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Measurement of the orientation of buffer-gas-cooled, electrostatically-guided ammonia molecules

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ABSTRACT

The extent to which the spatial orientation of internally and translationally cold ammonia molecules can be controlled as molecules pass out of a quadrupole guide and through different electric field regions is examined. Ammonia molecules are collisionally cooled in a buffer gas cell, and are subsequently guided by a three-bend electrostatic quadrupole into a detection chamber. The orientation of ammonia molecules is probed using (2 + 1) resonance-enhanced multiphoton ionisation (REMPI), with the laser polarisation axis aligned both parallel and perpendicular to the time-of-flight axis. Even with the presence of a near-zero field region, the ammonia REMPI spectra indicate some retention of orientation. Monte Carlo simulations propagating the time-dependent Schrödinger equation in a full basis set including the hyperfine interaction enable the orientation of ammonia molecules to be calculated – with respect to both the local field direction and a space-fixed axis – as the molecules pass through different electric field regions. The simulations indicate that the orientation of $\sim$95% of ammonia molecules in $J_K = 1_1$ could be achieved with the application of a small bias voltage (17 V) to the mesh separating the quadrupole and detection regions. Following the recent combination of the buffer gas cell and quadrupole guide apparatus with a linear Paul ion trap, this result could enable one to examine the influence of molecular orientation on ion-molecule reaction dynamics and kinetics.

1. Introduction

A prevailing goal in the study of reaction dynamics is to develop a complete understanding of the reaction process. Studying chemical reactions under cold conditions can provide control over the internal quantum state population distribution, which typically collapses down into the lowest few levels in small molecules at temperatures $\leqslant$1 K. The long-range intermolecular forces experienced by slow-moving molecules can also affect the orientation of reactants during the collision process – and thus influence the properties of the resulting products [1,2]. Over the past half century, the development of methodologies to control the spatial orientation of reactants has seen the investigation of steric effects [3] as well as the direct measurement of "molecular-frame" photofragment distributions [4,5].

Spatially orienting molecules can allow one to control the outcome of reactive collisions. This was demonstrated in 1976, with the introduction of molecular beam scattering experiments: CH_3I molecules were state-selected using a hexapole and aligned with a static field, before reacting with K atoms. The production of KI showed a strong dependence on whether the methyl group was oriented towards or away from the K atom [6]. Orientation effects have been demonstrated under ultracold conditions with KRb molecules held in an optical lattice trap. The $2KRb \rightarrow K_2 + Rb_2$ reaction was suppressed when the dipoles of the KRb molecules were aligned, such that only unfavourable "side-by-side" collisions could occur; the reactive "head-to-tail" collisions were prevented and the reaction rate constant was significantly reduced from that recorded with no orientation of the reactants [7]. Recently, the total electronic angular momentum of O($^3P_2$), Ne($^3P_2$) and He ($^3S_1$) beams emerging from a bent magnetic guide have been found to exhibit a substantial degree of orientation to the quantisation axis – in spite of the absence of additional uniform magnetic fields after the guide [8]. A combination of weak fringe fields emanating from the guide, stray magnetic fields, and the way that the species are transmitted through the bent guide has been proposed as the cause of the observed orientation.

Electric fields serve to shift and split the energy levels of polar molecules, in addition to orienting the dipole moment of the

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species. The orientation of dipoles can be considered from a classical or a quantum mechanical perspective. Classically, molecules tend to adopt the most stable (*i.e.* lowest energy) configuration, which sees the dipole moment orient parallel to the local electric field, although the rotational kinetic energy may be sufficient to overcome the orientational force. Quantum mechanically, the orientation of the dipole is governed by the change in the rotational wave function induced by the field [9]. The electric fields in a quadrupole (or hexapole) guide enable one to state-select molecules and to orient them in the local electric field, which is not uniform in direction within the quadrupole. Typically, molecules exiting the guide enter a homogeneous field region provided by parallel electrodes. This post-quadrupole applied field adiabatically reorients the molecules from the inhomogeneous field in the quadrupole to a fixed laboratory axis, as molecules follow the direction of the local field [6]. Thus symmetric top molecules can be state-selected and oriented in the laboratory frame through the combination of a quadrupole guide and static electric fields. However, if the transmission into the homogeneous field region involves passage through a near-zero-field zone, non-adiabatic transitions could lead to loss of orientation.

In this paper, we probe the orientation of cold ammonia molecules after they exit a quadrupole guide and enter a reaction chamber, designed ultimately for the study of cold ion-molecule collisions. (2 + 1) resonance-enhanced multiphoton ionisation (REMPI) spectroscopy is employed, with the laser polarisation axis aligned both parallel and perpendicular to the time-of-flight (ToF) axis to determine the molecular orientation. The extent to which ammonia molecules can be oriented in the experimental apparatus in this work, and the conditions necessary to achieve orientation, is examined using Monte Carlo simulations. The ultimate goal is to gain control over all ion-molecule reaction parameters. While there is significant scrambling of the orientation of ammonia molecules as they pass through the different electric field regions, amendments to the experimental apparatus provide conditions appropriate for preserving the orientation of polar symmetric top molecules. This presents the exciting prospect of controlling the translational energy, rotational population distribution and orientation of polar reactants as they undergo reactive collisions with cold ions confined in a linear Paul trap.

2. Experimental methods

2.1. Experimental apparatus

The experimental apparatus, based on the design of Sommer et al. [10], has been described in Ref. [11], hence only a brief description is provided here. Ammonia molecules, either NH_3 or ND_3, are injected into a quadrupole guide after being collisionally cooled by helium buffer gas. A 20 × 40 × 40 mm (length × height × width) buffer-gas cell is attached to the second stage of a two-stage pulse-tube cryocooler. The buffer gas line thermalises with each of the nested temperature stages, and helium enters the cell at 6 K. The molecular line is thermally insulated from the cryogenic environment, with a small heating block ensuring that ammonia molecules enter the cell at 210 K. Ammonia molecules are cooled by collisions with helium buffer gas atoms in the cell, and pass out of the cell through an exit aperture. A 2 m-long three-bend electrostatic quadrupole then guides internally and translationally cold ammonia molecules (in low-field seeking states) through two differentially pumped regions and into a reaction chamber (see Fig. 1 of Ref. [11]). Previous work [11] has shown that a low rotational temperature, *ca.* 10 K, is maintained at the exit of the quadrupole guide. The transmission of the different J_K states through the quadrupole guide is discussed in detail in Ref. [11].

The quadrupole is assembled from hand-polished stainless steel rods with a circular cross section and 2 mm diameter. Voltages of ±5 kV are applied to the quadrupole electrodes, achieving maximal field strengths of up to 90 kV cm^{-1} at the electrode surfaces. After exiting the guide, molecules pass through a grounded Ni mesh covering an area with a 20 mm diameter. The ammonia molecules subsequently pass through a repeller electrode (inner diameter 25 mm) and are intersected by a REMPI laser between the repeller and extractor plates (see Fig. 1). The resulting ions are accelerated into a flight tube and onto microchannel plates (MCPs) for detection.

2.2. Orientation of molecules

Electric (magnetic) fields are commonly used to orient molecules that have a permanent electric dipole moment (magnetic moment). For a symmetric top molecule, the interaction energy between a permanent dipole, μ, and an external electric field, E, can be expressed in scalar terms as $-\mu E\langle cos\theta\rangle$, where $\langle cos\theta\rangle = KM/J(J+1)$ and θ is the angle between the dipole and the field axis [12]. J is the total angular momentum quantum number excluding nuclear spin, K is the projection of $\mathbf{J}$ onto the molecular axis, and M is the projection of $\mathbf{J}$ onto the external field axis. Hence orientation effects are molecule and state dependent. The magnitude of the electric field in the quadrupole guide, which near the axis varies linearly with distance from the axis and is approximately independent of azimuthal angle, is more than sufficient to influence the orientation of ammonia molecules (except very close to the axis).

Between the quadrupole guide and the point of ionisation – specifically, at the entrance to the mesh – the quantisation axis is rapidly rotated from the inhomogeneous electric field in the quadrupole (perpendicular to the quadrupole axis) to the homogeneous field between the repeller and extractor plates (parallel to the quadrupole axis). The extent to which ammonia molecules remain oriented to the field as they pass through these regions is dependent on the properties of the electric fields. Polar molecules typically follow the field adiabatically, and the adiabatic eigenstates can be quantized with respect to the axis of the electric field vector. The probability of a nonadiabatic transition occurring as molecules pass through different electric fields is dependent on a number of factors. Nonadiabatic transitions can occur when a molecule is not able to follow the changes in the electric field direction, such as when the frequency at which an electric field is rotated is comparable to the splitting between neighbouring M states, or when the molecule passes rapidly through a zero-field crossing, as described in Landau–Zener theory. Such situations are generally avoided inside the quadrupole guide, as the rate of rotation of the field is orders of magnitude slower than the minimum splitting between states (1.9×10^9 rad s^{-1} in ND_3, at a field of 2 kV cm^{-1}) [13]. However, in situations where the magnitude of the electric field is minimal, there is a near-degeneracy in states differing only in their orientation with respect to the electric field. At zero field, the ammonia energy levels are no longer split by the Stark effect – although the manifold is not entirely degenerate, owing to the presence of inversion and hyperfine splittings.

To maintain their orientation to the local field, molecules must follow the field adiabatically. It has been demonstrated that nonadiabatic transitions can be largely suppressed in an ensemble of trapped ammonia molecules through the use of an electrostatic trap with a non-zero field minimum at the trap centre [14]. This study also notes that nonadiabatic transitions are minimised when only the magnitude of the field – and not the direction – changes

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