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Orienting Polar Molecules in Molecular Beams. Symmetric Tops*

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Symmetric-top molecules exist in various orientations in even very weak electric fields, in contrast to diatomic molecules which are oriented only in fields so large as to be impractical. For symmetric tops these orientations can be separated in an inhomogeneous electric field, and calculations are presented for the separating properties of a hexapole field. The transmission and the final distributions of velocity and orientations have been calculated for several different molecules over a range of conditions. Experimental transmission measurements were made and are in good agreement with calculations. By fitting experimental points to calculated transmission curves dipole moments in good agreement with literature values have been determined. The molecules separated by the hexapole field are experimentally shown to make adiabatic transitions into a homogeneous electric field, providing evidence that the molecules can be oriented in the laboratory reference frame.

I. INTRODUCTION

Molecular-beam techniques allow one to study various aspects of the details of molecular interactions.[1] In particular, several investigators have recently studied steric effects in chemical reactions by intersecting a beam of atoms with a beam of oriented polar molecules.[2] These preliminary experiments have not yet been fully interpreted, partially because of lack of information about the orientation of the molecules. In this paper we discuss the technique of orienting molecules, present calculations describing the orientation, and show experimental data which support our assertions.

The method to be described is applicable only to symmetric-top molecules. In the presence of a very weak electric field (to provide a unique direction in space) these molecules rotate in such a fashion as to constitute three groups: those in which the average projection of μ on $\mathcal{E}$ is aligned against the field, those for which the average projection is with the field, and those in which the average projection is zero. If the latter two groups are removed,[3] those remaining are all aligned against the field.[4] The problem of obtaining a beam of oriented molecules is thus one of separating extant orientations, rather than a brute force twisting of the dipoles by application of a strong electric field.[5]

II. THEORY

A. Deflection.

The interaction energy between a rotating symmetric-top molecule with dipole moment μ and an applied electric field, $\mathcal{E}$, is[6]

$$W_{el} = -\mu\mathcal{E}MK/J(J+1) = -\mu\mathcal{E}\langle\cos\theta\rangle, \qquad (1)$$

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† Robert A. Welch Foundation Undergraduate Research Scholar.

[1] See for example, Advan. Chem. Phys. **10**, (1966).

[2] (a) P. R. Brooks and E. M. Jones, J. Chem. Phys. **45**, 3449 (1966); (b) R. J. Beuhler, R. B. Bernstein, K. H. Kramer, J. Am. Chem. Soc. **88**, 5331 (1966); (c) R. J. Beuhler and R. B. Bernstein, Chem. Phys. Letters **2**, 166 (1968); (d) P. R. Brooks, J. Chem. Phys. **50**, 5031 (1969).

[3] H. G. Bennewitz, W. Paul, and Ch. Schlier, Z. Physik **141**, 6 (1955).

[4] K. H. Kramer and R. B. Bernstein, J. Chem. Phys. **42**, 767 (1965).

[5] It is possible, of course, to twist the dipoles by application of enormous electric fields. In a gas the orientation is obtained from the well known [see, for instance, N. Davidson, *Statistical Mechanics* (McGraw-Hill Book Co., New York, 1962)] Langevin equation, $\cos\theta = L(y) = \coth y - 1/y$, where θ is the angle between μ and $\mathcal{E}$ and $y = \mu\mathcal{E}/kT$. In a molecular beam the relaxing collisions necessary for the Langevin equation to apply are absent, but nevertheless this is a reasonable approximation up to $y \approx 1$. This brute-force method is equally applicable to diatomic molecules, but for either diatomics or symmetric tops enormous electric fields (10^7 V/cm) are necessary to effect a significant degree of orientation. [As an example, for HCl at 300°K in a field of 10^7 V/cm, direct calculation yields $\langle +\cos\theta\rangle = 0.21$, but $L(y) = 0.26$.] These laboratory field strengths are impractical. Symmetric tops may be much more easily aligned by the techniques described in this paper, but no other method except the brute-force technique is available for diatomics. This method could be made feasible for diatomics if only the $J=0$ level were present [only 380 kV/cm is required for $\langle +\cos\theta\rangle = 0.21$ for HCl, $J=0$]. This level could be separated with an inhomogeneous electric field and the "ten-pole" field has been suggested to be especially suited for this purpose. [T. G. Waech, K. H. Kramer, and R. B. Bernstein, J. Chem. Phys. **48**, 3978 (1968).]

[6] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955).
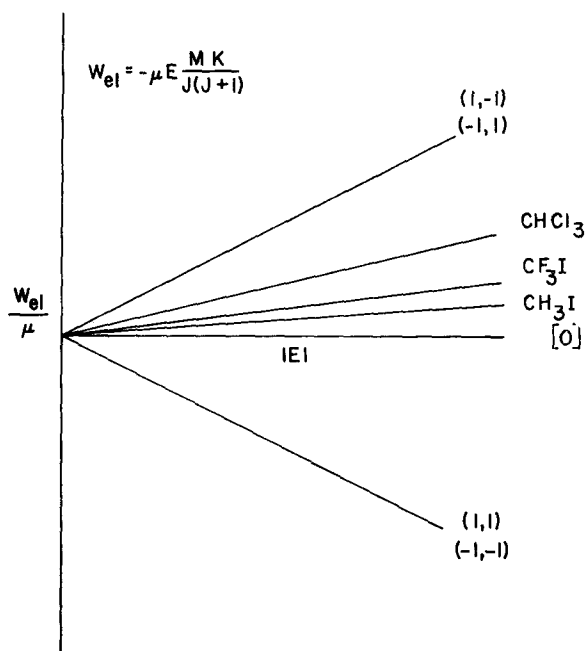
FIG. 1. Variation of symmetric-top energy levels in an electric field for $J=1$. Of the nine possible M, K states, five do not interact with the field to first order and are denoted by [0]. Also illustrated is the median level for each of three gases at room temperature: for each gas, half of the rotational states which can be focused have slopes less than that indicated. These median slopes $(-\cos\theta)$ are 0.24, 0.12, and 0.07 for $CHCl_3$, CF_3I, and CH_3I, respectively.

where θ is the angle between μ and $\mathcal{E}$ averaged over rotation, and M, K, and J are the usual quantum numbers. If the molecule is placed in an inhomogeneous field, it experiences a force

$$F = -\nabla W = \mu \langle\cos\theta\rangle \nabla \mid \mathcal{E} \mid, \qquad (2)$$

and molecules with various orientations are deflected in different directions depending on whether $\langle\cos\theta\rangle$ is positive, negative, or zero. (See Fig. 1.) Separation of these component orientations could be effected by passing the beam through an inhomogeneous electric field. The "two-wire" or Stern–Gerlach type of field[7] used extensively in molecular-beam electric resonance spectroscopy[7b,8] would be suitable in principle, but in practice the deflections are so small[9] that in order to obtain good separation of the component orientations a very narrow, well-collimated (and hence low-intensity) beam is necessary.

In order to overcome the obvious intensity limitations of the Stern–Gerlach type of field, we have employed an

inhomogeneous electric field created by six alternately charged rods placed at the corners of a regular hexagon.[3,4] As shown in Fig. 2, the beam travels along the axis of this array. By symmetry the electric-field intensity is zero on the axis; consequently, molecules in the upper levels of Fig. 1 will be deflected toward the axis. The array is made optically opaque by appropriate stops so that it will transmit only those molecules in the upper states (for which $MK<0$) which undergo a sufficient deflection toward the axis.

In addition to removing the undesired molecular orientations, this six-pole field *focuses* the molecules which are selected.[3] All upper-state molecules entering the field parallel to the axis with the same velocity v and quantum state will undergo simple harmonic motion inside the field and will be focused to a point on the axis at a distance

$$l = (\pi^2 m v^2 r_L^3 / 24 V_0 \mu \langle\cos\theta\rangle)^{1/2} \qquad (3)$$

where m is the molecular mass and other symbols are defined in Fig. 2. This criterion has been used by Kramer and Bernstein[4] (KB) to predict that the orientation of a velocity-selected beam would be given by

$$\langle-\cos\theta\rangle = V_{th}/V_0, \qquad (4)$$
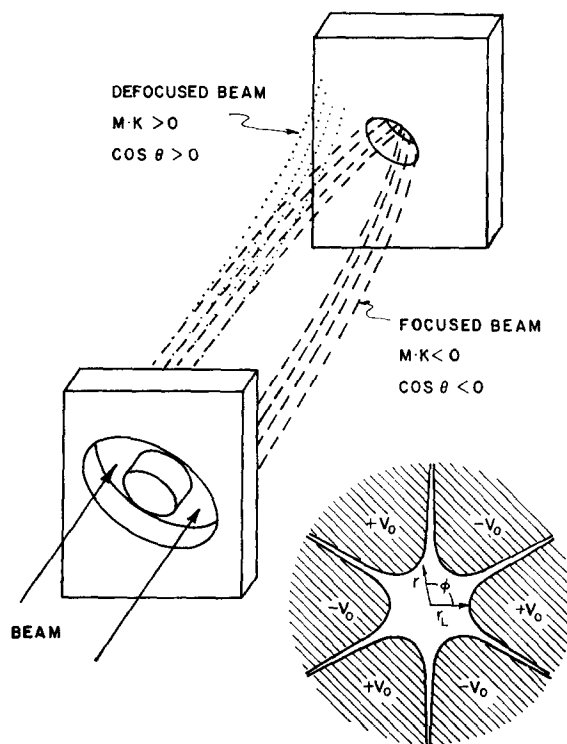
FIG. 2. Schematic view of hexapole field with rods removed, showing exaggerated beam deflection and details of beam stops. These stops allow only levels with $MK<0$ to pass through field when rods are charged.

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[7] (a) R. R. Herm and D. R. Herschbach, Lawrence Radiation Laboratory, Berkeley, Calif., UCRL Rept. 16039, 1965. (b) A. J. Hebert, Lawrence Radiation Laboratory, Berkeley, Calif., UCRL Rept. 10482, 1962.

[8] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956).

[9] A typical angular divergence of the $\pm\cos\theta$ components of the beam is $1°$ (CH_3I, $300°K$, $\cos\theta = \pm1$, $\mu = 1.6D$, $\partial E/\partial x = 30$ kV/cm², $l = 10$ cm).

where V_{th} is a "threshold" voltage given by

$$V_{th} = \pi^2 m v^2 r_L{}^3 / 24 \mu L^2,$$

and L is now the length of the field. This description is complete only if the beam is velocity selected and if the apertures are infinitesimal. In general the apertures will have some finite size, and the focusing field will pass molecules which have focal lengths somewhat different from L. As a consequence, a distribution of orientations will emerge, not a single orientation as predicted by Eq. (4). (For unselected beams there is no threshold voltage.)

To completely specify the states of the molecules which are transmitted by the field we must average over all initial conditions: velocity, quantum state, and radial position of entrance. A molecule is assumed to be transmitted if at the end of the field its radial distance is less than the radius of the exit aperture. This makes allowance for transmission of molecules with a large range of focal lengths. If the focal length is sufficiently short, however, molecules may cross the axis and then

FIG. 4. Calculated distribution functions for orientation, $G(\eta)$. For the incident beam (IN) $g(\eta)d\eta$ is the fraction of the incident beam (considering only the focusable states) in the interval η to $\eta + d\eta$, where $\eta = -\cos\theta$. For the beams transmitted, $G(\eta)d\eta$ is the fraction of the number transmitted in the same interval. Ordinates for both distributions are identical. The calculations assume that no molecules are transmitted with $MK \geq 0$. Results for $CHCl_3$ are essentially continuous and have been reproduced as a continuous distribution for clarity.

undergo enough of a diverging quarter cycle as not to be transmitted (too strong focusing).

The details of this calculation are contained in the Appendix for the general case in which the incident beam has a modified Maxwell–Boltzmann velocity distribution. Typical results for the transmission, final distribution of orientation, and final velocity distribution are summarized in Figs. 3–7. In most figures the dimensionless field parameter B is used, where

$$B = 3\mu L^2 V_0 / k T r_L{}^3,$$

L is the field length, k is Boltzmann's constant, T is the temperature of the beam source, and V_0 and r_L are defined in Fig. 2.

B. Orientation

The six-pole electric field selects quantum states; the molecules leaving the field are not oriented in the
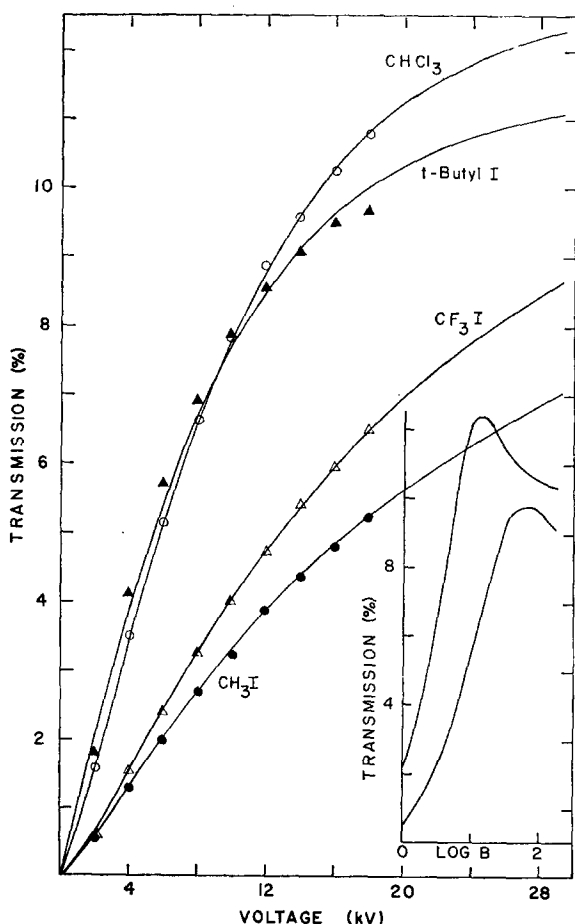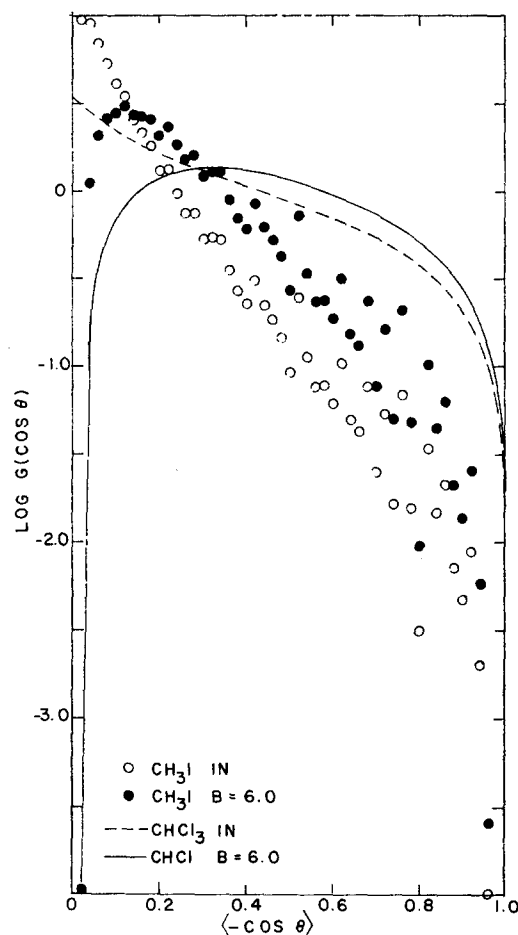

FIG. 3. Calculated transmission of inhomogeneous hexapole field for several molecules. Experimental measurements are normalized to theoretical curves at 12 kV. Inset shows transmission of $CHCl_3$ and CH_3I over a large range of B.
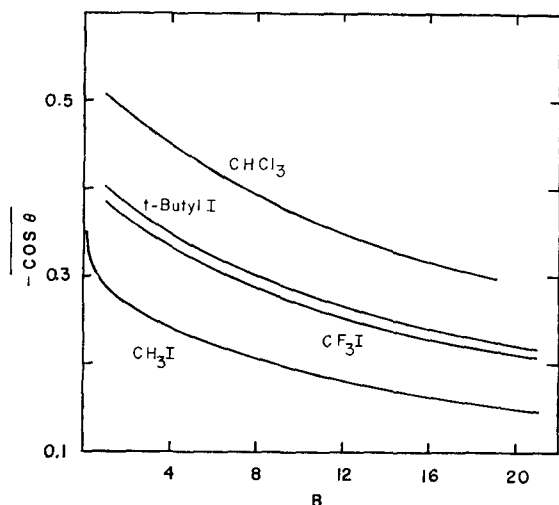
FIG. 5. $\cos\theta$ averaged over transmitted distributions similar to those in Fig. 4 for various values of B.

laboratory. However, as KB point out, the molecules may be oriented in the laboratory by allowing them to pass adiabatically into a region of uniform field.

III. EXPERIMENTAL

A. Transmission

Relative transmission measurements were made for several molecules as a function of field voltage in order
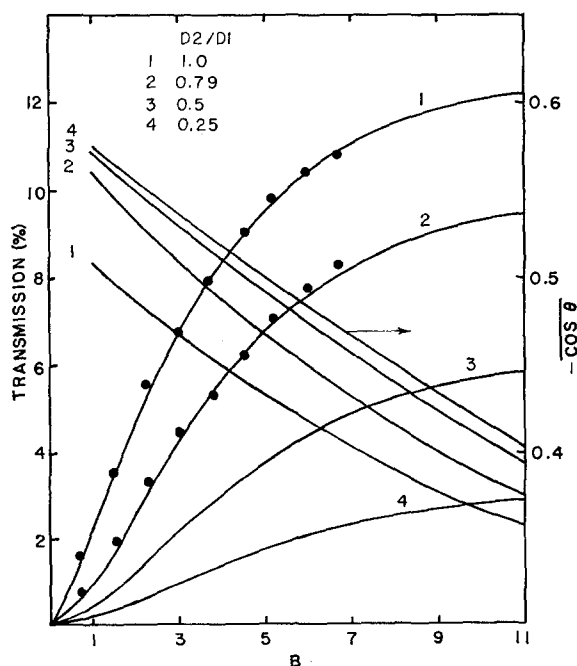

FIG. 6. Transmission and average $(-\cos\theta)$ for CHCl₃ for various diameters of exit aperture. $D2$ is the radius of the exit aperture; $D1$ is the radius of the stop in the center of the entrance aperture. Points are experimental and are normalized to the curves at 12 kV $(B=4.46)$.

to test the validity of the calculations. The six-pole field was constructed of six $\frac{3}{8}$-in. stainless-steel rods $8\frac{1}{2}$-in. long with centers equally spaced on a circle $1\frac{5}{8}$-in. diam[10] $(r_L=\frac{9}{32}$ in.$)$. The initial field stop defined a beam with a doughnut-shaped cross section ($\frac{3}{8}$-in. outside diam, 0.160-in. inside diam). The exit hole was 8.5 in. from the entrance and was usually 0.160-in. diam, but several runs were made with a 0.125 in. hole.[11] The rods were charged symmetrically with respect to ground with a simple voltage-doubler power supply which could supply ±20 kV.
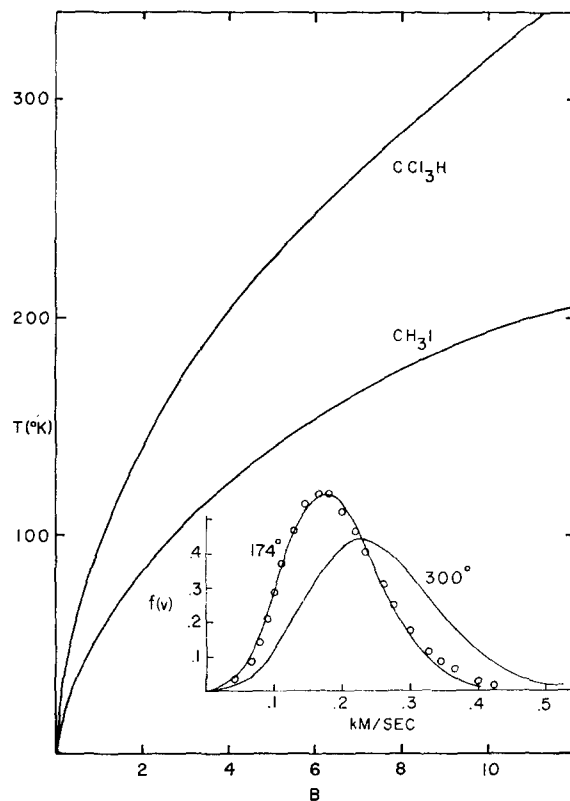

FIG. 7. Inset shows calculated velocity distribution of CH₃I $(B=7.0)$, transmitted through hexapole field compared to a modified Maxwell–Boltzmann distribution with source at 174 and 300°K. Oven temperatures yielding velocity maxima identical to the transmitted velocity maxima are shown for a range of B. Temperature of beam entering field is assumed to be 300°K.

The beam effused from a glass multichannel array mounted on a gimballike mechanism so that the beam could be adjusted to enter the field paraxially. The oven was located 8 in. from the entrance to the field because it was observed that the focused intensity decreased at

[10] The equipotential surfaces of the hexapole field are sections of 60° hyperbolas. At small r, the field due to rods of circular cross section is identical to that created by the hyperbolic rods. The good agreement between theory and experiment suggests difference at larger r are not of practical importance.

[11] Further details of the construction of the hexapole field and of the transmission measurements will be contained in the Ph.D. thesis of E. M. Jones.

shorter distances. The focused-beam intensity was measured by the steady-state pressure it built up in a GCA BA100P ionization gauge mounted with its orifice 6 in. from the exit of the field. The tube was powered by a Granville–Phillips Ionization Gauge Controller, and the collector current was measured with a Keithley 610BR Electrometer in combination with an external zero-suppression circuit. Total pressure in the chamber was usually $\sim 5 \times 10^{-8}$ mm; maximum detector pressures built up by the focused beam were $\sim 5 \times 10^{-8}$ mm.

In order to compare experiment with theory we need to measure the transmission, or the fraction of incident molecules which are passed by the field, as a function of voltage. This unfortunately requires a measurement of the incident intensity and would necessitate both moving the high-voltage field aside and changing the position of the ionization gauge; this was not feasible. However, in the course of these experiments it was observed that the optically opaque field passed a beam even if no voltage was applied to the field. This "shadow beam" appears to be due to incomplete collimation and scattering from slit edges. The shadow-beam intensity was determined to be directly proportional to the oven pressure, and we have therefore used it as a measure of the incident intensity.

The focused intensity (hexapole voltage on–off signal difference) was measured over a range of incident intensities (monitored by measuring the shadow-beam intensity) for each voltage displayed in Fig. 3. Plots of focused intensity vs shadow intensity were linear, and interpolation of these data then yielded an averaged signal at a single-reference shadow intensity for each voltage. These reference signals were normalized to the theoretical transmission plots at an arbitrary voltage (± 12 kV) and are shown in Fig. 3.

While measurement of absolute transmission is still precluded, it was possible to compare the transmission of different molecules. We assume that the intensity of the shadow beam is the same fraction of the incident intensity for all molecules. The relative transmission for each gas may then be obtained by referring all focused intensities to the same shadow intensity. These results are shown in Table I for an arbitrary focusing voltage (± 12 kV), although equally good agreement is obtained at other voltages. This agreement between calculation and experiment furnishes a convincing check on the calculations, and measurement of the absolute transmission of one gas does not seem worthwhile.

B. Orientation

The motivation for this work was to describe accurately the orientation of the molecules transmitted through the field. The preceding section (as well as KB) showed that molecules are transmitted. It was previously noted that these will be oriented in the laboratory

TABLE I. Transmission of hexapole field relative to CH_3I.

Gas	μ(D)	Transmission	
		Theory	Exptl.
CH_3I	1.65	1	1
CF_3I	0.93	1.18	1.16
CCl_3H	1.20	2.33	2.40
$t\text{-}C_4H_9I$	2.13	2.26	2.10
	2.40	2.35	2.10

reference frame *if* they make adiabatic transitions from the hexapole field to some uniform laboratory field. Although such adiabatic transitions are well-known in molecular-beam resonance experiments with atoms and diatomic molecules,[8] the question remains, do symmetric tops, in fact, make adiabatic transitions? The answer appears to be yes on the basis of the reactive scattering experiments, but since little is presently understood about the reaction of oriented molecules, it is essential to obtain evidence for orientation from independent experiments.

A simple deflecting field cannot be used to determine the laboratory orientation, because the molecules emerging from the six-pole field may all make adiabatic transitions into the analyzing field, independent of their prior laboratory orientation. We can, however, investigate the conditions which allow the adiabatic transitions necessary for orientation. The apparatus used is shown schematically in Fig. 8; it consists of a state-selecting field (*A* field) previously described, a shielded box containing a parallel-plate type of homogeneous field (*C* field), and a refocusing field (*B* field) similar to the *A* field, but one in which both entrance and exit apertures are $\frac{3}{8}$ in. diam.[12] An NRC-type 507 ionization gauge was used as a detector in these experiments.

With this apparatus essentially no increase in signal was observed with either the *A* field or the *B* field on separately, because molecules which are state selected in *A* have trajectories which do not allow them to enter the detector. If, however, *both A and B* were turned on, a considerable increase was observed as long as the field strength in the *C* field was $\gtrsim 10$ V/cm. This increase is due to molecules which are state selected in field *A* and which are in the same state in field *B* where they can be focused into the detector. This refocusing in *B* is possible only if the molecules remain in the same quantum state, i.e., make adiabatic transitions, in going from *A* to *C*

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[12] This, of course, is simply a molecular-beam electric-resonance apparatus with "flop out" geometry. Transitions are caused if the rate at which the field changes is greater than a transition frequency (Ref. 6). Since the various M states of a J, K set will become degenerate at zero field, the slightest perturbation (from a nearby polar molecule or from slight field inhomogeneities) will be sufficient to cause a nonadiabatic transition.
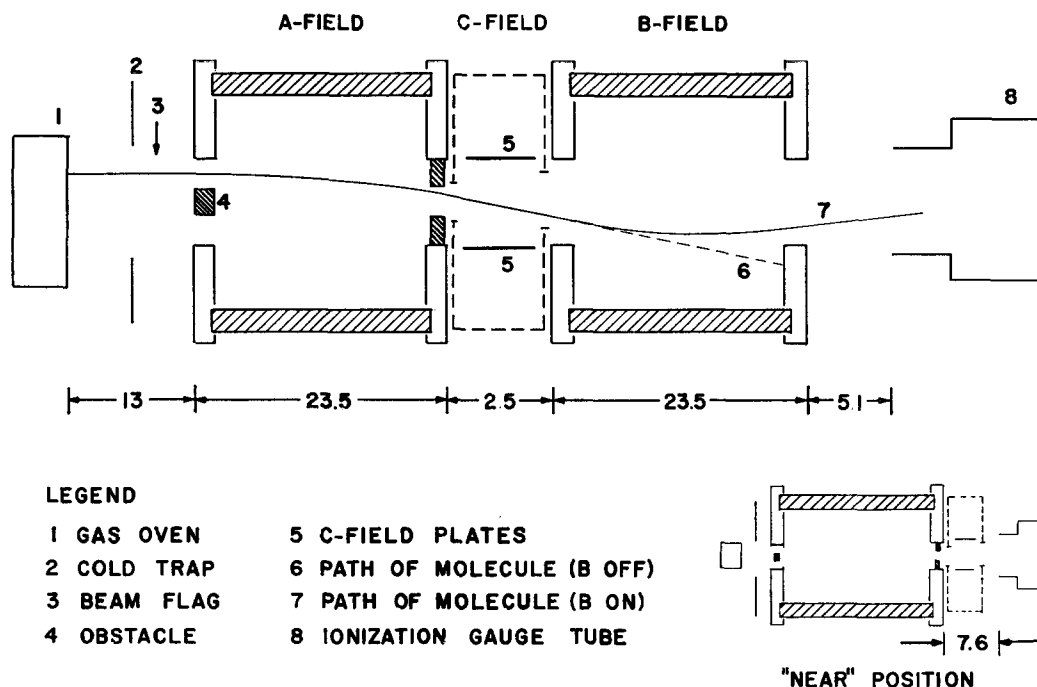
FIG. 8. Apparatus for studying nonadiabatic transitions. Dimensions are in cm, and beam deflections are exaggerated for illustration. Molecules are state selected in A, but will not enter the detector unless they are refocused in B. In order to be refocused in B, they must remain in quantum states with essentially the same focusing characteristics as those states selected in A. Inset shows "near" configuration used to measure flux leaving C.

to B. The experimental observations (see Fig. 9) thus show that at least some of the molecules make adiabatic transitions from A to C to B. This conclusion is strengthened by results obtained upon varying the field strength in C. The results[13] (Fig. 10) clearly show that *nonadiabatic* transitions occur when the applied field strength in C is very low. Above $\sim$10 V/cm, however, there is no evidence for nonadiabatic transitions.

TABLE II. Signal observed in "near" and refocused positions.

Gas	Pressure (μ)	Signal ratio (refocused/near)
$CHCl_3$	100	1.20
	170	1.15
	220	1.13
CH_3I	120	1.21
	170	1.11

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[13] The behavior shown in Fig. 10 was observed for a number of different pressures; it was independent of direction or magnitude of fields created by very small guard plates at the entrance and exit of the shield surrounding the C field (not shown in Fig. 8). The experimental data indicate that the minima do not occur at exactly zero voltage applied to the C-field electrodes, and this suggests the presence of a small stray field in the C region. The slight difference in the applied voltage at the minimum for the two curves may be due to experimental error and has not been further investigated.

In separate experiments field B was removed and replaced with the ionization gauge (Fig. 8, "near" position). To within the reproducibility of the oven pressure, essentially the same focused signal was obtained with the ion gauge in the near position as was obtained in the refocused position. These data (Table II) show that most (and probably all) of the focused molecules which emerge from A will be refocused in the B field. (The C field was observed not to impede the beam in any fashion.) The correlation of intensities in near and refocused positions and the apparent absence of nonadiabatic transitions for C-field strengths $\gtrsim$10 V/cm show that essentially all molecules will make adiabatic transitions into a homogeneous field if $\varepsilon \gtrsim$ 10 V/cm. In the homogeneous field the molecules are oriented in a laboratory reference frame, and it is this fact that the reactive scattering experiments confirm.

IV. DISCUSSION

A. Orientation

As pointed out previously by KB, the qualitative features of the focusing for symmetric-top molecules are mainly dictated by whether the molecule is a prolate or oblate top. The rotational energy depends on the quantum number K as well as on J, and the Boltzmann factor discriminates against high K states for prolate tops. Consequently, few states of high $|MK/J(J+1)|$ (or $|\langle\cos\theta\rangle|$) are populated for prolate tops. (This can

TABLE III. Molecular parameters for symmetric tops.

Molecule	B^a (GHz)	C(GHz)[b]	Percent orientation (300°K)		
			$\cos\theta < 0$	$\cos\theta = 0$	$\cos\theta < -0.5$
$CHCl_3$	3.301	1.72	48.91	2.18	10.37
CF_3I	1.523	5.75	48.20	3.51	3.28
CH_3I	7.501	148.7	42.31	15.38	0.86
CD_3I	6.040	75.760	45.63	9.73	1.26
$C(CH_3)_3I$	1.562	4.63	48.70	2.60	3.93

[a] Reference 6. [b] Calculated from bond distances and bond angles.

be illustrated classically by the fact that the most stable rotation of a pencil is about an axis perpendicular to its symmetry axis.) For oblate tops high K is favored, and consequently more states of high $|\langle\cos\theta\rangle|$ are populated. These effects are illustrated in Table III and Fig. 4, which show the results of numerical calculations of the population distribution for $-\langle\cos\theta\rangle$ for representative prolate and oblate tops.

The state-selecting field transmits molecules only by deflecting them, and this strongly discriminates against

low values of $\langle-\cos\theta\rangle$, as is illustrated in Fig. 4. For lack of a better method of display, Fig. 5 shows $\langle-\cos\theta\rangle$ averaged over the final population distribution as a function of B for several molecules. At higher voltages, molecules with small values of $\langle-\cos\theta\rangle$ will be deflected sufficiently to be transmitted; consequently the average orientation is less. The advantages of oblate tops are obvious.

The orientation can be enhanced (at the expense of the intensity) by making the exit hole smaller, as shown in Fig. 6. Also, for prolate tops higher values of K will be more populated at higher temperatures, and this will
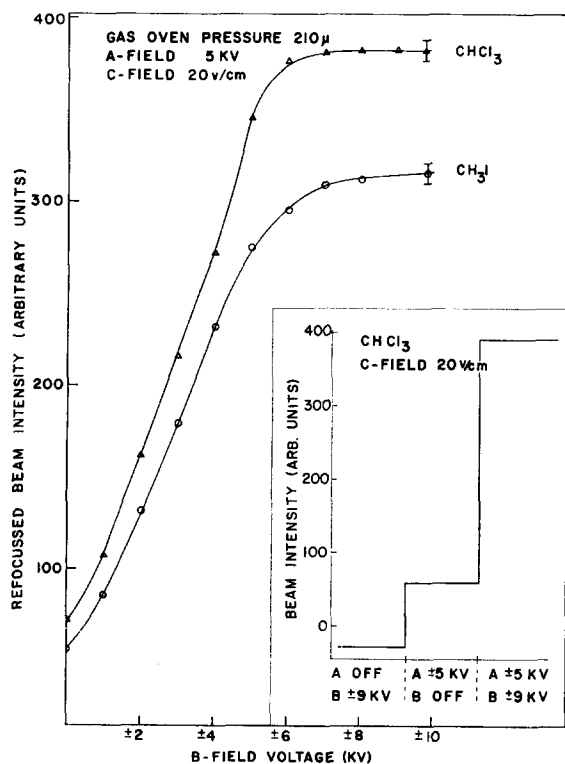

FIG. 9. Refocused signal vs B field voltage. The saturation of the refocused signal indicates that all molecules which emerge from C in focusable states reach the detector. Inset shows detector signal for various combinations of A and B voltages for $CHCl_3$. A slight defocusing of the shadow beam occurs when B alone is charged but maximum signal is obtained only when A and B are both on.
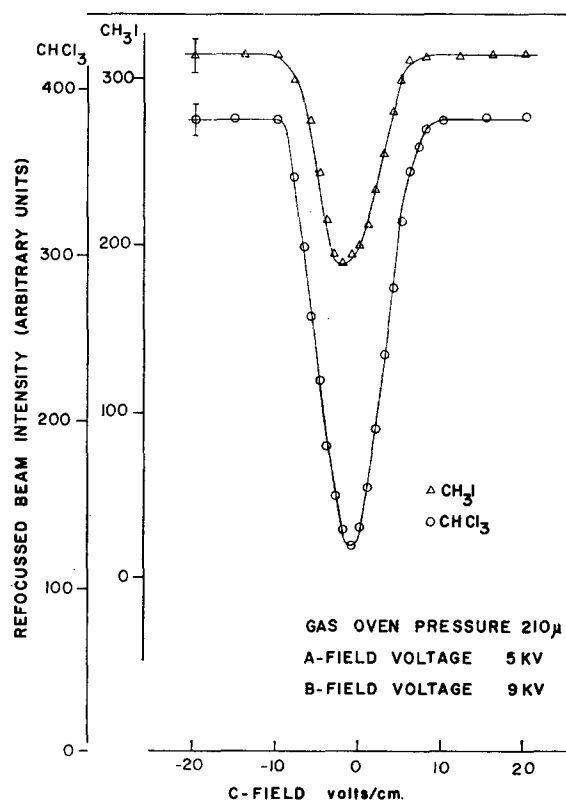

FIG. 10. Refocused signal vs C field (homogeneous) voltage. Decrease in signal (flopout) is due to nonadiabatic transitions occurring in C field.

TABLE IV. Dipole moments from deflection properties.

Gas	Dipole moment (D)	
	Transmission	Literature
CH_3I	1.64 ± 0.05	1.65[a]
CCl_3H	1.24 ± 0.02	1.20[a]
CF_3I	0.94 ± 0.05	1.0 ± 0.1[b] 0.93[c]
$t\text{-}C_4H_9I$	2.40 ± 0.05	2.13[a]

[a] Reference 6.

[b] F. Sterzer, J. Chem. Phys. 23, 762 (1955).

[c] A. DiGiacomo and C. P. Smyth, J. Am. Chem. Soc. 77, 774 (1955).

enhance the orientation. Calculations for CD_3I showed that for the same value of the field parameter B, the transmission and orientation were independent of T over the range 200–500°K. However, B varies as $1/T$, so at high T a fixed voltage would give greater orientation and smaller transmission.

We have not quantitatively measured the orientation of the molecules emerging from the state-selecting field. However, the results schematically illustrated in Fig. 9 indicate that molecules do make adiabatic transitions from the six-pole field to a homogeneous field. The results shown in Fig. 10 confirm that the transitions are adiabatic since it is possible to observe nonadiabatic transitions by allowing the homogeneous field strength to become very small. If the molecules make adiabatic transitions from the six-pole field to a homogeneous field, and we have shown that they can, then they must be oriented in the laboratory.[14]

B. Velocity Distribution

Faster molecules spend less time in the field than slower molecules; consequently few fast molecules will be transmitted. The calculated velocity distribution before and after transmission is shown in the inset in Fig. 7. The distribution of transmitted velocities is approximated by the modified Maxwell–Boltzmann distribution for a beam from a source at a lower temperature. For reference we plot as a function of B that source temperature at which the most probable beam velocity would be equal to the most probable velocty transmitted through the six-pole field. It is interesting to note that for CCl_3H above $B \sim 9$ the transmitted beam is "hotter" than the incident beam. This is a manifestation of the low-velocity molecules being focused at distances less than the length of the field and being deflected too far to pass through the exit aperture. The fraction of molecules with low speeds decreases relative to that with high speeds and the output "temperature" is greater than the input temperature.

[14] Because $MK < 0$, the dipole is oriented with its negative end closest to the negative field electrode.

C. Transmission

The only result of the calculations subject to quantitative experimental verification is the transmission. As shown in Figs. 3 and 6 and Table I the agreement between experiment and calculation is very good. (It should be noted that this agreement does not confirm the calculations for the velocity distribution, or more important, the orientation distribution. These distributions would be much more sensitive to the various assumptions made in the calculation, such as a collision-free, perfectly collimated beam. As a consequence those calculations should be regarded with some caution.) The agreement for CH_3I and for CCl_3H in Fig. 3 was so good that we questioned an initial disagreement for CF_3I. Considerably better agreement was obtained with a slightly different dipole moment for CF_3I, and this led us to investigate the possibility of using this technique to determine dipole moments. We have calculated the dipole moments shown in Table IV by least-square fitting the experimental focused intensities to the calculated transmission curves. Our predictions are in good agreement with results obtained from microwave spectroscopy, except for CF_3I. In that case we agree with gas-phase polarization measurements, and the microwave value appears to be imprecise.[15]

Figure 3 shows that oblate tops are more easily focused than prolate tops, as expected. However, it is interesting to note that the maximum transmission is roughly the same, $\sim 10\%$, regardless of the type of top. The inset of Fig. 3 shows this most clearly. For sufficiently large voltages the focusing is "too strong," and the transmission decreases. We are unable to observe these maxima because they occur at very high V_0 (38 kV for CCl_3H, 127 kV for CH_3I). However, this effect may explain the maxima observed by KB for the very oblate top, CI_3H.

ACKNOWLEDGMENTS

APPENDIX: TRANSMISSION IN THE HEXAPOLE FIELD

An array of six equally spaced and alternately charged rods of hyperbolic cross section will produce a field in which symmetric-top molecules can be focused (KB). The electric potential V in terms of the symbols of Fig. 2 is

$$V = V_0 (r/r_L)^3 \cos 3\phi,$$

[15] Similar agreement is not obtained with t-butyl I in which the focusing properties predict a dipole moment of 2.40 D rather than 2.13 D (Ref. 6). However, in the t-butyl I beam experiments a number of low-lying vibrational levels are populated which may well have different dipole moments and/or focusing properties. This has not been investigated further.

and for symmetric tops the radial force is[16]

$$F_r = \mu \langle \cos\theta \rangle 6 V_0 r / r_L{}^3 = \rho\beta r,$$

where

$$\beta = 6 V_0 / r_L{}^3 \quad \text{and} \quad \rho = \mu \langle \cos\theta \rangle.$$

The beam enters the optically opaque field with a doughnut-shaped cross section (inner radius d_1, outer radius r_s) and a molecule must be deflected in order to pass through the exit hole (radius d_2) a distance L away. The beam is well-collimated before entering the field, so all molecules enter with velocities parallel to the axis, and the equation of motion of a molecule incident at radius r_0 is

$$r = r_0 \cos(\rho\beta t^2/m)^{1/2}.$$

The molecule will pass through the field if $r < d_2$ at distance L (or $t = L/v$), or if $-d_2 \le r_0 \cos(\rho\beta L^2/mv^2)^{1/2} \le d_2$. This takes into account the fact that molecules can cross the axis. It is now necessary to average over the initial entry points in the field, the modified Maxwell–Boltzmann velocity distribution in the beam $f(v)$ and the distribution of values of $\cos\theta$, $g(\cos\theta)$.

The fraction of molecules with effective moments in the range ρ to $\rho + d\rho$ ($\rho = \mu \cos\theta$) and speeds in the range v to $v + dv$ which are incident on an annular ring of radius r and thickness dr is $2(r_s{}^2 - d_1{}^2)^{-1} f(v) dv\, g(\rho) d\rho r dr$. Molecules of moment ρ incident at r will be transmitted if the velocity is in the range

$$\frac{(\rho\beta L^2/m)^{1/2}}{\arccos(-d_2/r) + n\pi} \le v \le \frac{(\rho\beta L^2/m)^{1/2}}{\arccos(d_2/r) + n\pi},$$

where n is an index related to the number of times the molecule has crossed the axis.

After integrating over the transmitted velocity, the fraction of molecules transmitted with moments in the range ρ to $\rho + d\rho$ is then given by the fraction incident

[16] At the maximum field strengths in our apparatus ($\mathcal{E} \sim 37$ kV/cm) Eq. (1) agrees to 1% for $J \ge 4$ with exact calculations of J. H. Shirley, J. Chem. Phys. **38**, 2896 (1963). Since $J_{mp} \sim$ 50–100 and since the field strength is usually far less, Eq. (1) should be completely adequate. Again at this high field a moment may be induced by the field, but for a polarizability of 10^{-23} cc, the induced moment is only 1.3×10^{-6} D, and we completely ignore it.

in that range multiplied by a transmission, or

$$G(\rho) = \frac{2g(\rho)}{r_s{}^2 - d_1{}^2} \int_{d_1}^{r_s} W(\rho, r) r dr,$$

where $G(\rho)$ is the normalized distribution of orientations emerging and $g(\rho)$ the normalized distribution of *focusable* orientations in the initial beam, and where

$$W(\rho, r) = \sum_{j=0}^{\infty} e^{-\alpha_j}(\alpha_j + 1) - e^{-\beta_j}(\beta_j + 1),$$

$$\alpha_j = B \cos\theta [(j+1)\pi - \arccos(d_2/r)]^{-2},$$

$$\beta_j = B \cos\theta [j\pi + \arccos(d_2/r)]^{-2},$$

$$B = 3\mu L^2 V_0 / kT r_L{}^3.$$

Integrating over all ρ gives the transmission of the field:

transmission = incident intensity/transmitted intensity

$$= \int_0^{\mu} G(\rho) d\rho.$$

Finally the velocity distribution of the selected beam, $h(z)$ is related to the modified Boltzmann distribution, $f(z)$ by

$$h(z) = A f(z) \int_{R_1}^{R_2} r dr \sum_{n=0}^{\infty} \int_{L_1}^{L_2} g(\rho) d\rho,$$

where

$$z = v/\alpha = v/(m/2kT)^{1/2},$$

$$R_1 = d_1/d_2,$$

$$R_2 = r_s/d_2,$$

$$L_1 = z^2 B^{-1}(\arccos d_2/r + n\pi)^2,$$

$$L_2 = z^2 B^{-1}(\arccos -d_2/r + n\pi)^2,$$

A = normalization constant obtained by numerically integrating $h(z)$.

The distribution of orientations in the incident beam was calculated numerically as in KB, except those states for which $MK = 0$ were separately enumerated and the fraction of molecules with a specified $MK/J(J+1)$ was calculated for increments of 0.005 in $\langle \cos\theta \rangle$. Nuclear-spin effects were included.