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COMMUNICATIONS

Rotational alignment of NO desorbing from Pt(111)

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Researchers have used a variety of state selective detection schemes to probe the energy distribution of molecular desorbates.¹ These methods have included the measurements of velocity distributions, electronic and vibrational excitation efficiencies, and rotational energy distributions. For the well-studied case of NO desorption from Pt(111),²⁻²⁰ energy disposal into these degrees of freedom was determined to be fairly well accommodated with the surface for temperatures $T_s < 450$ K.¹⁴⁻²⁰

A sensitive measure of desorption dynamics might be the degree of rotational alignment in the desorbing molecule.²¹ Such a measurement would provide information about the last interaction which the molecule makes with the surface before escaping. Novakoski and McClelland²² observed a preference in molecular orientation for the desorption of CHF₃ from Ag(111). We have carried out experiments to determine the degree of rotational alignment in NO as it desorbs isothermally from Pt(111) by measuring how the resonance enhanced multiphoton ionization (REMPI) signal varies with the linear polarization direction of the laser beam.

The Pt(111) crystal was cut, polished, and cleaned using standard metallographic techniques. A differentially pumped pulsed nozzle dosed a 0.2 cm² region of the 1 cm² surface. The Pt(111) sample was maintained at a temperature of 553 K. Following the 140 μs dose, the molecules desorbed isothermally from the surface. Helmholtz coils reduced the stray ambient magnetic field, and hence eliminated scrambling of the alignment of the NO free radical. A laser probed the alignment distribution of the ground state rotational levels via 1 + 1 REMPI.²³ Production of the necessary 225 nm radiation for excitation of the NO $A^2\Sigma^+ - X^2\Pi(0,0)$ band is described elsewhere.²⁴ A photoelastic modulator alternated the linear polarization of the laser beam between two orthogonal directions. The laser fired 200 μs after the end of the dose pulse and passed 2 mm above the surface with a 1 mm² cross section. The REMPI ions were mass selected using the time-of-flight technique, detected by multichannel plates, and recorded on a computer. The dose-desorb-probe cycle repeated at 10 Hz while the laser polarization switched between orthogonal linear polarizations at 5 Hz. Under these conditions, the surface coverage from

which the detected molecules desorb is accurately reproduced but presently unknown.

The quadrupole moment of the alignment distribution, $A_0^{(2)}(J)$, was determined for various rotational levels J of the NO ground state. $A_0^{(2)}(J)$ was calculated from the measured polarization dependence of a particular transition, while including the effects of saturation and intermediate state alignment.²⁴ In the classical limit, the value of $A_0^{(2)}(J)$ represents the ensemble average of $3 \cos^2 \theta - 1$ where θ is the angle between the angular momentum vector \mathbf{J} of the molecule and the surface normal $\hat{\mathbf{n}}$. $A_0^{(2)}(J)$ ranges from 2 to -1 , where positive values represent a preference for \mathbf{J} along $\hat{\mathbf{n}}$, negative values \mathbf{J} perpendicular to $\hat{\mathbf{n}}$. The former corresponds to "helicopter" motion of the departing molecule, the latter to "cartwheel" motion (see Fig. 1).

Figure 2 shows $A_0^{(2)}(J)$ as calculated from different rotational branches. We observe little to no rotational alignment for $J < 12.5$, while higher rotational levels exhibit a slightly positive quadrupole moment. An alignment moment of $+0.14$ implies that 20% more molecules desorb with their plane of rotation resembling that of a helicopter [Fig. 1(a)] than those resembling a cartwheel motion [Fig. 1(b)], assuming that the spatial distribution of \mathbf{J} is described by an ellipsoid. We found that both Λ -doublet states exhibited the same degree and direction of alignment, within the uncertainty of our measurements. This latter observation discounts an electronic orbital alignment effect²⁵ as the source of the observed rotational alignment. It should be noted that our detection scheme is a measure of number den-

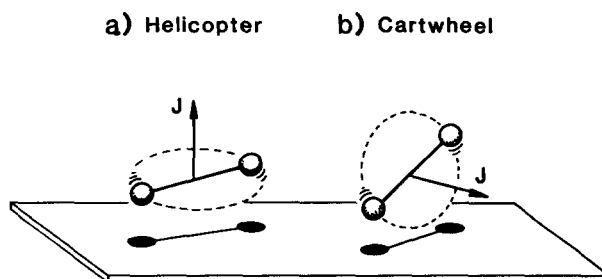


FIG. 1. Rotational alignment relative to the surface plane. The helicopter motion (a) is favored for $A_0^{(2)} > 0$ while the cartwheel motion (b) is favored for $A_0^{(2)} < 0$.

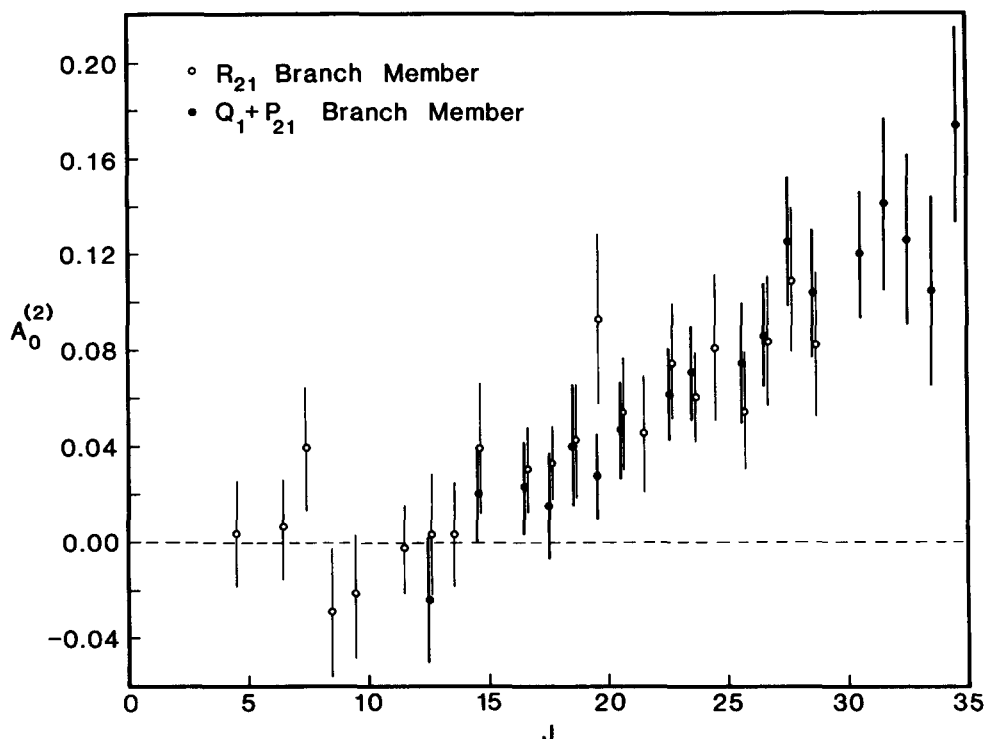


FIG. 2. The quadrupole moment of the rotational alignment distribution as a function of the quantum number J . $A_0^{(2)}(J)$ was calculated from the polarization dependence of two different branches, each originating from the same Λ doublet of the $\text{NO}^2\Pi_{1/2}$ ground state. The dashed line corresponds to no alignment. The error bars represent one standard deviation.

sity, not flux. Hence the observed alignment can be attributed to an alignment-dependent desorption rate, an alignment-dependent velocity distribution, or a combination thereof. However, because of the high degree of translational accommodation measured for this system,¹⁶ we argue the first interpretation holds.

This work is the first study to observe rotationally-resolved alignment of molecules desorbing from a surface. Ertl, Walther, and co-workers reported no polarization preference in their scattering experiments of $\text{NO}/\text{Pt}(111)$ ¹⁸ and $\text{NO}/\text{graphite}$,²⁶ although the effect was probably smaller than their error bars. Our results are consistent with the $\text{NO}/\text{Pt}(111)$ desorption measurements of Mantell, Cavanagh, and King²⁰ who observed no alignment at low J .

Our results cannot be reconciled with the simple picture of a direct transition from the known low-temperature equilibrium position (NO bound normal to the surface)⁴⁻⁷ to the gas phase free rotor, without the existence of an intermediate state. It is hoped that measurements such as these will distinguish between various models in the literature that propose desorption transition states similar to that of a free rotor²⁷ or that of a frustrated rotor undergoing a restricted wagging motion.²⁸

Through microscopic reversability and detailed balance arguments, we assert that adsorption at 553 K is alignment-dependent for molecules having a large amount of rotation. In particular, molecules approaching the surface with rotational motion similar to that of a helicopter have a better chance of sticking than those molecules with a cartwheel motion.

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