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Spatial deorientation of upper-Stark-state-selected supersonic beams of CH_3F, CH_3Cl, CH_3Br, and CH_3I

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The spatial scrambling of upper-Stark-state ($KM_J<0$)-selected beams of CH_3F, CH_3Cl, CH_3Br, and CH_3I in field-free space has been investigated. It has been proposed that the mechanism for spatial deorientation as the electric-field strength is reduced to zero is the change in precessional frequency and loss of spatial direction as the total angular momentum **J** decouples from the collapsing electric field and couples with the nuclear spin. Supersonic beams were quantum-state selected in a hexapole inhomogeneous electric field and directed between a pair of parallel field plates before being focused through a second hexapole field to a quadrupole mass spectrometer detector. Exposure of the beam to zero field in the parallel-plate region leads to an attenuation of the beam signal relative to the non-zero-field case due to defocusing of newly formed lower Stark states and $KM=0$ states in the second hexapole field. This phenomenon can be used to determine the effect of field strength on the orientation of upper Stark states within the beam. The beam signal at the detector was shown to remain constant for uniform field strengths greater than approximately 3 V cm^{-1}, with a signal attenuation of around 40% relative to this level at zero field. Attempts were made to measure the mean lifetime for spatial scrambling by pulsing the uniform field to ground potential for increasing intervals and observing the beam attenuation. However, these measurements were complicated by the effect of the beam velocity distribution on the signal and it was found that reproducible values could not be obtained, though the results of these experiments are consistent with lifetimes lying in the expected range from 100 to 300 μs.
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I. INTRODUCTION

. In an earlier investigation into the effects of molecular orientation on electron-impact ionization of symmetric top molecules [1,2] a hexapole field was used to select and focus the upper-Stark-state component of a molecular beam into a uniform orienting field maintained between a pair of parallel field plates, where it was intersected by an electron beam. In order to collect and count the positive ion products of electron-impact ionization processes occurring in the crossing region, the homogeneous field used to orient the molecules was rapidly switched (<100 ns) from 20 V cm^{-1} to 0.1 V cm^{-1} (a small potential was maintained in order to preserve the field polarity). Product ions were then guided out of the beam crossing region by an electrostatic lens assembly and collected over a period of 300 μs from field switching. It was assumed that the beam molecules subjected to the homogeneous field prior to its collapse would remain oriented long enough for asymmetry effects to be observed. Significant differences in the ionization cross sections were measured for electron impact at the positive and negative ends of the molecular dipole for several prolate and oblate symmetric top molecules, indicating that complete scrambling did not occur on the time scale of these experiments.

Brooks *et al.* [3] were the first to use a split hexapole in conjunction with a central uniform field to investigate the effect of the uniform electric-field strength on dipole scrambling of quantum state selected beams of symmetric top molecules. These experiments indicated that a minimum uniform field of 10 V cm^{-1} is required to preclude deorientation with subsequent degradation of focusing in the second hexapole field.

Kaesdorf *et al.* [4] used a hexapole field to state select CH_3I molecules for a study of the angular resolved photoelectron spectroscopy of oriented molecules. In order to minimize the effects of electric field on the photoejected electrons, the molecular beam was directed through a slowly decreasing uniform orienting electric field. The beam experienced a change in field strength from 10 to 0.3 V cm^{-1} over a distance of 360 mm. Since an orientation effect was reported in these experiments, some degree of spatial orientation was preserved during passage through the weak field.

Ghandi and Bernstein [5,6] investigated the effect of the uniform orienting field strength on spatial orientation, over the range of field strengths from 0 to 1.0 kV cm^{-1}, through the spatial distribution of product ions produced from polarized laser photofragment photoionization [7] of CH_3I. The ratio of upper to lower Stark states for the $|111\rangle$ and $|222\rangle$ states at a given orienting field was determined from the ratio of product ions scattered into each of the two hemispheres. The original degree of orientation for a molecular beam of CH_3I could be recovered providing the uniform field strength exceeded 0.3 V cm^{-1} for the $|222\rangle$ state and 0.6 V cm^{-1} for the $|111\rangle$ state. In addition, it was shown that even though the rotational angular momentum **J** should couple with the nuclear spin **I** through the hyperfine interaction in the weak orienting field to give an ensemble of $|FJKIM_F\rangle$ states, decoupling occurs to give the original $|JKM\rangle$ distribution when a strong field (>500 V cm^{-1}) is restored.

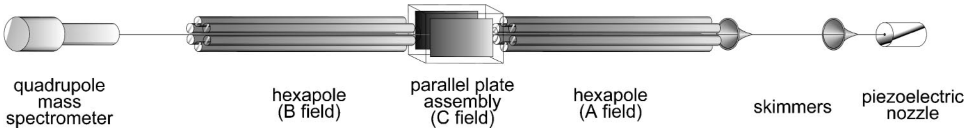

FIG. 1. Schematic of experimental configuration.

II. EXPERIMENT

The rotational motion of a symmetric-top molecule is defined by three quantum numbers: *J*, the total angular momentum quantum number; *K*, describing the projection of the vector **J** onto the molecular axis; and M_J, the projection of **J** onto the local electric field vector. When a symmetric top molecule enters a hexapole field it experiences a radial force, which depends on its rotational state $|JKM_J\rangle$. The hexapole field, established by applying positive and negative potentials of several kilovolts to adjacent hexapole rods, is strong near the rods and zero on the axis. Molecules in lower Stark states, for which the rotational quantum number product $KM_J>0$, minimize their energy by moving to high field. This motion results in divergent trajectories through the hexapole and subsequent loss of these states from the beam. Upper-Stark-state molecules, for which $KM_J<0$, minimize their energy by moving to low field, following convergent trajectories, which focus to the axis. Molecules for which $KM_J=0$ are unaffected by the field and are subject to the usual attenuation with distance from the nozzle.

The experiments described in this communication use an experimental arrangement consisting of two identical hexapoles separated by a set of parallel field plates. According to convention, the hexapole fields are referred to as the *A* and *B* fields, while the uniform field established between the parallel plates is called the *C* field. After passing through the *A* field the beam consists predominantly of upper Stark states. The molecular trajectory through the remainder of the system depends on the strength of the electric field maintained in the *C* field region, specifically to the magnitude of the Stark splitting relative to the energy splitting due to spin-rotation coupling between the rotational motion **J** of the molecule and the nuclear spin **I**. There are two limiting cases. In the weak-field case the Stark energy is much smaller than the hyperfine energy, and the hyperfine levels are only slightly perturbed by the electric field. In this case the molecular dipole $\boldsymbol{\mu}$ precesses about the total angular momentum **J**, **J** precesses about the total angular momentum $\mathbf{F}(=\mathbf{I}+\mathbf{J})$, and **F** precesses about the electric-field vector **E**. In this case the molecular state is described by the quantum numbers *I, J, F*, and M_F; M_J is no longer a good quantum number since it is not a constant of the molecular motion. Conversely, in the strong field case, the Stark energy is much greater than the hyperfine energy. The precession of **J** about **E** is so fast that the nuclear orientation cannot respond on the same time scale, and **I** and **J**, are said to be decoupled. In this case the system is described by the quantum numbers *I*, M_I, *J*, and M_J, and the Stark energy levels are essentially the same as for the case with no hyperfine coupling. Radiofrequency resonance spectra carried out in the present system [8,9], in which the observed peaks correspond to ΔM_J rather than ΔM_F transitions, indicate that the strong field regime provides an appropriate description of the hyperfine coupling in the current experiment arrangement when *C* fields of greater than a few volts per centimeter are established. The upper limit for breakdown of the ''strong field'' description is set by the position of the resonance peak corresponding to the $J=1$, $K=1$ rotational state, appearing at a field strength of 4.2 V cm^{-1}. This conclusion is supported by rough calculation of the expected hyperfine splittings based on tabulated spin–rotation coupling constants for the symmetric tops studied [10]. Estimated hyperfine energies are of the order of 4×10^{-30} J, compared to a Stark energy of 1.3×10^{-27} J for the $|111\rangle|JKM\rangle$ rotational state at a field strength of 4.2 V cm^{-1}.

As the beam exits the *A* field and enters a nonzero *C* field, the beam molecules make adiabatic transitions from the *A* field to the *C* field, and from the *C* field to the *B* field. They remain in the same rotational state throughout their trajectories through the system and will nearly all be transmitted through the *B* field to the detector. If the *C* field is zero then the Stark energy levels become degenerate and the absence of an electric-field vector means that there is no preferred spatial orientation for a given state. In the absence of the Stark effect, spin-rotation coupling between the rotational motion **J** of the molecule and the nuclear spin **I** becomes the dominant interaction, and the precessional motion of **J** about **F** means that the molecular dipoles scramble relative to the initial direction of orientation.

If complete deorientation occurs in the *C* field region the molecules will have random orientations as they enter the *B* field, and the orientation of any given molecule with respect to the field direction in the hexapole will determine whether it is projected into an upper Stark state, lower Stark state, or $KM_J=0$ state on entering the *B* field. Upper Stark states are transmitted to the detector, but a considerable fraction of the beam will be lost as nonfocusing states, leading to a significant drop in the beam signal relative to the non-zero *C* field case. It might be expected that since spatial deorientation occurs through the hyperfine interaction the mean lifetime for scrambling should be of the order of the hyperfine precessional period. Consideration of the spin-rotation coupling constants for the four molecules studied [10] indicates that the precessional frequencies are around 6 kHz, corresponding to a lifetime of around 150 μs. This should be accessible to experimental measurement.

A schematic of the experimental arrangement is shown in Fig. 1. Molecular beams are generated using a piezoelectric nozzle source (Physikalisch-Chemisches Institut der Universität, Zürich) which can be operated in pulsed or continuous mode. In the present experiments, continuous mode is used, and the high voltage applied to activate the piezoelectric crystal is varied to control the effective size of the nozzle aperture. This allows stagnation pressures of greater than 1000 Torr to be used without exceeding the pumping capacity of the vacuum system, maintaining a low beam temperature. Molecular-beam translational and rotational temperatures are estimated to be around 30 K based on fits to beam velocity distributions and the measurement of rotational state population distributions using radio-frequency resonance spectroscopy [8,11].

The beam passes through two skimmers (Beam Dynamics) with aperture diameters of 1.0 and 1.5 mm before entering the hexapole field. The *A* and *B* fields are provided by two sections of hexapole, each 530 mm long with an inscribed radius of 4.74 mm. The hexapoles are separated by a pair of polished copper parallel field plates, of length 150 mm and separation 10 mm, between which the *C* field is established. In order to minimize field penetration from the hexapole rods into the *C* field region, the field plates are enclosed in an aluminum Faraday cage with 10-mm entrance and exit apertures. After passage through the *A*, *C*, and *B* fields the beam exits the hexapole field through a 2.0-mm aperture at ground potential and is brought to focus at the electron-impact ion source of an Extranuclear Laboratories 4-270-9 quadrupole mass spectrometer located on the axis 20 cm from the exit aperture.

III. RESULTS AND DISCUSSION

Several kinds of measurement have been carried out and are reported here. Inititially, the overall effect of scrambling in the *C* field region on the total beam signal detected after passage of the beam through the *C* field was investigated. Following this, a set of experiments aimed at establishing the minimum uniform field strength required to keep beam molecules spatially oriented in the *C* field region was carried out. Attempts were then made to determine the time required for an upper-Stark-state selected beam to spatially scramble after entering a field-free region in which the M_F and M_J quantum numbers are undefined, usually expressed as a mean lifetime for deorientation. Each experiment exploits the decrease in beam signal when field-free conditions are experienced in the *C* field region to extract information on orientation properties of the beam.

A. Beam attenuation due to dipole scrambling

The effect of spatial scrambling in the *C* field region on the total beam signal was investigated by measuring hexapole transmission curves (beam signal as a function of hexapole voltage), first with a field of 20 V cm^{-1} between the parallel plates, then with zero field. The results of these measurements for the four symmetric-top molecules studied are shown in Fig. 2.

Focusing of upper Stark states to the beam axis when voltages are applied to the rods during passage through the hexapole leads to an increase in signal, the ‘‘hexapole enhancement.’’ The numerical value for the enhancement is taken as the ratio of the beam signal with the hexapole field on to that with the hexapole off. At a hexapole voltage of ± 5000 V the enhancement is found to decrease by around 40% when the homogeneous field in the *C* region is switched off. The overall signal attenuation has contributions from each of the $|JK\rangle$ rotational states present in the beam according to the differing numbers of possible M_J states. If it is assumed that after spatial scrambling has occurred in the *C* field region, a given $|JK\rangle$ state entering the *B* field reprojects in the strong inhomogeneous field to give equal populations of the possible M_J states, it may be expected that the fractional drop in signal for the state should be roughly equal to $K/(2K+1)$, the fraction of beam molecules entering nonfocusing lower Stark states. This was tested by carrying out Monte Carlo simulations of molecular trajectories through the system. The simulations average the number of successful trajectories (those that reach the detector) over the rotational state distribution calculated using statistical thermodynamics. The hexapole enhancements for the zero and nonzero *C* field were determined from the fate of 10 000 trajectories flown through the system. If the *C* field is on, molecules remain in the same rotational state for the entire trajectory. If the field is zero, they are randomly assigned to a new M_J state as they enter the *B* field. The simulations were found to reproduce experimental results fairly accurately. Simulated and measured ratios of the hexapole enhancement with the *C* field off to that with the *C* field on at a hexapole voltage of ± 5000 V and beam rotational and translational temperatures of 30 K are shown in Table I.

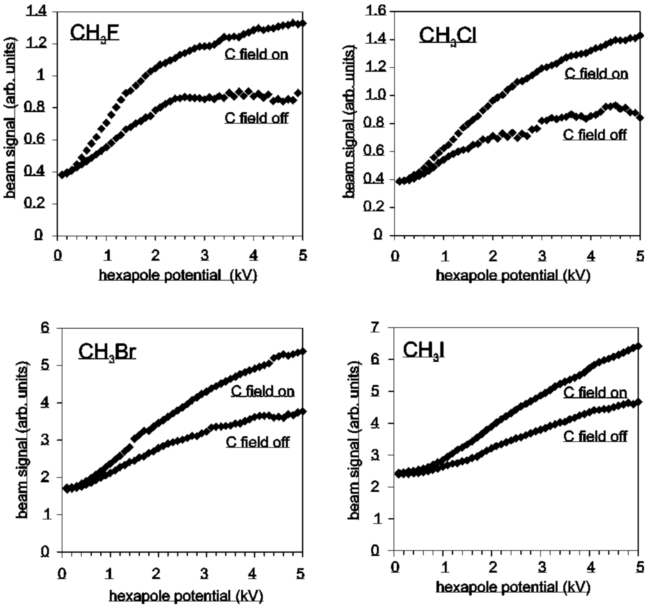

FIG. 2. Hexapole transmission curves for beams of CH_3F, CH_3Cl, CH_3Br, and CH_3I for *C* fields of 20 and 0 V cm^{-1}.

B. Orienting field requirements

The experimental arrangement described above allows the minimum orienting field to be measured directly by monitoring the beam signal as a function of the electric field established between the two parallel plates. The experiments were carried out with potentials of ± 5000 V on both sets of hexapole rods. As shown in Fig. 3, as the field is increased the

TABLE I. Simulated and experimentally measured ratios of hexapole enhancements for zero and nonzero *C* field for CH_3F, CH_3Cl, CH_3Br, and CH_3I.

	Enhancement ratio	
Beam	Expt.	Calc.
CH_3F	0.67	0.74
CH_3Cl	0.62	0.74
CH_3Br	0.69	0.69
CH_3I	0.73	0.68

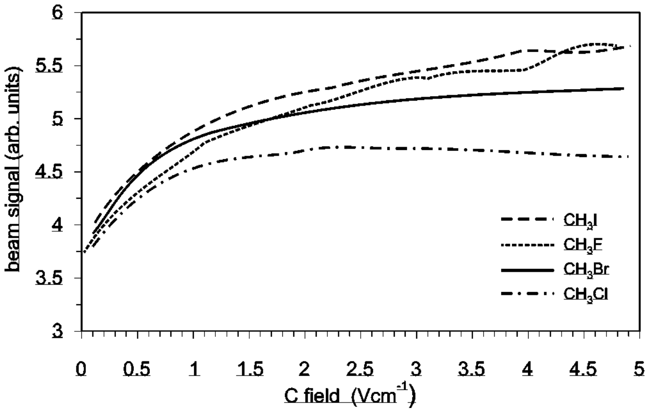

FIG. 3. Rise in beam signal with increasing *C* field as adiabatic transitions into and out of the uniform field become possible.

beam signal rises as it becomes possible for molecules to undergo adiabatic transitions into the *C* field and remain in upper Stark states which focus in the *B* field. The rise in signal is steep at first, but starts to level off above field strengths of 1 V cm^{-1}. Orientation is essentially complete at field strengths greater than 3 or 4 V cm^{-1}. The field strength required for complete orientation appears to vary slightly over the CH$_3X$ series, with CH$_3$Cl and CH$_3$Br orienting at lower fields than CH$_3$F, and CH$_3$I, though the differences are quite small. The reason for the differences observed is not immediately apparent since there are several factors present that could affect orientation and that differ among the four methyl halides studied, such as the molecular dipole moment, total nuclear spin, beam velocity (which determines the length of time for which molecules experience the *C* field), and beam rotational temperature (which determines the distribution of rotational states within the beam).

The minimum orienting field requirements established in the present paper are considerably lower than the >10 V cm^{-1} determined by Brooks *et al.* [3] in a series of almost identical experiments. The only major difference between the two experimental arrangements is the geometry of the hexapoles and parallel-plate region. Brooks *et al.* used two 235-mm-long hexapoles separated by a 25-mm-long pair of parallel plates. When the electric field in the *C* field region is modeled using SIMION6.0 [12] the reason for the discrepancy becomes clear. The experimental arrangement used by Brooks *et al.* suffers from significant field penetration from the hexapole rods into the *C* field region, resulting in a highly nonuniform electric field, even when the *C* field is nominally zero, i.e., when the parallel plates are held at ground potential. Orientation will not be observed until the applied field exceeds the penetrating field, leading to the higher-orienting field requirements noted in the earlier experiments. The presence of inhomogeneous penetrating fields in the *C* field region also explains the fact that considerable signal depletion was observed for beams of CH$_3$I and CHCl$_3$ due to dipole scrambling even though the flight time of the beams through the parallel-plate region are significantly less than the scrambling lifetimes determined in the current experiments. Subsequent experiments carried out by Brooks *et al.*, for which the results have not been published, support this analysis, giving results that are much more consistent with those obtained from the experiments described here. In the experimental arrangement used here, the *C* field is considerably longer and is also more effectively screened from the hexapole rod voltages so that field penetration is much less of a problem. This is confirmed by computer simulation of the *C* field region, which predicts minimal field penetration beyond the edges of the parallel-plate region.

These measurements of the minimum orienting field are for a distribution of rotational states determined by the rotational temperature of the beam. It is interesting to compare these results with the experiments carried out by Ghandi and Bernstein [6], in which the field dependence of orientation for single rotational states of CH$_3$I was determined. The measured field strengths of 0.3 V cm^{-1} and 0.6 V cm^{-1} required for complete orientation of the $|111\rangle$ and $|222\rangle$ states are significantly lower than the values reported here for a distribution of states. A possible explanation for the observed dependence of the required orienting field on rotational state emerges from a consideration of the orienting process: symmetric top molecules orient through an interaction between the molecular dipole μ and the electric field E. The energy of interaction is simply the Stark energy $\mu E\langle\cos\theta\rangle$, where θ is the angle between the two vectors and $\langle\cos\theta\rangle = KM/J(J+1)$. Presumably orientation becomes possible when the interaction energy reaches some threshold value W_{thresh}, so that the required minimum orienting field for a given state is

$$E_{JKM} = \frac{W_{\mathrm{thresh}}}{\mu}\,\frac{J(J+1)}{KM}. \tag{1}$$

If this hypothesis is correct, plotting the beam orientation data from single-state experiments against $\mu E\langle\cos\theta\rangle$ rather than against E should give similar curves for each rotational state, with the signal reaching a constant value at a similar value of the ordinate. Though Ghandi and Bernstein made measurements for only the $|111\rangle$ and $|222\rangle$ states of CH$_3$I this appears to be the case. Figure 4 shows third-order polynomial fits through the data of Ghandi and Bernstein plotted (a) as a function of electric-field strength E and (b) as a function of $\mu E\langle\cos\theta\rangle$. The improved agreement between the two sets of data in the second figure is clearly evident. Radio-frequency resonance spectra of CH$_3$F and CH$_3$Cl beams [8,9] measured using our apparatus show peaks for rotational states up to $J=7$. Higher J states will tend to increase the required orienting field measured in experiments that average over all rotational states present, consistent with the higher measured values when compared with the single-state data of Ghandi and Bernstein. If the value of W_{thresh} determined from the data of Ghandi and Bernstein is used to average E_{JKM} for CH$_3$I over the states up to $J=7$, complete orientation is predicted at a field strength of 3.9 V cm^{-1}, in good agreement with the field strength at which the beam signal levels off for CH$_3$I in Fig. 3.

C. Mean deorientation lifetimes

The most straightforward way to measure a deorientation lifetime would be to use a fast oscilloscope to record the beam signal as a function of time after switching the orienting field between the parallel plates to zero. Unfortunately, the signal decay due to spatial scrambling is convoluted with

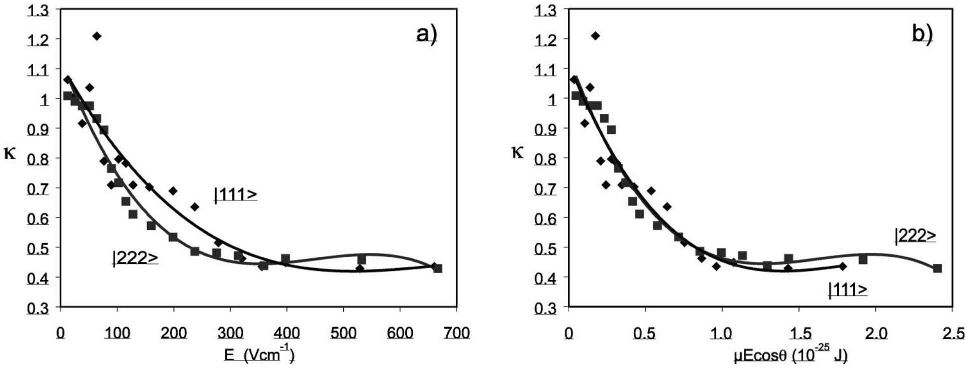

FIG. 4. Ratio of upper to lower Stark states for the $|111\rangle$ and $|222\rangle$ states of CH_3I plotted as a function of (a) homogeneous field strength E and (b) $\mu E\langle\cos\theta\rangle$. Third-order polynomial fits to the two data sets are shown in each case. Data from Ghandi and Bernstein [6].

the much broader time-of-flight decay signal due to the beam velocity distribution, making extraction of a decay constant impracticable.

The length of time for which the beam experiences field-free conditions may be controlled by pulsing the potential applied to the parallel plates to ground for set intervals. If the pulse is longer than the time it takes for the molecular dipoles to spatially scramble, a dip in the beam signal is observed, as shown in Fig. 5 for a broad pulse width of 200 μs. The observed dip is delayed relative to the voltage pulse by the flight time of the beam from the parallel plates to the detector and broadened by the beam velocity distribution. The ''height'' of the dip should be directly proportional to the amount of spatial scrambling occuring within the zero-field interval, and it was hoped that this could be used in the measurement of deorientation lifetimes. Experiments were conducted in which the dip was measured as a function of zero-field time. If it is assumed that spatial scrambling follows first-order kinetics, the dip in beam signal $S(\Delta t)$, where Δt is the zero-field interval, is given by

$$S(\Delta t)=S_{\max}(1-e^{-k\Delta t})=S_{\max}(1-e^{-\Delta t/\tau}), \qquad (2)$$

where $S_{\max}$ is the maximum dip in the signal, k is the first-order rate constant, and τ is its reciprocal, the mean lifetime for scrambling.

A plot of the signal dip against the zero-field time should, therefore, be an inverted exponential function, which can be fitted to obtain the time constant for deorientation. In practice, however, it was not possible to fit the data in this way to obtain reasonable, reproducible values for the decay constant, though the results indicated a lifetime lying somewhere in the range from 100 to 300 μs, not inconsistent with the predicted value of around 150 μs. It is thought that there are two major problems with the approach employed. The first is the fact that the maximum zero-field time is limited to the flight time of the beam through the parallel-plate region. For CH_3F this is around 200 μs, roughly the same as the expected value for the time constant, which severely limits the range over which meaningful data can be collected. A second, related consideration is that many of the beam molecules will exit the C field region before experiencing the entire width of the zero-field pulse. Because the distribution of velocities within the beam leads to a broad time-of-flight distribution of molecules arriving at the detector, the signal detected at a given instant will consist of contributions from molecules, which have experienced zero-field conditions for the entire range of times from 0 up to Δt. This means that the signal is not strictly described by the first-order rate equation given above, but is in fact some kind of integral over this function. The distribution of velocities within the molecular beam therefore precludes using the split hexapole arrangement to measure accurate time-dependent orientation properties. However, it should be possible to measure deorientation lifetimes using a variant of the technique adopted by Ghandi and Bernstein [5,6] described earlier. By switching the orienting field to ground and measuring the ratio of ions detected in the two hemispheres as a function of laser delay from field switching rather than as a function of a static-field strength, determination of deorientation lifetimes should be straightforward.

It is in fact possible to extract an approximate orientation lifetime for CH_3I from the published results of the experiments carried out by Ghandi and Bernstein, in which the required field strength was investigated [6]. Based on the degree of orientation measured under zero-field conditions after the 640 μs flight time to the ionization region for the $|222\rangle$ state, the orientation lifetime can be estimated to be around 220 μs, in accord with the value predicted from a consideration of hyperfine frequencies.

A deorientation lifetime on the order of a few hundred microseconds is also consistent with the data obtained by Kaesdorf *et al.* [4], who reported small orientation effects for the photoionization of CH_3I with orienting fields as low as 0.3 V cm^{-1}. While this field strength is lower than that required to fully orient a beam of symmetric-top molecules, the present experiments show that a significant fraction of

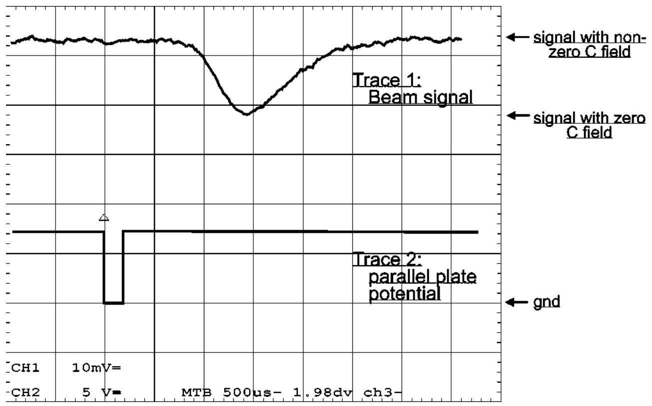

FIG. 5. Dip in the CH_3F beam signal observed on pulsing the C field to ground. The upper trace shows the beam signal while the lower trace shows the potential difference applied across the parallel field plates.

the beam should be oriented at this potential, and small orientation effects should be observable. In addition, the experiments of Kaesdorf *et al.* involved a reduction in the orienting field strength from 10 V cm^{-1} to 0.3 V cm^{-1} over a distance of 360 mm, with the CH_3I molecules experiencing fields of less than 3 V cm^{-1} for only around 530 μs. Based on the scrambling lifetime of 220 μs determined from the data of Ghandi and Bernstein, a retention of orientational integrity of around 10% would be expected.

IV. CONCLUSIONS

Beams of symmetric-top molecules have been found to show complete orientation at uniform field strengths of 3–4 V cm^{-1}. These measurements are complementary to other published experimental studies and are also supported by computer modeling. Attempts have been made to measure mean deorientation lifetimes, but were complicated by the beam velocity distribution. However, available data support a lifetime of the order of 200–300 μs, consistent with predictions based on a consideration of the hyperfine coupling frequencies associated with the deorientation process. A lifetime of this magnitude has important implications for studies of collisions between beams of charged particles and oriented molecules, indicating that orienting fields can be switched off before the beams cross, precluding effects of the field on the charged particle beam without compromising the observation of orientation effects on the collision.

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