

Orientation of CHF_3 Desorbed and Scattered from $\text{Ag}(111)$: Measurements Using Electrostatic Focusing

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A hexapole focusing field provides a general method for determining the orientation of polar polyatomic molecules. In the first application of this method to surface scattering we find that at 620 K CHF_3 is 27% more likely to desorb with the fluorine end of the symmetry axis pointing directly away from the surface than with the opposite orientation. As the temperature is lowered, the desorption anisotropy decreases. Direct scattering gives a preferential orientation opposite to that of desorption.

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The recent application of optical spectroscopy to detect molecules leaving surfaces¹⁻⁵ is contributing greatly to our understanding of inelastic and reactive gas-surface collisions. These techniques detect the distribution of individual quantum states of molecules leaving a surface and distinguish the role of the various translational, rotational, and vibrational motions in the collision. However, with few exceptions,^{3,4} these spectroscopic techniques are limited to diatomic molecules, because the complexity of the spectra of energetic polyatomics generally prevents analysis. Here we introduce a new technique, electric deflection, for studying the orientation of polyatomic molecules colliding with surfaces. This technique,⁶ which has been used extensively for studying gas-phase collisions,⁷ can be used for complex polyatomics because it does not require resolution of individual quantum states. The deflection of any polyatomic with an electric-dipole moment component along the *A* and/or *C* principal axis is sensitive to the rotationally averaged moment along the field. Thus, in contrast to spectroscopic techniques, it can be determined whether the electrically positive or negative end of a polyatomic molecule is more likely to leave a surface first. Electrostatic focusing techniques have also recently been used to study nuclear-spin equilibrium in gas-surface encounters.⁴ In contrast to time-of-flight, angular distribution, and most optical methods, the focusing technique, as implemented in this paper, is particularly suited for detecting small deviations from thermal equilibrium, because it gives a null result (no dependence of the transmitted signal on field polarity) at thermal equilibrium. Here we find that CHF_3 tends to desorb from $\text{Ag}(111)$ with its hydrogen atom oriented toward the surface, while direct scattering leaves the molecule with weak orientation in the opposite direction.

For orientation studies, nonlinear polyatomics are actually preferable to linear molecules, because the planar

rotation of a linear molecule quickly destroys information about which end of the molecule first left the surface. Several groups have used lasers to characterize the distribution of planes of rotation of diatomic molecules leaving surfaces,⁵ and orientation effects have been deduced from the effect of a magnetic field on Knudsen gas flow.⁸

Our apparatus (Fig. 1) is a standard surface-analysis chamber to which a capillary-array doser and differentially pumped deflection, buffer, and quadrupole-mass-spectrometer chambers have been added. The fixed doser and detector axes are both in the horizontal plane, separated by 60°.

The energy of a symmetric-top molecule with permanent electric dipole μ in a field E is⁶ $-\mu\rho E$, where ρ is expressed in terms of the symmetric-top quantum numbers J , K , and M by $\rho = KM/J(J+1)$. ρ is essentially the average cosine of the angle between the dipole moment along the molecular symmetry axis and the electric field, which is equal to the product of M/J , the cosine of the angle between the precessing angular momentum \mathbf{J} and \mathbf{E} , and K/J , the cosine of the angle between the molecular symmetry axes and \mathbf{J} . The strength of a hexapole field generated by six cylindrical electrodes

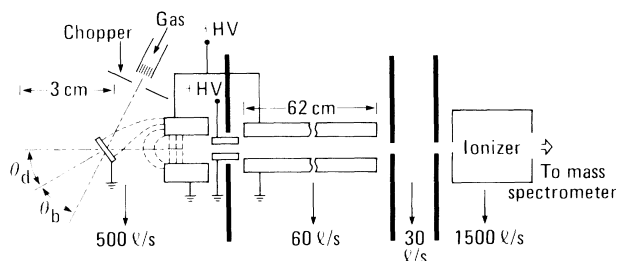


FIG. 1. Schematic diagram of apparatus. Except for the focusing field, the drawing is to scale.

increases quadratically with distance from the center. If the molecule leaves the surface with its dipole moment along the field direction, ρ is positive, the Stark energy of the molecule is negative, and the molecule is pulled into regions of higher field strength ("defocused"). Similarly, for negative values of ρ , the molecule is focused toward the center of the field. The value of ρ describing the molecule is determined by its rotational motion, as it desorbs, relative to the local field which is perpendicular to the grounded Ag surface. The polarity of the field at the surface is determined by the sign of the voltage on the three nongrounded electrodes of the hexapole.

For a typical field voltage, the fringing field at the sample surface is about 2 kV/cm, giving a typical precession period for \mathbf{J} about \mathbf{E} of 1 ns. This is small enough compared to the molecular transit time from the surface to the hexapole (40 μ s) to guarantee that the precession is adiabatic (ρ is conserved), while the field rotates between 60° and 90° (depending on surface orientation) over the flight path from the surface to the hexapole. To collimate the molecular beam while maintaining a definite quantization axis, an aperture of six miniature biased electrodes is located near the entrance of the larger hexapole field.

We characterized the orientation of molecules leaving the surface by

$$P = 100 \frac{S_+ - S_-}{(S_+ + S_-)/2}, \quad (1)$$

where S_+ and S_- are the signals focused into the detector with the electrode polarity positive and negative, respectively. If P is positive, then molecules with positive Stark effects predominate, indicating that molecules tend to leave the surface positive end first.

Before collecting focusing data, we prepared the single-crystal Ag(111) surface by polishing, sputtering, and annealing, and confirmed its cleanliness and crystallinity by Auger spectroscopy and low-energy electron diffraction. The dosing rate on the crystal was typically $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$. To obtain each value of P , the field polarity was alternated at 10-s intervals for about 20 cycles. The deflecting voltage was typically 4.6 kV, but the observed P values did not change significantly for voltages between 3 and 5 kV. Since molecular deflection depends on the ratio E/v^2 , this implies that the orientation distribution is not strongly coupled to the velocity distribution.

To check for artifacts giving spurious molecular polarization, the surface chamber, with its pump off, was filled with 10^{-6} Torr of CHF₃. To within the $\pm 0.6\%$ uncertainty, P for molecules effusing into the field was zero with either our Ag sample or unpolished stainless steel positioned in front of the hexapole.

In Fig. 2, crude angular distributions for molecules leaving the surface are displayed as the detected signal versus the surface orientation. (In Figs. 2 and 3, the

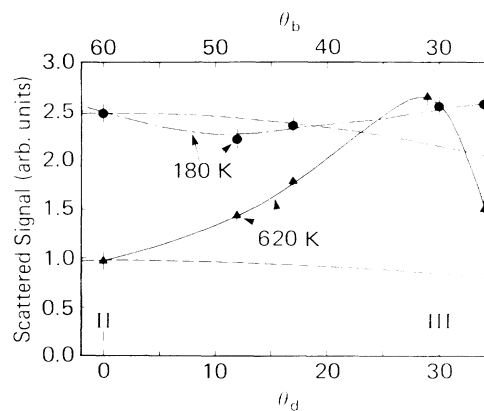


FIG. 2. Scattered signal vs surface orientation. Dashed lines are cosine distributions.

solid lines have simply been drawn through the data points.) Starting with the surface oriented with its normal parallel to the detector axis ($\theta_d = 0$), the surface is rotated about the axis perpendicular to both the beam and detector axes, with the angles θ_b and θ_d indicating the angles between the surface normal and the beam and detector axes, respectively. For Fig. 2, the azimuthal orientation of the crystal puts the $[10\bar{1}]$ direction in the scattering plane. The points displayed include a factor $\cos(\theta_d)/\cos(\theta_b)$ multiplying the raw data to correct for the fact that the doser always illuminates a larger region of the surface than that viewed by the detector. The difference in the total signal intensities at the two surface temperatures can be attributed to the inverse velocity dependence of our detector efficiency and to the different velocity distributions of the molecules scattered from the surface at the two temperatures.

The marked contrast between the angular plots at surface temperature $T = 180$ and 620 K reflects a difference in sticking probability at these two temperatures. The 180-K data are nearly a cosine distribution, suggesting a trapping-desorption mechanism, with the trapping probability near unity (estimated as 0.9 ± 1), while the 620-K data have a distinct peak at the specular angle, indicating that direct scattering, as well as trapping-desorption, occurs. From the estimated area of the specular peak, we calculate that at 620 K the probability for trapping is approximately 0.7 ± 0.1 . However, in our apparatus we cannot directly measure the trapping probability.

In Fig. 3, P is plotted as a function of temperature for three surface orientations, two of which, II and III, are included and indicated in Fig. 2. A third orientation, labeled I, is generated by rotation of the surface upward from position II until its normal points 30° above the detector axis. Here, the detector axis is 75° from the specular direction and 28° below the scattering plane, so that only molecules desorbed after trapping should be observed.

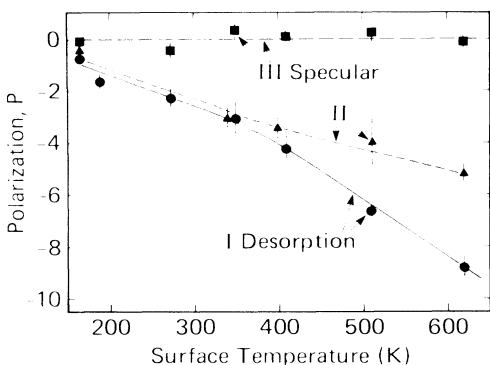


FIG. 3. Measured polarization P vs surface temperature at three surface orientations.

The fact that P is near zero at low temperatures is consistent with a near-unity trapping probability at these temperatures. (By trapping, we mean a collision which leaves the molecule thermally equilibrated and adsorbed on the surface.) For unity trapping probability, the desorbing molecules must be at thermal equilibrium (i.e., unoriented), because the ensemble of molecules leaving the surface are just those which would be leaving the surface if it were in an equilibrium environment. At a temperature where the sticking probability is less than unity, the desorbing molecules need not be at thermal equilibrium, since molecules leaving the surface “remember” that they arrived at the surface from a beam and not from an equilibrium distribution. Although a desorbing distribution in equilibrium with the surface will always give $P=0$ in our experiment, measurement of $P=0$ does not imply that the distribution is in overall thermal equilibrium, but merely that the desorbing molecules at the angle and velocity selected by the detector have no preference for one end over the other leaving the surface first.

Orientation I, which emphasizes the trapping-desorption channel, shows a negative polarization signal, which increases in magnitude as temperature increases. This temperature dependence is consistent with the fact that the orientation distribution of molecules desorbing along some particular direction from a surface at temperature T is the same as the orientation dependence of the sticking probability for molecules at temperature T incident along the same direction onto the surface held at T . When the temperature is very low, nearly all such slow incident molecules would stick, so that the orientation dependence of the sticking probability would be very weak.

Scattering near the specular direction (III) gives nearly zero polarization at all surface temperatures. As noted earlier, this is to be expected at low surface temperature, where the sticking coefficient is near 1. At higher temperatures, it must be taken into account that both directly scattered and desorbing molecules are scattered

at this angle. From Fig. 2, the signal from the desorbing molecules can be estimated from the dashed line drawn from the II orientation, which assumes a cosine distribution for desorption, and a constant probability for trapping desorption versus surface orientation. With correction for this signal, the polarization for the scattering signal component is $5.3 \pm 0.5\%$ at 620 K. The polarization at orientation II is midway between that of I and III, as is to be expected from the relative scattering angles.

We also attempted to observe polarization of CH_3NO_2 desorbing from Ag(111), but found it to be zero within our uncertainty. We believe that this results from a high sticking probability.

Because the measured polarizations are averages over all focused molecules, information about an actual orientation distribution cannot be generated, except by comparison to a model. We model the distribution of desorbing molecules by a product of three distributions: a Boltzmann velocity distribution at the surface temperature T , a rotational-state distribution at T , and a factor which depends on the orientation parameter ρ ,

$$I = P_B(J, K, M) P_B(v) (1 + a\rho) / v. \quad (2)$$

The v in the denominator corrects for the velocity dependence of the detector sensitivity. Equation (2) is clearly arbitrary, in that it assumes that the sticking probability varies linearly with the orientation parameter, while the velocity and rotational distributions are thermal. To simulate the focusing behavior of the field, the transmission probability P_t was determined numerically as a function of ρ/v^2 , which, for a given field, is proportional to the curvature of the trajectory. P_t is simply the fraction of the initial positions and directions of molecules entering the deflecting field with particular ρ/v^2 which eventually reach the detector. The detected signal is

$$S = \sum_{J, K, M} \int I P_t dv. \quad (3)$$

Numerical calculations using these expressions indicate that the measured percentage polarization P depends linearly on the distribution parameter according to $P = -78a$. Thus, the maximum polarization measured, -9.5% , gives a value for a of 0.12, indicating that, within this model, the ratio of probabilities for molecules leaving the surface with the H end pointed directly toward the surface to those with the opposite orientation is 1.27 to 1.

Applying microscopic reversibility as described above, we will discuss our desorption results in terms of the greater sticking probability of the H end of CHF_3 . The Ag(111) surface is quite inert,⁹ and is expected to be particularly so toward CHF_3 . There should be no activation energy for adsorption, so that whether an incident molecule physisorbs depends on whether the incident kinetic energy is transferred to other degrees of freedom

during the collision. Because the efficiency of energy transfer generally increases with the well depth, one possible source of the orientation we observe might be that the H end of the molecule is attracted more strongly to the surface than the fluorine end. Our impulse-model calculations, which study a rigid rotating CHF_3 undergoing multiple collisions with a thermally excited "hard-cube" model of the surface, show that the observed orientation cannot be a simple result of the mass distribution and shape of the repulsive potential of CHF_3 , but must indeed involve the orientation dependence of the attractive potential.¹⁰

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