Diffractive Scattering of Hydrogen Dimers from LiF(001)

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The weakly bound hydrogen dimer has been detected in diffraction from LiF(001) along the $\langle 100 \rangle$ direction. The incident dimer energy is 48 meV and the crystal surface temperature is 150 K. The data are analyzed with a simple eikonal elastic scattering calculation and inelastic phonon scattering attenuation is estimated with a measured Debye-Waller factor. These calculations suggest that at least 5% of the dimers survive fragmentation. The well-defined first-order diffraction peak has an intensity of order 5×10^{14} dimers/sec str which could be useful for further beam studies.

The most precise knowledge of the neutral gas-surface interaction has come from the coherent scattering studies of helium and hydrogen from single crystals [1,2]. The experimental systems are well defined and quantum-mechanical calculations can be completed so that the diffraction and bound state resonance experiments have become a spectroscopy. While the elastic scattering is now understood, the inelastic scattering is still evolving. We have been able to demonstrate coherent scattering, without fragmentation, of hydrogen dimers from a solid surface through elastic diffraction channels. These results suggest that a third class of gas-surface systems, involving dimer combinations of $He/H_2/D_2$, can also be studied in these types of coherent experiments. For the present case of hydrogen dimers, because the free hydrogen rotors behave approximately like spectators, these dimers may have the feature that their internal states are quite simple, so that we may be able to study the dynamics of a simple pseudodiatomic molecule interacting with a surface in the quantum-mechanical regime. We believe such studies can be extended to several combinations of light atom (He, H_2, D_2) clusters in order to investigate the interaction of clusters with solid surfaces and ordered adsorbates, and to prepare well-defined beams of such clusters for investigation of their physical and chemical properties.

The weakly bound hydrogen dimer is of fundamental interest because it is accessable to quantum chemical calculations [3], its infrared spectra have been reported and analyzed [3,4], and it is of interest to astrophysics. The interaction of a cluster with a solid surface is an interesting dynamics problem in inelastic energy transfer and a useful technology in thin film growth. While some molecular beam scattering experiments for clusters interacting with surfaces and analysis [5–7] have been reported in the classical regime, the details are convoluted by the large number of inelastic channels and energies involved, which give rise to broad scattering distributions and insensitivity to the potential parameters.

Only the lowest van der Waals stretching state is bound for the hydrogen dimer $(H_2)_2$, incorporating two bound $(l=0,1)$ and two quasibound orbiting resonances $(l=2,3)$. The individual molecules are freely rotating "pseudoatoms" and the binding energies are less than 0.4 meV [3,4]. In some sense this may represent the simplest diatomic "pseudomolecule" that can be studied with coherent scattering from surfaces and whose internal states are accessible to single phonon interactions. Because the binding energy is small compared with incident beam energies and the surface phonon energies, one would not expect the complex to survive the interaction with a surface classically. However, the quantum coherent scattering channel provides elastic channels, and we are able to detect the scattering process.

The clusters are formed by a free-jet expansion [8] of normal hydrogen into a source chamber pumped by a 20-in. diffusion pump. The nozzle diameter is 25 μm, and the nozzle temperature and pressure are typically 110 K and 5 bars, respectively. The beam is collimated, modulated for equal beam-on and beam-off periods, and scattered in a 10^{-10}-torr UHV chamber from the LiF(001) crystal along the $\langle 100 \rangle$ direction; the crystal is held near 150 K. The crystal is rotated and the differentially pumped detector, a quadrupole mass spectrometer, is held fixed such that the sum of the incident and scattering angle, measured from the surface normal, is fixed at 96.0°. The LiF surface was chosen for these initial studies because it has been calibrated and characterized with helium scattering by many investigators and it is reasonably straightforward to clean and characterize. Helium and hydrogen scattering were both used to calibrate the scattering experiments, not only for correct geometries but in comparison to earlier scattering amplitudes and theory [1,2,9,10].

The incident beam is characterized in-line with a second mass spectrometer and the two mass spectrometers were cross calibrated by moving the detector to the incident beam station. Since the dimer ionizes to H_3^+ [11], the primary noise in the mass spectrometer is due to the naturally occurring mass three isotope (0.015% of the incident beam), which provides a background level noise, but which is small compared to the dimer signals. In addition, since the diffraction process scatters the mass three isotope and the mass four dimer into different angu-

lar directions the isotope does not contribute to the coherent scattering in the diffraction channels of the dimer.

The other primary concern is with fragmentation of the trimer cluster in the mass spectrometer to provide signals at mass three. Again, the coherent diffraction scattering will separate the dimer diffraction peaks spatially, but the specular peak could be contaminated. To reduce this effect we have selected beam source conditions such that the amount of measured trimer signal is small, less than 2% compared to the measured dimer signal. Such source conditions require a balance between source temperature and source pressure. Figure 1 shows a typical relative beam analysis for our apparatus suggesting that at 110 K the dimer dominates up to 5 bars before the larger clusters are formed. The data are not quantitative because the fragmentation ratios in the mass spectrometer ionization process are not known. As the source temperature is increased the source pressure at which the larger clusters rapidly form also increases so that the optimum conditions, maximum dimer intensity and minimum trimer, vary considerably. For example, we have confirmed the diffraction results below with source conditions of 165 K and 20 bars. We have also purposely increased the source pressure to verify that the trimer does not affect our dimer coherent diffraction results. The dimer results presented below are for conditions near 110 K and 5 bars for which we have measured the incident dimer beam velocity resolution $(\Delta v/v)$ to be 3% (FWHM).

Figure 2(a) shows results for the coherent scattering of the dimer at an incident energy of 48 meV. The elastic scattering conditions are given by $k_i(\sin\Theta_f - \sin\Theta_i) = G(m,n)$, where $k_i = k_f$ is the wave vector of the dimer (9.58 Å), $G = 2\pi m/a + 2\pi n/a$ $(a = 2.84$ Å) is the two-dimensional surface reciprocal lattice vector for the LiF crystal, and (m,n) are the diffraction peak indices [1,2]. The (1,1) surface direction is along the $\langle 100 \rangle$ crystal direction. The second-order peaks (2,2) are also allowed
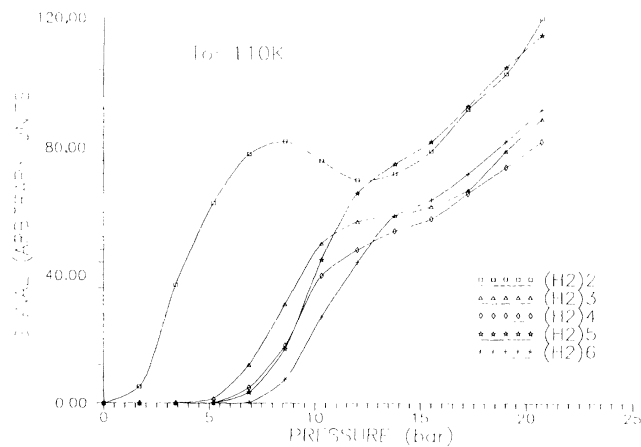
for our geometry but we have not been able to reproducibly measure them; the theory mentioned below confirms that their intensity will be small. As an example of the separation of the coherent dimer peaks, the hydrogen molecule, the mass three hydrogen isotope, and the hydrogen trimer cluster would give first-order $(-1,-1)$ diffraction peaks at angles of 77°, 67°, and 57°, respectively, in Fig. 2, all at least 5° from the dimer peak.

Figure 2(b) shows the results for the most simple elastic scattering calculation, the eikonal hard wall [1,12], which is known to be reasonable for the hydrogen molecule. The calculation is shown for a hard-wall sinusoidal corrugation amplitude of 0.15 Å. This corrugation amplitude is a fitting parameter in the theory and is a qualitative measure of how a surface of constant electron charge density, or repulsive turning potential varies across the surface [1]. For example, the hydrogen molecule is fitted by a corrugation amplitude of about 0.25 Å and the helium scattering is typically fitted with a corru-
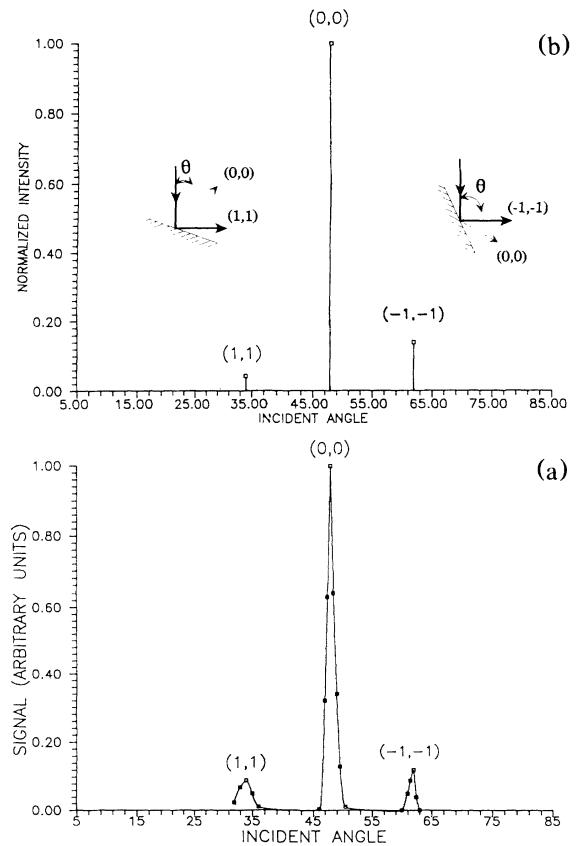

FIG. 2. Diffraction of 48-meV hydrogen dimers from 150 K LiF(001) along $\langle 100 \rangle$ $(\Theta_i + \Theta_f = 96°)$; (a) experimental and (b) elastic eikonal intensity calculation for a hard wall sinusoidal corrugation 0.15 Å. The insets indicate the crystal orientation necessary to observe the first-order peaks with the fixed 96° source-to-detector angle. The incident angle Θ is measured from the surface normal and the specular (0,0) ray is indicated for reference.

FIG. 1. Incident beam cluster mass spectrometer signals as a function of nozzle pressure at a fixed temperature of 110 K.

gation of about 0.32 Å. The 0.15-Å "fit" for the dimer provides the correct ratio of $I(-1,-1)/I(0,0)$ intensity. This smaller corrugation is indicative of the expected result, that the dimer is larger than helium or the hydrogen monomer so that the surface appears smoother.

Assuming that fragmentation (inelastic scattering) is approximately the same for both zero and first-order diffraction channels, we have used this simple eikonal calculation, fitted to the diffraction peaks, to estimate the fraction F of dimers which scatter elastically and do not fragment as

$$F = [(D/M)_{oo}/(D/M)_i][P(M)/P(D)]_{oo}, \qquad (1)$$

where the first bracket is the dimer-to-monomer ratio in the specular beam (oo) to that in the incident beam (i), and the second bracket is the calculated ratio of specular scattering probabilities for the monomer $P(M)$ and dimer $P(D)$. The measured ratio in the first bracket cancels effects due to dimer-to-monomer fragmentation in the mass spectrometer detection. The result for the data here is that F is approximately 0.05, i.e., at least 5% of the dimers survive based on this elastic calculation.

There are two mechanisms which would lead to fragmentation: inelastic scattering due to interaction with surface phonons, and elastic scattering in which there is translational-to-rotational transfer of energy within the molecule. In order to estimate the contribution due to phonon scattering we have performed Debye-Waller experiments [1], coherent elastic peak attenuation versus surface temperature (T_s), for both the dimer and molecular hydrogen coherent peaks. These are fitted by the usual Debye-Waller form for the reduction of the ideal elastic intensity (I_e), $I/I_e = \exp(-2W)$ where $W = \frac{1}{2}\langle(\mathbf{u}\cdot\Delta\mathbf{k})^2\rangle$, $\mathbf{u}$ is the thermal displacement of the surface atoms, proportional to T_s, and $\Delta\mathbf{k}$ is the momentum transfer in the scattering event. Since $\Delta\mathbf{k}$ is larger for the dimer than the monomer, due primarily to its larger mass, the inelastic phonon attenuation is larger for the dimer. These results will be presented elsewhere, but they permit us to scale out the loss in elastic scattering intensity to be expected from inelastic phonon scattering. Applying this experimentally determined factor as a correction to the elastic calculation of $[P(M)/P(D)]_{oo}$ in Eq. (1) accounts for 25% of the dimer loss. Obviously this result must be made more quantitative with energy resolved data and with the use of a more rigorous theory [10].

The coupling effect of the inelastic rotational transitions within the "free" hydrogen molecules on the dimer are minimized because at our beam source conditions the hydrogen molecules are predominantly in the ground para and ortho states ($j = 0,1$). The rotational transitions ($\Delta j = 2$) are too large (44 and 73 meV) for substantial interaction with single surface phonons. Coupling the elastic translation-to-rotation transfer within the free hydrogens is also minimized. In the present experiments,

the incident energy and angle kinematics are such that the elastic translation-to-rotation scattering from the surface is not allowed for the free hydrogen rotors. Based on previous work with molecular hydrogen scattering from surfaces [9,13] we expect such effects to be on the order of a few percent so that they should not affect the dimer scattering. The fragmentation of the dimer should therefore be due primarily to the dynamics of the coupling of the two ($l = 0,1$) internal states of the dimer bond directly with the surface phonons (inelastic scattering) or with the incident translational energy in an elastic surface collision. As mentioned above these two mechanisms can be probed by varying surface temperature, and even more directly by using time-of-flight detection to resolve inelastic scattering.

We are in the process of improving our experimental signal-to-noise ratio, compared to this initial study, so that we can detect the (2,2) diffraction channels, and so that we can use time-of-flight energy analysis on the scattered coherent beams to better probe the inelastic dynamics. We are also installing an azimuthal rotation capability on the crystal holder so that the elastic selective adsorption scattering can be used to probe the bound states of the dimer-surface interaction potential, in analogy to the helium and hydrogen studies [1,13]. Using a magnetic catalyst it is also possible to generate beams of nearly pure para hydrogen [13], so that under our beam formation conditions it will be possible to prepare dimers in the $l = 0$ state (the $l = 1$ state is not allowed for para dimers due to symmetry) for extremely well-defined coherent elastic and inelastic studies.

In addition to the studies of the interaction between clusters and surfaces, with and without ordered adsorbates, which may become possible, it should interest researchers that a beam of rather well-defined hydrogen dimers can be generated by this coherent diffraction process. As a matter of interest to other investigators, we have *estimated*, from monomer beam flux gauges and the mass spectrometer ratios, that the diffracted beam intensity in these experiments for the $(-1,-1)$ dimer beam is of order 5×10^{14} dimers/sec str. An analogous separation of the more strongly bound argon dimers has been obtained by crossed molecular beam scattering in the gas phase [14] and used to measure ionization fragmentation probabilities. While the separation of the hydrogen dimers is much better using the coherent surface scattering reported here, the present technique is limited to the light hydrogen/helium systems, whereas the crossed beam technique can be used to disperse larger and heavier clusters.

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