Rotationally Inelastic Scattering of C_2H_2 from LiF(100): Translational Energy Dependence

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(Received 18 December 1995; revised manuscript received 23 April 1996)

We report the first results from a new experimental apparatus designed for the general investigation of energy transfer in molecule-surface scattering. The translational energy dependence of the rotational temperature of C_2H_2 scattered from LiF(100) has been measured, yielding results which are different from any data of this type previously reported. Our preliminary interpretation of the results is in terms of vibrational excitation with increasing incident translational energy. [S0031-9007(96)00726-0]

PACS numbers: 82.65.–i, 34.50.Dy, 34.50.Pi, 82.20.Rp

The transfer of energy and the ensuing chemistry that occurs between molecules and surfaces is of both fundamental and practical importance, yet the depth of our understanding of these and many of the associated processes is quite limited compared with analogous processes in unimolecular and bimolecular chemistry [1], due, in part, to the greater complexity of molecule-surface interactions. The most comprehensive data to date are from studies of NO/surface scattering [2–9], which include measurements of the rotational, vibrational, and angular distributions, along with their dependencies on translational energy (E_i) and surface temperature (T_s). For the other molecules which have been studied, which include HCl [10], NH_3 [11], CO_2 [12], CO [12,13], HF [14], H_2 [15], D_2 [15], SF_6 [16], HD [17], CH_4 [18], and N_2 [18,19], the data are much less complete. Thus most of the literature is limited to diatomic molecules, with the data for polyatomic molecules being inadequate to claim a general understanding of these processes. Notwithstanding, these experiments provide the current *de facto* standard for the classification of molecule-surface scattering mechanisms, namely, (1) elastic, (2) direct inelastic, (3) indirect inelastic, and (4) trapping-desorption [5].

The data presented in this Letter are the first results from a new apparatus that is designed to overcome many of the experimental limitations experienced previously in the study of molecule-surface scattering. The coupling of a high-resolution infrared laser, an ultrahigh-vacuum surface scattering apparatus, and the highly sensitive optothermal detection method [20] provides the means for studying a wide range of molecules and surfaces. By carrying out an extensive study of the C_2H_2/LiF(100) system as a function of the energy of the collision, we have identified two scattering regimes: a low energy regime where the degree of rotational excitation upon scattering is strongly dependent on the incident energy, and a high energy regime where the degree of rotational excitation is essentially invariant with incident energy. The novel form of this incident energy dependence is indicative of rich scattering dynamics and may be explained in terms of phonon energy transfer, frustrated rotation (“chattering”), and/or excitation of the bending modes of the C_2H_2 molecule.

Figure 1 shows a schematic diagram of the apparatus, which, for the present study, is configured to determine the rotational state population distribution of the molecules before *and* after the surface encounter. A molecular beam is formed by expanding mixtures of C_2H_2 in He into vacuum from a source pressure of 2 bars, and the molecular velocity is changed by varying both the beam composition and the nozzle temperature. The LiF(100) surface was cleaved in air and heated *in vacuo* to 550 K overnight (base pressure $\approx 2 \times 10^{-8}$ mbar). The scattering azimuth, $\langle 100 \rangle$, and surface cleanliness were then confirmed via He atom diffraction, which is known to be highly sensitive to surface contamination. These measurements, carried out at various times during the experiment, showed that the 300 K surface remained clean.

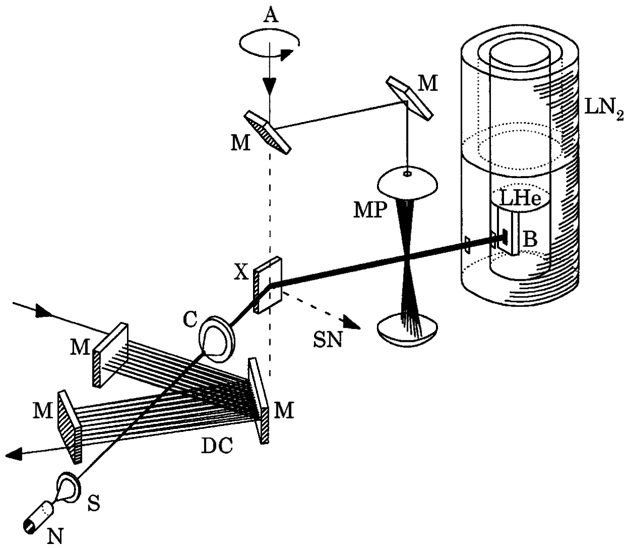

FIG. 1. Schematic diagram of the apparatus showing the nozzle (N), skimmer (S), collimator (C), Doppler cell (DC), crystal (X), surface normal (SN), probe multipass cell (MP), bolometer (B), liquid helium dewar (LHe), liquid nitrogen dewar (LN_2), axis of rotation of the detector flange (A), and various mirrors (M).

As indicated in Fig. 1, the laser can be directed into the apparatus upstream of the crystal surface where a folded multipass cell is used to collect Doppler shift spectra to measure the molecular velocity. C_2H_2 rovibrational transition frequencies were located using a wave meter and published frequencies [21] for the P branch of the upper member of the $\nu_3/\nu_2 + \nu_4^1 + \nu_5^1$ Fermi diad.

Angular distributions were measured for rotational state-selected molecules by rotating the bolometer about the crystal while pumping the $P(3)$ transition prior to the molecule-surface collision, as shown in Fig. 1. Since the laser excitation occurs upstream from the crystal, these angular distributions correspond to the scattering of vibrationally excited molecules from the surface. Although, in principle, there could be a difference between the precollision and postcollision pumped angular distributions, a comparison of the experimental data showed that they were the same within experimental uncertainty. This result is not surprising considering the reports of NO/LiF(100) scattering of Misewich *et al.* [22] which suggest that (at least for high-frequency vibrations) the scattering process is nearly vibrationally elastic.

For postcollision pumping measurements of the internal state populations, the laser was directed into the spherical multipass cell, yielding an infrared spectrum of the scattered molecules. Rotational state populations were determined from the measured transition line intensities by correcting for the rotational state degeneracy, laser power, and line strength. Analogous measurements were made for the incident molecular beam, yielding incident rotational temperatures (T_r) of 24–42 K for the beam conditions used to access the entire range of E_i considered here. Figure 2 shows an example of a Boltzmann plot of the rotational population measured for C_2H_2 scattered from LiF(100). The line through the data points represents a 392 K Boltzmann distribution, which clearly provides an excellent description of the data. For all the measurements reported here, the angle of incidence was fixed at 60° and the bolometer detector was positioned at or near the angle of maximum intensity in the measured angular distribution.

Figure 3 shows a series of T_r measurements carried out as a function of E_i. The dependence of T_r on the normal incident translational energy ($E_n = E_i \cos^2 \theta_i$) can be divided into two regimes: at low energies ($23 < E_n < 65$ meV), T_r varies linearly with E_n (in kelvin) with a slope of 20%; while at high energies ($E_n > 65$ meV), T_r is essentially independent of E_n. Figure 4 shows three angular distributions representative of the same incident energy range. In the low energy regime, the angular distributions [e.g., Fig. 4(a)] are relatively broad and subspecular, while at higher energies we observe narrower and more specular scattering lobes [Fig. 4(b)] that become pregressively supraspecular [Fig. 4(c)] with increasing E_i.

To interpret the above observations we must take several factors into account: (1) the direct conversion of translational energy into rotational and vibrational excitation of the scattered molecule, (2) surface corrugation, (3) phonon creation and annihilation, (4) kinematic effects, and (5) multiple scattering (including chattering [23,24] and multiple bounces [25]). The observed narrowing of the angular distribution with increasing E_i can be largely understood in terms of the kinematics associated with the changing magnitudes of the energies involved. In an uncorrugated, rigid-surface, vibrationally elastic, direct scattering system, inelastic scattering involves only the intramolecular conversion of E_n into rotation—giving rise to supraspecular scattering since the parallel component of the energy is unchanged. In our experiments E_n varies from ≈25 to ≈155 meV, while the range of rotational states populated corresponds to a loss of 0–54 meV of E_n to rotation. As E_i is increased over the range studied, this energy loss becomes less significant in proportion to E_n, and the angular distributions become narrower

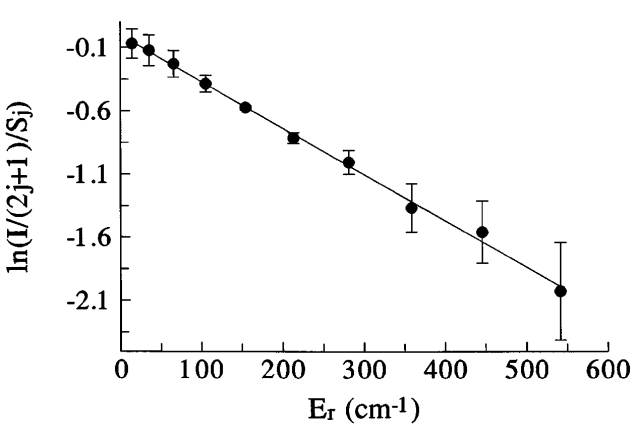

FIG. 2. Semilogarithmic Boltzmann plot of the rotational distribution of C_2H_2 scattered from LiF(100) for $E_i = 244$ meV ($E_n = 61$ meV) at $\theta_i = 60°$. The line is a fit to the experimental data from which T_r is found to be 392 ± 10 K.

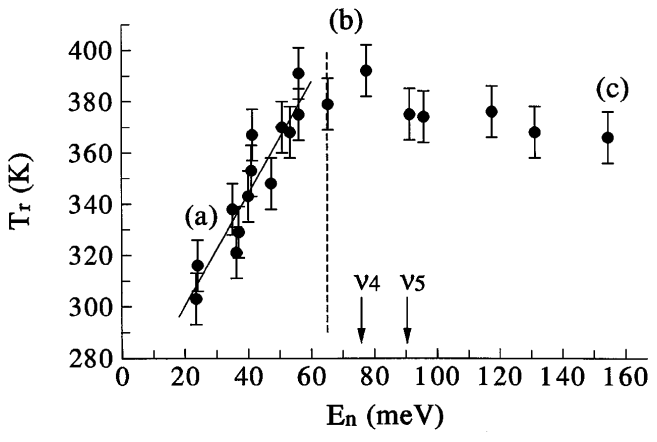

FIG. 3. Dependence of the final rotational temperature of C_2H_2 scattered from LiF(100) as a function of E_n for $\theta_i = 60°$. Labels (a), (b), and (c): the values of E_n which correspond to the angular distributions in Fig. 4.

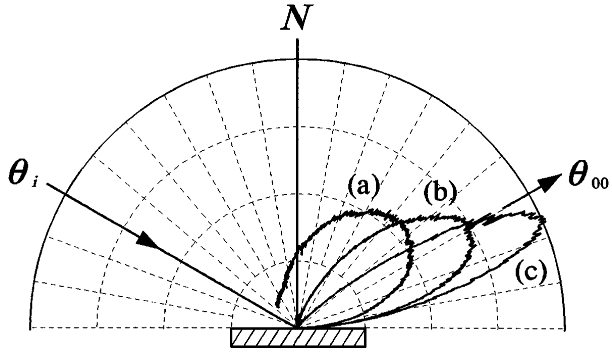

FIG. 4. Angular distributions of vibrationally excited C_2H_2 scattered from LiF(100) at $\theta_i = 60°$. Incident energies are (a) 110 meV, (b) 275 meV, and (c) 618 meV.

and more specular. Model calculations [26] show that, in the absence of corrugation, phonons, and finite residence times, these kinematic effects will focus the scattered molecules into a narrow angular range of approximately 4° centered at 62° for $E_i \approx 618$ meV.

This simple model of energy transfer fails in that it predicts angular distributions far narrower than those actually observed and cannot explain the observed subspecular scattering. Inclusion of surface corrugation, phonons, and multiple scattering effects will tend to broaden the angular distributions, as well as allow for nonconservation of surface parallel energy which would lead to subspecular scattering. Multiple scattering effects resulting in finite surface residence times (and a trapping-desorption-type scattering mechanism) are expected to be the major cause of the backscattered intensity ($\cos\theta$-like scattering) observed in the angular distributions at low E_i. However, the backscattered molecules comprise a relatively small fraction of the total scattered intensity [see Fig. 4(a)], indicating that relatively few molecules are temporarily trapped at the surface. Therefore, the observed subspecular scattering must be a consequence of surface corrugation, phonon interactions, and/or chattering. Any one or combination of these effects could also explain the rather large degree of rotational excitation observed in the low energy regime.

The narrow specular and supraspecular C_2H_2 scattering observed in the high energy regime is quite similar to the measured angular distributions for the NO/Ag(111) system [3,4]. The extensive studies of this system reveal narrow specular and supraspecular scattering, with T_r varying linearly with E_n (slope $\approx$10%) and showing only a weak dependence on T_s. The authors attribute this behavior to a direct inelastic scattering mechanism. In contrast, the present results indicate that T_r is independent of E_i above a threshold of $\approx$260 meV. Therefore, although the high E_i angular distributions suggest a scattering dynamics which is in the "direct inelastic" regime, the near independence of T_r from E_i suggests that something more is needed to fully explain the results.

Elastic and direct inelastic scattering trajectories involve a single center-of-mass (COM) turning point. The fact that C_2H_2 is rather long and less spherical than the diatomic molecules previously studied suggests that an impact of one end of the molecule could lead to sufficient rotational excitation to enable the *other* end of the molecule to impact the surface before the COM experiences its turning point (chattering). This mechanism is different from indirect inelastic scattering which involves multiple COM turning points and is best thought of as an intermediate between trapping-desorption and direct inelastic scattering. In contrast, chattering involves only a *single* COM turning point even though there are multiple encounters of the ends of the molecule with the surface. To test the plausibility of such trajectories, we have employed model classical trajectory calculations [26] which show that multiple encounter, single-turning-point collisions are, in fact, likely. This chattering concept is appealing because it can provide an explanation for the lack of a rotational rainbow [2] in the present data, even in the regime where the measured angular distributions indicate direct inelastic scattering dynamics. In the diatomic studies, the rotational distributions have all been rationalized based on a direct scattering process that leads to a deviation from Boltzmann statistics evidenced by an enhanced probability of scattering into high J states because of the presence of a maximum in the rotational excitation as a function of impact angle (the angle between the surface normal and the bond axis). For C_2H_2 we expect the rainbow may be washed out by these multiple encounters. Chattering may frustrate the transfer of translational to rotational energy and could play a role in the observed decrease in translational to rotational energy transfer ($T \rightarrow R$) efficiency at high E_i. However, our initial theoretical treatments indicate that chattering is a minor contributor to the overall dynamics and we do not expect that it is the cause of the dramatic change in behavior observed at $E_n \approx 65$ meV.

The dramatic break in the curve shown in Fig. 3 occurs roughly at an energy corresponding to the bending vibrational modes of C_2H_2 (76 and 90 meV for ν_4 and ν_5, respectively [21]), and it is tempting to invoke vibrational excitation as an explanation for the change in dynamics. The fact that the break occurs slightly before the energy threshold could be due to (1) the acceleration of the molecule into the surface due to the attractive component of the interaction potential, (2) the effect of surface corrugation and the nonconservation of parallel momentum, and/or (3) energy transfer from surface modes to the molecular vibrations. For collisions occurring "end-on" or "side-on," there is no torque on the molecule and, hence, no bending deformation of the molecule. On the other hand, collisions occurring at intermediate angles result in large torques and are also those that could induce bending of the C_2H_2. Thus the same trajectories which give rise to highly rotationally excited molecules also have the potential to excite the bending vibrations. Since the present experiments probe molecules only in the ground vibrational state, such a correlation between rotational and vibrational excitation would give rise to an apparent depletion of the high J state populations relative to the low J states, thus lowering T_r. This mechanism could also account for the slightly negative slope of the curve beyond the break in Fig. 3. Although vibrational excitation in molecule-surface scattering has been observed previously, for example, in the $NH_3/Au(111)$ system [11] where the umbrella mode was excited at incident translational energies close to energetic threshold, the dependence of T_r on E_n was reported to be linear with a slope of 20% over the entire range studied. If the effect we are observing here is the result of the proposed rotational-vibrational correlation, it is perhaps not surprising that the nature of this correlation depends strongly on molecular structure and may very strongly from system to system.

At the present time we are unable to say much about how phonon interactions influence the scattering dynamics. It is interesting to note, however, that the curve in Fig. 3 extrapolates to a finite rotational temperature of $\approx$255 K for zero incident energy, indicative of energy transfer from the surface to the molecule. In fact, decoupling from the heat bath of the surface with increasing E_i may account at least in part for the observed rollover in the T_r vs E_i curve: given a y intercept of zero, a slope of 20% extrapolated to an E_n of 155 meV would give $T_r \approx 360$ K. Future experiments designed to further investigate the role of energy transfer from the surface to the molecules will involve measurements of initial and final state-selected angular distributions, surface temperature studies, and measurements of final velocities.

In summary, the overall behavior of the $C_2H_2/LiF(100)$ system is distinctly different from that of all other systems which have been reported. The angular distribution measurements indicate that the scattering mechanism is direct, and the internal state measurements show that the scattering is strongly rotationally inelastic. The T_r data indicate a dramatic change in the dynamics over the range of incident energies used in our study. At low E_i, where the dependence of T_r on E_i is linear, the results are consistent with $T \rightarrow R$, surface corrugation, and phonon energy transfer mechanisms. At higher energies ($E_i > 260$ meV), we observe a saturation (and possible decrease) in T_r, indicative of the onset of another mechanism which has not previously been observed. We propose that the low frequency bending vibrational modes of C_2H_2 are excited above the energetic threshold, resulting in a depletion of high J, vibrational ground state molecules. Further work is underway to verify the existence of vibrationally excited scattered molecules by direct laser probing of these states, which should provide us with the information necessary to define the detailed nature of the proposed rotational-vibrational correlation.

This work was supported by the National Science Foundation (CHE-93-18936). The donors of the Petroleum Research Fund, administered by the ACS, are also acknowledged for partial support. T. W. F. acknowledges partial support from the U.S. Department of Education.

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