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Rotational Energy Transfer in Direct Inelastic Surface Scattering: NO on Ag(111)

A. W. Kleyn, A. C. Luntz, and D. J. Auerbach
IBM Research Laboratory, San Jose, California 95193

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Rotational state distributions for NO scattered from Ag(111) have been measured over the incident kinetic energy range of 0.1 to 1.7 eV with use of rotationally cold molecular beam and laser-induced–fluorescence detection. The measured distributions divide into two parts: a low rotational state portion ($J \lesssim 20.5$) which is described by a Boltzmann distribution and a high-J portion which shows a broad structure tentatively interpreted as resulting from a rotational rainbow.

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The understanding of trapping and sticking of atoms and molecules at surfaces requires an understanding of the various energy-loss mechanisms involved in collisions with surfaces. For atoms, momentum distribution measurements of scattered particles are providing much insight into the underlying dynamics; for molecules, however, measurements of internal-energy distributions are also required. Rotational energy transfer is of particular interest because both experiment[1] and theory[2] provide indirect evidence for a facile interchange of translational and rotational energy in molecular scattering.

Recently there has been considerable interest in the direct measurement of rotational state distributions for surface-scattered molecules by laser-induced–fluorescence (LIF) detection. Using LIF detection, one can determine molecular internal-state distributions by tuning a laser through an adsorption band of the molecule and measuring total fluorescence to provide a very sensitive measure of the adsorption spectrum. Using this technique, Frenkel *et al.*[3] observed a 280-K Boltzmann rotational distribution for a rotationally cold beam of NO scattered from (NO-covered) Pt(111) at 290 K and conclude that this results from trapping and complete accommodation followed by desorption. Measurements from a carbon-covered Pt(111) surface[3] showed small departures from a Boltzmann distribution for low rotational states. McClelland *et al.*[4] reported that making a 300-K thermal beam of NO collide with an Ag(111) surface results in a Boltzmann rotational state distribution for the scattered particles with partial accommodation to the surface temperature. They were unable, however, to determine if this results from direct scattering or from trapping followed by desorption. Partial rotational accommodation has also been observed for CO scattered from LiF.[5]

To distinguish and characterize the various energy-transfer channels involved in atom-surface scattering, it has proven extremely useful to measure scattered-particle energy distributions as a function of surface temperature, incident energy, and incident and final angle.[6] For molecular scattering, such measurements are needed not only of the translational energy distributions, but for internal-energy distributions as well. We report here LIF measurements of internal-energy distributions of a rotationally cold beam of NO molecules scattered from an Ag(111) surface. The dependence on incident kinetic energy, E_i, and incident angle, θ_i, has been measured for the first time as have angular and velocity distributions for molecules scattered in specific rotational states, J. Measurements carried out for higher J than previously reported[3,4] reveal interesting new phenomena; sharp departures from a Boltzmann distribution are observed for the higher incident energies. The results support a direct scattering mechanism for the range of conditions studied here and show the inadequacy of the physical picture of partial accommodation to the surface temperature suggested in earlier work.

The experiment is based on measuring the laser-induced-fluorescence excitation spectrum for the $A^2\Sigma(v'=0)\leftarrow X\,^2\Pi_{1/2,\,3/2}(v''=0)$ transition of NO before and after scattering from a clean Ag(111) surface. The NO originated from a seeded, supersonic beam source and had rotational temperatures of 5 to 50 K, depending on source conditions. A 1%-duty-factor beam chopper and five stages of pumping on the source and scattering chamber reduced NO background to a negligible value. Auger-electron spectroscopy with use of a cylindrical mirror analyzer and low-energy electron diffraction were used to ensure that the surface was clean and well ordered during the course of the experiments. The tunable uv ($\lambda \approx 226$ nm), generated by summing the output of a frequency-doubled neodymium:yttrium aluminum garnet (Nd:YAlG)-pumped dye laser with the 1.06-μm light from the Nd:YAlG laser in a potassium dihydrogen phosphate (KDP) crystal, had a linewidth of approximately 0.5 cm^{-1}. The exciting radiation was introduced perpendicular to the scattering plane 8 mm from the surface in a manner which allowed the scattering and incident angles to be independently varied.

Spectra were analyzed by selecting lines which were estimated to have $\gtrsim 90\%$ of their intensity originating from a single transition and dividing the measured intensities by laser power and rotational line strengths to yield the relative populations, N_J, of the various rotational levels, J, of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-orbit states. Since the LIF detection is sensitive to density, independent knowledge of the velocity is required to convert the measurements to flux populations. Here we have assumed the velocity distributions to be independent of rotational state as has been implicitly done in previous work.[3,4] This assumption is expected to introduce negligible errors, except when the internal energy of the scattered particles is a substantial fraction of E_i. For high energies this assumption of constant velocity distribution was checked by direct measurement. As a test of the detection system and analysis procedure the scattering chamber was filled with NO gas at 295 K and N_J was found to be given by a Boltzmann distribution: $N_J \propto (2J+1)\exp(-E_J/kT_R)$ with a rotational temperature $T_R = 290 \pm 10$ K.

Measurements of several types were made on molecules scattered from the surface. Internal-energy distributions at given initial and final angles were measured for various beam energies and surface temperatures. Angular distributions were measured by setting the laser to a given spectral line and scanning the final angle. Velocity distributions were measured by time of flight with the delay between the beam chopper and the firing of the laser used to determine the flight time.

Internal-energy distributions for specularly scattered molecules are shown in Fig. 1 for different incident angles and normal kinetic energies E_n, where $E_n = E_i\cos^2(\theta_i)$. In the figure $\ln[N_J/(2J+1)]$ is plotted versus total internal energy, $E_{\rm int}$, the sum of rotational and spin-orbit energy, so that a Boltzmann distribution is given by straight line. Although not shown in the figure, measurements for various values of E_i and θ_i yield similar distributions if E_n is held constant. Clearly the measured distributions divide into two regions. For low J ($J \lesssim 20.5$ or $E_{\rm int} \lesssim 0.06$ eV) a Boltzmann distribution is observed whereas for high J the measured distributions are non-Boltzmann. A broad structure in $N_J/(2J+1)$ vs $E_{\rm int}$ becomes apparent at the higher energies. Let us discuss these two regions in turn.

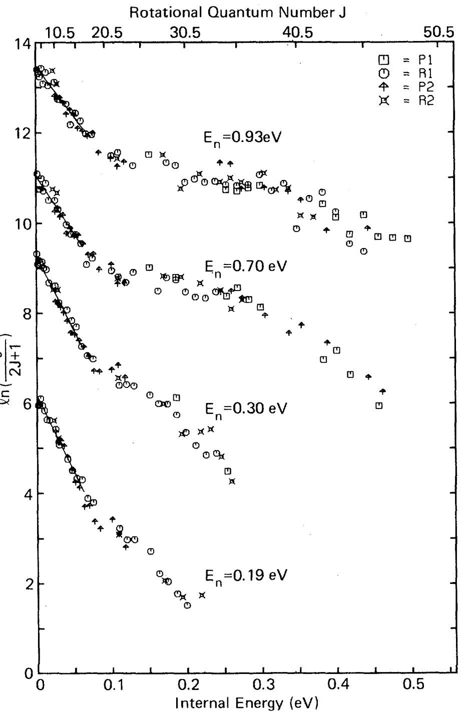

FIG. 1. Rotational-state distributions for scattered NO molecules as a function of internal energy (bottom) or rotational quantum number J (top). The J scale shown applies to the $^2\Pi_{1/2}$ spin-orbit state. $P1$ and $R1$ are the populations derived from the P and R transitions of the $^2\Pi_{1/2}$ state and $P2$ and $R2$ from the $^2\Pi_{3/2}$ state. From top to bottom: $E_i = 1.0$ eV, $\theta_i = 15°$; $E_i = 0.75$ eV, $\theta_i = 15°$; $E_i = 0.32$ eV, $\theta_i = 15°$; $E_i = 0.32$ eV, $\theta_i = 40°$.

For low J, each curve in Fig. 1 shows a single straight line for both spin-orbit states indicating that not only is the rotational energy distribution Boltzmann-like but also spin-orbit and rotational temperatures are equal. From the slope of this line T_R was determined with a typical standard deviation of 25 K. The existence of a temperature might at first suggest equilibration with the surface. If this were the case we would expect the measured T_R to be nearly equal to and strongly dependent on T_S and largely independent of E_i. The measurements show exactly the opposite. For specular scattering the variation of T_R with incident energy is shown in Fig. 2, where T_R is plotted versus E_n. The variation is seen to be of the form

$$T_R = a(E_n + \epsilon). \tag{1}$$

A line least-squares fitted to the $T_S \approx 650$ K data is also shown in Fig. 2 which yields $\epsilon = 0.78 \pm 0.08$ eV and $a = 320 \pm 26$ K/eV. The variation of T_R with T_S at a given E_n, shown in the figure by the use of different symbols, is found to be very small and almost within 1 standard deviation.

Angular distributions, measured for scattered molecules in individual rotational states with $J \lesssim 27$, are peaked near specular. This provides further evidence for direct inelastic scattering.[7] Velocity-distribution measurements also support this conclusion although because of technical limitations of our present setup these measurements were restricted to $E_n \gtrsim 0.5$ eV and $J \lesssim 27$. The occurrence of trapping for very high J has not yet been checked.

The measurements of the variation of T_R with E_n [Fig. 2 and Eq. (1)] show that large values of E_n are required to produce a substantial change in the distribution. This suggests that a strong attractive potential is involved in the collisions of NO with the Ag(111) surface. Furthermore we conclude that the surface corrugation plays little role in rotational energy transfer since the rotational-state distribution of scattered particles depends far more strongly on E_n than on $E_t = E_i \times \sin^2(\theta)$. Further theoretical work is required to extract detailed information on the potential from these studies; however, if we suppose that the exchange of momentum with the repulsive wall is fairly impulsive, the energy transfer would scale with the energy at the bottom of the well. This would imply [cf. Eq. (1)] a well depth $\approx \epsilon$ or 0.78 eV. An adsorption energy of 1.0 eV and a saturation coverage of 0.05 monolayers have been previously reported[8] for NO adsorption on Ag(111) from flash desorption measurements. Because of the small saturation coverage it might be tempting to interpret these observations in terms of adsorption at defect or other minority sites on the surface. The present results, however, suggest a strong attractive interaction over the entire surface.

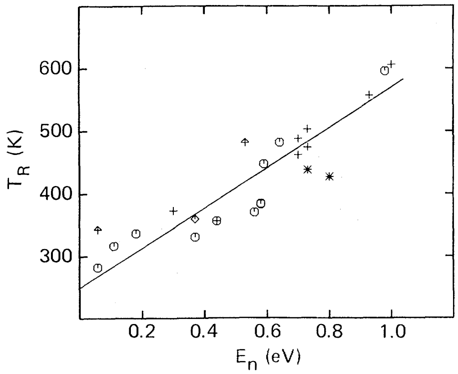

FIG. 2. Rotational temperature T_R of the low-J region as a function of the normal incident energy E_n. For the circles $(\theta_i, T_S) = (40°, 650$ K), for plusses (15°, 650 K), for arrows (40°, 780 K), and for the asterisks (15°, 590 K).

Perhaps the most striking feature of the results shown in Fig. 1 is the large departure from a Boltzmann distribution observed for high J and high incident energy. The variation of this portion of the distributions with E_n is far stronger than that observed for the low-J portion. For the higher incident energies the curves show a broad maximum as a function of J. A possible explanation for this maximum can be found by considering the expected variation in rotational energy transfer as a function of orientation angle, χ, for a molecule interacting with a smooth surface. For an initially nonrotating molecule a maximum in the energy transferred, $\Delta E_{\max}$, will be found for some value of the initial orientation. This is exactly the condition required to give the rotational rainbow effect which has been recently observed in gas-phase scattering.[9, 10] Classically the rotational rainbow is a singularity in N_J arising from a term $(d\Delta E/d\chi)^{-1}$ in the cross section; quantum mechanically a similar result is obtained by considering the "orientation interference structures" which result from a coherent superposition of contributions from different χ to the scattering.[11] Tentatively then we ascribe the broad maximum observed to a rotational rainbow. In the surface scattering case additional complexities arise because of the averaging required over surface thermal motion which will tend to mask the rainbow. The high energies used here tend to minimize this averaging effect. Trajectory calculations on model systems are underway to help in the interpretation of this phenomenon.

From a variety of evidence presented above we conclude that for the conditions employed in this study NO undergoes direct inelastic scattering. Qualitatively the results are consistent with a picture based on a strong attractive interaction, a small surface corrugation, and a highly anisotropic repulsive interaction. Further work is required on the role of anisotropy in the attractive potential as well as quantitative comparison of the results with theoretical calculations. By such comparison, measurements of the type presented here can provide detailed information on the potentials and dynamics of molecular interactions with surfaces.

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Measurement of the Anomalous Nuclear Magnetic Moment of Trivalent Europium

R. M. Shelby and R. M. Macfarlane
IBM Research Laboratory, San Jose, California 95193

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An order-of-magnitude reduction of the nuclear magnetic moment of trivalent europium due to hyperfine-induced magnetic shielding was predicted by Elliott in 1957. With use of optical hole burning and optically detected nuclear quadrupole resonance in $YAlO_3:Eu^{3+}$, this shielding has been measured for the first time. We find that the ground-state moment is reduced to 21% of its intrinsic value, while the moment in the excited $^5D_0$ state is unaffected.

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More than twenty years ago Elliott[1] predicted that the nuclear magnetic moment of the trivalent europium ion in its ground $^7F_0$ state would be anomalously small. The reason for this is that the electronic contribution to the moment due to second-order hyperfine coupling with the $^7F_1$ levels $\sim 400\ \mathrm{cm}^{-1}$ higher in energy is of opposite sign to, and almost cancels, the intrinsic moment of the Eu nucleus. Since the $^7F_0$-$^7F_1$ splitting is spin-orbit in origin and does not vary greatly from host to host, this cancellation is expected to be a general phenomenon with small modifications depending on the crystalline environment. As Elliott pointed out, this effect makes conventional NMR or nuclear quadrupole resonance (NQR) observations of trivalent europium very difficult and no such experiments have yet been reported. For this reason Elliott's prediction of the small Eu^{3+} moment has, until now, remained unconfirmed.

In $YAlO_3:Eu^{3+}$ we have used hole burning and optically detected NQR in an external magnetic field parallel to the *b* axis to measure the effective nuclear moment of ^{151}Eu and ^{153}Eu in both the ground $^7F_0$ and the excited $^5D_0$ states. In the $^7F_0$ state we obtain values of $0.743\mu_N$ for ^{151}Eu and