Observation of rotational polarization produced in molecule-surface collisions

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The rotational polarization produced by scattering a rotationally cold beam of NO from Ag(111) has been measured by laser-induced fluorescence. A strong rotational polarization perpendicular to the surface normal is observed. The degree of polarization depends strongly on final rotational state, incident energy, and incident angle.

Molecular-beam scattering experiments on surfaces have focused primarily on measurements of angular and velocity distributions of the scattered particles. Quite recently, measurements of final internal state distributions of the scattered particles have become available by laser-induced-fluorescence (LIF) detection.[1-3] In gas-phase scattering experiments, in addition to these techniques, directional or vector properties are also accessible and provide information on many new features of the dynamics.[4] For example, in gas-phase reactive scattering both the dependence of reactant orientation on reaction probability[5] and the spatial alignment or polarization of product rotation[6] have been measured. We report here observation of the rotational polarization produced by scattering a rotationally cold beam of NO from an Ag(111) surface. A strong dependence of the degree of polarization is found on final rotational quantum number J and initial angle of incidence θ_i. These results clearly demonstrate that many new aspects of the surface-molecule dynamics can be revealed by measuring vector properties.

The experiments are based on measuring the distribution of orientations of the final angular momentum vector $\vec{J}$, by observing the dependence of LIF intensity on the direction of linear polarization of the exciting radiation. Any anisotropic distribution of a given $\vec{J}$ can be described classically by the distribution function $n(\theta,\phi)$ where θ and ϕ are the polar angles of $\vec{J}$ relative to some axis such as the surface normal $\hat{n}$. Since the azimuthal dependence of the surface corrugation is expected to be quite small, we assume that $n(\theta,\phi)$ is isotropic in ϕ and can be represented generally by the Legendre expansion

$$n(\theta) = \sum_{1=0}^{\infty} b_1 P_1(\cos\theta) , \qquad (1)$$

where θ is the angle between $\vec{J}$ and $\hat{n}$.

The polarization properties inherent in LIF detection are capable of measuring several moments of this distribution.[7,8] In the experiments reported here, the detected fluorescence is spectrally unresolved, representing an unweighted sum over P, Q, and R branches. In this case, the fluorescence is isotropic, and the LIF intensity I depends only on absorption,[8] i. e.,

$$I \sim \int n(\theta) |\hat{u} \cdot \hat{\epsilon}_L|^2 \sin\theta \, d\theta , \qquad (2)$$

where $\hat{u}$ is the transition dipole and $\hat{\epsilon}_L$ is the direction of the linear polarized laser. For LIF detection of NO via the $^2\Sigma \leftarrow ^2\Pi$ electronic transition, $\hat{u}$ is parallel to $\vec{J}$ for Q branch absorptions.[7] In the classical limit $(J \gg 1)$, evaluation of Eq. (2) with the distribution given in Eq. (1) yields for Q branch transitions

$$I(\theta_0) \sim b_0 \left[1 + \frac{2}{5} \left[\frac{b_2}{b_0} \right] P_2(\cos\theta_0) \right] , \qquad (3)$$

where θ_0 is the angle of $\hat{\epsilon}_L$ relative to $\hat{n}$. The total population of the state b_0 is measured when $\theta_0 = 0.955$, i. e., the "magic angle" where $P_2(\cos\theta_0) = 0$. The polarization anisotropy $\mathscr{P}$ is given by

$$\mathscr{P} = \frac{b_2}{b_0} = 5 \left[\frac{I(0) - I(\pi/2)}{I(0) + 2I(\pi/2)} \right] , \qquad (4)$$

where $-2.5 \leq \mathscr{P} \leq 5.0$. These two limits correspond to perfect alignment of $\vec{J}$ perpendicular to and parallel to $\hat{n}$, respectively. Thus, measurements of $I(\theta_0)$ yield both the population and the polarization anisotropy for the state J. Small J-dependent corrections are necessary for the coefficients $\frac{2}{5}$ in Eq. (3) and 5 in Eq. (4) due to the spectral overlap of the weak P_{21} or R_{12} bands with the Q branch transitions.

The LIF spectrum of specularly scattered NO is measured when a supersonic nozzle beam of NO seeded in He is incident on a AG(111) surface as described previously.[3] The LIF intensity is monitored as the angle θ_0 is varied by rotating the plane of polarization of the lineraly polarized uv laser beam with a Soleil-Babinet compensator set for $\lambda/2$ phase shift. Three pairs of mutually orthogonal coils were used to reduce stray magnetic fields in the scattering region to $\leq$ 10 mG. This feature is necessary in order to preserve the rotational polarization produced in the scattering. Since NO is paramagnetic, the precession of $\vec{J}$ about the earth's magnetic field in the 8 mm flight path before detection would be significant.

Three types of measurements were performed. Firstly, the LIF intensity of selected Q branch transitions were monitored as a function of θ_0. Secondly, θ_0 was set at the "magic angle" and the state populations b_0 measured as a function of J. Thirdly, the polarization anisotropy $\mathscr{P}$ was measured for Q branch transitions as a function of J by repeated alternate measurements for each transition at $\theta_0=0$ and $\theta_0=\pi/2$ and application of Eq. (4).

Measurements of the LIF intensity as a function of θ_0 have been made for various initial conditions. In many cases, a strong polarization was observed. An example is show in Fig. 1. Here the LIF intensity of a $J=31.5$ Q_1 transition[9] is shown as a function of θ_0. This clearly demonstrates that the distribution $n(\theta)$ is strongly polarized perpendicular to $\hat{n}$. A fit of Eq. (3) to the data yields $\mathscr{P}=-1.44$. Similar results were obtained for Q_2
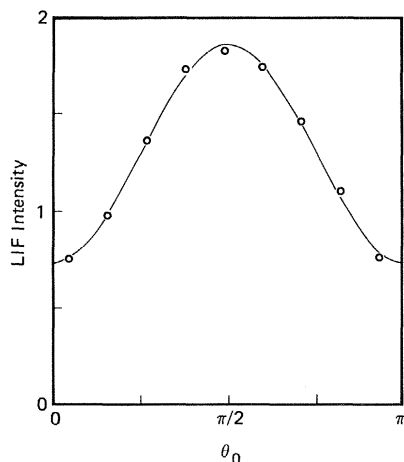
transitions[9] as well. Quantum mechanically, the rotational polarization is described as a nonuniform distribution over the M substates of J. The observed polarization means that there is a strong preferential population of the substate $M=0$, where the natural axis of quantization is given by the surface normal $\hat{n}$. The fact that J is polarized perpendicular to $\hat{n}$ can be understood from the analysis of rotational state distributions produced in the direct inelastic scattering of NO from Ag(111).[3] It was demonstrated there that the rotational excitation scaled with the normal component of the incident kinetic energy E_n. This implies that the rotational excitation is caused principally by forces acting normal to the surface, and suggests that the final angular momentum vectors $\vec{J}$ should as a result be preferentially aligned perpendicular to the surface normal. That the observed polarization is defined with respect to $\hat{n}$ indicates that no static electric or magnetic fields, either due to experimental artifact or to the surface scattering, adiabatically reorient the axis of quantization prior to probing by LIF. Although substantial, the observed polarization anisotropy is significantly less than the smooth surface limit $\mathscr{P}=-2.5$ suggested by the E_n scaling of the rotational state populations.

A representative spectrum of the total populations, plotted as $\ln(b_0/2J+1)$, as a function of the final internal energy is given in Fig. 2. This spec-

FIG. 1. LIF intensity as a function of θ_0 for a $J=31.5Q_1$ transition for the conditions $T_S=$ 650 K, $\theta_i=40°$, and $E_i=0.75$ eV. The points are experimental while the solid line is a fit of Eq. (3) to the data.
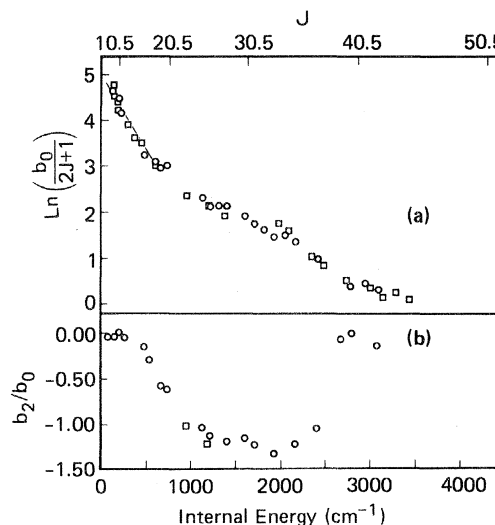

FIG. 2. Rotational state distribution $\ln[b_0/(2J+1)]$ (a), and the rotational polarization b_2/b_0 (b), as a function of NO internal energy (bottom) or rotational quantum number for the $^2\Pi_{1/2}$ state (top). The $\bigcirc$ are for Q_1 transitions and the $\square$ are for Q_2 transitions. Initial conditions were $T_S=$ 650 K, $\theta_i=40°$, and $E_i=0.75$ eV.

trum, similar to the ones published earlier[3], exhibits two distinct regions, at low J the distribution corresponds to a temperature and at high J it is non-Boltzmann. This high-J part has been tentatively attributed to a direct repulsive interaction, in particular a rotational rainbow.[3] The two regions are very distinct in the corresponding specturm $\mathscr{P}$ presented in Fig. 2 as well. In the low-J region, no polarization is observed for these initial conditions. For other θ_i, a small $\mathscr{P}$ is observed for this region, both parallel to $\hat{n}$ at $\theta_i \approx 0°$ and perpendicular to $\hat{n}$ at $\theta_i > 40°$. In the high-J region the polarization reaches a plateau of $\mathscr{P} \approx -1.3$. At very high J, a sharp cutoff occurs in the polarization at $J \approx 37.5$, while no sharp feature occurs for b_0. Further measurements show that the state J where this sharp cutoff occurs depends strongly on E_n.

From Fig. 2 it is clear that the low- and high-J parts of the spectra behave quite differently, both in terms of b_0 and $\mathscr{P}$. Preliminary trajectory calculations suggest these differences may be related to the initial orientation of the molecule relative to the surface.

The observed strong rotational polarization reported here provides additional evidence for rotational excitation in direct inelastic scattering with very little effect of surface corrugation. More importantly, the rotational polarization appears to be a very sensitive probe of the actual dynamics. Many intriguing questions remain as to what ultimately determines the degree of polarization and its dependence of J, T_S, and incident beam conditions.

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[9]Q_1 and Q_2 refer to Q branch transitions in the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-orbit states, respectively.