State-selective velocity and angular distributions of NO molecules scattered from a graphite surface

J. Häger, Y. R. Shen,* and H. Walther

Max-Planck-Institut für Quantenoptik and Sektion Physik der Universität München,
D-8046 Garching, Federal Republic of Germany

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Laser ionization was used to measure the state-selective angular and velocity distributions of NO molecules scattered from a graphite surface. The data showed that at sufficiently low surface temperatures, the scattered molecules were generally composed of a quasispecular reflected part and a diffusive scattered part with different translational and rotational behavior.

Molecular-beam scattering from solid surfaces has long been recognized as a powerful means for investigation of gas-surface reaction dynamics.[1] With the help of the recently developed laser-induced fluorescence or ionization technique for state-selective detection of molecules, one can now measure not only the angular and velocity distributions of molecules before and after scattering from a surface, but also their internal energy distribution.[2-9] Such measurements will then fully describe the average energy and momentum exchanges between the molecules and the surface in the scattering process. Experiments reported so far, however, have been short of providing the complete information. In this Rapid Communication, we describe an experiment using laser-induced fluorescence and resonance ionization to measure the internal energy distribution of molecules as well as their state-selected angular and velocity distributions. The experiment dealt with scattering of a supersonic NO beam against a pyrographite surface. We found that at sufficiently low surface temperatures, there appeared, in general, two scattering channels.[10] One led to scattered molecules in a lobular angular distribution, peaked near the direction for specular reflection, with a mean velocity slightly lower than the incoming velocity; the other yielded diffusively scattered molecules in a presumably cosine angular distribution with a much lower mean velocity. The rotational temperatures which characterized the rotational energy distribution of these two groups of scattered molecules also appeared to be somewhat different.

The experimental arrangement was quite similar to the one described earlier[2] except for a modification of the detection system. A state-selective laser-ionization together with time-of-flight measurements were used to analyze the scattered NO molecules. For this purpose a cylindrical cage was mounted in front of the pyrographite sample (see Fig. 1). Molecules crossing the cage axis were selectively ionized by a pulsed tunable dye laser beam along the axis via the $X(^2\Pi) \rightarrow A(^2\Sigma) \rightarrow$ continuum transition. An ion multiplier together with a transient recorder was then used to record and average the time-of-flight spectrum of the ions leading to the velocity distribution of the parent scattered molecules. By scanning the laser wavelength and changing the position of the sample in the direction of the molecular beam, the internal energy as well as the velocity distributions of the scattered molecules could be measured as a function of the scattering angle (θ_s). The pyrographite sample was prepared as earlier.[2]

The time-of-flight arrangement was tested by measuring the known velocity distribution of room-temperature NO gas filled into the chamber. In this case a suitable aperture selected only ions leaving the cage in the direction to the multiplier. The total flight time of the ions in the high electrical field region between cage and multiplier is about 1 μs; time-of-flight changes of ions leaving the cage at different spots in the scattering plane can therefore be neglected. No fringe field effects inside the cage were observed when the multiplier was placed in a distance of at least 4 cm. The error in the determination of the absolute velocities was less than 10%. Further details of the experimental setup will be discussed elsewhere.

In the present experiment, the incidence angle (θ_i) of the molecular beam on the sample was fixed at 70°. Figure 2 shows the angular distributions of the scattered NO molecules measured by the rotatable mass spectrometer for several sample temperatures (T_s). They are shown in comparison with the angular distribution of scattered He atoms. The NO data are generally composed of a quasispecular scattering or lobular part peaked at a scattering angle θ_s significantly less than the specular reflection angle and a diffusive scattering or cosine distribution part. The ratio of both parts is dependent on sample temperature and incidence angle which leads, for the present high incidence angle of 70°, to a reduced diffusive contribution compared with earlier measurements.[2] The results are characteristic of the so-called trapping dominated scattering process.[2,10] In the present experiment, however, they can be correlated
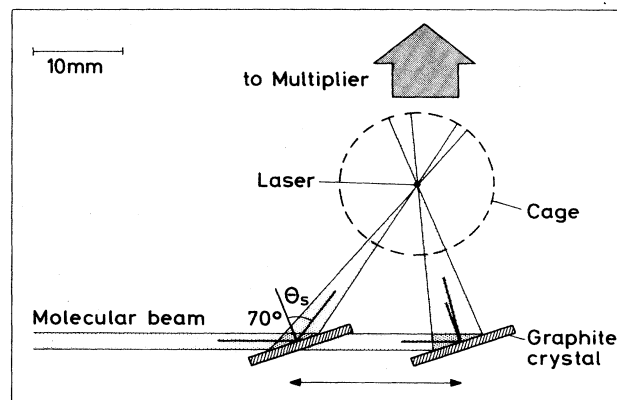

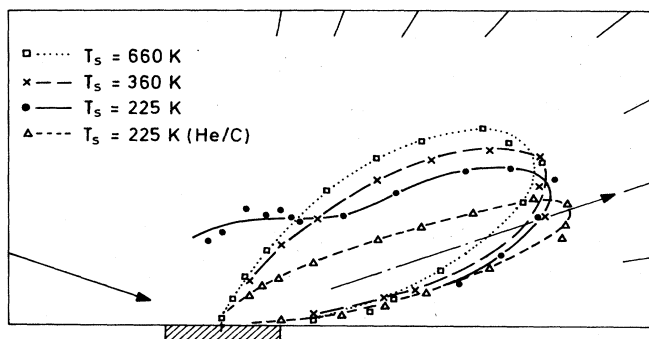FIG. 1. Schematic of the time-of-flight measurements.

FIG. 2. Normalized angular distributions of NO and He scattered from a graphite surface at various T_s, directly obtained from the mass spectrometer signals.

with the velocity distributions of the scattered molecules.

In Fig. 3 we show, as an example, the velocity distributions of molecules in the $J = \frac{9}{2}$, $^2\Pi_{1/2}$ state scattered into different θ_s and at $T_s = 200$ K. Each distribution curve can be resolved into two peaks as follows. One with a mean velocity (~ 650 m/s) somewhat less than the incoming mean velocity (~ 750 m/s) and the other with a much lower mean velocity (~ 400 m/s). The former is broader than, while the latter almost as broad as, the incoming velocity distribution. As θ_s deviates from the direction of maximum quasispecular scattering towards the surface normal
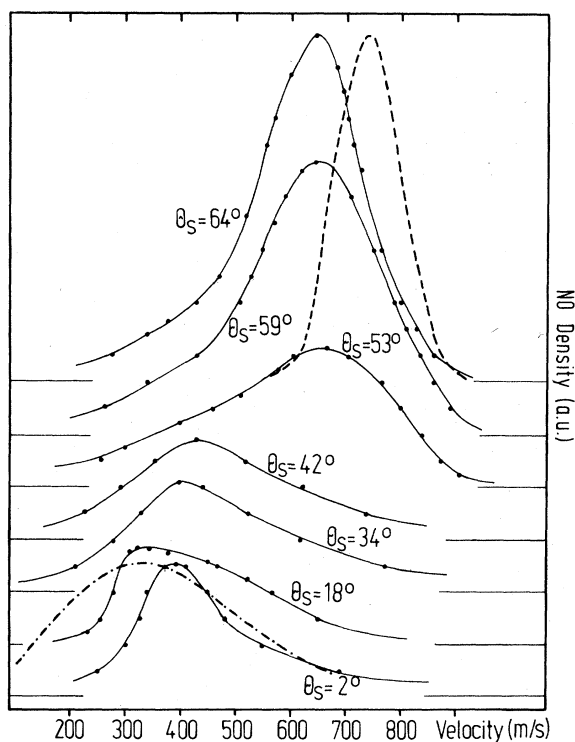

FIG. 3. Velocity distributions of scattered NO molecules ($J = \frac{9}{2}$) along different directions (θ_s) in comparison with the incoming velocity ($-\,-\,-$) and a 200-K Maxwellian distribution ($-\,\cdot\,-\,\cdot$) ($T_s = 200$ K, $\theta_i = 70°$).

($\theta_s = 0$), the former decreases in intensity and the latter increases. The two peaks can therefore be associated with quasispecular scattering and diffusive scattering, respectively. At higher T_s, the peak associated with diffusive scattering was found to diminish against the quasispecular peak as one would expect from the angular distribution in Fig. 2. With the diffusive scattering part greatly reduced, the quasispecular peak becomes better defined also at smaller θ_s. We found, interestingly enough, that the peak velocity of the quasispecular peak increases with increasing T_s (650 m/s at $T_s = 200$ K, 685 m/s at $T_s = 300$ K, 710 m/s at $T_s = 470$ K, and 750 m/s at $T_s = 660$ K, as compared with 750 m/s for the peak incoming velocity). At high T_s, the peak velocity increases with decreasing θ_s (710 m/s at $\theta_s = 64°$, 770 m/s at $\theta_s = 59°$, 820 m/s at $\theta_s = 53°$, and 850 m/s at $\theta_s = 48°$ with $T_s = 470$ K and the peak incoming velocity at 750 m/s).

That the velocity distribution of the quasispecular scattering is broader and exhibits a shift, as compared with the incoming velocity distribution, indicates a non-negligible molecule-surface interaction with energy exchange. It correlates well with the broadening and shift of the angular distribution of the quasispecular scattering relative to the angular distribution of the quasielastically scattered He beam.[10] The latter has a width presumably governed by the surface roughness of the pyrographite and the angular resolution of the mass spectrometer (5°). At low T_s (< 300 K), the quasispecular part of NO has a significantly smaller mean velocity than the incoming one. This can be explained only by a molecule-surface interaction which allows the molecules to impart to the solid a net average momentum along the surface and is contrary to the assumptions of the hard cube model. In the surface-normal direction, however, the quasispecularly scattered molecules do appear to gain in average momentum from the surface at sufficiently high T_s. For example, the fact that the peak velocity of the scattered molecules increases with decrease of θ_s at high T_s is a clear indication of momentum and energy transfer from the surface to the molecules in the surface-normal direction.

The diffusive scattering part has a mean velocity almost two times less than the incoming mean velocity. This large energy loss of molecules to the surface can only result from a trapping-desorption process. However, the mean velocity of the diffusively scattered molecules is not as low as that expected for molecules desorbed from a surface at $T_s = 200$ K, and the velocity distribution ($\theta_s = 2°$ in Fig. 3) is not broader than the incoming one, which is much narrower than the Maxwellian distribution at 200 K. Thus, the diffusive scattering part cannot arise from an equilibrium trapping-desorption process, but is more likely the result of a transitional trapping-desorption process. The sharp velocity distribution suggests that each molecule transfers about the same amount of energy to the surface irrespective of its incoming velocity.

The time-of-flight spectra of the scattered molecules in various J states were quite similar. We present a set of them at three different θ_s's in Fig. 4. The relative intensities of the quasispecular and the diffusive scattering peaks are, however, different for different J; when J increases, the quasispecular scattering peak decreases relative to the diffusive scattering peak. Since the $J > \frac{9}{2}$ states were hardly populated in the incoming molecular beam, both the quasispecularly scattered and the diffusively scattered molecules gained rotational energy in the molecule-surface
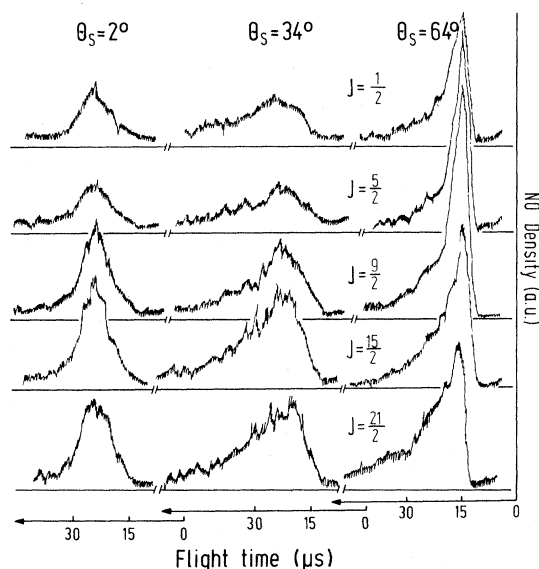
FIG. 4. Time-of-flight spectra of NO molecules in different rotational states after scattering into different angles θ_s ($T_s = 200$ K, $\theta_i = 70°$).

collisions. The curves in Fig. 4 indicate that the higher-J states were more heavily populated in the diffusively scattered molecules, corresponding to a larger rotational energy gain. More quantitatively, we find that the rotational energy distributions of the two types of scattered molecules can be characterized by two different rotational temperatures. For $T_s = 200$ K, the quasispecular reflection part (evaluated at $\theta_s = 64°$) has a rotational temperature $T_{rot}^{qs} = 180 \pm 20$ K, and the diffusive scattering part (evaluated at $\theta_s = 2°$) has a $T_{rot}^d = 230 \pm 30$ K. The latter appears to be larger than T_s, but this could be the result of experimental inaccuracy. In any case, it is clear that $T_{rot}^d > T_{rot}^{qs}$. Similar measurements at $T_s = 250$ K and $T_s = 300$ K yielded $T_{rot}^{qs} = 190$ K, $T_{rot}^d = 250$ K, and $T_{rot}^{qs} = 200$ K, $T_{rot}^d = 250$ K, respectively. The data here show that, indeed, the diffusively scattered molecules in their multiple collisions with the surface pick up more rotational energy. Also, for both scattering components, the energy transferred to the rotational degree of freedom must be somehow governed by the surface temperature. This suggests that while the translation → rotation energy conversion may still be operative, the surface must play an important role in limiting the rotational energy exchange.

The diffusive scattering is believed to be the result of molecules bouncing around on the surface in the trapping well before desorption. The residence time is long compared with a vibrational period, but short compared with the time required for complete thermal equilibrium between the molecules and the surface. This is analogous to the case of gas-phase molecular collisions through a transitional bound state. In contrast, the quasispecular scattering is believed to be a single-collision process, analogous to the case of collisional excursion in the gas-phase scattering. The molecule-surface interaction time is comparable to the vibrational period; although it is short, energy transfer to the molecular rotational degrees of freedom can still be efficient. The translational energy exchange between the molecules and the surface can be more or less determined by the hard cube model, but more properly, the momentum exchange along the surface should also be taken into account. There is a net momentum transfer to the molecules in the surface-normal direction; however, only at a sufficiently high surface temperature, the molecules can gain a net translational energy from the surface in the quasispecular scattering.

We believe that the qualitative features of our results described here are common to all molecule-surface scattering. Scattering composed of a quasispecular part and a diffusive part has also been observed in rare-gas scattering from surfaces.[10] We have compared the angular distributions of Ar and NO molecules scattered from the same graphite surface with the same incoming velocity. At high T_s (> 400 K), both exhibited only the quasispecular part, and appeared roughly the same. At low T_s (200 K), diffusive scattering becomes important in both cases, but is much more pronounced in the case of NO. This is easily understood from the much weaker interaction between Ar and graphite. The existence of internal degrees of freedom in NO should only slightly influence the angular and velocity distributions of the scattered molecules.

*Permanent address: Physics Department, University of California, Berkeley, California 94720.

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