Dynamics of NO Molecular-Beam Scattering from a Ge Surface

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(Received 3 March 1986)

Translational and rotational energy distributions of NO molecules scattered from an oxidized Ge surface were determined by means of laser two-photon ionization and time-of-flight techniques. Trapping-desorption and direct inelastic-scattering channels are clearly separated in state-resolved measurements: The former shows a mean kinetic energy $\langle E_{f,J''} \rangle$ corresponding to the surface temperature, while the latter exhibits "rainbow" features and a $\langle E_{f,J''} \rangle$ which is, for high-J" states, much larger than expected from pure translational to rotational energy conversion.

PACS numbers: 79.20.Rf, 61.16.Fk

The interaction dynamics of molecules with a surface is usually divided into two channels¹: trappingdesorption and direct inelastic scattering. In trappingdesorption the molecule releases its incident kinetic energy completely to the solid and is intermediately trapped at the bottom of the interaction potential. After a certain residence time at the surface it returns back into the gas phase by uptake of thermal energy from the solid. In direct inelastic scattering, on the other hand, the energy exchange of the incident molecule with the surface is not sufficient-it returns into the gas phase after single (or multiple) collision(s). These two channels manifest themselves in the angular and velocity distributions of the scattered molecules: The anguler distribution for trapping-desorption is symmetric with respect to the surface normal, while for direct inelastic scattering it is peaked near the specular direction. The velocity distribution in the former case corresponds in principle to complete translational accommodation and can usually to a first approximation be described by a Boltzmann distribution corresponding to the surface temperature T_s , while in the latter it is non-Boltzmann and strongly correlated with the incident kinetic energy.

Different effects are also observed corresponding to the populations of the rotational levels after scattering of initially rotationally cold molecules: In trappingdesorption the rotational population can be described by a Boltzmann distribution with rotational temperature T_R . Interestingly, $T_R = T_s$ only at low surface temperatures, while it reaches a limiting value $(T_{R, \lim} \approx 400 \text{ K in the case of NO})$ at higher T_s .² This effect is denoted as "rotational cooling in desorption," whereby $T_{R, \lim}$ is essentially only determined by the rotational constant of the desorbing molecule, but not by its interaction potential with the surface.³ In direct inelastic scattering, on the other hand, with high incident kinetic energy, E_i , the rotational distribution becomes clearly non-Boltzmann as a result of the "rotational rainbow" effect.⁴⁻⁷ This effect is ascribed to the transformation of translational into rotational energy during the collision process. According to current theoretical treatments,⁸ energy exchange with the phonon bath of the solid should be of minor importance for this effect, but experimental verification of the full energy balance was so far still lacking and will be reported in this Letter for the first time. This goal was achieved by state-resolved experiments: A beam of rotationally cold NO molecules with defined initial kinetic energy E_i was scattered at an oxidized Ge surface, and the molecules coming off the surface in a certain direction were analyzed with respect to their velocity distributions in individual rotational levels. These measurements allowed, in addition, a clear separation between the two scattering channels and therefore their relative contributions to the total flux of scattered molecules could be determined as a function of J''. It should be noted that the oxidized Ge showed some surface roughness.

The experimental arrangement involving a UHVmolecular beam and an excimer-dye-laser frequency doubling system is the same as that used in our earlier laser-induced-fluorescence study,² except that the laser-induced-fluorescence detecting system is now replaced by a device combining resonantly enhanced multiphoton ionization and time-of-flight (TOF) techniques. This device consists of a cylindrical cage, 17 mm in diameter and 6 mm in height, which is made of metal wire mesh and set at ground potential in front of the sample. The axis of the cage is perpendicular to the incident NO beam, but does not intersect it. The laser pulses are focused along the cage axis to ionize the NO molecules from individual rotational states. The ions produced have the same velocity as the parent molecules. After passing the radius of the cage, they are accelerated towards an electron multiplier and detected. The resulting TOF distributions can subsequently be converted into velocity distributions. By translating the sample along the NO beam axis with respect to the detection axis formed between the



FIG. 1. TOF signals of scattered NO at various rotational states (J''); (a) density vs time and (b) converted into flux vs velocity under the experimental conditions $E_i = 730$ meV, $\theta_i = \theta_f = 45^\circ$, and $T_s = 190$ K. The characteristics of the incident NO-He seeded beam are also displayed. Dashed lines in (b) indicate the maxima of the high- and low- v_f components in the velocity distributions.

center of the cage and the multiplier, we can measure the molecular density as a function of scattering angle θ_f . To obtain the velocity (v_i) of the incident molecules, the cage is moved into the center of the primary beam and the photoions are detected in line of sight by a second multiplier. The v_i can be changed by control of the nozzle temperature and by seeding of the beam with He. The angle of incidence with respect to the surface normal (θ_i) can be varied by rotation of the sample. A full account of experimental details as well as of data-handling procedures will be published elsewhere.⁹ Our TOF measuring scheme is very similar to that used by Häger, Shen, and Walther¹⁰ to study scattering of NO graphite. Hamers, Houston, and Merrill¹¹ applied also resonantly enhanced multiphoton ionization and TOF to investigate NO scattering from Ir(111).

A typical set of TOF distributions and the corresponding final velocity distributions (v_f) at different rotational levels (J'') of the scattered NO molecules are shown in Fig. 1 for $T_s = 190$ K. Separation into two different contributions is clearly evident which allows evaluation of the two scattering channels individually. Measurements at a higher T_s (up to 450 K) yield similar TOF structures with double peaks, although the relative intensities of the two components vary with T_s . the high-velocity component is highly non-Boltzmann and is attributed to direct inelastic scattering. With increasing J'', its peak maximum shifts to lower velocities suggesting decreasing mean translational energy. The intensity of this high v_f component becomes much larger near the specular scattering angle. It also increases with increasing E_i and decreasing θ_i . In contrast, the low-velocity component is due to trapping-desorption: Its peak maximum depends on T_s but is independent of J'' and incident E_i . Its intensity increases with decreasing θ_f (varied from 60° to 0°). Furthermore, the high-J''states which are absent in the incident beam ($T_{rot} = 120$ K) are appreciably populated in the high- v_f component, but exhibit only very small intensity for the low- v_f component. It should be noted, however, that the low- v_f component has a TOF line shape somewhat different from a pure Maxwell-Boltzmann distribution at low T_s . The reason for such a behavior is being further studied.

For quantitative analysis, each of the (density) time-of-flight distributions is converted into a flux velocity distribution and then integrated to scale the total flux (= population $N_{J'', \text{tot}}$) of scattered particles. The low- v_f part is fitted by a flux velocity distribution given by $Av^3 \exp[-B(v-v_0)^2]$, where A is a normalization factor, v_0 a flow velocity which is zero for a pure Maxwell-Boltzmann distribution, and B a width parameter.⁹ Its integration yields the fraction of molecules which have undergone trapping-desorption. Its difference from the total flux then corresponds to the particle flux originating from direct inelastic "Boltzmann plots," scattering. The resulting $\ln[N_{J''}/(2J''+1)]$ versus internal energy E_{int} (= E_{rot} $+ E_{el}$), for both components are reproduced in Fig. 2.

The data from the trapping-desorption channel can be fairly well approximated by a straight line, yielding a rotational temperature of $T_R = 210 \pm 20$ K, which equals within experimental error the surface temperature T_s . This result is in agreement with previous investigations of NO desorption,² according to which



FIG. 2. Plots of rotational state distributions. $\ln[N_{j''}/(2J''+1)]$ vs E_{int} , for both the high- v_f (direct inelastic scattering) and the low- v_f (trapping-desorption) components observed in TOF spectra under the same conditions as described in Fig. 1. Rotational "rainbow" is clearly evident for the high- v_f component (open circles).

 $T_R = T_s$ up to about 300 K from where on the "rotational cooling" effect becomes increasingly important. By contrast, the data from the high- v_f component are strongly non-Boltzmann and show the "rotational rainbow" features characteristic for direct inelastic scattering at higher incident kinetic energies.^{4,5} The numbers of NO molecules scattered from the surface via the two channels vary with the rotational energy. For example, with $E_i = 730$ meV, $\theta_i = \theta_f = 45^\circ$ and $T_s = 190$ K, about 76% of all molecules in the $J'' = \frac{5}{2}$ state originate from trapping-desorption and the rest from direct inelastic scattering, whereas for the $J'' = \frac{67}{2}$ state, nearly all molecules stem from the latter process.

The average translational energies $\langle E_{f,J''} \rangle$ for both components were determined through $\langle E_{f,J''} \rangle = M_2 / M_0$, where $M_n = \int_0^\infty v^n f(v) dv$ and f(v) is the respective flux velocity distribution.¹² The resulting data are displayed in Fig. 3. For the trapping-desorption channel $\langle E_f \rangle$ is equal within the experimental limits to the value $2kT_s$, irrespective of J''. On the basis of arguments of microscopic reversibility for a system in which the sticking coefficient (= trapping probability) is < 1, the mean translational energy of the desorbing particles should be even smaller than $2kT_s$.¹³ The calibration of *absolute* velocities was perhaps not sufficiently accurate with the present experimental system to detect such an effect of "translational cooling."

The results for the direct inelastic-scattering component are most remarkable: With $E_i = 730$ meV and at low J'', $\langle E_f \rangle$ amounts only to about 35% of the incident kinetic energy; 65% (or 474 meV) is lost to the heat bath of the solid, which means that the scattering



FIG. 3. Plots of the mean kinetic energy $\langle E_{f,J''} \rangle$ of scattered NO vs the rotational energy E_{rot} for (curve *a*) the direct inelastic scattering and (curve *b*) the trappingdesorption components. The solid line (curve *c*) indicates the expected behavior if pure translational-to-rotational energy conversion were the mechanism for the "rainbow" effect.

is highly inelastic. $\langle E_f \rangle$ decreases with increasing J'', but to a much lesser extent than what would be expected if the rotational energy originates solely from the incident translational energy.

The population of higher rotational levels in molecule-surface scattering, leading to the effect of "rotational rainbows," has been treated theoretically in numerous papers.^{6, 14-20} The simplest picture -which also underlies most of these studies-is that with an aspherical molecule bouncing off a hard wall, part of the initial translational energy is transformed into rotational energy, depending on the orientation of the molecular axis with respect to the surface normal. If this were the dominant mechanism, the rotational energy stored in the molecules with a given J'' should be missing in the associated mean translational energy $\langle E_{f,J''} \rangle$, i.e., the latter should follow the solid line in Fig. 3. This is obviously not the case, but $\langle E_{fI''} \rangle$ decreases only weakly with J'', and we have to conclude that the final translational energy is largely decoupled from rotational excitation.

These experimental findings can, however, be tentatively interpreted on the basis of the theoretical work of Muhlhausen, Williams, and Tully.²⁰ These authors conclude that the NO molecule is not aspherical enough to produce the rotational-rainbow effects on the basis of the hard-wall model. (Thermal averaging and surface roughness as in this case would, in addition, largely wash out effects caused by repulsive interactions.) Instead, rotational excitation is mainly caused by a strongly orientation-dependent *attractive* potential: If a NO molecule approaches the surface with its wrong end (i.e., the O atom) foremost, it is spun around, and the forces that reorient the molecule produce rotational motion which is not effectively damped when the molecule returns into the gas phase. Detailed calculations for $\langle E_{f,J''} \rangle$ on the basis of this model would clearly help to confirm this picture.

In short, the present results show the clear separation of the two scattering channels in both velocity and state-resolved measurements. The earlier work by Hamers, Houston, and Merrill¹¹ on NO/Ir demonstrated the occurrence of two scattering channels in their TOF spectra which, however, were not state resolved. Häger, Shen, and Walther¹⁰ on the other hand, investigated the NO/graphite system, but could not clearly separate the two components. In our study on NO/Ge, we are able to distinguish the two scattering channels and separately analyze the state-resolved energy exchange. The results allow us for the first time to conclude that pure translational to rotational energy transfer cannot be the dominant mechanism for rotational excitation in the scattering process.

The authors wish to thank Dr. J. Segner and Dr. W. Vielhaber for their contributions in the early stages of the experiment and Dr. P. M. Ferm for his assistance with data analysis. This work was supported by the Deutsche Forschungsgemeinschaft Sonderforschungsbereich. One of us (T.J.C.) would like to express his gratitude to the Alexander von Humboldt-Stiftung for a Senior U.S. Scientist Award. One of us (F.B.) would like to thank the Studienstiftung des Deutschen Volkes for a scholarship. ^(a)Permanent address: IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.

¹See J. A. Barker and D. J. Auerbach, Surf. Sci. Rep. 4, 1 (1985), and references therein.

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