Rotationally Inelastic Molecule-Surface Scattering

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Time-of-flight measurements have been performed on the inelastic scattering of room-temperature beams of H_2 and D_2 molecules from a LiF (100) surface. The results show discrete inelastic peaks corresponding to energy losses approximately equal to the molecular rotational excitation energy but shifting with scattering angle. This indicates that rotationally inelastic scattering is dissipative rather than diffractive; i.e., it includes phonon excitations in the solid. The phonons involved can be identified as single Rayleigh surface phonons.

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The scattering of atoms or molecules from solid surfaces has recently attracted increasing attention. This arises both from a better theoretical understanding of the interaction process[1] and distinct progress in the experimental techniques. It has now been demonstrated[2] that molecular beam scattering from surfaces can give information on the atom-solid interaction potential,[3] the geometrical surface structure,[4,5] and the dynamic properties of the solid surface.[6] The present Letter[7] considers particular aspects of this scattering process, namely the interaction of a molecule having internal degrees of freedom with a surface, and the coupling of the corresponding molecular quantum states to the elementary excitations of the solid. The interest in this problem arises from the fundamental energy-transfer processes concerned, and their implications on problems like the accommodation of molecules on solid surfaces or the energy balance between dust and gas in interstellar clouds.

In the following we will be concerned with a system including a simple diatomic molecule like H_2. Using a room-temperature supersonic nozzle beam (energy 65 mV) we can limit the internal excitations considered to $J=0 \rightarrow J=2$ rotational transitions. Two possibilities are open for molecule-surface collisions. In the *diffractive*[8] case, rotationally inelastic events may occur where no energy or momentum is exchanged between the molecule and the solid.[9-11] The surface merely acts to transform translational into rotational energy in the scattering process. The inelastic events lead to scattering into discrete directions as determined by parallel-momentum conservation to within a surface reciprocal-lattice vector. Energy analysis should show a single energy loss amounting to the rotational excitation energy ΔE_{rot}. In contrast, a *dissipative* scattering process implies participation of the solid by its phonon excitations. The transformation of translational into rotational molecular energy occurs via the simultaneous creation or annihilation of a phonon, which ensures energy and momentum conservation over a wide range of scattering parameters. A variety of scattering angles and energy losses may therefore be found depending on the phonon involved.

Elastic measurements (not including energy resolution) have been performed previously for the scattering of H_2 and D_2 from LiF (Ref. 12) and MgO (Ref. 13) single-crystal surfaces. The results show additional diffraction maxima due to rotationally inelastic events. The analysis of these results[14,15] has led to the conclusion that rotationally inelastic scattering is predominantly diffractive. The present study is the first to include energy resolution into a molecule-surface scattering experiment. For H_2 and D_2 scattering from LiF, it is shown that an inelastic peak is found corresponding to an energy loss approximately equal to the rotational excitation energy, but varying in position with scattering angle. This is indicative of a dissipative scattering process, involving creation or annihilation of phonons in the solid. The phonons involved can be identified as single Rayleigh surface phonons.

The experimental setup consisted of a UHV system equipped with a flight tube for time-of-flight measurements. The molecular beam was generated in a fast valve with variable opening time, working on the principle of induced current repulsion in an Al disk.[16] Pulse widths of 10 μsec at speed ratios of 12 were used with pulse repetition rates of 0.1 Hz. The pulses were detected at a distance of 905 mm from the sample by a commercial nude ion gauge. Spectra were compiled by adding 100 to 200 pulses in a multichan-

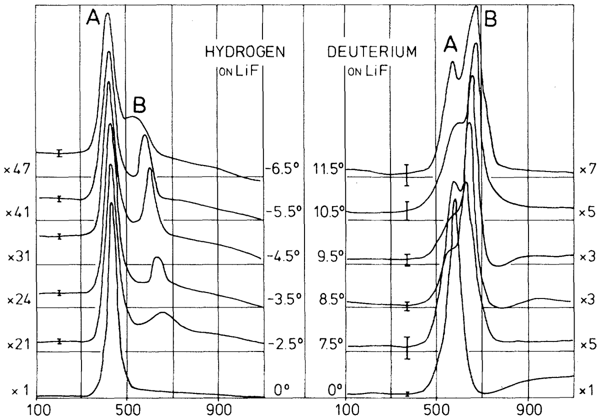

FIG. 1. Time-of-flight spectra of H_2 (left-hand side) and D_2 (right-hand side) scattered from a (100) room-temperature LiF surface along a ⟨10⟩ azimuth for various sample angles (as given along the centerline), relative to the specular condition. Fixed source-detector angle is 135°, flight distance from the surface is 905 mm, and beam energies are 79 meV for H_2 or 89 meV for D_2. All curves are normalized to the specular intensities (0°) by factors as indicated. Specular intensities are 30 times higher for H_2 than for D_2.

nel system with a resolution of 10 μsec per channel. Scattering took place along a ⟨10⟩ azimuth on a LiF (100) surface, with a fixed angle of $\theta_s = 135°$ between source and detector. Angular variation was achieved by rotating the crystal through an angle $\Delta\theta$, with positive values referring to a decreased angle of incidence. The angular range scanned extended from 45° to grazing angles of incidence or observation ($\Delta\theta = \pm 22.5°$).

Measurements were performed with H_2 and D_2 molecules in order to provide internal consistency by use of two similar molecules with different rotational excitation energy. Typical time-of-flight spectra for scattering of H_2 and D_2 beams are shown in Fig. 1. The lowest curve represents specular scattering at 67.5° angle of incidence. Only the elastic peak is seen, at a position corresponding to the initial molecular energy E_i. In a narrow angular range as indicated, a second structure *B* is observed that changes position with scattering angle. The flight time of peak *B* is longer, so that it corresponds to a loss of translational energy of the molecule. The half width of peak *B* amounts to about 6 meV in energy space and corresponds to the width of the elastic peak. The separation between structures *A* and *B* is markedly different for the two molecules. At least for H_2, a slight shift towards shorter flight times can be observed for peak *A*.

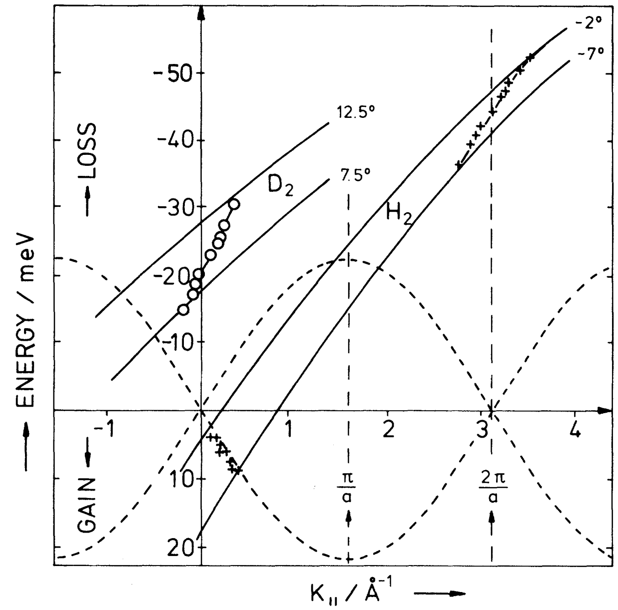

FIG. 2. Plot of energy vs parallel-momentum transfer for H_2 and D_2 scattering from LiF (100) surface. The solid lines represent coupling parabolas derived from Eq. (1) for sample angles as indicated. Crosses and circles are peak positions for H_2 and D_2, respectively. The broken line gives the Rayleigh-phonon dispersion (Ref. 18) in an extended-zone scheme for phonon creation (upper trace) and annihilation (lower trace).

The time-of-flight spectra shown in Fig. 1 can be converted into the corresponding energy spectra by use of the independently measured molecular-beam velocity. This allows one to obtain the *energy transfer* ΔE corresponding to a particular loss (or gain) structure. In addition, a *momentum transfer* $\Delta\vec{K}$ parallel to the surface is inherent in a molecular scattering event, with a size not negligible on the scale of reciprocal-lattice vectors. A unique relation exists between energy and momentum transfer, depending on the geometrical scattering conditions,[17] which can be written in the form

$$\frac{\Delta E}{E_i} = 1 - \left(1 - \frac{\Delta K}{K_i}\right)^2 \frac{\sin^2(\theta_s - \Delta\theta)}{\sin^2(\theta_s + \Delta\theta)} \qquad (1)$$

with K_i being the parallel component of the incident wave vectors. Using this relation, the energy and momentum transfers corresponding to the spectra in Fig. 1 have been compiled in Fig. 2, where the crosses and circles indicate measured points for H_2 and D_2, respectively. Figure 2 shows ΔE vs ΔK parabolas according to (1) for the sample angles $\Delta\theta$ as indicated, and a calculated[18] dispersion relation for Rayleigh phonons.

The group of measured points for H_2 near 10 meV gain energy arises from the observed shift of peak *A* in Fig. 1 towards shorter flight times. Such a shift has been observed earlier for He scattering from LiF (Ref. 19) and can be attributed to the direct annihilation of Rayleigh phonons in the scattering process. This interpretation is confirmed by the close correlation of these points with the predicted Rayleigh dispersion curve (dashed in Fig. 2). A similar evaluation of the corresponding peak for D_2 was not possible because of a lower signal-to-noise ratio. It is, however, assumed that in both cases the maximum *A* near the elastic position arises from direct coupling to Rayleigh phonons.

The loss peaks *B* in Fig. 1 give rise to the two groups of points in the loss region (Fig. 2) marked H_2 and D_2. Both groups appear to be centered to either zero momentum transfer (D_2) or transfer of a full reciprocal-lattice vector (H_2). At these center points, which correspond to diffractive scattering, loss energies are found close to the $J=0 \rightarrow J=2$ rotational transition, which is 44 meV for H_2 and 22 meV for D_2. However, deviating from these points the peak does not just decrease in intensity while occurring at constant energy, as would be expected for a diffractive event. In contrast, the structure stays discrete and shows a clear dispersion, which is approximately parallel for both molecules. This is indicative of a dissipative scattering process, involving discrete phonon excitations in the solid.

In order to identify the phonons involved in the dissipative scattering, we present a closer inspection of the loss structures in Fig. 3. Here the phonon contribution to the loss peak (i.e., the absolute value of the loss energy after subtraction of a constant rotational excitation energy) is plotted in a reduced-zone scheme. The observed points fall clearly outside the cross-hatched region, which indicates the bulk phonon continuum.[18] In particular, the points measured for H_2 scattering (which have been obtained with a better signal-to-noise ratio) closely follow the lower curve representing the dispersion of Rayleigh surface phonons as calculated for a surface with a polarizability different from the bulk[18] and confirmed experimentally.[20]

From the measurements presented here we conclude that rotationally inelastic scattering of H_2 and D_2 from a LiF (100) surface is a dissipative rather than diffractive process. This implies a direct coupling of the internal excitations of the molecule and the solid. In the scattering process, translational energy of the molecule is converted into a rotational excitation, with simultaneous emission or absorption of a phonon to satisfy the scattering conditions away from the diffractive case. The phonons involved are shown to be single Rayleigh phonons in the crystal surface. A remarkable feature is the fact that this process seems to occur with a strong selection rule on the direction of the phonon momentum, namely with antiparallel $\vec{K}$ for phonon creation and parallel $\vec{K}$ for phonon annihilation. The background of this selection rule is yet unclear.

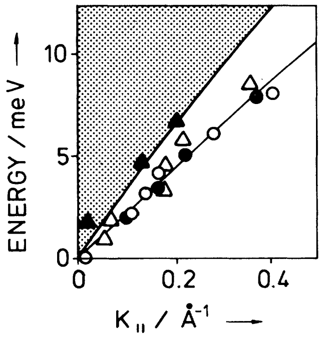

FIG. 3. Phonon contribution to rotationally inelastic scattering, obtained by plotting the absolute value of the loss energy, after subtraction of the rotational transition energy, vs momentum transfer in a reduced-zone scheme. Full and open symbols refer to phonon annihilation and creation, respectively; open circles, H_2; open triangles, D_2. Hatched area, bulk phonon continuum; solid line, Rayleigh-phonon dispersion.

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Atomic Displacements in the Si(111)-(7×7) Surface

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The parallel and perpendicular displacements of atoms in the first few layers of Si(111)-(7×7) have been determined with use of ion scattering. It was directly observed that the major reconstruction of this surface involves ~ 0.4 Å displacements perpendicular to the surface.

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The determination of the atomic positions of atoms in reconstructed semiconductor surfaces is a continuing challenge to the surface scientist. The primary structural tool, low-energy electron diffraction (LEED), can be used in a straightforward manner to determine the periodicity of the surface arrangement, but has been less successful in unambiguously establishing the actual atomic positions. In this Letter we report on an ion-scattering study of the Si(111)-(7×7) surface. The experimental results provide the first straightforward and definitive evidence that the major reconstruction in this surface involves vertical displacements of ~ 0.4 Å. We have also found that the lateral strain is small, much less, for example, than that observed in the Si(001)-(2×1) case.[1] In this paper we discuss the acquisition and analysis of these results and their implications for the various models of the Si(111)-(7×7) surface.

The ion-scattering technique for surface-structure determination makes use of the shadowing effect[2] which occurs for an ion beam incident along a major crystal axis direction. The first atom in an ideal string of atoms parallel to the incident beam forms a shadow cone which reduces the probability of close encounters between the incident ions and atoms further along in the string. In a reconstructed surface the first atom may not be aligned with the atomic row and the shadowing is reduced. The energy spectrum of the backscattered ions contains a high-energy surface peak (SP) due to interactions of the beam with the exposed surface atoms. The SP is a quantitative measure of the shadowing effect.

The apparatus for this study has been described elsewhere.[1] Briefly, it consists of a UHV system coupled to a Van de Graaff accelerator which produces He^+-ion beams collimated to ~ 1 mm^2 over the range of 0.1–4.0 MeV. The system contains visual-display LEED apparatus, Auger apparatus, sample-cleaning equipment, and a sample manipulator for channeling orientation. Also held on the manipulator is a scattering standard consisting of a heavy element implanted at low energy into Si. Scattering from this standard, calibrated against a known implanted standard,[3] can be compared to the scattering from the sample to obtain an absolute determination of the areal atomic density in the SP.