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Vibrational and Rotational Energy Distribution of NO Scattered from the Pt(111) Crystal Surface: Detection by Two-Photon Ionization

M. Asscher, W. L. Guthrie, T.-H. Lin, and G. A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Department of Chemistry, University of California, Berkeley, California 94720

The vibrational and rotational state distributions of a supersonic nitric oxide beam, scattered from a Pt(111) single crystal surface, were investigated. A two-photon ionization technique was applied to monitor the internal energy content of the scattered molecules. Vibrational distributions were found to be colder than that corresponding to the crystal temperature between 450–1100 K. Rotational temperatures were also found to be colder than expected for thermal equilibrium with the platinum surface.

The dynamics of gas-molecule–surface interactions has received increasing experimental and theoretical attention in recent years. Laser-induced fluorescence or bolometer detection techniques were used to investigate the excitation of rotational states in NO molecules scattered from metal surfaces,[1-4] and of CO and HF molecules scattered from the LiF surface.[5,6] Atomic recombination of nitrogen on an iron foil produces vibrationally hot N_2 molecules, as determined by high-energy electron beam excitation.[7] Theoretical studies have attempted to predict the rotational excitation of diatomic molecules upon scattering from smooth solid surfaces.[8-10]

We report the direct observation of vibrationally excited NO molecules scattered from a clean Pt(111) crystal surface using a two-photon ionization (TPI) technique. The vibrational and rotational energy distributions were determined as a function of crystal temperature and angle of scattering. We found that the population of excited vibrational $(v''=1)$ and rotational states is less than the population when thermal equilibrium between the crystal and the desorbed NO is assumed.

The molecular-beam–surface scattering apparatus was described elsewhere[11]; the modified version used in this laser ionization study will be described in detail in a future publication.[12] The scheme of the scattering and ionization detection is shown in Fig. 1. Briefly, a supersonic molecular beam from a differentially pumped source impinges upon a single-crystal sample, located in the ultrahigh vacuum scattering chamber. The beam characteristics are 100 meV incident kinet-
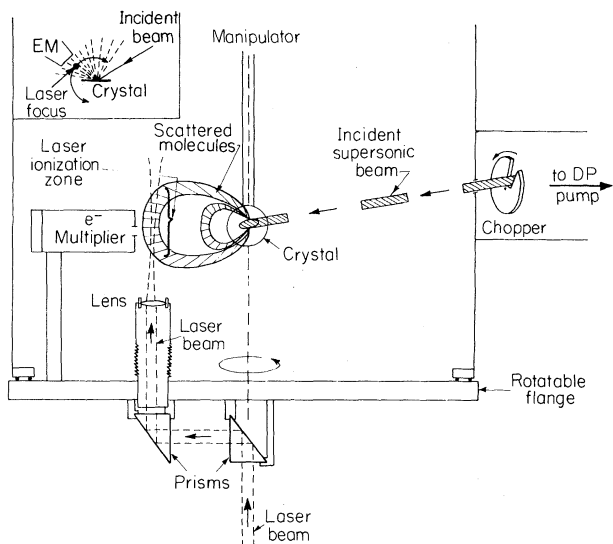

FIG. 1. Schematic of the molecular-beam–surface scattering experiment with laser-induced two-photon ionization as a probe for internal-state energy distributions.

ic energy,[13] 45 K incident rotational temperature, and 52°–64° incident angle with respect to the surface normal. A variable-speed, low-frequency chopper (1–20 cps) is used to obtain beam pulses in order to reduce the background NO pressure in the scattering chamber and improve the signal-to-background ratio. The background NO contributes up to 10% of the detected signal of the ground-state molecules ($v'' = 0$). The base pressure in the scattering chamber was 2×10^{-10} Torr and 5×10^{-10} in the presence of the chopped NO beam. The crystal sample was cleaned by ion sputtering and annealed up to 1200 K. Crystal cleanliness was determined by Auger electron spectroscopy, and the temperature in the range of 295–1100 K was monitored with a Pt-Pt 10%-Rh thermocouple that was spot welded to the crystal. A tunable uv laser beam focused with a 12.5-cm $f/1$ quartz lens intercepts the scattered molecules at a distance of 2.5 cm from the Pt(111) crystal. The laser beam and detector apparatus rotate about the crystal, allowing measurements of angular distributions and internal energy distributions at each angle. The ion signal detector is an electron multiplier (Hamamatsu Cu-Be R-595) operated at bias voltages in the range of 2000–3500 V. The electron multiplier located near the laser beam focus collects all ions generated by the radiation. A delay of 1 μsec between the laser pulse and the appearance of the ion signal allowed the effective separation of the ion signal from the scattered-laser-light pulse. For each laser pulse, the ion current pulse was divided by the laser intensity. The normalized signal was typically averaged over 20–100 laser shots. Data digitization and control of the dye laser grating were carried out by a Nova-2 minicomputer. The laser system[14] (Quanta-Ray) is a neodymium--doped yttrium-aluminum-garnet (DCR-1A) pumped dye laser (PDL-1) with a wavelength extention unit (WEX-1), capable of generating tunable uv radiation in the range 217–400 nm. Maximum energy near the wavelength range of 225 and 236 nm was about 1 mJ/pulse. Rotational distribution spectra were obtained at energies not exceeding 200 μJ/pulse, with a typical resolution of 2 cm^{-1} (full width at half maximum).

The use of two-photon or multiphoton ionization techniques as a probe of internal-state distributions in the UHV range of molecular densities depends on two major factors: (a) The first electronic transition should be to a bound or predissociative state, and accessible by a one-photon

absorption process. (b) The first electronic transition should be the rate-limiting step in the path to ionization[15] unless all successive transitions are to unbound states.

For the NO molecule the first requirement is satisfied since the first transition is to the $A^2\Sigma^+$ ($v'' = 0$) state, which is a bound state with a fluorescence lifetime of 200 nsec. The second requirement is also satisfied because the second transition is to the ionization continuum. The NO ion signal was found to be linearly dependent on the laser energy in the range 40–800 μJ/pulse. Calibration of the rotational spectra was carried out with gas-phase NO at room temperature. Using the $Q_{11} + P_{21}$ and $R_{11} + Q_{21}$ rotational branches we always obtain rotational temperatures of 290 ± 20 K. The experimental rotational line intensities $N_{J''}$ are plotted as $\ln[N_{J''}/(2J'' + 1)]$ versus the rotational energy. A straight line emerges, from which a rotational temperature can be extracted. The rotational line intensities directly reflect the ground-state rotational population and are not corrected for the Honl-London rotational line strength factors. This is due to saturation of the first electronic transition under our experimental conditions.[16] Studies of the sensitivity of the TPI technique that were carried out as a function of pressure yielded detectable ion signals at molecular densities equivalent to as low as 10^{-12} Torr of NO. For NO, TPI is at least one order of magnitude more sensitive than the optimum laser-induced fluorescence measurements.[1-5,12]

In Fig. 2 the vibrational population of scattered NO molecules is shown as a function of crystal temperature (T_s). The population ratio NO($v'' = 1$)/ NO($v'' = 0$) for $T_s = 450$–1100 K (crosses on the short-dashed line in Fig. 2) deviates substantially from the ratio (solid line) that is expected if there was complete accommodation of the scattered NO molecules with the surface and there were no interfering processes during desorption. The accommodated ratio can be expressed by the Boltzmann factor: NO($v'' = 1$)/NO($v'' = 0$) = $\exp(-E_v/kT_s)$, where E_v is the energy of the first vibrationally excited state, $E_v = 1876$ cm^{-1}, and T_s is the corresponding crystal temperature. The NO($v'' = 1$) population was measured by tuning the laser to the $A^2\Sigma^+$($v'' = 0$) $\leftarrow X^2\Pi$($v'' = 1$) transition near 236 nm. The intensity of the $Q_{11} + P_{21}$ bandhead was used to determine the relative $v'' = 0$ (filled circles in Fig. 2) and $v'' = 1$ populations as a function of T_s. The normalized ratios ($v'' = 1$)/ ($v'' = 0$) that appear in Fig. 2 (crosses on the short-dashed line) are obtained by direct measurement
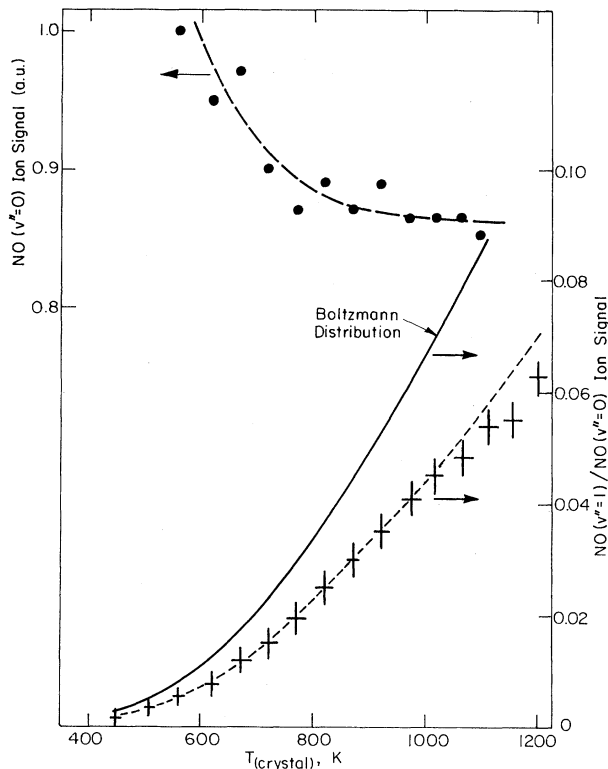
FIG. 2. Vibrational excitation of NO molecules scattered from the Pt(111) surface as a function of surface temperature. Solid line represents the calculated Boltzmann ratio of $NO(v'' = 1)/NO(v'' = 0)$ at a given surface temperature (right ordinate). Long-dashed line and filled circles show the $NO(v'' = 0)$ experimental signal (left ordinate). Crosses are the normalized $NO(v'' = 1)/NO(v'' = 0)$ experimental ratio (right ordinate). The short-dashed line represents the expression $0.67 \exp(-E_v/kT_s)$, where $E_v = 1876$ cm^{-1} and T_s is the crystal temperature.

of this ratio[12] at $T_s = 620$, 820, 990, and 1155 K; the rest of the experimental points are relative to these.

A cosine angular distribution was found for the $NO(v'' = 1)$ molecules at $T_s = 820$ K. Thus, the vibrationally excited NO molecules adsorb on the surface long enough to desorb with a cosine distribution. Modulated molecular beam[17] and angular distribution[13] studies of the same system carried out in our laboratory indicate that the mean surface residence time of NO becomes shorter than 200 μsec very rapidly above $T_s = 600$ K. It was found before,[13] and confirmed in this work, that in the angular distributions of ground vibrational state molecules, an increasing portion of the scattered molecules appear near the specular angle (52° from the normal to the surface in

this study) with increasing T_s via an inelastic scattering mechanism.

Three temperature-dependent processes affect the degree of vibrational excitation observed experimentally: the decrease of the adsorption probability at higher T_s, the rate of multiphonon excitation of the originally cold NO to the first vibrational state, and the rate of NO desorption.

The NO flux at the surface normal, where the vibrational ratios were measured, appears to originate primarily from the desorption process, at least up to $T_s = 900$ K and possibly higher temperatures.[13] The decrease in the sticking coefficient leads to an increase in the inelastically scattered fraction, which appears away from the surface normal. Therefore the ratio measured at the normal should reflect the vibrational population for the trapped and then desorbed molecules rather than those that are inelastically scattered, and should be nearly unaffected by variations of the sticking probability at the above temperature range.

The measured $(v = 1)/(v = 0)$ ratio (crosses in Fig. 2) could be fitted by the empirical expression $0.67 \exp(-E_v/kT_s)$ (short-dashed line in Fig. 2), where T_s is the crystal temperature and $E_v = 1876$ cm^{-1} is the vibrational energy. The constant preexponential factor, 0.67 (lower $v'' = 1$ population compared with the Boltzmann population at the crystal temperature), may originate from different desorption kinetics for $v'' = 1$ and $v'' = 0$ NO molecules. The rate constant for the desorption of NO in the $v'' = 0$ vibrational state may be larger than the rate constant for desorption of NO in the $v'' = 1$ vibrational state. Under the assumption of first-order desorption rate constants and identical activation energy for desorption, the preexponential factors must be different to explain the temperature-independent ratio of the rate constants.

The rotational distributions of a rotationally cold (45-K) incident nitric oxide beam upon scattering were determined as a function of platinum crystal temperature in the range 295–870 K. The results are summarized in Table I. The rotational temperatures of scattered NO molecules from a clean Pt(111) surface are colder than what is expected if complete accommodation between the trapped NO molecules and the surface occurs. These results can be qualitatively rationalized by assuming that the NO desorbs directly from a rotationally frozen chemisorbed state as suggested by Cavanagh and King.[4] If the NO cannot equilibrate in a more rotationally free physisorbed

TABLE I. Rotational temperature (T_{rot}) at various crystal temperatures.

$T_{crystal}$ (K)	T_{rot} (K)	Comments
295	325 ± 30	scattering from an overlayer of NO
465	360 ± 35	detector at normal to the surface
485	350 ± 35	detector at normal to the surface
580	390 ± 40	detector at normal to the surface
580	470 ± 45	detector at specular angle ($\equiv 52°$)
580	465 ± 45	He/NO 4:1 seeded beam, detector at specular angle
820	440 ± 45	detector at normal to the surface
870 $(J'' < 18\frac{1}{2})$	330 ± 35	detector at normal to the surface
870 $(J'' \geqslant 23\frac{1}{2})$	580 ± 60	detector at normal to the surface

state, the experimental rotational temperature should not necessarily be equal to the crystal temperature. The colder rotational distributions observed in the NO-Pt(111) system are in agreement with other observations obtained recently in other[4] and identical[18] diatomic-surface scattering systems.

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