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Rotationally Inelastic Gas-Surface Scattering Investigated by Laser-Induced Fluorescence

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Variations of the rotational energy distributions of NO molecules scattered at a Pt(111) surface have been determined by means of laser-induced fluorescence. Scattering of a rotationally cold (32 K) supersonic molecular beam at a NO-covered surface results in full rotational accommodation due to trapping/desorption. No Boltzmann distribution of the rotational energies is observed if the molecules are directly (specularly) scattered at a graphitic overlayer.

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A complete description of the dynamics of the interactions between gaseous molecules and solid surfaces includes the transition probabilities between the various quantum states. Measurements of angular and velocity distributions in molecular-beam experiments provide this kind of information with respect to the translational motion. These techniques could also be used to identify indirectly variations of the rotational state in scattering of H_2 at surfaces of ionic crystals.[1-3]

Separation of energy accommodation coefficients into contributions arising from translational and internal excitations[4] provides another qualitative approach to this problem.[5-7] What would be needed, of course, is an analysis of the population of the internal (vibrational plus rotational) states of the molecules before striking and after leaving the surface. To our knowledge, so far only the second part of this task has been tackled in two studies applying the technique of electron-beam-induced fluorescence[8]: Ramesh and Marsden determined the rotational accommodation coefficient for N_2 on various metal surfaces,[6] and Thorman, Anderson, and Bernasek[9] reported on the vibrational-energy distributions of N_2 molecules formed by recombination of N atoms at an Fe surface. Whereas this technique has so far been restricted to N_2 molecules, the method of laser-induced fluorescence (LIF)[10] offers a much wider range of applications and has also recently been successfully used to study rotationally inelastic scattering in homogeneous gas phase.[11,12] We report here on the first application of this technique concerning the determination of the variation of internal-energy distribution in gas/solid scattering. The sensitivity in the present configuration allows detection of less than 10^7 molecules per cubic centimeter per state.

The experimental arrangement is reproduced schematically in Fig. 1. A supersonic beam of NO molecules is formed in a bakable beam-gen-

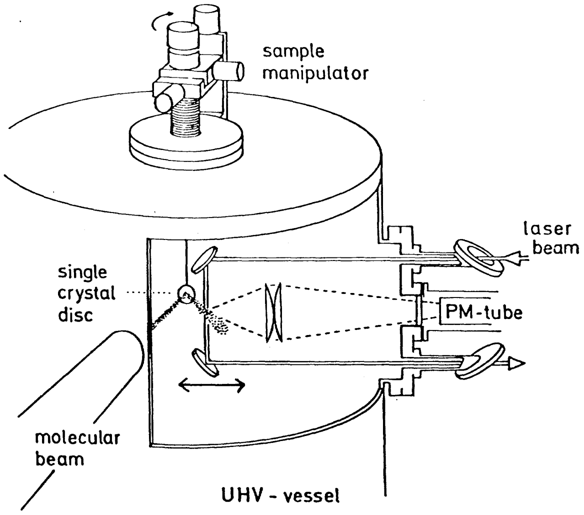

FIG. 1. Experimental arrangement (schematic).

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erating system consisting of a nozzle, a skimmer, collimating apertures, and three diffusion-pump stages.[13] The Pt(111) sample is mounted on the rotatable axis of a manipulator within a UHV system with base pressure below 1×10^{-10} Torr. The effective pressure of the NO beam at the sample surface was about 3×10^{-7} Torr for the 45° incidence angle used in these measurements. The adsorption properties of the system NO/Pt(111) have been studied separately.[14]

The tunable frequency-doubled dye laser was pumped by a XeCl excimer laser and delivered 5-ns pulses at a rate of 5 Hz. The pulse power was 10 μJ in the desired wavelength range (~ 226 nm), with a linewidth of 0.1 cm^{-1}. The laser beam enters and exits from the analysis chamber through Brewster-angle quartz windows as shown. Inside the chamber, it is deflected by aluminum-coated mirrors which are displaceable to the left and right as shown, so that the incoming NO beam or the scattered molecules can be excited and observed. The laser-induced fluorescence was collected by an $f/1$ quartz lens system and focused through the quartz window onto the photomultiplier (PM) tube. The photomultiplier signal was amplified and recorded by means of a boxcar integrator.

The ground state of the NO molecule is split by spin-orbit interaction into the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states with an energy difference of 123 cm^{-1}, consisting of the usual set of rotational levels.[15] The molecules are excited from the $^2\Pi_{1/2}(v''=0)$ state to the $v'=0$ vibrational level of the $A^2\Sigma^+$ electronic state, which has a fluorescence lifetime of about 200 ns.[16] Spectra were recorded by measuring the total fluorescence yield while varying continuously the laser wavelength.

The fluorescence intensity is dependent on the population density $N_{J''}$ of the respective rotational level of the electronic ground state, its quantum number J'', and the Hönl-London factor $S_{J'J''}$ for the $J''\rightarrow J'$ transition,[17] where the quantum number J' refers to the rotational level in the $A^2\Sigma^+$ state to which excitation occurs[18]:

$$I_{J'J''}\propto[S_{J'J''}/(2J''+1)]N_{J''}. \qquad (1)$$

In thermal equilibrium, the population densities follow a Boltzman distribution:

$$N_{J''}\propto(2J''+1)\exp(-E_{J''}/kT_{\text{rot}}), \qquad (2)$$

where $E_{J''}$ is the rotational energy and T_{rot} the rotational temperature. Thus, in thermal equilibrium, a plot of $\ln[N_{J''}/(2J''+1)]$ [as derived from Eq. (1) through the measured $I_{J'J''}]$ vs $E_{J''}$ should yield a straight line whose slope is determined by T_{rot}.

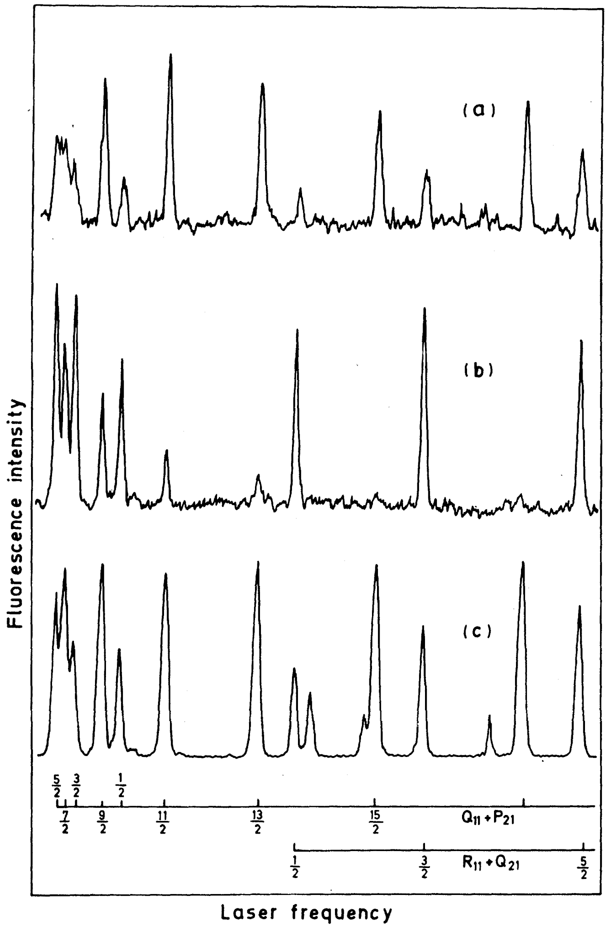

FIG. 2. LIF spectra from NO. Curve a, after scattering at a graphitic surface (330 K). Curve b, incident supersonic molecular beam. Curve c, reference data from a gas cell at 300 K.

Apart from measurements with the impinging and scattered molecular beam, spectra from NO in a gas cell kept at 300 K were also recorded. This allows easy identification of the various spectral lines, even in the case of a poor signal-to-noise ratio. Typical data of the $Q_{(11)}+P_{(21)}$ and $R_{(11)}+Q_{(21)}$ branches are shown in Fig. 2. These spectra reflect the populations of the lower electronic ground state in the supersonic beam before scattering (curve b), after scattering (curve a), and in the reference cell (curve c), respectively. Comparison between spectra b and c clearly shows differences in the relative populations. In the beam spectrum, the lines with rotational numbers $>\frac{15}{2}$ are very weak, reflecting

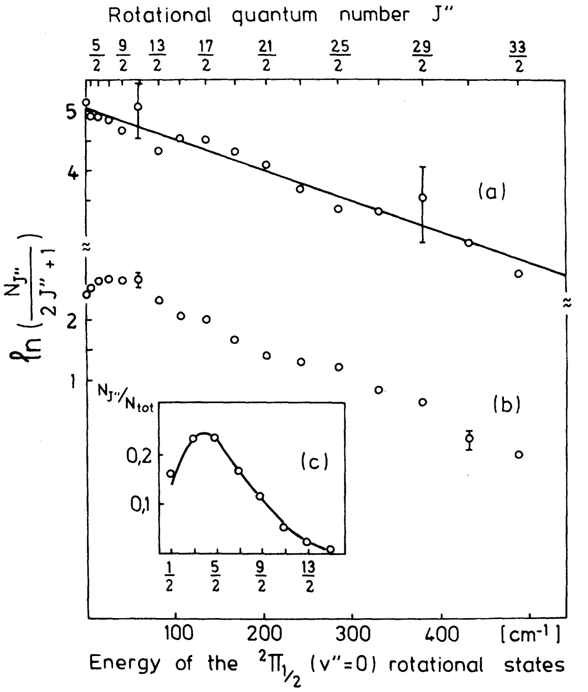

FIG. 3. Data evaluation: (a) After scattering at an NO-covered surface (290 K), (b) after scattering at a graphitic surface, and (c) rotational-energy distribution of the incident beam.

only low populations of the higher rotational levels. A plot of $N_{J''}$ vs J'' [as derived from the $Q_{(11)} + P_{(21)}$ branch] for the incident beam is reproduced in Fig. 3(c). The size of the data points reflects the magnitude of the error bars, which were in all cases determined by the signal-to-noise ratio. The experimental data are quite accurately fitted by the solid line which was calculated by Eq. (2) for $T_{\mathrm{rot}} = 32$ K, thus confirming the existence of a Boltzmann distribution over the rotational degrees of freedom in the supersonic beam.

A further set of fluorescence measurements yielded the population distribution of the NO molecules after scattering at the surface. In this case, the laser beam passed the scattered NO molecules at 45° from the surface normal region at a distance of 11 mm. The Pt(111) surface was initially kept at 290 K and exposed to the NO beam. Under steady-state conditions, the surface will be saturated with a layer of adsorbed NO. Scattering then occurs at this adlayer and is characterized by an almost perfect cosine angular distribution. This effect is caused by a trapping/desorption process in the second layer ("precursor state"), giving rise to full accommodation of the translational motion.[14] Analysis of the data according to Eqs. (1) and (2) from three sets of experiments yields a straight line for a plot of $\ln[N_{J''}/(2J''+1)]$ vs $E_{J''}$ [Fig. 3(a)]. From the slope, a rotational temperature $T_{\mathrm{rot}} = 280 \pm 30$ K is derived. This result shows that, under these conditions, full rotational accommodation of the NO molecules into a Boltzmann distribution also occurs, which is further confirmation of the dominance of the trapping/desorption mechanism.

In a second experiment, the Pt(111) surface was first covered by a graphite overlayer (formed by thermal decomposition of ethylene). The angular distribution of scattered NO is predominated by a lobular peak in the specular direction which indicates a strong contribution from direct inelastic scattering events, i.e., without full translational accommodation. A LIF spectrum from the scattered beam recorded in specular direction is reproduced in Fig. 2, curve *a*. At small energies the corresponding plot of $\ln[N_{J''}/(2J''+1)]$ vs $E_{J''}$ [Fig. 3(b)] exhibits deviations from a straight line, indicating that the rotational distribution of the scattered molecules no longer follows a Boltzmann distribution. This effect is outside the limits of error and is attributed to the transformation of translational energy into rotational energy. Evidence for such an effect has been observed in time-of-flight measurements for the system O_2/W.[19] A simple hard-cube model as developed by Nichols and Weare[20] on the basis of classical mechanics predicts, for incoming beams with small rotational temperature, a pronounced maximum at nonzero rotational energy in the distribution of the scattered molecules which is identified with the experimental effect just described.

Measurements of the present type also allow determination of the rotational accomodation coefficient as defined by $\alpha_{\mathrm{rot}} = (\varphi - \varphi_0)/(\varphi_T - \varphi_0)$. φ_0 is the incident energy flux in the rotational degree of freedom, φ the actual flux in the scattered beam, and φ_T the flux if the rotational energy in the scattered beam is in thermal equilibrium with the surface. For the example represented by Fig. 3(b), we obtain $\alpha_{\mathrm{rot}} \approx 0.8$.

The presented application of the LIF technique offers promising prospects for further invesitgations on the dynamics of gas-solid interactions including also other internal degrees of freedom. It is, in principle, also possible to study the vibrational-energy change or variations of the electron angular momentum upon scattering at a surface. Questions concerning vibrational de-

activation or ballistic vibrational-rotational transfer can be tackled. It should also be possible to study phonon-molecule interactions. The technique demonstrated here thus opens up a new class of experiments in the field of molecule-surface interactions.

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