PHYSICAL REVIEW LETTERS

Laser-Induced Alignment and Orientation of Quantum-State-Selected Large Molecules

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(Received 1 October 2008; published 12 January 2009)

A strong inhomogeneous static electric field is used to spatially disperse a supersonic beam of polar molecules, according to their quantum state. We show that the molecules residing in the lowest-lying rotational states can be selected and used as targets for further experiments. As an illustration, we demonstrate an unprecedented degree of laser-induced one-dimensional alignment ($\langle \cos^2 \theta_{2D} \rangle = 0.97$) and strong orientation of state-selected iodobenzene molecules. This method should enable experiments on pure samples of polar molecules in their rotational ground state, offering new opportunities in molecular science.

For many applications in physics and chemistry an ensemble of molecules all in the rotational ground state is desirable. Such targets would provide unique possibilities, for example, for manipulating the external degrees of freedom with static electric fields [1,2] or optical fields [3,4], or both [5,6]. A supersonic expansion of molecules in an inert atomic carrier gas can—to some degree—provide such a desired molecular target: At least in the case of small molecules (consisting of just a few atoms) the low rotational temperatures that are obtainable result in the population of only a few rotational states. For larger polyatomic systems rotational cooling down to or even below 1 K still leaves the molecular ensemble distributed over a considerable range of rotational states, thereby often masking quantum-state-specific effects. State selection of large molecules can be performed using inhomogeneous electric or magnetic fields. For instance, static fields have been applied to deflect polypeptides [7], whereas dynamic focusing schemes [8] have recently been used in the deceleration and state selection of benzonitrile [9] and in the selection of structural isomers of 3-aminophenol [10].

Here we exploit that the lowest-lying rotational states, and, eventually, the rotational ground state, of a polar molecule can be spatially isolated by deflecting a molecular beam with a strong inhomogeneous static electric field. The state-selected molecules are used for laser-induced alignment [4,11] and mixed-field orientation experiments [12,13]. Here, alignment refers to confinement of a molecule-fixed axis along a laboratory-fixed axis, and orientation refers to the molecular dipole moments pointing in a particular direction. The state selection leads to strong enhancement in the degree of orientation and alignment of iodobenzene molecules compared to that achieved when no deflection is used. For small molecules, state selection can be achieved using a hexapole focuser, and it has recently been suggested that this can be used for improved alignment and orientation experiments [14]. The method demonstrated here will apply broadly to both small and large polar molecules.

The possibility to deflect polar molecules in a molecular beam with an electric field was first described by Kallmann and Reiche in 1921 [15,16] and experimentally demonstrated by Wrede in 1927 [17]. As early as 1926, Stern suggested that the technique could be used for the quantum-state separation of small diatomic molecules at low temperatures [18]. In 1939 Rabi *et al.* introduced the molecular beam resonance method, by using two deflection elements of oppositely directed gradients in succession, to study the quantum structure of atoms and molecules [19]. Molecular beam deflection by static inhomogeneous electric fields has also been used extensively as a tool to determine dipole moments and polarizabilities of molecular systems ranging from diatomics over clusters to large biomolecules [7]. The present work builds on Stern's original proposal and exploits that the force experienced by a molecule from the inhomogeneous field depends on the rotational quantum state. In particular, the ground state has the largest Stark shift. Molecules residing in this state are deflected most and can, therefore, be spatially separated from molecules in other states. Our goal is to isolate and use rotational ground state molecules (or at least molecules in the few lowest-lying states) as targets for various experiments. It is crucial that the population of ground state molecules in the molecular beam is initially as large as possible since the deflection does not change the initial state distribution but merely disperses it. Therefore, the rotational temperature of the molecular beam is made as low as possible using a high-pressure supersonic expansion.
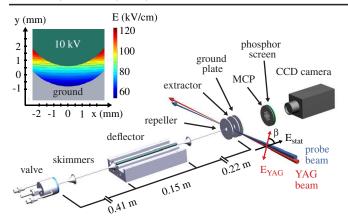
FIG. 1 (color online). Scheme of the experimental setup. In the inset, a cut through the deflector is shown, and a contour plot of the electric field strength is given.

A schematic of the experimental setup is shown in Fig. 1. About 1 mbar of iodobenzene is expanded in 90 bar of helium into a vacuum using a pulsed Even Lavie valve [20] to produce a molecular beam with a rotational temperature of ~1 K. After passing two 1-mm-diameter skimmers the molecular beam enters a 15-cm-long electrostatic beam deflector. The deflector consists of a trough (at ground potential) with an inner radius of curvature of 3.2 mm and a rod (at high voltage) with a radius of 3.0 mm. The vertical separation of the two electrodes across the molecular beam axis is 1.4 mm. This electrode geometry creates a two-wire field with a nearly constant gradient over a large area around the molecular beam axis [21]. In the inset of Fig. 1 a cross-sectional view of the deflector with the created electric field is given. The deflector is mounted such that the deflection occurs vertically, and molecules in high-field-seeking states are deflected upwards. After passing the deflector, the molecular beam enters the target area through a 1.5-mm-diameter skimmer, where it is crossed by one or two focused laser beams. One laser beam, consisting of 25-fs-long pulses (800 nm, beam waist of $\omega_0 = 21$ μm), is used to probe the molecules. In the first part of the experiment, this laser is used to characterize the deflection by determining the density at a given height in the molecular beam via photo-ionization. This laser is also used for Coulomb exploding the molecules to enable the determination of their alignment and orientation. The second laser beam, consisting of 10-ns-long pulses from a Nd:YAG laser (1064 nm, $\omega_0 = 36$ μm), is used to align and orient the molecules. For these experiments, the probe pulse is electronically synchronized to the peak of the YAG pulse. Ions produced by the probe pulses are accelerated, in a velocity focusing geometry, towards a microchannel plate (MCP) detector backed by a phosphor screen. The two-dimensional (2D) ion images are recorded with a CCD camera. The experiments are conducted at 20 Hz, limited by the repetition rate of the YAG laser.

To demonstrate the effect of the deflector we measure the vertical intensity profile of the molecular beam. This is done by recording the signal of I^+ ions, created by ionization with a circularly polarized probe pulse, as a function of the vertical position of the probe laser focus (see Fig. 2). When the deflector is turned off, the molecular beam extends over ~1.5 mm, mainly determined by the diameter of the skimmer before the target area. When the deflector is turned on, the molecular beam profiles broaden and shift upwards. The broadening and the shift become more pronounced as the voltage on the deflector is increased from 5 kV to 10 kV. In order to simulate these beam profiles, we first calculate the Stark curves for all rotational states from spectroscopic constants [22]. The Stark energies for the lowest-lying rotational states are displayed in the inset in Fig. 2. Then we perform trajectory calculations for molecular packets of individual rotational states, which yield single-quantum-state deflection profiles. These individual profiles are averaged according to the populations for various rotational temperatures. A comparison of calculated and experimental profiles yields a rotational temperature of the molecular beam of 1.0 K. The resulting calculated profiles are also shown in Fig. 2 and agree well with the observations. The calculations indicate that the most deflected molecules are indeed those initially residing in the lowest-lying rotational quantum states. In the measurements described below, experiments are conducted on these quantum-state-selected molecules simply by positioning the laser focus close to the upper cutoff region in the 10 kV profile, as indicated by an arrow in Fig. 2. Similarly, experiments can be conducted on the least deflected molecules, corresponding to molecules in
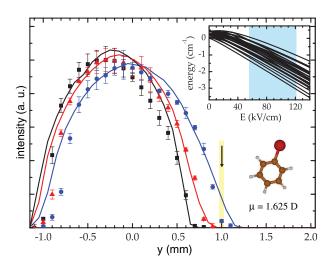

FIG. 2 (color online). The vertical profile of the molecular beam measured by recording the laser-induced I^+ signal (see text). The experimental data are shown by (black) squares (deflector off), (red) triangles (5 kV), and (blue) circles (10 kV), together with the corresponding simulated profiles. In the inset the energies of the lowest quantum states of iodobenzene are shown as a function of the electric field strength. The shaded area represents the range of field strengths present in the detector for a voltage of 10 kV. The value of the dipole moment of iodobenzene [22] is given below the molecular model.

high-lying rotational states, by moving the lens position to the lower part of the beam profile.

We now turn to studying alignment and orientation due to the ac field from the YAG pulse, E_{YAG}, and the static electric field, E_{stat}, from the spectrometer electrodes that projects the ions onto the MCP detector. The basic experimental observables are 2D images of I^+ ions recorded when the molecules are irradiated with both the linearly polarized YAG pulse and the probe pulse. The angular distribution of the I^+ ions provides direct information about the spatial orientation of the C-I bond axis of the iodobenzene molecules [4,23]. Examples of images are displayed in Fig. 3.

Image A2 is recorded with the YAG pulse linearly polarized parallel to the detector plane (vertical in Fig. 3), corresponding to an angle between E_{stat} and E_{YAG} of $\beta = 90°$. In these alignment experiments (row A of Fig. 3) the Coulomb explosion laser is linearly polarized perpendicular to the detector plane. The I^+ ions appear as angularly narrow rings. The innermost (and brightest) ring results from I^+ ions when iodobenzene is doubly ionized by the probe pulse and fragments into an $I^+ + C_6H_5^+$ ion pair, whereas the outermost ring results from I^+ ions formed from triple ionization and fragmentation into an $I^+ + C_6H_5^{2+}$ ion pair [23]. The pronounced angular confinement, quantified by $\langle \cos^2\theta_{2D} \rangle = 0.93$ (calculated from the outer ring, where θ_{2D} is the angle between the projection of the I^+ recoil velocity on the detector plane and E_{YAG}), shows that the C-I axis of the iodobenzene molecules is strongly aligned along E_{YAG}. For comparison,
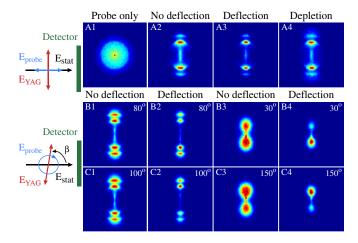

FIG. 3 (color online). I^+ ion images, recorded when the probe pulse Coulomb explodes the iodobenzene molecules, illustrating alignment and orientation. The polarization state of the YAG and the probe pulse with respect to the detector plane and the static field is shown schematically at the left. Images labeled "no deflection" are recorded at lens position $y = 0.0$ mm, "deflection" at $y = 1.0$ mm, and "depletion" at $y = -0.9$ mm, the latter two with the deflector at 10 kV (see Fig. 2). The value of β is shown for each image in row B and C. The intensity of the YAG pulse is 8×10^{11} W/cm^2 and 5×10^{14} W/cm^2 for the probe pulse. $E_{stat} = 595$ V/cm.

an image without the YAG pulse is shown (A1). As expected it is circularly symmetric and $\langle \cos^2\theta_{2D} \rangle = 0.51$. These observations are fully consistent with previous experiments on adiabatic alignment of iodobenzene [4]. When the experiment is conducted on the most deflected molecules (image A3), the angular confinement sharpens even further and $\langle \cos^2\theta_{2D} \rangle$ increases to 0.96 [24]. By contrast, when the experiment is conducted on the least deflected molecules (image A4), corresponding to the molecules in the highest rotational states, the alignment weakens and $\langle \cos^2\theta_{2D} \rangle$ decreases to 0.90.

When the polarization of the YAG pulse is rotated away from the detector plane, the up-down symmetry characterizing the images in row A is broken. This is illustrated by the images in row B and C. In these experiments, the Coulomb explosion laser is circularly polarized [25]. For images with $\beta < 90°$ (row B) more I^+ ions are detected in the lower part, whereas for $\beta > 90°$ (row C) more I^+ ions are detected in the upper part. The asymmetry becomes more pronounced as the YAG polarization is rotated closer to the axis of the static field (compare, for instance, images B1 and B3, or B2 and B4). We interpret these observations as orientation due to the combined effect of the YAG laser field and the static electric extraction field [5,6]. The orientation is expected to place the I end of the molecules towards the repeller plate (see Fig. 1), where the electrical potential is highest. For iodobenzene all states are high-field seeking. Therefore, the permanent dipole moment of the molecule, which is directed along the C-I axis from I ("negative end") towards the phenyl group ("positive end"), is oriented parallel to the electric field. Thus, for $\beta > 90°$ the I^+ ions are expected to preferentially be ejected upwards, and for $\beta < 90°$ they will be ejected downwards. This is in agreement with the up-down asymmetry on the images.

The significant improvement of the up-down asymmetry, or equivalently the orientation, obtained by using the most deflected molecules is clear by comparing image B1 with B2 (or C1 with C2) and B3 with B4 (or C3 with C4). To quantify the degree of orientation, we determine for each image the number of I^+ ions, $N(I^+)_{up}$, in the upper part of the $I^+ + C_6H_5^+$ and $I^+ + C_6H_5^{2+}$ channels (i.e., ions detected in the upper half of the images) as well as the total number of ions, $N(I^+)_{total}[= N(I^+)_{up} + N(I^+)_{down}]$. In Fig. 4 the ratio $N(I^+)_{up}/N(I^+)_{total}$ is plotted as a function of β for deflected and undeflected molecules and for two different extraction fields. The difference between the data for the most deflected molecules and the data obtained with the deflector turned off is striking and shows the advantage of selecting the lowest-lying rotational states for strongly increasing the degree of orientation. From the data for deflected molecules it is also obvious that increasing the static electric field by a factor of 2 leads to better orientation. In addition, Fig. 4 shows the results obtained for the least deflected molecules in the depleted region ($y = -0.9$ mm). The degree of orientation is sig-
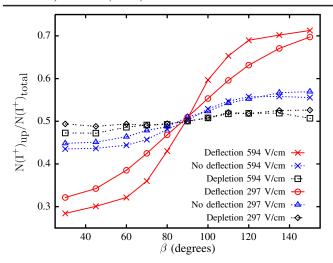
FIG. 4 (color online). Orientation, represented by $N(I^+)_{up}/N(I^+)_{total}$, as a function of β; see text for details.

nificantly reduced compared to that obtained without deflection.

Deflection of cold molecular beams enables the selection and the spatial separation of the most polar quantum states, i.e., the lowest-lying rotational states, for a wide range of molecules, from diatomics to large biomolecules. In many cases it may even be possible to completely isolate the rotational ground state. Although the deflection of iodobenzene seeded in helium, treated here, is already sufficiently selective that laser-induced alignment and orientation is significantly improved, we point out that more stringent state selection is possible by (a) lowering the speed of the molecular beam, for instance by using Ne rather than He as the carrier gas, and (b) increasing the deflection field gradient or the length of the deflector. Generally, deflection will be more pronounced for lighter molecules and for more polar molecules.

Adiabatic alignment and orientation, discussed in this Letter, is one example where state selection by deflection is highly advantageous. Pronounced effects are also expected in nonadiabatic alignment [26] and orientation [27], both, in terms of achieving strong field-free alignment and orientation, as well as in revealing quantum effects usually obscured by the averaging over many rotational states in a typical molecular ensemble. Moreover, the deflection spatially separates the selected molecular states from the background of atomic carrier gas, which could be useful for isolating a molecular signal in high-harmonic generation and attosecond experiments. Finally, the ability to disperse molecular beams by inhomogeneous electric fields is not limited to rotational state selection but naturally differentiates between individual structural isomers of molecules [10]. This is expected to become of significant importance not just in spectroscopic studies but also in emerging structural and dynamical studies employing pulses from coherent x-ray sources.

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