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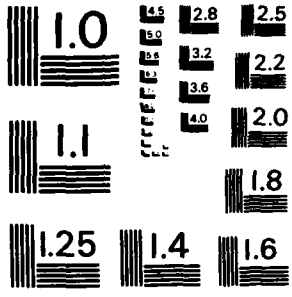

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The scattering of nitric oxide (NO) from a clean single-crystal of silver [the (111) face] has been studied. The rotational and fine structure distributions of NO $X^2\Pi$ have been determined as a function of surface temperature and of incident kinetic energy normal to the surface plane. The analysis technique is that of laser-induced fluorescence using a Nd:YAG pumped dye laser which is both frequency doubled and Raman shifted to overlap the NO (γ) band system in the UV. It is found that the energy transferred into the NO rotational degree of

NO $X_{2\pi}$

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freedom in a single gas-surface encounter is expressed by

$$\langle E_r \rangle = a(E_n) + (E_w) + b(E_s)$$

where $\langle E_r \rangle$ is the mean rotational energy, E_n the normal component of the NO kinetic energy, E_s the surface temperature, E_w a parameter characterizing the NO/Ag(111) well depth, and a and b are coefficients that express the fraction of kinetic and surface energy appearing as rotational excitation. For NO $X^2\Pi_{1/2}$ we find that E_w = 2850 K, a = 0.88 and b = 0.18 and for NO $X^2\Pi_{3/2}$, E_w = 2080 K, a = 0.132, and b = 0.11.

STUDY OF GAS-SURFACE INTERACTIONS BY LASER-INDUCED FLUORESCENCE DETECTION

FINAL REPORT

RICHARD N. ZARE

MAY 1, 1984

U. S. ARMY RESEARCH OFFICE

DAAG 29-80-K-0035

STANFORD UNIVERSITY

STATEMENT OF PROBLEM STUDIED

AND SUMMARY OF EXPERIMENTAL RESULTS

We have studied the interactions in a gas-surface system by the laser-induced fluorescence (LIF) techniques. Specifically, we have studied the rotationally inelastic scattering of a molecular beam of nitric oxide (NO) from a single-crystal silver surface (the (111) face) under ultrahigh-vacuum conditions. Using a tunable UV laser, we were able to probe the rotational and electronic state distributions of the scattered NO. Measurements were performed as a function of surface temperature, incident NO kinetic energy, and incident scattering angle.

The important results from this study are, first to demonstrate the feasibility of using LIF techniques in surface scattering experiments, and also to show the usefulness of doing so.

The experimental results can be summarized as follows:

1) The scattered NO rotational distributions were Boltzmann in nature, i.e., were characterized by a single temperature, for $E_n \leq 1160$ K, where E_n represents the component of the incident NO kinetic energy that is normal to the surface. The distribution was non-Boltzmann at $E_n = 2321$ K, showing a broad maximum at rotational quantum numbers (J) between 22.5 and 32.5, which corresponds to the highest J's observed. This maximum is interpreted as a rotational rainbow due to a maximum in the rotational excitation function.

2) Due to the nature of the molecular beam, the incident NO is almost completely relaxed in the the $\Omega = \frac{1}{2}$ fine structure state (the lower in energy) and into the lowest few rotational levels. Significant

excitation of the upper fine structure level is observed on scattering and at higher beam energies the fine structure populations scale monotonically with E_n just as the rotational populations do.

3) It was found that energy transferred into the NO rotational degree of freedom in a single collision with a clean Ag(111) surface could be expressed by the following equation:

$$\langle E_r \rangle = a(E_n + E_w) + b(E_s)$$

where $\langle E_r \rangle$ is the mean rotational energy (the temperature if the distribution is Boltzmann), E_s is the surface temperature, E_w is the depth of the NO/Ag(111) potential well, and a and b are constants which express the fraction of kinetic and surface energy appearing as rotational excitation. For the $\Omega = \frac{1}{2}$ fine structure component our best fit values for these parameters are $E_w = 2850$ K, $a = 0.88$, $b = 0.18$, while for the $\Omega = \frac{3}{2}$ component $E_w = 2080$ K, $a = 0.132$, $b = 0.11$.

We have also considered theoretical aspects of the diatom-surface scattering problem. In particular, within an impulsive potential framework (the 'hard cube' model), we explored the role surface atom motion plays in rotationally inelastic scattering. We found that inclusion of a range of surface cube velocities strongly affects such features as rotational rainbows and cutoffs in higher rotational state populations due to trapping by the surface.

In conclusion, we have completed a detailed experimental study of gas-surface dynamics by investigating the rotationally inelastic scattering of nitric oxide by an Ag(111) surface using a laser-based detection scheme; and we have carried out complementary theoretical computations.

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