential energy on a circle. The advantage of a storage ring over a trap is that packets of particles with a nonzero mean velocity can be confined. While circling the ring, these particles can be made to interact repeatedly, at well-defined times and at distinct positions with electromagnetic fields and/or other particles.

The most straightforward way to obtain a storage ring is by bending a single hexapole focuser into the shape of a torus, as demonstrated by Crompvoets et al. Such a ring, however, does not confine molecules along the longitudinal direction; an injected packet of molecules will spread out and eventually fill the entire ring. This problem can be overcome by breaking the symmetry of the ring.

Heiner et al. demonstrated a storage ring composed out of two half rings separated by small gaps; packets of ammonia molecules were kept together by changing the electric fields synchronously with their passage through the gaps. This is the neutral analogue of a synchrotron for charged particles. A more elaborate design for a synchrotron was published by Nishimura et al.

The main motivation for a synchrotron is its anticipated use as a low energy collider; counter-propagating molecules meet many times when they revolve around the ring. The number of times that counter-propagating packets meet scales with the number of packets in the ring, which depends on the number of segments, and the number of roundtrips that these packets make (see section 8.3).

A hexapole torus can be approximated by many short straight hexapole segments. A synchrotron consisting of 40 straight hexapoles was demonstrated by Zieger et al. The 37 mm long hexapoles are separated by 2 mm-wide gaps, while the axes of adjacent hexapoles make an angle of 9° with each other. A photograph of the resulting circular structure with 0.5 m diameter is shown in Figure 39. Below the setup, the density of ammonia molecules at the detection zone inside the synchrotron is shown as a function of time after injection. The velocity of the stored packets is 125 m/s, implying that the molecules take about 12.5 ms to complete one round trip. The zoom-in shows the TOF-profile of the molecules after completing 1025 round trips, that is, after the molecules have traveled a distance of over a mile. The measurements in Figure 39 have been performed with 13 packets being stored in the ring simultaneously. In principle, more packets could be stored, but this is limited by the fact that at least two hexapoles need to be switched off to allow for new packets to enter the ring. The density of ammonia molecules in the synchrotron is seen to decrease exponentially with time at a rate of about 0.31 per second, determined equally by collisions with background gas and excitation due to blackbody radiation in the room-temperature chamber.

7. PHASE-SPACE MATCHING

In the preceding sections, we have described the various elements, deflectors, focusers, decelerators, traps, and rings, that are used to manipulate the motion of polar molecules. In this section, we discuss how the various elements may act together to transport molecules through the machine. In particular, we will discuss how one can make sure that the phase-space density of the beam remains constant throughout the machine.

7.1. Liouville’s Theorem

Liouville’s theorem states that in a system that is only acted upon by forces that can be derived from a potential, that is, in a
system with forces that only depend on the position of the particles but not on their velocity, the number of particles per unit volume in six dimensional phase-space is conserved.\textsuperscript{205} It was shown by Ketterle and Pritchard\textsuperscript{206} that Liouville’s theorem also applies to particles in time-varying electric or magnetic fields.

Two important properties of phase-space can be inferred from Liouville’s theorem.\textsuperscript{207} First, different trajectories in phase-space do not intersect at any given instant of time. This is evident from the fact that in a system with conservative forces the initial conditions completely determine the subsequent evolution. Hence, if two trajectories would cross at a certain time, they would have the same position and momentum at that time, and their subsequent motion would be identical. Second, a boundary \( C_1 \) in phase-space, which bounds a group of particles at time \( t_1 \), will transform into a boundary \( C_2 \) at time \( t_2 \), which bounds the same group of particles. This follows directly from the first property. As a consequence, the motion of a group of particles in phase-space can be calculated by tracking the boundary of that group in phase-space. In phase-space representation, the group of particles behaves as an incompressible fluid: the shape of the six-dimensional volume can change, but the volume itself cannot.\textsuperscript{208} This has major consequences for the molecular beam experiments described in this review. The phase-space density is defined during the supersonic expansion and is not increased throughout the beamline. The velocity spread, which is a measure for the translational temperature of the molecules in the beam, can be lowered (“cooling”) but only at the expense of the number density.

Although the phase-space density cannot be increased, it can actually decrease or, more correctly, it can be diluted, when a group of molecules is transferred from one element to the next and these elements are not properly matched. Figure 40 illustrates this by showing a group of molecules being loaded in a potential well. The exact details are unimportant, but for concreteness one could think of a beam of molecules entering an electrostatic trap or a synchrotron. The panels on the left-hand side of the figure show the situation when the potential has just been switched on, while the panels on the right-hand side of the figure show the situation some time later. The red shaded area shows the position and velocity of a group of molecules, the so-called emittance of the beam. Note that the emittance may refer either to the area in phase-space occupied by the molecules, that is, a number with units of m·m/s, or to the shape of the boundary, depending on the context. The solid curves show lines of equal (potential + kinetic) energy of the molecules in the electric or magnetic trapping potential. The bold curve shows the outermost closed equipotential, the so-called separatrix. Molecules that are inside the separatrix will remain trapped in the potential. We will refer to the phase-space area enclosed by the separatrix as the acceptance. Note that with the same sloppy use of terminology as before, the acceptance may refer either to the enclosed phase-space volume or more generally to the shape of the equipotential lines.

The loading process depicted in the upper panels of Figure 40 is imperfect in three different ways: (i) The emittance of the beam is larger than the acceptance of the potential. This leads to a partial loss of molecules. (ii) The emittance and the acceptance are not centered around the same point in phase-space; that is, the average position of the beam is not at the center of the trap, or the average velocity of the beam is nonzero when the trap is switched on. As a result of this, the whole beam will (collectively) oscillate back and forth in the potential. (iii) The emittance of the beam and the acceptance of the trap do not have the same shape in phase-space; that is, the ratio of the spatial distribution to the velocity distribution of the beam is different from that of the acceptance diagram of the potential. As a result, the beam will perform a “breathing” motion in the potential well. Problem (i) leads to loss of molecules, but not necessarily to a decrease in phase-space density. Problems (ii) and/or (iii) do lead to a decrease in phase-space density, or rather to phase-space dilution. Although the area occupied by the molecules remains constant, the original phase-space distribution is in practice irretrievable, and the effective area in phase-space is increased.

The lower panels of Figure 40 show the perfect loading process. The emittance is perfectly matched to the acceptance, and the shape and volume of the phase-space distribution do not change during subsequent evolution.

To avoid the loss of phase-space density, one needs to shape the emittance properly, a process known as phase-space matching.\textsuperscript{207} Phase-space matching is performed by adding interposed elements that map the emittance at the exit of one beamline section to the acceptance of the next element. The principle of phase-space matching is shown schematically in Figure 41.

In molecular beam deceleration experiments, phase-space matching is performed using electrostatic and magnetic focusing lenses and bunchers in the transverse and longitudinal

![Figure 40](image-url). The loading of a package of molecules into a potential well with (a) imperfect and (b) perfect phase-space matching.

![Figure 41](image-url). Schematic representation of phase-space matching. The gray shaded emittance of section A is mapped onto the acceptance, or the equipotential lines, of section B using an interposed transformation section. Note that the volume in phase-space, that is, the shaded area in this two-dimensional plot, remains constant under this transformation.
dimension, respectively. For instance, in the experiments with a molecular synchrotron, a hexapole is used to match the emittance of the molecular beam to the acceptance of the decelerator. A combination of two hexapoles and a buncher is used to match the emittance of the decelerated beam onto the acceptance of the synchrotron. Electrostatic and magnetic lenses have been discussed in detail in section 4.1. In the next section, we will discuss the operation principle of a buncher.

7.2. Longitudinal Focusing of a Stark Decelerated Molecular Beam

In a buncher, a beam of polar molecules is exposed to a harmonic potential in the forward direction, that is, along the molecular beam axis. This results in a uniform rotation of the longitudinal phase-space distribution of the ensemble of molecules. By switching the buncher on and off at the appropriate times, it can be used either to produce a narrow spatial distribution at a certain position downstream from the buncher or to produce a narrow velocity distribution. Both effects have been demonstrated experimentally using a Stark decelerated beam of ND₃ molecules.¹⁰⁴,²¹⁰,²¹¹

Figure 42 shows schematically the bunching principle. When the Stark decelerator is operated at a phase angle of 70°, the decelerator, except for an overall scaling factor. The fields are switched such that the synchronous molecule spends an equal amount of time on the downward slope and on the upward slope of the potential well, and the synchronous molecule will therefore keep its original velocity. Molecules that are originally slightly ahead of the synchronous molecule, that is, molecules that are originally faster, will spend more time on the upward slope than on the downward slope of the potential well and are therefore decelerated relative to the synchronous molecule. Vice versa, molecules that are originally slightly behind the synchronous molecule, that is, molecules that are originally slower, will spend less time on the upward slope than on the downward slope of the potential well, and are therefore accelerated relative to the synchronous molecule. The calculated distribution at the time that the buncher is switched on is also shown in Figure 42. In this figure, the contours of equal energy for the molecules in the potential well are shown, relative to the position in phase-space of the synchronous molecule. As the potential well is approximately harmonic, the phase-space distribution of the molecules rotates uniformly. When the buncher is switched off, the slow molecules are ahead while fast molecules are lagging behind, leading to a longitudinal spatial focus at some position downstream. The angle over which the packet is rotated, and thus the exact position where the packet will come to a spatial focus, can be changed by varying the voltage on the buncher electrodes or by varying the duration that the buncher fields are on.²¹¹ Similar to the situation in optics, the magnification of the distribution is determined by the distance from the decelerator to the buncher divided by the distance from the buncher to the detection zone.

8. APPLICATIONS AND OUTLOOK

The controlled molecular beams that are produced with the techniques outlined above can be used for a number of applications. Slowly moving molecules, for instance, are ideally suited for high-resolution spectroscopy and metrology, taking advantage of the increased interaction times. These beams also enable novel molecular beam collision studies, in particular, the study of (in)elastic collisions and scattering processes as a function of collision energy. Trapped samples of neutral molecules can be used to measure lifetimes of metastable states, which is of particular relevance for free radicals, for which basically no other reliable methods exist to obtain this information. These samples of cold molecules also provide good starting conditions for the application and testing of various cooling schemes to produce samples of ultracold molecules. In the following sections, examples of these applications are given, and future prospects are discussed.

8.1. High-Resolution Spectroscopy and Metrology

Ultimately, the precision in any spectroscopic measurement is limited by the interaction time of the particle to be investigated with the radiation field. In conventional molecular beam experiments, this interaction time is typically a few hundred microseconds. The ability to produce slow molecular beams significantly enhances the obtainable interaction time and hence resolution. The improved resolution can potentially be used for stringent tests of fundamental physics theories.

As a proof-of-principle experiment, high-resolution microwave spectroscopy was carried out on Stark-decelerated beams of ¹⁵ND₃,²¹² and OH²¹³ molecules. Figure 43a shows the setup used by Hudson et al.²¹³ Figure 43b shows Ramsey fringes recorded on the transition between the F = 2 hyperfine states of...
obtained in atoms is far better than the precision obtained in molecules, in a number of cases this is compensated by the fact that the structure (and symmetry) of molecules makes them inherently more sensitive.

For instance, the most stringent limit on time-symmetry violating interactions leading to a permanent electric dipole moment of the electron (EDM) is set by an experiment on YbF.\textsuperscript{53} Using the dipolar molecule YbF instead of the spherical Tl atom previously used in these tests has two great advantages. First, at the modest operating field used by Hudson et al., the interaction energy of YbF is, due to the electric dipole moment, 220 times larger than that obtained using Tl in a much larger field. Second, the motional magnetic field, a source of systematic error that plagued the Tl experiment, has a negligible effect on YbF. Because of these advantages, it was possible to improve on the Tl experiment by using YbF molecules, even though the molecules are produced in much smaller numbers.\textsuperscript{53}

The possibility of improving the resolution of the EDM experiment by the use of cold molecules has been an important motivation for the work on AG deceleration\textsuperscript{74} as well as for the work on cryogenic molecular beam sources currently in progress at Yale and Harvard.\textsuperscript{213} It should be noted, however, that the actual implementation of cooling techniques in the EDM-experiment is extremely demanding, as discussed, for instance, by Tarbutt et al.\textsuperscript{156} Heavy molecules are also considered for measuring nuclear spin-dependent parity violation,\textsuperscript{216,217} and in the search for a difference in transition frequency between chiral molecules that are each other’s mirror image.\textsuperscript{218–220} Polar molecules may also be used to test the time-variation of the fundamental constants, and in particular of the proton-to-electron mass ratio, \( \mu \). For instance, the inversion invariance in ammonia is determined by the tunneling rate of the protons through the barrier between the two equivalent configurations of the molecule and is exponentially dependent on the reduced mass, which is closely linked to the proton-to-electron mass ratio.\textsuperscript{212,214} Even larger sensitivities to variations of the fundamental constants occur for transitions between accidentally degenerate levels that have a substantially different dependence on the fine-structure constant \( \alpha \) and/or on \( \mu \). This enhanced sensitivity forms the basis of an experiment that is currently being performed on Dysprosium to test the time-invariance of \( \alpha \).\textsuperscript{221} In molecules, accidental degeneracies are ubiquitous, and a number of suitable candidate molecules have been identified,\textsuperscript{222,223} including molecules such as metastable CO\textsuperscript{224} and methanol\textsuperscript{225} that can be cooled with the techniques discussed here.

8.2. Collision Experiments

Interesting applications of controlled molecular beams can also be found in scattering experiments. In conventional molecular beam scattering experiments, the most serious limitations to obtain ever higher collision energy resolutions and to accurately measure inelastic scattering channels are the velocity and angular distributions of the molecular beams and the population distribution over the various quantum states, respectively. The ability to manipulate the 3D velocity distribution of molecules with electric and magnetic fields prior to the collision offers the possibility of studying molecular encounters under well-controlled and unexplored conditions and enables scattering experiments in which molecular interaction potentials are probed in unprecedented detail.\textsuperscript{226}

8.2.1. Crossed Beam Scattering Experiments. The first scattering experiment using Stark decelerated molecules was

![Figure 43. High-resolution spectroscopy using Stark-decelerated beams. (a) Schematic diagram of a microwave spectroscopy experiment at JILA in which a beam of OH radicals is Stark decelerated to 200 m/s, and interrogated in a 10 cm-long microwave cavity. (b) Ramsey microwave spectroscopy for the transition between the \( F = 2 \) hyperfine states of the two \( \Lambda \)-doublet components of the rotational ground state of the OH radical with 0.2 ms pulse separation time. Reprinted with permission from ref 213. Copyright 2006 American Physical Society.](image)
performed in 2006 by Gilijamse et al. In this experiment, a Stark decelerated beam of OH radicals was scattered with a conventional beam of Xe atoms in a crossed molecular beam geometry. By changing the velocity of the OH radicals from 33 to 700 m/s using the Stark decelerator, while the velocity of the Xe atoms was kept fixed at 320 m/s, the total center-of-mass collision energy in this system could be varied from 50 to 400 cm$^{-1}$. Studies of this kind had thus far only been possible by crossing molecular beams under a variable angle. With Stark decelerated beams, these experiments can be performed with a high energy resolution in a fixed experimental geometry. As the deceleration process is quantum-state specific, the bunches of slow molecules that emerge from the decelerator are extremely pure, and quantum state purities of better than 99.5% can be reached. The state-to-state rotational inelastic scattering cross sections were measured for a number of scattering channels as a function of the collision energy. The collision energy was varied over the energetic thresholds for inelastic scattering into the first excited rotational levels of the F$_1$(X$^2\Pi_{3/2}$) and the F$_1$(X$^2\Pi_{1/2}$) spin–orbit manifolds are shown in the top and bottom rows, respectively. The relative cross sections that result from quantum close-coupled calculations based on recent high-quality ab initio OH-Ar PES’s are given by the solid curves. Reprinted with permission from ref 229. Copyright 2010 RSC Publishing.

This benchmark experiment clearly demonstrated the feasibility of the approach; however, the sensitivity of the experiment was limited by the rather low number densities of the decelerated OH radicals. An improved Stark decelerator, exploiting the $s = 3$ higher-order resonance, was constructed to overcome this limitation. In 2010, Scharfenberg et al. used this 2.6 m-long Stark decelerator to scatter OH radicals with Ar atoms as a function of the collision energy. The OH(X$^2\Pi$)−Ar system is one of the benchmark systems for the scattering of open-shell radicals with rare gas atoms and has been studied both experimentally and theoretically by many groups in the past. Scharfenberg et al. showed that this improved Stark decelerator enabled state-to-state scattering experiments to be performed with a sensitivity that even exceeds that obtained in conventional crossed beam scattering experiments. In Figure 44 are shown the measured relative inelastic cross sections as a function of the center-of-mass collision energy for scattering into 13 different inelastic channels. The largest cross section is observed for scattering into the (X$^2\Pi_{3/2}$, $J = 3/2$, f) state. This $\Delta$-doublet changing collision is the only exoenergetic channel, and the relative cross section for this channel therefore approaches 100% at low collision energies. The other channels show a clear threshold behavior. The solid curves that are shown in the figure are the relative inelastic scattering cross sections that result from quantum scattering calculations, which
are seen to be in excellent agreement with the experiment.\textsuperscript{229} Recently, the same experimental approach was used to study the collision energy dependence of the state-to-state inelastic cross sections for the scattering of Stark decelerated OH radicals with He, Ne, Ar, Kr, and Xe atoms as well D\textsubscript{2} molecules.\textsuperscript{230,231}

Thus far, an energy resolution of $\geq 13$ cm\textsuperscript{-1} could be reached. This energy resolution is almost exclusively determined by the angular and velocity spreads of the rare gas atom beam, which are large as compared to the corresponding spreads of the Stark decelerated beam. A large improvement in the energy resolution would be obtained when the crossing angle between both beams is chosen optimally,\textsuperscript{232} or when the scattering partner is also brought fully under control using electric or magnetic fields.\textsuperscript{226} The latter approach has been pioneered recently in the scattering of a beam of Stark-decelerated OH radicals with a beam of hexapole state-selected NO radicals,\textsuperscript{233} which represents the first crossed beam inelastic scattering experiment with full quantum state control over both scattering partners, and with quantum state selective detection of the scattering products.

In future experiments, the experimental approaches can be further optimized to reach lower collision energies and higher energy resolutions. Sophisticated laser-based detection methods can be implemented to measure the quantum state, velocity, and angular distribution, as well as the alignment or orientation of the scattering products, and even the correlations between these variables. The extension of these methods to study molecular reactive scattering is another exciting avenue and would allow one to study elementary reactions at low collision energies, or to tune the collision energy over the reaction barrier. At low collision energies, the scattering becomes sensitive to externally applied electric or magnetic fields, allowing the unique possibility to control and steer the outcome of a chemical reaction.\textsuperscript{234,235}

### 8.2.2. Collision Studies in Traps and Storage Rings.

The advantage of the crossed beam approach is the purity of the experiment. Molecules scatter in a field-free region under well-defined and single collision conditions. In addition, the collision products are detected state-selectively, enabling the measurement of state-to-state scattering cross sections. This allows for a clear interpretation of the scattering data and enables a precise and unambiguous comparison with the outcome of theoretical calculations. The disadvantage, however, is the small interaction time of both beams and the consequent small product count rates. Longer interaction times can be obtained with experimental approaches that employ molecules that are confined in traps or storage rings. Ye and co-workers developed a trap consisting of permanent magnets to confine OH radicals.\textsuperscript{187} Collisions with the OH radicals were studied by sending supersonic beams of He atoms or D\textsubscript{2} molecules through the trap.\textsuperscript{187} Information on the total collision cross sections could be inferred from the beam-induced trap loss that occurs through elastic as well as inelastic collisions; the observed trap loss is most likely dominated by elastic scattering.\textsuperscript{256} Recent calculations by Tscherbul et al. indicate that the presence of the trapping field significantly influences the collision energy dependence of the measured trap loss.\textsuperscript{256}

Recently, collision experiments using trapped molecules have enabled studies at collision energies below 5 cm\textsuperscript{-1}. Ye and co-workers combined the Stark deceleration and trapping technique with the buffer gas cooling technique.\textsuperscript{188} A continuous buffer gas cooled beam of state-selected ND\textsubscript{3} molecules was directed via a curved hexapole through a magnetically trapped sample of OH radicals, allowing interaction times of $\sim 1$ s. The total cross section for collisional trap loss was measured at a mean collision energy of 3.6 cm\textsuperscript{-1}. A polarizing electric field was applied to the magnetic trap, and first indications for the influence of an applied field on the cross sections were observed.

Lower collision energies can be obtained if cold atoms are used as target species. Lewandowski and co-workers superimposed a sample of electrostatically trapped ND\textsubscript{3} molecules with a sample of magnetically trapped Rb atoms.\textsuperscript{237} A packet of ND\textsubscript{3} molecules was Stark decelerated and loaded into an electrostatic trap, while a cloud of cold Rb atoms was laser cooled and trapped separately by magnetic fields. Both traps were then spatially overlapped by mechanically moving the magnetic trap to the electrostatic trapping region. Collisions between the ND\textsubscript{3} molecules and Rb atoms were studied at millikelvin temperatures by monitoring the decay of the ND\textsubscript{3} density in the trap. The observed inelastic collision cross sections were larger than expected for field-free collisions. This increased collision rate was rationalized via quantum-mechanical scattering calculations on Rb–ND\textsubscript{3} collisions in the presence of an electric field. It is noted that novel collision experiments have also been conducted between atoms and molecules that are cotrapped (via buffer gas cooling) in a magnetic trap.\textsuperscript{238,239}

In Rydberg decelerators, low-energy collisions between atoms from the carrier gas of the supersonic expansions and the decelerated Rydberg atoms or molecules can occur. These collisions are actually unwanted and deteriorate the deceleration efficiency. This problem is particularly significant in Rydberg decelerators because the deceleration is strong and a large velocity slip builds up before the trailing part of the gas pulse has overtaken the decelerated molecules. This problem has been overcome by adiabatically deflecting a beam of Rydberg hydrogen atoms by 90°, before the Rydberg atoms are decelerated and trapped.\textsuperscript{240} The deflection has allowed the suppression of collisions with atoms in the trailing part of the gas pulse and enabled the study of trap loss mechanisms over extended periods of time.

Increased interaction times can also be achieved in a molecular synchrotron, as discussed in section 6.6. In Figure 45 is shown a variety of possible experimental arrangements that can be used to study collisions using a molecular synchrotron. In Figure 45a is shown the simplest arrangement, in which the synchrotron is loaded with multiple packets of molecules from adjacent pulses of a single injection beamline. The velocity of each packet is set by the Stark decelerator, allowing multiple trailing packets of molecules in the ring that overtake each other. Collisions between different species can be performed using the arrangements that are shown in Figure 45b and c. The open electrode geometry of the synchrotron allows the positioning of magnetic or optical traps for molecules or atoms in the beam path. For instance, the combination of a molecular synchrotron with a sample of ultracold atoms enables the study of collisions that are relevant for sympathetic cooling schemes in molecular traps. Collisions between different molecular species are most easily performed when two separate injection beamlines are used. In Figure 45c, an arrangement is shown to load multiple counterpropagating packets of molecules in the ring. A molecular synchrotron that is loaded with multiple counterpropagating packets of ammonia...
molecules from two Stark decelerators has just become operational at the Fritz Haber Institute in Berlin.

The longer interaction time that is offered by the synchrotron, however, is compromised by disadvantages that also apply to scattering experiments that use samples of molecules confined in static traps. In a synchrotron, the total (elastic + inelastic) scattering cross section is deduced from a measured loss of molecules stored in the ring, and it is challenging, if not impossible, to extract state-to-state cross sections from the experiment. In addition, the molecules scatter inside the trapping fields of the ring, potentially complicating the unambiguous interpretation of the scattering results.

The synchrotron technology can also be exploited for detailed studies of bimolecular state-to-state inelastic scattering in the low temperature (1−10 K) regime by merging two molecular beams. A possible experimental arrangement for this is shown in Figure 45d. A Stark-decelerated packet of molecules with a forward velocity in the 100−150 m/s range is bent using a quarter segment of a synchrotron. The synchrotron technology ensures that the trajectory of the packet is manipulated while keeping the molecules together in a compact bunch. A second beam of atoms or Stark-decelerated molecules is merged with the first beam, and the molecules can be made to interact in free flight some distance downstream from the exit of the bend. The velocities of both beams can be made slightly different from each other, providing access to collision energies as low as 1 K. This experimental arrangement allows the controlled variation of the collision energy and allows for full flexibility to control experimental parameters in the interaction region. In addition, the low collision energies are obtained with molecular beams with a relatively high forward velocity and number density; for cold collisions, an interesting alternative to traps and crossed beam geometries.

8.2.3. Surface Scattering. Molecular beams with a tunable velocity also offer new possibilities in surface scattering studies. The use of directed molecular beams to probe the interaction of molecules with well-defined single crystal surfaces is a mature field of research. Beams of state-selected molecules, in particular ground-state CO and NO molecules, are routinely used for these studies. After scattering from the surface, the internal ro-vibrational energy, the kinetic energy, and the angular distribution of the scattered molecules are probed to obtain information on the molecule−surface interaction. Although the velocity of the incoming beam of molecules can normally only be changed by changing the carrier gas or the temperature of the source, the component of the velocity perpendicular to the surface, which is assumed to be the only relevant one, can be varied by simply changing the angle of incidence of the beam with the surface. It is actually an interesting question whether changing the perpendicular component of the velocity by rotating the sample, for instance, indeed has the same effect as changing the speed of the molecules under normal incidence conditions. At very low velocities of the incoming molecules, this is most likely no longer true, and the Stark decelerator offers the possibility to experimentally address this issue.

A novel apparatus in which molecule−surface interactions can be studied using velocity-controlled molecular beams is currently under construction at the Fritz Haber Institute in Berlin, in collaboration with the group of Wodtke in Göttingen, Germany. CO molecules in the metastable a^3Π state that exit a

Figure 45. Schematic presentation of four different experimental configurations that can be used to study molecular collisions, all making use of (parts of) a molecular synchrotron. Reprinted with permission from ref 226. Copyright 2009 RSC Publishing.

Figure 46. Schematic representation of the setup as used by Willitsch et al. to study reactive collisions between Ca^+ ions stored in a linear Paul trap and a continuous beam of velocity selected CH3F molecules. Reprinted with permission from ref 244. Copyright 2008 American Physical Society.
Stark decelerator will be optically pumped back to selected ro-vibrational levels in the \( X^3\Sigma^+ \) electronic ground state. Stark deceleration, used in combination with stimulated emission pumping, thus produces fully state-selected beams of ground-state CO molecules with a continuously tunable velocity and with a narrow velocity distribution. Here, the fact that a packet of molecules stays confined throughout the deceleration process is exploited, thus enabling efficient transfer in a pump–dump scheme even if the individual optical transfer steps are separated by a long distance. The ground-state CO molecules then scatter with the temperature-controlled surface and are subsequently state-selectively detected.

### 8.2.4. Ion–Molecule Reactions

Beam manipulation methods have also been used to study ion–molecule reactions at low collision energies. In 2008, Willitsch et al. combined a source of laser-cooled ions in a linear Paul trap with a quadrupole-guide velocity selector.\(^{244}\) A schematic representation of this experiment is shown in Figure 46. Reactive collisions between trapped Ca\(^+\) ions and translationally cold CH\(_3\)F molecules were studied at temperatures \( \geq 1 \) K by monitoring the decrease of the number of Ca\(^+\) ions observed in the fluorescence images. The disappearance of individual ions could be observed as a function of the time of exposure to the flow of CH\(_3\)F, yielding directly the bimolecular rate constant of the reaction. An extension of the experimental approach for the study of low-temperature reactions with sympathetically cooled molecular ions (translational temperature \( T > 10 \) mK) was presented by Bell et al., together with first results on the charge-transfer reaction between OCS\(^+\) ions and velocity filtered ND\(_3\) molecules.\(^{113}\) Experiments to perform these studies using a Stark decelerated beam of ammonia molecules are underway.

### 8.3. Direct Lifetime Measurements of Metastable States

The long observation time afforded by a trap can be exploited to directly measure the radiative lifetime of excited rovibrational or electronic states with high precision. This was first demonstrated by Van de Meerakker et al. by monitoring the temporal decay of electrostatically trapped OH radicals in the first vibrationally excited \( X^3\Pi_{1/2} \) \( v = 1, J = 3/2 \) state.\(^{245}\) The OH radicals were prepared in this excited state via laser excitation and Franck–Condon pumping prior to the deceleration and trapping process. The measured population in the vibrationally excited state as a function of the storage time in the trap is shown in the left panel of Figure 47. From the observed exponential decay, a radiative lifetime of this state of 59.0 ± 2.0 ms is deduced, in good agreement with the calculated value of 58.3 ms.\(^{246}\) This experiment benchmarks the Einstein A coefficients in the important Meinel system of OH.

The same experimental approach has also been applied to accurately measure the electronic lifetimes of CO molecules in the metastable \( a^3\Pi \) state. CO molecules in this state can only decay to the \( X^3\Sigma^+ \) electronic ground state (the Cameron bands), and this spin-forbidden transition is weakly allowed because of spin–orbit mixing of the \( a^3\Pi \) state with \( ^1\Pi \) states.\(^{248}\) The latter process makes the lifetime of the \( a^3\Pi \) state strongly quantum state dependent. To measure these quantum state specific lifetimes, the CO molecules are laser prepared in either the \( a^3\Pi_1 \) \( (v = 0, J = 1) \) state or in the \( a^3\Pi_2 \) \( (v = 0, J = 2) \) state, both of which can be decelerated and trapped. The measured trap decay curves are shown in the middle and right panels of Figure 47, yielding lifetimes of 2.63 ± 0.02 and 143 ± 4 ms for the \( a^3\Pi_1 \) \( (v = 0, J = 1) \) and the \( a^3\Pi_2 \) \( (v = 0, J = 2) \) states, respectively. Although the absolute values of these lifetimes were not accurately known before these measurements, the ratio of these lifetimes follows from the known energy levels of the \( a^3\Pi \) state with spectroscopic precision as 1:54.7. The independently determined lifetimes of the two different quantum states are seen to agree perfectly with this ratio.

Similar trap lifetime measurements have also been performed on molecules that are magnetically trapped using helium buffer gas loading. Campbell et al. trapped NH radicals in their \( v = 1 \) first vibrationally excited state and measured the spontaneous emission lifetime.\(^{249}\) A value of 37.0 ms was measured for the NH \( (X^3\Sigma^+, v = 1, N = 0) \) state, in excellent agreement with the calculated radiative lifetime.

In these lifetime measurements, the observed population decay curves have to be corrected for the inherent trap lifetime. For this, a quantitative understanding of all trap loss mechanisms is essential. The trap losses due to optical pumping by blackbody radiation and due to collisions with the background gas have been studied by monitoring the population decay of OH and OD radicals in a room-temperature electrostatic trap.\(^{72}\) By comparing these two isotopes under otherwise identical conditions, both trap loss mechanisms, which are coupled as they both depend on the temperature, could be disentangled and quantified. The optical pumping rate by room-temperature blackbody radiation was determined as 0.49 s\(^{-1}\) for the OH radical and 0.16 s\(^{-1}\) for the OD radical. Trap loss due to blackbody radiation is thus a major limitation for the room-temperature trapping of OH radicals. Most polar molecules exhibit strong electric dipole allowed rovibrational transitions within the room temperature blackbody spectral region. In Table 3 are given the calculated blackbody pumping rates out of the specified initial quantum state for a number of polar molecules for which trapping is being pursued using the currently available techniques. If longer
trapping times are required, the trapped molecules would have to be shielded from thermal radiation.

8.4. Ultracold Molecules in Traps

The ability to confine samples of cold molecules in traps offers interesting possibilities to investigate molecular interactions and quantum collective effects at ultralow temperatures. At sufficiently low temperatures, the de Broglie wavelength of the molecules becomes comparable to, or even larger than, the interparticle separation. In this exotic regime, quantum degenerate effects dominate the dynamics of the particles, and a Bose Einstein condensate can be formed. Of particular interest for these experiments is the presence of a permanent electric dipole moment in the molecules. The anisotropic, long-range, dipole–dipole interaction is predicted to give rise to new and rich physics in these cold dipolar gases. Recently, tremendous progress in this direction has been made with ultracold samples of polar molecules that are produced via association of cold atoms.

This kind of experiment might also become possible with chemically stable molecules that are loaded into a trap from a beam, provided that methods are found to further cool the trapped molecules toward quantum degeneracy. For this, the number density of the trapped molecules needs to be made higher, and/or the temperature needs to be reduced. Several approaches have been proposed to either increase the number density of the trapped sample or reduce its temperature, or both.

8.4.1. Trap Reloading Schemes

The most straightforward way to increase the number density of trapped molecules would be the accumulation of several packets of molecules in the trap. Simply reloading the trap, however, requires opening up the trapping potential, thereby losing or heating the molecules that are already stored. Two different schemes that work specifically for the NH radical and the SO molecule, respectively, have been proposed to circumvent this fundamental obstacle.

The trap reloading scheme for NH radicals was proposed in 2001 by Van de Meerakker et al. and can be realized by producing NH molecules in the metastable aΔ state. The metastable NH radicals are slowed to a complete standstill using a Stark decelerator and are subsequently forced to decay to the XΣ- electronic ground state by exciting the spin-forbidden aΠ ← aΔ transition. In the ground state, the NH molecules are rather insensitive to electric fields, but experience a significant Zeeman shift allowing their confinement in a magnetic trap. The laser-driven spontaneous decay process effectively switches off the electric-field interaction of the molecules, enabling the accumulation of several packets of molecules in the magnetic trap, and provides a unidirectional pathway to the ground state. This reloading scheme has recently been implemented experimentally, and the subsequent loading of six packets of NH molecules in a magnetic trap has been demonstrated. A similar accumulation scheme has been proposed and implemented recently to load Cr atoms in a conserve potential from a guided atomic beam. With subsequent evaporative cooling, a Bose–Einstein condensate of Cr could thus be produced.

The accumulation of different packets in a trap has also been proposed for the SO radical. In this scheme, a beam of SO2 molecules is Stark-decelerated to rest. The cold SO2 molecules are then photodissociated, producing SO radicals and O atoms. The dissociation can be performed at the threshold, such that the SO and O fragments are produced without recoil energy. The SO radical has a electronic ground state and can be trapped magnetically. The Stark deceleration of a beam of SO2 molecules to low final velocities has been demonstrated, but the confinement and accumulation of SO radicals has so far not been reported upon.

8.4.2. Sympathetic Cooling

The phase-space density of the trapped gas can also be increased by decreasing the temperature of the molecules. Various cooling schemes have been proposed to achieve temperatures below 1 mK. One of the most promising schemes is sympathetic cooling, in which the cold molecules are brought into contact with an ultracold atomic gas and equilibrate with it via elastic collisions.

Sympathetic cooling has been used in traps of laser-cooled atomic ions to cool atomic and molecular ions and is the key process of the buffer gas cooling technique, which produces trapped atomic and molecular samples in the cold regime, which can in favorable cases be cooled further to quantum degeneracy using evaporative cooling.

To date, the applicability of sympathetic cooling to bring particles from the cold regime into the ultracold regime has been experimentally demonstrated for atomic species but not yet for molecular species. However, there have been a number of theoretical studies addressing the optimal choice of system and apparatus for sympathetic cooling of molecular species.

Sympathetic cooling of cold molecules relies on elastic collisions with an atomic coolant at ultracold temperature. Elastic collision rates must be high enough to ensure thermalization while the molecular and atomic cloud overlap. In practice, this requires that both species are trapped at the same place for long times; experiments to spatially overlap a sample of electrostatically trapped molecules with cold atoms have already been performed. Inelastic collisions can harm sympathetic cooling, however, as they result in a change of the molecular quantum state. Molecules are most easily trapped in an atomic gas and equilibrate with it via elastic collisions. Sympathetic collisions of cold molecules can harm sympathetic cooling, however, as they result in a change of the molecular quantum state. Molecules are most easily trapped in an atomic gas and equilibrate with it via elastic collisions.
covalent potential energy surfaces, introducing mechanisms for three-body recombination and inelastic losses. Recently, Lara et al. have identified general properties that an atom–diatom system should fulfill to minimize the effect of inelastic collisions. The use of a light atom, together with a small van der Waals C₆ coefficient of the atom-molecule system, would result in high centrifugal barriers and therefore inhibit some inelastic channels. In addition, a diatomic molecule in which the electronic spin is weakly coupled to the molecular axis (i.e., best described in Hund’s case (b)) would also reduce the coupling to spin-changing exit channels of the atom-molecule collision. Moreover, atom–diatom systems with an interaction potential as weak as possible are desirable and could be found by using closed-shell atomic partners, such as alkaline-earth atoms. Recent calculations by Tscherbul et al. suggest that it may be possible to create ultracold gases of polyatomic molecules by sympathetic cooling with alkaline-earth atoms in a magnetic trap.

The imidogen radical NH has received a lot of attention in the context of sympathetic cooling, and its collisional properties with a number of atomic partners have been theoretically investigated. Soldán and Hutson pioneered these theoretical studies by examining the interaction of NH(X ³Σ⁺) with rubidium atoms and pointed out the important role of ion-pair potential energy surfaces and of harpooning mechanisms in cold collisions. Later, Tacconi et al. have extended these interaction studies to the NH–Cs system and performed quantum dynamics studies of ultracold collisions of NH with Rb and Cs atoms. Collisional cross sections of NH with Cs were found to be much smaller than with Rb, disqualifying Cs as an efficient partner for sympathetic cooling. Soldán et al. have systematically investigated the interaction of NH with alkaline-earth atoms. The interaction with heavy collision partners (Ca and Sr) shows strong anisotropy, while with light partners (Be and Mg) the anisotropy is much smaller. In addition, in both the Be–NH and the Mg–NH systems, the ion-pair states are inaccessible at low collision energies. Quantum scattering calculations by Wallis and Hutson have confirmed that Mg is a good candidate atom for sympathetic cooling of imidogen radicals in a magnetic trap. Recently, ab initio calculations of the Li–NH system, followed by quantum scattering calculations, have shown that the elastic cross section greatly exceeds the total inelastic cross section, irrespective of the details of the potential energy surfaces of Li–NH. Indeed, spin-relaxation collisions induced by the strong anisotropy of the atom–diatom system are suppressed by high centrifugal barriers. Lithium could thus be an efficient ultracold atomic coolant for NH, provided that the imidogen radicals can be precooled to about 20 mK.

Lara et al. have performed quantum scattering calculations for the Rb–OH system, including the hyperfine structure of both collision partners. Although elastic cross sections were found to be large enough to ensure sympathetic cooling, equally large inelastic cross sections hamper the cooling process. Further studies confirmed that the only way to eliminate the large inelastic losses would be to remove all exoergic collision channels by producing and trapping both atomic and molecular species in their absolute ground state. Similarly, Tokunaga et al. numerically studied the sympathetic cooling of LiH molecules stored in an electrostatic trap by an ultracold Li atom cloud. They concluded that sympathetic cooling is hampered by inelastic collisions that induce dramatically high losses while the temperature of the molecular cloud goes down.

Zuchowski and Hutson have considered sympathetic cooling of NH₃ and ND₃ using alkali and alkaline-earth atoms as ultracold coolants. They have investigated the anisotropy of the interaction potential in detail, which in all cases was found to be large and is likely to induce strong rates for all energetically allowed inelastic collisions. Therefore, once again, unless both atomic and molecular species are produced and trapped in their absolute ground state, sympathetic cooling would be hampered by inelastic collisions. Note that Zuchowski and Hutson have calculated an interestingly weak anisotropy for the interaction in the Xe–NH₃ system, which thus holds promise for sympathetic cooling of ammonia. Later, Zuchowski and Hutson investigated the ultracold collisions between ammonia and rubidium atoms. Inelastic collisions were found to be smaller than expected in such a heavy atom-molecule system. Nevertheless, the elastic-to-inelastic cross section ratio is still 1 order of magnitude too small to be promising for sympathetic cooling of ammonia in low-field-seeking states. However, due to the closed-shell singlet state of ammonia, atomic spins were found to be less affected by Rb–ammonia inelastic collisions than in other systems (e.g., Rb–OH). As a consequence, sympathetic cooling might be feasible between high-field seeking states of ammonia and rubidium atoms in low-field-seeking states. Recently, Lewandowski et al. have taken the first experimental steps toward sympathetic cooling of ND₃ molecules by studying inelastic collisions between trapped samples of low-field seeking ND₃ molecules and Rb atoms (see section 8.2).

Recently, Zuchowski and Hutson investigated cold and ultracold collisions of NH radicals with N atoms in a magnetic field. Collisions between N and NH both in spin-stretched low-field-seeking states were found to be dominated by elastic processes. Sympathetic cooling of NH with cold N atoms, cotrapped in a magnetic trap, could therefore be feasible. To sympathetically cool NH to ultracold temperatures, the atom cloud should be brought first to ultracold temperatures, which could, for instance, be achieved by evaporative cooling, thanks to long, experimentally achievable trap lifetimes. However, at atomic temperatures below 1 mK, Hummon et al. found that sympathetic cooling of NH radicals would be disturbed by inelastic collisions between nitrogen atoms (both for ¹⁴N and for ¹⁵N).

Beside static traps, which can only confine low-field seeking states, optical dipole traps and microwave traps have been proposed to confine ground-state high-field seeking molecules around an electric field maximum. Inelastic collisions in such traps do not lead to trap losses and open new schemes for sympathetic cooling. Barletta et al. have proposed a method to cool optically trapped molecules by cold collisions with cotrapped, ultracold rare-gas atoms. Metastable rare-gas atoms can be laser-cooled to ultracold temperatures and subsequently be quenched to their electronic ground state. Barker and coworkers evaluated the feasibility of their method with H₂ as a benchmark molecule, and with each of the five stable rare-gas atoms. Thanks to the high optical lattice trap frequencies, atom-molecule collision rates are increased and compensate for the spatial mismatch between the “warm” molecular cloud and the ultracold atom cloud. It yields thermalization times that are within experimentally accessible trapping times, thereby offering good prospects for sympathetic cooling, especially with Ar and He atoms. These studies have been extended to the...
case of benzene molecules, yielding large cross sections, which might be exploited for sympathetic cooling. Numerical studies of sympathetic cooling of hydrogen and benzene molecules by ultracold ground-state Ar atoms have been carried out. In both cases, experimentally accessible initial density and temperature conditions can be found, which enable the sympathetic cooling of the molecular species to well below 1 mK.

Tokunaga et al. numerically studied the sympathetic cooling of LiH molecules by an ultracold Li atom cloud trapped in a standing wave microwave field. Although the details of the cooling process (cooling rate, successfully cooled molecule fraction) depend on the initial overlap of the molecular and atomic cloud, a large fraction of the molecules can be sympathetically cooled below 1 mK within a few seconds. The microwave trap therefore appears to be a suitable trap for sympathetic cooling of LiH molecules by ultracold Li atoms, and the method might apply to a broader range of atom-molecule species.

8.4.3. Laser Cooling. Another approach to decrease the temperature of the trapped gas is laser cooling, in which the molecular sample is cooled by cycling on an optical transition. Laser cooling has been the most successful method to produce samples of cold atoms, and its development led to rapid advances in this field. The extension of laser cooling to molecules has been considered almost unfeasible for a long time because of the complex molecular energy level structure that involves a large set of rotational and vibrational levels. A molecule would typically only scatter a few photons before it is pumped into an internal state that is no longer part of the cooling cycle. Rotational transitions are governed by strict selection rules, and cycling transitions can be found that are rotationally closed. Vibrational transitions, however, are governed by Franck-Condon factors that express the overlap of vibrational wave functions. For a typical molecule, the population will be distributed over a large number of vibrational levels after absorption of a photon from the cooling laser. A number of molecular species have been identified that possess an energy level scheme that may make them suitable for laser cooling, such as NH$_2$, CaH, CaF, RaF, OH, and others. Stuhl et al. identified a class of polar molecules that can potentially be cooled and trapped in a magneto-optical trap. The scheme exploits $J = J' - 1$ transitions to rotationally close the cycling transition and has been worked out in detail for the TiO molecule. Pulsed electric fields are used to mix the magnetic sublevels, such that all molecules spend some time in bright states.

A breakthrough in the experimental realization of laser cooling of molecules has been achieved recently by DeMille and co-workers. Using carefully chosen transitions in SrF that has highly diagonal Franck-Condon factors, a beam of buffer gas cooled SrF molecules was deflected and transversely cooled. The $\Delta \Pi_{1/2} \leftrightarrow \Xi \Sigma^+$ electronic transition is used as the cycling transition. Rotational branching is eliminated by driving a $N = 0 \leftrightarrow N' = 1$ transition. Two vibrational repump lasers and radio frequency sidebands of the lasers effectively close the transitions and address all hyperfine and spin-rotation quantum levels. Similar schemes could be applied to a number of diatomic molecules and are expected to result in the three-dimensional laser cooling of diatomic molecules in the near future.

Other cooling schemes that combine carefully chosen trap designs with laser excitation schemes have been proposed as well. These include optoelectrical cooling schemes based on Sisyphus-like cooling cycles in tailored electric traps, single photon cooling that is implemented in trap reloading schemes, and laser cooling using stimulated Raman transitions. Methods to cool the rotational, vibrational, and translational degrees of freedom of molecules in high Q optical cavities in which molecules scatter laser light into a resonant cavity mode are currently being investigated.

9. CONCLUSIONS

The different tools that were developed in the past to manipulate the transverse motion of molecules in a beam, dating back to the Stern and Rabi era, have proven to be crucial for developments beyond molecular physics alone. The development of decelerators, bunchers, traps, and storage rings now enable the complete control over the full three-dimensional motion of molecules in a beam. These techniques have only matured recently; experiments that were unthinkable 10 years ago seem routine by now. This improved control over molecules can be, and has been, used to advantage in a broad variety of research fields, ranging from ultrahigh-resolution spectroscopy, crossed beam (reactive) scattering, and ultracold molecule physics. These tools add a new dimension to the long and rich history of the manipulation of molecules with electric and magnetic fields and have the potential to cause a renaissance in molecular physics in the years to come.

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Notes

The authors declare no competing financial interest.

Biographies

Sebastiaan van de Meerakker (born 1977) studied physics at the University of Nijmegen, The Netherlands. For his Ph.D. research at the FOM Institute for Plasmaphysics in Nieuwegein, The Netherlands (2000–2005), he worked on the Stark deceleration and electrostatic trapping of OH radicals. As a postdoc, he joined David Chandler’s group at Sandia National Laboratories (Livermore, CA) to work on crossed beam inelastic scattering experiments. In 2006, he became a group leader at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany, where he launched a program to use Stark-decelerated molecular beams in crossed beam scattering experiments. Since 2011, he is an assistant professor at the Radboud University

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Nijmegen, The Netherlands, and develops methods to perform precise studies of molecular scattering processes.

Hendrick L. Bethlem (born 1972) studied physics at VU University Amsterdam. As a Ph.D. student at the University of Nijmegen and at the FOM-Institute for Plasma Physics in Nieuwegein, he developed and demonstrated the first Stark decelerator and used it to load ammonia molecules in an electrostatic trap. In 2002, he obtained his Ph.D. degree at the University of Nijmegen. As a postdoc at Imperial College London, he worked on techniques to decelerate heavy molecules. As a postdoc and later as group leader at the Fritz-Haber-Institut in Berlin, he was involved in several experiments on different types of traps and storage rings for polar molecules, as well as experiments to trap molecules on a chip. Since 2008, he is assistant professor at the VU University Amsterdam where he leads experiments that use cold molecules to test fundamental physics theories.

Nicolas Vanhaecke (born 1975) studied mathematics and physics at the Ecole Polytechnique in France, where he obtained his Ph.D. in 2003, with studies on formation and trapping of ultracold cesium molecules. As a postdoc, he worked on the Stark deceleration and electrostatic trapping of OH radicals at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany (2003–2005), and then he joined Frédéric Merkt’s group at the ETH Zürich to develop and demonstrate the first Zeeman decelerator for neutral paramagnetic species (2005–2006). Appointed on a CNRS research position in 2005 at the Laboratoire Aimé Cotton in Orsay, France, he launched a program on the manipulation of Rydberg atoms and of paramagnetic molecules with electric and magnetic fields. In 2011, he joined the Molecular Physics department at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin.

Gerard Meijer (born 1962) studied physics at the University of Nijmegen, The Netherlands, and obtained his Ph.D. degree from there in 1988, with spectroscopic studies on small molecules in the gas phase. As postdoc at IBM (San José, CA), he was involved in the early characterization of fullerenes. He was installed as full professor in Nijmegen in 1995, where he worked on cavity ring down spectroscopy and launched experimental methods to decelerate and trap neutral polar molecules. As director of the FOM-Institute for Plasma Physics in Nieuwegein, The Netherlands (2000–2003), he pioneered the use of infrared free electron lasers for the structural characterization of gas-phase clusters and biomolecules. Since 2002, he is the director of the Molecular Physics department at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin.

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