

State-to-State Molecular-Beam Scattering of Vibrationally Excited NO from Cleaved LiF(100) Surfaces

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Survival of vibrational excitation has been observed for the scattering of NO prepared by a laser in a single well-defined quantum state, $\text{NO}(v=1, J=\frac{3}{2}, \Omega=\frac{1}{2})$, from a cleaved LiF(100) surface. State-selective angular, velocity, rotational, and electronic distributions of these vibrationally elastically scattered molecules have also been obtained for the first time.

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Exchange of vibrational energy during gas-surface collisions has recently attracted a great deal of theoretical¹⁻³ and experimental⁴⁻⁷ interest. Direct vibrational relaxation experiments on various static gas samples and polycrystalline metal surfaces carried out by use of a laser-excitation and fluorescence-decay-rate measurement technique have reported survival probabilities between 0.3 and 0.8 depending on the vibrational level excited, nature of the surface, and surface temperature.^{4,5} Rosenblatt⁶ has also reported small vibrational energy accommodation coefficients (i.e., large survival probability) for metal surfaces using a vibrating-surface technique. However, in an earlier experiment on the scattering of a vibrationally excited molecular beam of NO from a polished LiF surface, we were unable to detect any survival of the initial vibrationally excited molecules.⁷ This result stimulated a theoretical investigation of the scattering of NO from LiF by Lucchese and Tully¹ which predicted a survival probability near unity. The contrast between the low survival probability in our experiment and the high survival probability from the theory is striking, and we believe could be, in part, due to the surface roughness of the polished LiF surface used in the experiment compared to the atomically smooth surface assumed in the theory. In order to investigate this possibility, we have performed experiments using *cleaved* LiF(100) where the surface is atomically smooth and free of contaminants. In this case, a survival probability of 0.9 was observed, and, in addition, state-selective angular, velocity, rotational, and electronic distributions of these vibrationally elastically scattered molecules have been obtained for the first time.

In our experiments, two laser beams intersect a molecular beam. First, tunable infrared radiation excites part of the incident beam to a single vibrational-rotational state, $(v=1, J=\frac{3}{2}, \Omega=\frac{1}{2})$. Then, tunable ultraviolet radiation state-selectively probes the molecular beam both before and after interaction with a LiF(100) surface in an UHV scattering chamber. Rotational distributions are obtained by scanning of the probe-laser frequency. Angular distributions for

specific final states are obtained by moving of the probe-laser beam in the scattering plane. Also, because of the short duration of the exciting infrared-laser pulse, the beam of vibrationally excited molecules is well defined in time as well as energy. The short duration of the probe pulse then allows the determination of velocity distributions for specific final scattering channels by scanning of the delay time between the two laser pulses. This laser-spectroscopic time-of-flight velocity analysis is the state-specific analog of chopped-beam-mass-spectroscopic time-of-flight velocity analysis.

The vacuum system and laser excitation and detection scheme used in this experiment have been described previously.⁷ Experiments were performed with LiF(100) cleaved *in situ* under ultrahigh-vacuum conditions (5×10^{-10} Torr), and also with LiF(100) cleaved in air just prior to pump down. Results from vacuum-cleaved and air-cleaved samples were indistinguishable. All results reported here were reproducible on separate cleaves. The incident NO molecules are expansion cooled by their seeding in He and He-Ar mixtures, through a pulsed nozzle valve. Most of the NO molecules are then in the lowest few rotational states in $v=0$.⁸ About 230 μsec after the start of the 600- μsec molecular-beam pulse, the infrared-laser pulse excites molecules initially in the $v=0, J=\frac{1}{2}$ level of the ${}^2\Pi_{1/2}$ electronic state, producing a short pulse of vibrationally excited $\text{NO}(v=1, J=\frac{3}{2}, \Omega=\frac{1}{2})$ on top of the 600- μsec background pulse of $\text{NO } v=0$ molecules. By taking time-of-flight spectra at two different positions along the incident beam, we determined the incident flow velocity, for pure He seeding, to be 1.42×10^5 cm/sec, giving an incident translational energy of $E_{t,i} = 310$ meV. The incident angle was $\theta = 45^\circ$. Expansion in a mixture of helium and argon produced an incident beam with a flow velocity of 7.5×10^4 cm/sec, corresponding to an incident beam energy of $E_{t,i} = 100$ meV.

In Fig. 1, a scattered-beam time-of-flight spectrum is presented along with an incident-beam spectrum. The scattered beam was detected at the specular angle

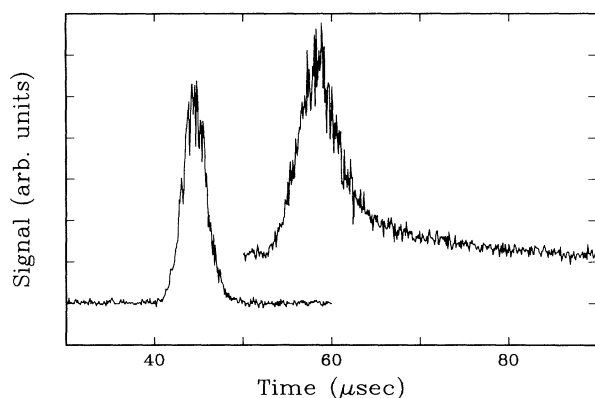


FIG. 1. (Left) Incident-beam and (right) scattered-beam time-of-flight spectra. The incident NO molecules are in the $v=1, J=\frac{3}{2}$ state. The scattered molecules, detected at the specular angle of 45° , are in the $v=1, J=\frac{11}{2}$ state. The vertical scales for the two traces are different.

(45°) with the uv probe-laser frequency set to detect only NO molecules in the final state ($v=1, J=\frac{11}{2}, \Omega=\frac{1}{2}$). (Similar time-of-flight spectra were taken for other J states in $v=1$, ranging from $J=\frac{3}{2}$ to $\frac{41}{2}$.) It is seen that the scattered-beam spectrum was broadened in time compared to the incident-beam spectrum, indicating some translational-energy spreading from the collision with the surface. In addition to this energy spread, the change of the total translational energies of the molecules can also be obtained from our time-of-flight analysis. For NO in pure He, with $E_{i,t}=310$ meV, we found a final average velocity of 1.1×10^5 cm/sec, corresponding to an average final translational energy of $E_{t,f}=190$ meV. There is also a small background ionization signal of NO $v=1$ molecules which is independent of the ir-light pulse. This background signal is 600 μ sec long and is probably produced by collision of $v=0$ incident molecules with the surface and a small contribution from $v=1$ leftover from the supersonic expansion. This is currently under investigation in our laboratory. Angular distributions for NO ($v=1, J=\frac{3}{2}, \Omega=\frac{1}{2}$) scattered into various J 's in $v=1$ have been obtained, and all have narrow, nearly specular angular distributions similar to that shown in Fig. 2, which was for the final state of $v=1, J=\frac{31}{2}, \Omega=\frac{1}{2}$. Full width at half intensity for the angular distribution was found to be $\lambda_f \sim 40^\circ$. The narrow angular width and the narrow translational-energy distribution of the scattered molecules are clear signatures of a direct inelastic scattering process with most of the molecules making single collisions with the surface.

Rotational distributions for NO $v=1 \rightarrow v=1$ scattering were obtained from the ultraviolet-multiphoton-ionization spectra. To be sure that we

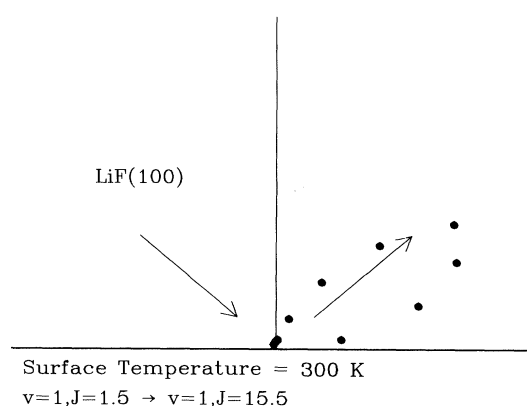


FIG. 2. Angular distribution of vibrationally elastically scattered molecules.

were observing the distribution for those that are produced by infrared-laser excitation, the background $v=1$ peaks were subtracted out by taking the difference between spectra taken with the ir laser on and spectra taken with the ir laser off. Rotational populations could be described quite well by a Boltzmann distribution and the rotational temperatures obtained in this manner are summarized in Table I. Rotational distributions in the $^2\Pi_{3/2}$ spin-orbit electronic state gave the same rotational temperature as the $^2\Pi_{1/2}$ distributions. A comparison of rotational lines originating in the $^2\Pi_{1/2}$ spin-orbit electronic state and lines originating in the $^2\Pi_{3/2}$ state allow the determination of the relative populations of the two states. Electronic temperatures based on these relative populations are 200 K for NO in He and 300 K for NO in He and Ar. For comparison, the rotational and electronic distributions for the scattering of the unexcited NO (i.e., $v=0 \rightarrow v=0$ scattering) were studied by tuning of the probe laser to the region of the $\gamma(0-0)$ band. Rotational and electronic temperatures for $v=0 \rightarrow v=0$ scattering were identical to temperatures obtained for $v=1 \rightarrow v=1$ scattering to within our experimental error.

From the above data it is now possible to calculate a probability of survival for the vibrationally excited molecules. We do this by summing over the scattered $v=1$ rotational and spin-orbit states and integrating over spatial and temporal distributions and comparing with an integration over the incident-beam spatial and temporal distribution. In this way we determine the survival probability to be 0.9 for scattering of NO seeded in pure helium ($E_i=310$ meV) and 0.7 for scattering of NO seeded in a mixture of helium and argon ($E_i=100$ meV). We estimate an uncertainty of about 10% in the relative values and slightly higher in the absolute values.

The main results of the scattering of

TABLE I. $E_{t,i}$ and $E_{t,f}$ are incident and final translational energies in millielectronvolts. Incidence angles are 45° in all cases. T_{rot} is rotational temperature in kelvins, and λ_f is the full width at half maximum of the angular distribution of the scattered molecules, in degrees. Survival probability (S.P.) is the probability for an incident $v=1$ molecule to remain in $v=1$ after the collision with the surface. The theoretical values in the middle row are from Lucchese and Tully (Ref. 1).

	$E_{t,i}$	$E_{t,f}$	T_{rot}	λ_f	S.P.
NO in He	310	190	340	40	0.9
Theory	217	107	292	60	0.95
NO in He and Ar	100	50	300	40	0.7

NO($v=1, J=\frac{3}{2}, \Omega=\frac{1}{2}$) [$E_i=310$ meV (He), $E_i=100$ meV (He-Ar)] from freshly cleaved LiF(100) ($T_s=300$ K) and with $\theta_i=45^\circ$ into NO($v=1, J, \Omega$) are then as follows: (1) The vibrational-energy survival probabilities for cleaved LiF(100) are *large*. (2) $v=1 \rightarrow v=1$ scattering is similar to $v=0 \rightarrow v=0$ scattering in terms of rotational and electronic distributions. (3) Translational energies are reduced after scattering for specularly scattered molecules. (4) Final rotational states $\frac{3}{2} \leq J \leq \frac{41}{2}$ have similar angular and velocity distributions.

The most striking result of these experiments is the large vibrational-energy survival probability for scattering from cleaved LiF when compared with the small probability previously reported from our laboratory for scattering from polished LiF.⁷ Two properties of the scattering surface have changed in going from polished LiF to cleaved LiF: the surface roughness and the surface contamination. Polished LiF, although optically smooth, is certainly microscopically rough, whereas cleaved LiF is atomically smooth, leading to significantly different gas-surface interaction potentials. Microscopic roughness will also lead to multiple collisions and can significantly increase the trapping probability. Molecules trapped for a period longer than the vibrational lifetime on the surface are deactivated. In studies of the vibrational relaxation of CO₂(101) in collision with polycrystalline surfaces, the deactivation probability was observed to decrease from 0.72 at 300 K to 0.37 at 440 K.⁵ The authors suggested that this temperature dependence and the magnitude of the deactivation probabilities were a reflection of trapping at the surface. Surface contamination might also play a major role in vibrational relaxation. One possibility is that contaminants could increase the trapping probability. Another is that molecularly adsorbed contaminants introduce vibrational frequencies on the surface much closer in energy than surface phonons to that of the incoming vibrationally excited NO. Transfer of

energy to surface vibrations is expected to be much more efficient if the surface vibrations are closer in energy to the NO vibrational frequency.¹

It would be of interest to find the dominant mechanism for quenching. Our experimental results showed that there were no discernible differences in $v=1$ to $v=1$ scattering from vacuum-cleaved versus air-cleaved LiF surfaces. Thus contaminants that might adsorb from exposure to atmosphere are desorbed during pump down, in agreement with earlier secondary-ion-mass-spectroscopy studies by Estel *et al.*,⁹ or these contaminants do not affect the survival probability. To investigate the effect of surface roughness, we again started with a clean, well-ordered, vacuum-cleaved LiF(100) surface, from which vibrationally elastic time-of-flight and angular distributions identical to those shown in Figs. 1 and 2 were obtained. This surface was then roughened *in situ* by Ar⁺ ion bombardment. The $v=1$ to $v=1$ scattering signal was shown to decrease with ion bombardment until it finally fell below our detection limit. This clearly shows that a roughened, but clean, surface will greatly increase the quenching of vibrational energy in gas-surface scattering.

Theoretical investigations thus far have concentrated on scattering from atomically smooth surfaces and so a comparison of these predictions with results obtained for scattering is only appropriate for experiments with cleaved LiF. Quantum mechanical calculations on the scattering of diatomics from rigid surfaces performed by Bawagan *et al.*² imply that deactivation probabilities should be less than 0.1; however, the energies used in these calculations were much larger than that used in our experiments. Stochastic classical mechanical calculations using a generalized Langevin equation approach and scattering conditions very similar to our experiment were recently carried out by Lucchese and Tully.¹ A summary of a comparison of our results with the generalized Langevin equation calculations is presented in Table I. In general there is an excellent agreement; however, the predicted angular distributions are broader, indicating that perhaps the corrugation used in their potential was too large.

Continued work in our laboratory includes a further exploration of the effect of changing the incident kinetic energy and normal energy by changing both the incident angle and the expansion seeding gas to other mixtures of He and Ar. In addition, because of the highly polarized nature of laser radiation, it is conceivable to perform scattering experiments with molecules that are not only in a selected initial state but also oriented. Also, the effect of conduction electrons could be explored by scattering studies from metal surfaces.

In summary, laser-spectroscopic techniques have been utilized to perform state-to-state molecular-beam

scattering experiments, allowing us to follow the scattering from a well-defined initial vibrationally excited state into specific vibrationally elastic rotational, electronic, and translational channels. Integration over these channels has allowed the determination of the vibrational-energy survival probability in scattering from a well-defined surface. While the vibrational-energy survival probability is of interest for comparison with accommodation experiments on polycrystalline surfaces with static gas samples, the specific-channel information for the case of scattering from an atomically smooth surface should allow a more detailed comparison with theory and an easier deconvolution of the data to obtain the gas-surface interaction potential.

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