Characterization of Oriented Molecule Beams by Radio Frequency Spectroscopy

Susan D. Wiediger, Peter W. Harland,[†] Judson R. Holt,[‡] and Philip R. Brooks*

Chemistry Department and Rice Quantum Institute, Rice University, Houston, Texas 77005

Received: July 28, 1997

Molecular-beam electric-resonance spectroscopy is used to interrogate the rotational states present in a molecular beam of oriented symmetric-top molecules produced for scattering experiments. $\Delta M = \pm 1$ transitions are observed between Stark energy levels in weak electric fields and depend on the rotational quantum numbers J and K. Substantial rotational cooling is apparent in both neat and seeded beams. Each resonance signal has a complicated dependence upon the high voltage applied to the hexapole focusing fields because molecules in the newly transformed states have vastly different focusing properties from the original. These effects can be unified using a "reduced" focusing voltage that allows intensity comparisons between rotational states, giving rotational temperatures of 3−4 K for CF_3H seeded in He or Ar. Under favorable circumstances, radio frequency "labeling" might allow one to selectively remove one rotational level at a time from an oriented molecular beam and thereby to study the orientation dependence of different rotational states.

Introduction

Geometrical considerations play an intuitive role in chemical reaction dynamics as well as in molecular structure. Although crystal-structure determinations provided a firm basis for these geometrical notions in molecular structure, the role played by molecular orientation in chemical reactions has been mainly based on indirect evidence. But over the past 30 years or so, direct evidence for the preferred reactivity at one end of a molecule has been obtained using beams of molecules that are *oriented* prior to reaction.[1−4,11,14,15,18,22] The effect of molecular orientation on reactivity can be very large, and in some cases reactivity vanishes for unfavorable approach of the reagents.[26,27]

Calibration of our chemical intuition required confirmation that reaction occurred preferentially on one end, and these needs were met by early experiments that relied on a "heads" vs "tails" comparison of reactivity.[2] But more detailed consideration of the steric dependence of chemical reaction requires a knowledge of the distribution of molecular orientations before reaction depending upon the experiment.

Aside from "brute-force" techniques[16,9] not considered here, oriented molecules can be prepared by using inhomogeneous hexapole electric fields to sort symmetric-top molecules into broad categories, roughly characterized as "up", "down", or "sideways", to correspond with the various possible rotations of a child's top. Molecules in different rotational states $|JKM\rangle$ are deflected in the hexapole field, and the category transmitted is comprised of all rotational states for which the energy *increases* with electric field (i.e., those with $MK < 0$). The distribution of rotational states, and thereby the distribution of molecular orientations selected by the hexapole field, depends on the molecule used, the temperature of the beam, and the experimental parameters of the hexapole field, such as the voltage and the size of the beam apertures.

The simplest distribution is obtained by using apertures so small that only one rotational state is transmitted, and several reactions have recently been studied[10,12,13] with molecules in the $|1\ \pm1\ \mp1\rangle$ state. Unfortunately, selection of a single rotational state severely reduces the intensity of an already weak selected beam. The intensity is reduced not only by the fraction of molecules originally present in that state but also by the small apertures required to separate the selected rotational state from other states. Selection of molecules in single states will thus be favored mainly for the methyl halides because their large rotational constants allow appreciable population to be prepared in lower rotational states.

A complementary experimental approach, and one that is especially appropriate for molecules heavier than the methyl halides, is to use larger apertures in the hexapole field to produce higher-intensity beams of oriented molecules, albeit in several rotational states. The orientation distribution is obtained by using the equations of motion in the hexapole field to computer-model the probability of transmission of a molecule in a given $|JKM\rangle$ state.[3] The overall distribution of molecular axes is obtained from the quantum probability of orientation[7,21] weighted by the probability of finding that state in the selected beam. This approach is particularly well-suited for heavier molecules that can populate many rotational states, even at temperatures of a few degrees Kelvin. The distributions of orientations calculated in this manner are relatively insensitive to the parameters assumed in the calculations and lend confidence to this approach.[27]

It would be desirable to have ways to obtain quantum-state information but still have enough beam intensity to perform reactive scattering experiments on molecules other than the methyl halides. The experiments reported here were undertaken to see if radio frequency techniques could provide rotational-state information for beams of oriented molecules using large-aperture hexapole focusing fields that produce molecules in a range of quantum states. Some information about state populations can be gleaned, and irradiation of the beam at a radio frequency resonance may provide a means of "labeling" molecules in scattering experiments.

[†] Permanent address: Chemistry Department, University of Canterbury, Christchurch, New Zealand.

[‡] Present address: Chemistry Department, MIT, Cambridge, MA.

S1089-5639(97)02448-1 CCC: $15.00

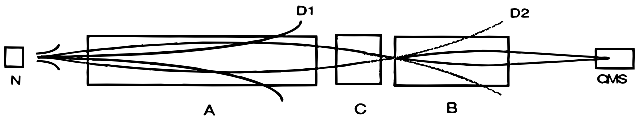

Figure 1. Schematic diagram of apparatus. Supersonic beam expands from nozzle N. Hexapole electric fields A and B focus molecules into the mass spectrometer (QMS), provided that the state-selected molecules fly adiabatically through the C field. If a resonant radio frequency field is applied in C, molecules can undergo a transition to a state that can defocus in the B field, following a trajectory along D2 and resulting in a decrease in intensity at the detector.

Experimental Section

A low-resolution Rabi-type molecular-beam electric-resonance machine was constructed by inserting a radio frequency C field between sections of the hexapole field used in reactive scattering experiments, as shown in Figure 1. The hexapole state-selecting field was comprised of three sections each 45.7 cm long, and the C-field cell was inserted after the second of the three sections of the hexapole field, resulting in an A field 91.4 cm long and a B field 45.7 cm long. The C field was constructed[17] from copper plates 9.5 cm long spaced 1.21 cm apart parallel to about ±0.2 mm. A uniform dc field could be applied to these plates, and a radio frequency field could be applied to a central region 5.7 cm long, with the radio frequency field having both parallel and perpendicular components relative to the dc field.

Beams were a supersonic nozzle-expansion of gases, such as CH_3F, CF_3H, and CH_3Cl both neat and seeded in Ar or He, at stagnation pressures from 50 to 300 Torr, shown[6] to give translational temperatures of $\sim$1 K. An axial quadrupole mass spectrometer QMS with a 5-mm diameter aperture located 46 cm from the end of the B field detected the beam. An HP 3312A function generator provided the rf signal, modulated at about 300 Hz by an HP 8013B pulse generator. The rf was monitored on an oscilloscope, and frequencies were measured to within about 5%. The output of the QMS was detected by a phase-sensitive lock-in amplifier (PSD) and stored in a computer.

The objective of these experiments was to provide rotational-state information on symmetric-top molecules whose spectroscopy was already known. At low resolution, neglecting quadrupole effects, the energy of a symmetric top in an electric field is given by the first-order Stark effect, as shown in Figure 2:

$$W = -\mu E \frac{MK}{J(J+1)} \tag{1}$$

For states with values of $MK < 0$, the energy increases with E, and molecules in these states are focused by the hexapole A and B fields. Molecules with $MK > 0$ are defocused in the hexapole field, and those with $MK = 0$ are undeflected. Transitions between M levels can be induced by radiation with frequency depending on the applied electric field $\nu = \Delta W/h = \mu EK/[hJ(J+1)]$, again shown in Figure 2 for $J = 1$, $K = 1$. For fields of a few V/cm and dipole moments of a debye, these frequencies are of order 1 MHz, so low that the levels would be essentially equally populated in a gas. In the molecular beam, molecules in the $MK = 1$ level are removed by being defocused in the A field (schematically following trajectories D1 in Figure 1) and those in $MK = -1$ are focused, giving a population inversion in the C field. These molecules with $MK = -1$ are focused into the QMS by the B field and in reactive scattering experiments would be oriented by a uniform field at the end of the B field. In the present experiments, molecules can be interrogated by an rf field in the C region, which can induce $\Delta M = \pm 1$ changes. Molecules that would have been focused by the B field into the QMS will be transformed into states that are defocused or undeflected by the B field, giving a concomitant decrease in flux at the detector.

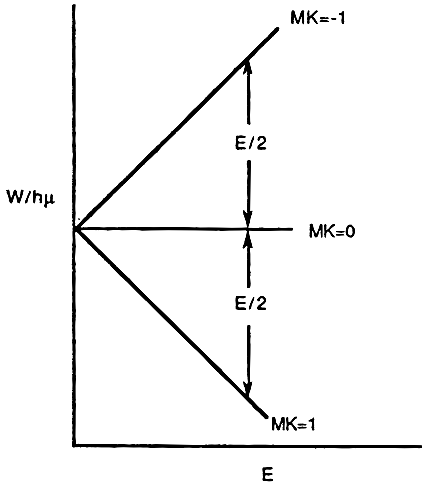

Figure 2. Stark effect energies for a symmetric-top molecule in the $J = 1$, $K = 1$ state.

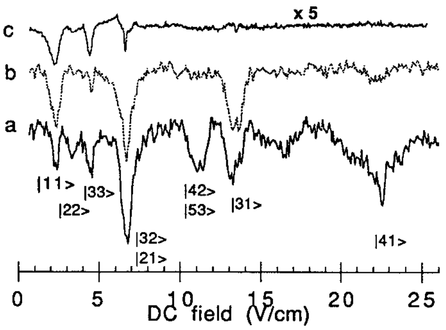

Figure 3. Spectra obtained by monitoring the beam intensity (PSD signal) while sweeping the magnitude of the DC field in the C region with $\nu = 1$ MHz: (a) neat CH_3F; (b) 10% CH_3F in Ar; (c) 10% CH_3F in He. $|JK\rangle$ denotes values of J and K in resonance. The field was calibrated using the $|32\rangle + |21\rangle$ line.

Results

Spectra were taken at constant rf by sweeping the dc electric field in the C region, and the electric field at resonance for $\Delta M = \pm 1$ transitions is

$$E = \frac{h\nu J(J+1)}{\mu K} \tag{2}$$

Typical spectra are shown in Figures 3 and 4 for CH_3F and CF_3H, which were chosen for study because F has no quadrupole moment and, to first order,[25] the energy is given by the simple Stark effect (eq 1). More data were taken with CH_3F because its large rotational constant allows a large fraction to be prepared in low rotational states at $T < 10$ K. (Extreme cooling needs to be avoided because the J and $K = 0$ states cannot be focused.) Some CH_3F transitions were assigned by taking data at various values of ν and plotting the resonance field E vs frequency (eq 2). A few transitions are strongly overlapped, and states are indicated that are calculated to contribute. As expected, low K levels are populated for the prolate-top CH_3F, whereas higher K states are populated for the oblate-top CF_3H and many more lines are observed.

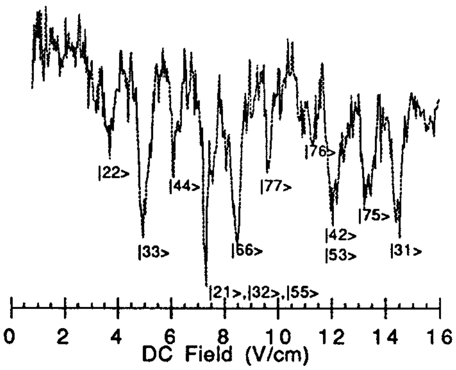

Figure 4. Spectrum of fluoroform, CF_3H: PSD signal versus electric field strength with hexapole voltage of 6 kV and radio frequency of 1 MHz. Assignments $|JK\rangle$ correspond to values of J and K calculated to be in resonance. The field strength is calibrated using the $|21\rangle$, $|32\rangle$, $|55\rangle$ line.

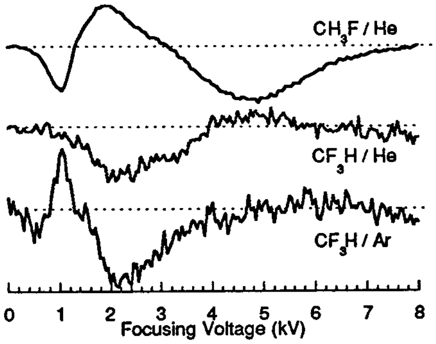

Figure 5. PSD signals vs focusing voltage. The high voltage on the focusing fields was varied at constant radio frequency of 1 MHz at the electric field in the C region for the $|11\rangle$ resonance.

Spectra were also obtained for CH_3Cl and CH_3Br, but the energy levels are no longer given by the simple Stark effect[5,24] because the quadrupole moments of both Cl and Br are nonzero. The resulting hyperfine structure leads to many more transitions. The spectra are much more complicated, and our limited resolution makes assignment difficult and beyond the scope of this report.

Figure 3 shows that the rotational population is cooled in the supersonic expansion and is cooled even further by seeding the beam. More dilute mixtures are even colder. Unfortunately, only qualitative temperature determinations are possible from these spectra because they are taken at fixed voltages on the focusing fields, usually 6 kV.

The focusing voltage has a strong influence on the relative intensities of the various resonance signals, so the ratio of the intensities of resonance signals corresponding to different rotational states cannot be simply related to the temperature. The focusing voltage can even change the *sign* of the signal. This is shown in Figure 5 for the $|11\rangle$ resonances in CH_3F and CF_3H where the signal amplitude at fixed rf and dc voltage is plotted vs the voltage on the hexapole focusing fields. For example, the CH_3F signal (top curve) is negative-going near 1 kV as expected for the flop-out geometry sketched in Figure 1. But as the focusing voltage is raised, the magnitude of the flop-out signal decreases, goes through zero, and then becomes positive as the intensity flops in. At higher voltages the signal again becomes negative. The CF_3H signal behavior is clearly different from the behavior of the CH_3F signal and depends on the seeding gas. Transitions for other states have even more complex focusing voltage dependencies.

Discussion

Effect of Focusing Voltage. The apparatus sketched in Figure 1 is a "flop-out" configuration; molecules undergoing a transition are presumed to be defocused by the B field and miss the detector. But as Figure 5 shows, at certain focusing voltages the signal is observed to *increase* and one sees either "flop-in" or "flop-out", depending on the voltage applied to the hexapole fields. This is a consequence of the scattering geometry used; the focusing voltage on hexapoles A and B is identical, and to maximize beam intensity, no beam-defining stops or apertures are used. A molecule making a transition in the C field has *different* focusing properties in the B field than it had in the A field, and the absence of beam-defining apertures allows molecules with a range of trajectories to hit the detector. The intensity of the transition can thus be a complicated function of the high voltage.

To model this behavior, molecular trajectories for transitions in the $|11\rangle$ state of CH_3F seeded in He were followed through the focusing A field, the uniform C field, the focusing B field, and finally the field-free region between the B field and the QMS. It was assumed that in the C field, molecules would make transitions with $\Delta M = \pm 1$, and the trajectory was continued in the B field with the molecule in the new state (focusing, nonfocusing, or defocusing). Figure 6 shows the results of these calculations. Only those molecules initially in the $MK = -1$ or 0 states contribute significantly to the final signal.

The top curve in Figure 6, labeled F−F, is the negative of the focusing curve for molecules in $MK = -1$ states (focusing). The first focus is near 1 kV. The second near 4.5 kV arises from an "overtone" in which molecules cross the axis and are refocused into the QMS. The intensities have a plateau because the apertures are large. If molecules are *removed* from this state by an rf transition in the C field, the focused intensity will decrease and the modulated signal will be negative near 1 and 4.5 kV as is observed. A schematic trajectory is shown in the right-hand panel.

Molecules originally in focusing $MK = -1$ states, which are transformed into nonfocusing $MK = 0$ states, make a contribution to the signal as shown in curve F−N in Figure 6. Molecules in the newly populated $MK = 0$ level are undeflected by the B field, but if the voltage in the A field is somewhat larger, sufficient focusing can be acquired in the A field alone, and at voltages of ~2 kV in the A field, molecules in these states can make a positive (flop in) contribution. A schematic trajectory is shown in the middle-right panel.

The third curve in Figure 6, denoted N−F, shows that molecules initially in $MK = 0$ can undergo a transition in the C field to $MK = -1$ and then be focused by the B field alone into the QMS at voltages of ~2 kV, giving a signal increase. The panel on the right shows schematically a diverging beam of molecules in nonfocusing states being transformed into states that could be focused by the B field into the QMS. This focusing occurs at somewhat higher voltages because the B field is shorter than the entire field.

The calculated signal is the sum of the signal possibilities, curves F−F, F−N, and N−F, and assumes that the $MK = -1$ and $MK = 0$ states are equilibrated by the rf. The agreement between experiment and the model calculation is good. Minor differences between the calculated and experimental signals are probably a consequence of our neglect of higher-order Stark effects, of the field in the hexapole rods deviating from the field created by ideal hyperbolic rods, and of the imperfect alignment of the QMS entrance relative to the rods.[19]

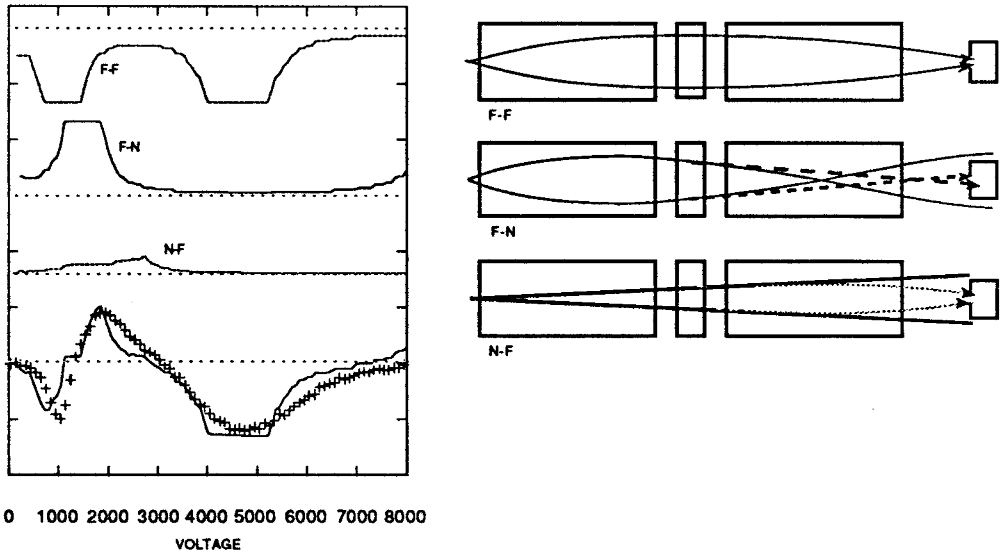

Figure 6. (Left) Effect of hexapole focusing voltage on the modulated QMS signal of CH_3F seeded in 90% He at 1 MHz and $E = 3$ V/cm, corresponding to $\Delta M = \pm 1$ for the $J = 1$, $K = 1$ state. Upper curves are model calculations. F−F is the negative (depletion) of the focusing curve for molecules in $MK = -1$ (focusing states). F−N denotes molecules entering the C field in focusing states and undergoing a transition to a nonfocusing state. N−F denotes molecules entering the C field in nonfocusing $MK = 0$ levels and changing in the C field to focusing $MK = -1$. Lowest calculated curve is the sum (F−F + N−F + F−N) and assumes $MK = 0, -1$ are equilibrated. Experimental points are normalized to the calculated curve. (Right) Schematic trajectories in apparatus corresponding to state focusing curves. Top panel (F−F) shows the focusing trajectory near 1 kV where molecules are focused into the detector. Panel F−N shows a schematic trajectory for a voltage ~2 kV where focusing molecules would be overfocused in the B field and miss the detector unless they undergo a transition into a state that is nonfocusing in B. Panel N−F shows nonfocusing molecules undergoing a transition to focusing states and being focused by the B field at a higher voltage near 3 kV.

Focusing Voltage and Temperature. The trajectory calculations offer a way to scale the focusing voltage to account for differing mass, speed, dipole moment, and state. In the hexapole focusing fields, the equations of motion are given by

$$\frac{d^2r}{dt^2} = \frac{6\mu V_0 r}{m r_0^{\,3}} \frac{MK}{J(J+1)} = \omega^2 r \tag{3}$$

where V_0 is the rod voltage, r_0 is the distance from the field axis to the (hyperbolic) rod, m is the mass, μ is the dipole moment, and J, K, M are the symmetric-top quantum numbers. States with $MK < 0$ are focusing, and the focal distance is $L = n\pi v/\omega$. If the length of the field is fixed, the quantity $\mu V_0 MK/[mv^2 J(J + 1)]$ will determine the trajectory and is more useful than the focusing voltage for comparing behavior among different states. In these experiments, the speed was not directly measured, but for different seeding mixtures, $v^2 \propto 1/\langle m\rangle$ and we define the reduced voltage as $U = \mu V_0 \langle m\rangle MK/[mJ(J + 1)]$, where m is the molecular mass and $\langle m\rangle$ the average mass in the seeded beam. This latter relationship offers a way to scale the focusing voltage to account for different molecules and speeds.

In Figure 7 the $|11\rangle$ resonances of CH_3F as well as the $|11\rangle$ and $|33\rangle$ resonances of CF_3H are plotted vs the reduced voltage U and show that the rf signals can be nicely scaled by the reduced voltage. This behavior is a manifestation of the deflection in *high field* and could be helpful in assigning spectra even for molecules with quadrupolar nuclei because the nuclear spin will couple to the field and the hyperfine structure is a perturbation to the Stark energy. Also, by comparison of rf intensities at the same values of the reduced voltage,[20] it is possible to compare populations of different rotational states, and the intensities of the $|11\rangle$ and $|33\rangle$ transitions can be used to get a rough measure of the rotational temperature for CF_3H seeded in Ar and He. (Comparable data were not taken for CH_3F because it is a prolate top with a large rotational constant and the population of $|K| > 1$ states in seeded beams was small.)

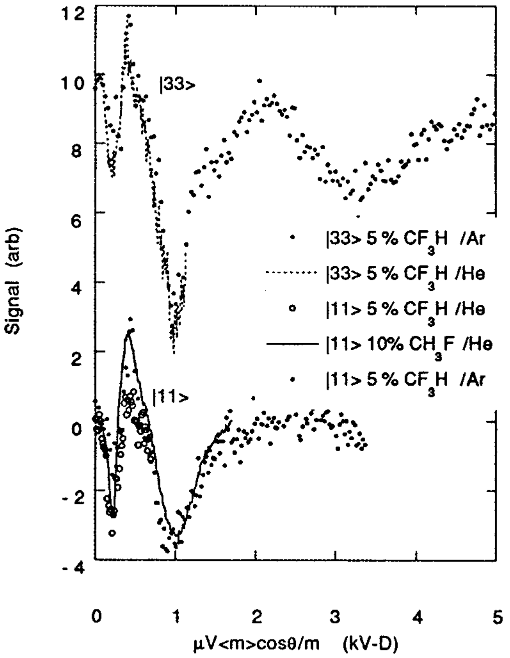

Figure 7. Resonance signals plotted against the reduced focusing voltage $U = \mu V\langle m\rangle MK/[mJ(J + 1)]$. Signals for the $|33\rangle$ transition in CF_3H seeded in He or Ar are offset for display.

Following the notation of Townes and Schawlow, the fraction of molecules in a given rotational state is

$$f_{JK} = \frac{(2J + 1)S(I, K)}{Z} \exp\left[\frac{-BJ(J + 1) + (C - B)K^2 h}{kT}\right] \tag{4}$$

where B and C are the rotational constants, Z is the partition function, and $S(I, K)$ is the extra spin and inversion degeneracy.[23] The signal intensities for the $|22\rangle$ and $|33\rangle$ resonances relative to the $|11\rangle$ resonance, I_{11}/I_{33} and I_{11}/I_{22}, were measured for CF_3H

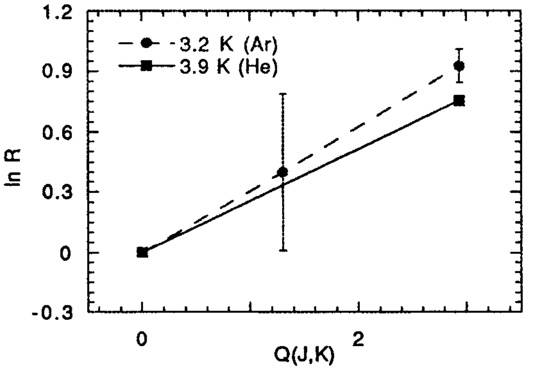

Figure 8. Intensity ratios measured at identical reduced voltages for the $|111\rangle$, $|222\rangle$, and $|333\rangle$ states of CF_3H plotted logarithmically against $Q(J, K)h/k$. The slope is $1/T$.

(Ar) and CF_3H (He). These ratios are given by

$$\frac{I_{11}}{I_{33}} = \frac{S(^1/_2, 1)}{S(^1/_2, 3)} \frac{\exp(-2Bh/(kT)) \exp([B - C]h/(kT))}{\exp(-12Bh/(kT)) \exp([B - C]h9/(kT))} = \frac{S(^1/_2, 1)}{S(^1/_2, 3)} \exp(Q_{33}h/(kT)) \quad (5)$$

and

$$\frac{I_{11}}{I_{22}} = \frac{S(^1/_2, 1)}{S(^1/_2, 2)} \exp(Q_{22}h/(kT))$$

where $Q_{33} = 8C + 2B$ and $Q_{22} = 3C + B$. The usual factor of $(2J + 1)$ does not arise because the experimental ratio is sensitive to molecules in a single M level. These expressions may be recast into a form suitable for determination of the temperature by defining

$$R_i = \frac{I_{11}}{I_{ii}} \frac{S(^1/_2, i)}{S(^1/_2, 1)} \quad (6)$$

and plotting $\ln R$ vs $Q(J, K)h/k$ as shown in Figure 8. The Ar data ratios are the average of those measured under conditions of maximum flop-out (the first and second minima) in the reduced focusing curves of Figure 6; the error bars span the extremes of this procedure. Focusing curves were not measured for the $|22\rangle$ state for CF_3H seeded in He, and for these rough measurements all rotational states including nuclear spins are assumed to be equilibrated.

The translational temperature of Ar was measured earlier[6] in this apparatus and determined to be 1 K at somewhat higher backing pressure. The rotational temperatures of 3−4 K for 5% mixtures of CF_3H in Ar and He are thus remarkably similar, very cold, and warmer than T_{trans}. Because of the paucity of comparable data, these temperatures are obtained assuming that all rotational degrees of freedom can be described by a single temperature, although for methyl fluoride, Douketis et al.[8] concluded that the relative J populations in a given K stack relaxed more rapidly than did the K population, and $T_J < T_K$. They also concluded that the A and E nuclear-spin modifications did not relax during the nozzle expansion. Although for fluoroform the smaller rotational constants may lead to more facile relaxation, in light of Douketis's conclusions we regard our temperatures as still somewhat tentative.

State Labeling. The preceding section shows that measurement of rotational temperatures is feasible for beams of oriented

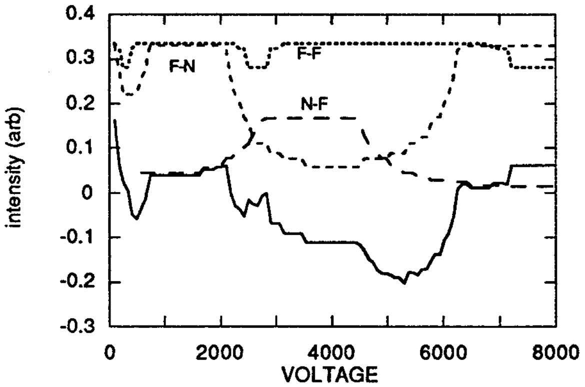

Figure 9. Calculated intensities expected at the scattering center for the $|111\rangle$ state of CH_3F. F−F is the intensity for molecules not undergoing a transition. F−N denotes signal from molecules that make transitions from focusing to nonfocusing states, and N−F are those making transitions from nonfocusing to focusing states. The solid curve is the PSD signal expected if the rf were modulated. Even with such large apertures, a focusing voltage can be found near 5300 V for which most molecules undergoing a transition would be removed from the beam.

molecules that, although selected according to Stark energy states, are still populated by a number of rotational states. These measurements can be made without beam-defining apertures, are not restricted to methyl halides, and could be performed during the course of reactive scattering measurements. Knowledge of the rotational population would then allow the orientation probability distribution to be calculated and compared with experimental reactivity measurements. This was the goal of these studies. But additional information might be obtained under favorable circumstances if the rotational states could somehow be individually labeled during the course of the scattering experiments.

The second minimum in Figure 6 near 4800 V (or $U \approx 1000$) corresponds to molecules making a transition and being *removed* from the beam without the new state being focused back into the beam. This raises the possibility that one could study a scattering process using a beam of oriented molecules comprised of many rotational states, selectively *label* states in the beam by irradiating at the resonance frequency for that state, and thereby study the effect of rotational state as well as of orientation. To investigate this possibility, trajectory calculations were performed to simulate the intensity that would be obtained for the worst-case scenario of an extended scattering center (9-mm diameter) located at the end of the B field. (In contrast, the rf measurements were made with a QMS with a 5-mm diameter aperture located 46 cm from the end of the B field.)

Results of these calculations are shown in Figure 9, which is similar to Figure 6 except that the enormous aperture results in very little selectivity. If one were to conduct a scattering experiment with a focusing voltage near, say, 1500 V, modulating the $|11\rangle$ rf voltage would produce very little change of beam *intensity*. Even though half of the molecules in the $MK = -1$ state would be converted into $MK = 0$, the trajectory would be sufficiently similar such that they would still enter the scattering center. The rf would produce a change in *state*; the orientation of these molecules would change from end-on to sideways, and it might be difficult to deconvolve the behavior of this state. At somewhat higher voltages, however, the $MK = 0$ molecules would follow trajectories that *remove* them from the beam, and near 5300 V the B field would reject all molecules making a transition, even those molecules initially in $MK = 0$ states. (A beam stop would make this separation a bit cleaner.) Modula-

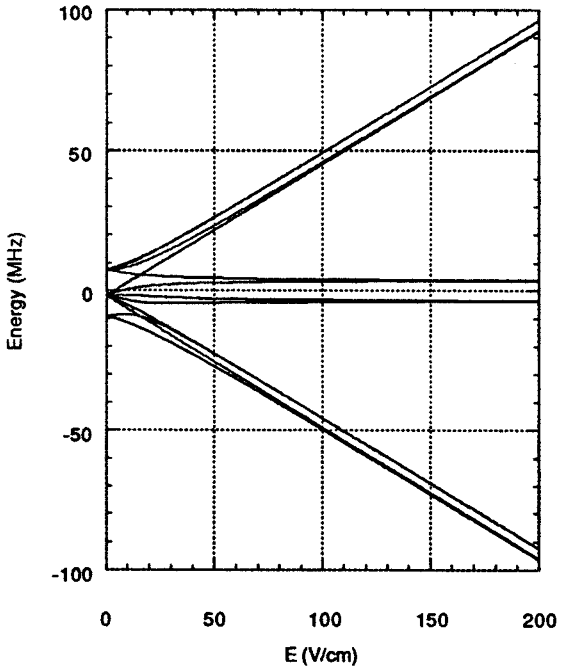

Figure 10. Energy levels calculated for CH_3Cl, $J = K = 1$. The spectrum is highly complex at a few V/cm but becomes much simpler at higher field strengths.

tion of the $|11\rangle$ rf transition with 5300 V on the rods would thus modulate the *intensity* of oriented molecules in the $J = 1$ state. Under favorable circumstances it might be possible to radio frequency label several rotational states to assess their contribution to the reactivity.

It thus appears feasible that the contribution to the reactivity by different rotational states could be probed by radio frequency labeling of the state in question. In order for this approach to be of general utility, it would be desirable to be able to do this also for molecules with hyperfine structure, especially those containing atoms that have quadrupole moments. The spectrum for these molecules is complex, especially at low fields. But if the electric field is sufficiently large, the hyperfine interactions are decoupled from the Stark interactions, and this is shown in Figure 10 for CH_3Cl. At field strengths of $\gtrsim$50 V/cm, the Stark effect is essentially linear but transitions would occur between several M_F levels. The "$MK = -1$" ↔ "$MK = 0$" transition at, say, 200 V/cm would include several lines ranging from $\sim$88 to 100 MHz. All of these lines could be excited using a single radio frequency by either ramping a uniform dc field or by having a C field with electrodes that are not quite parallel so that a given molecule would experience a dc field that would change during the time it would spend in the C field. A given radio frequency could then stimulate all possible $\Delta M = \pm 1$ transitions, and molecules in the $MK = -1$ states would be removed from the beam, resulting in the same selectivity for, say, CH_3Cl as we suggest for CH_3F. This is currently under consideration.

Summary

This study was motivated by a desire to be able to characterize in situ beams of oriented molecules *during the course of scattering experiments.* This approach would be particularly valuable for those molecules that are sufficiently heavy to populate a number of rotational states because hexapole state selection to give a single rotational state would result in a large loss of beam intensity.

The present work shows that radio frequency resonances can be observed and, as expected, that appreciable cooling results by seeding the beam molecules in a rare gas. But the scattering-experiment geometry used here is not optimal for rf spectroscopy, and the effect of the focusing fields must be considered in order to compare intensities of different rotational transitions to determine rotational temperatures. The equations of motion of the molecules in the focusing fields predict that the focusing is dependent upon the reduced voltage $U = \mu V_0\langle m\rangle MK/[mJ(J + 1)]$, and the intensities of the rf transitions in the $|11\rangle$ and $|33\rangle$ states of CF_3H and CH_3F are correlated well with the reduced voltage. We estimate the rotational temperatures for 5% CF_3H seeded in Ar or He to be about 3−4 K by comparing rf intensities at comparable reduced voltages. These temperatures are comparable to the translational temperature for Ar measured earlier (1 K) at somewhat higher backing pressure and suggest that $T_{\mathrm{rot}} \gtrsim T_{\mathrm{trans}}$.

By modulation of a given rf transition in a scattering experiment, it would be possible to modulate the population of oriented molecules in a given *MK* state, holding out the possibility of obtaining state-resolved scattering information even if the oriented beam is initially comprised of several rotational states.

Acknowledgment. We gratefully acknowledge support of this work by the Robert A. Welch Foundation and the National Science Foundation. P.W.H. thanks the Marsden Fund (NZ) for support. We thank John Muenter and Bob Curl for helpful comments, and we thank Nicholas Adams for generously loaning us his frequency generator, even at times that were inconvenient for him.

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(19) If the rf power were high enough, it might be possible that molecules in the focusing $MK = 1$ state could be transformed into defocusing $MK = +1$ states by sequential processes. At voltages a little larger than 2 kV, molecules undergoing C-field transitions to $MK = +1$ levels can acquire enough focusing character in the A field to still allow them to enter the QMS. Inclusion of the $MK = +1$ levels on the assumption that all *M* states

are equilibrated produces a similar result, and information about the population of the $MK = +1$ levels is inconclusive.

(20) The gases seeded in helium are in better accord with those in Ar if a small correction is made to account for a “slip” between the He speed and the speed of the seed molecule. For CH_3F the slip factor was 0.97, but for the heavier CF_3H it was 0.95 and 0.91 for $|11\rangle$ and $|33\rangle$, suggesting that molecules in different rotational states have slightly different speeds.

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