Rotational alignment of NO desorbing from Pt(111)

D. C. Jacobs, K. W. Kolaskinski, R. J. Madix, and R. N. Zare
Chemistry Department, Stanford University, Stanford, California 94305

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Researchers have used a variety of state selective detection schemes to probe the energy distribution of molecular desorbrates. 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), energy disposal into these degrees of freedom was determined to be fairly well accommodated with the surface for temperatures $T_s < 450$ K.

A sensitive measure of desorption dynamics might be the degree of rotational alignment in the desorbing molecule. Such a measurement would provide information about the last interaction which the molecule makes with the surface before escaping. Novakoski and McClelland observed a preference in molecular orientation for the desorption of CHF$_3$ 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 cm$^2$ region of the 1 cm$^2$ surface. The Pt(111) sample was maintained at a temperature of 553 K. Following the 140 $\mu$s 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 REMPI. Production of the necessary 225 nm radiation for excitation of the NO $A^2\Sigma^+ - X^2\Pi (0,0)$ band is described elsewhere. A photoelastic modulator alternated the linear polarization of the laser beam between two orthogonal directions. The laser fired 200 $\mu$s after the end of the dose pulse and passed 2 mm above the surface with a 1 mm$^2$ 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. In the classical limit, the value of $A_0^{(2)}(J)$ ranges from 2 to -1, where positive values represent a preference for $J$ along $\hat{n}$, negative values $J$ perpendicular to $\hat{n}$. 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 than those resembling a cartwheel motion, assuming that the spatial distribution of $J$ is described by an ellipsoid. We found that both $\Lambda$-doublet states exhibited the same degree and direction of alignment, within the uncertainty of our measurements. This latter observation discounts an electronic orbital alignment effect as the source of the observed rotational alignment. It should be noted that our detection scheme is a measure of number den-

\[ A_0^{(2)}(J) \]
A desorption transition states similar to that of a free rotor 27 or motion. 28 that of a frustrated rotor undergoing a restricted wagging state.

In particular, molecules approaching the surface with translational motion similar to that of a helicopter have a better chance of sticking than those molecules with a cartwheel dependence for molecules having a large amount of rotation.

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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 rotor 27 or that of a frustrated rotor undergoing a restricted wagging motion. 28

Through microscopic reversibility 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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FIG. 2. The quadrupole moment of the rotational alignment distribution as a function of the quantum number J. A_0(2J+1) (J) was calculated from the polarization dependence of two different branches, each originating from the same A doublet of the NO(211/2) ground state. The dashed line corresponds to no alignment. The error bars represent one standard deviation.