

Infrared-Induced Single-Phonon Desorption of HD from LiF(100)Paul M. Ferm,^(a) Sarah R. Kurtz,^(b) and Kathryn A. Pearlstine^(c)*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*

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Low-intensity (10^{-5} – 10^{-2} W/cm²) ir radiation at 9–15 μ m desorbs HD from 1.5–4.2-K LiF(100) at a rate (maximum 0.001 monolayer/s) proportional to the light intensity. This process is independent of temperature below 4.2 K, the velocity distribution is approximated by a temperature of 21 K, and the desorption efficiency increases with increasing wavelength. Desorption is attributed to single phonons created in a cascade following optical absorption. Thermal desorption is excluded as a possible mechanism except at high surface temperatures and coverages.

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Fifty years ago, Lennard-Jones and Strachan,¹ Strachan,¹ and Lennard-Jones and Devonshire¹ described gas-solid energy transfer in terms of transitions among discrete and continuum states of the gas-surface potential caused by the creation and annihilation of single phonons. This theory, which employed the Fermi "golden rule," was successful at explaining some of the scattering experiments of that time,² and despite the recent theoretical refinements³ which have been used to describe much improved experiments, the Lennard-Jones-Devonshire-Strachan approach is thought to be basically correct for light atoms and molecules (He and atomic and molecular hydrogen) and weakly interacting solids. According to the Lennard-Jones-Devonshire-Strachan theory, the final step in thermal desorption is the annihilation of a single phonon with the simultaneous transition of the absorbed particle from a discrete bound state to a continuum state. Unfortunately, this picture of single-phonon transitions is hard to verify by the study of thermal desorption directly, because it makes no dramatic qualitative predictions for major experimental observables such as the velocity distribution of the desorbing gas and the temperature dependence of the desorption rate.

The single-phonon picture can be verified by the observation of desorption from a specific nonthermal initial state of either the particle or the phonon. Lilienkamp and Toennies have done the former by diffracting an incident He beam into a metastable bound state and demonstrating that the speed and angle of the ejected atoms are consistent with single-phonon annihilation.⁴ Using another approach, Goodstein *et al.*⁵ and Hope, Baird, and Wyatt⁶ have confirmed a single-phonon contribution to He desorption by injecting a broad spectrum of high-temperature but low-intensity phonons into a sapphire crystal⁵ or liquid He.⁶ Here we report observations of single-phonon desorption of HD from 1.5–4.2-K

LiF(100). Desorption is initiated by high-energy phonons which are generated near the surface with use of low-intensity ir radiation.

Our work was prompted by the intriguing discovery of Chubb, Gowland, and Pollard in 1968 that the apparent vapor pressure of hydrogen in their apparatus was independent of temperature below 3 K, a fact they attributed to desorption by background blackbody radiation.⁷ Benvenuti, Calder, and Passardi confirmed this effect on a variety of uncharacterized metallic and nonmetallic substrates, showed that the anomalous pressure depended linearly on the incident radiation intensity, and postulated that light absorption by the solid was responsible for desorption.⁸ Both studies were concerned primarily with cryopump design and did not observe the desorbed molecules directly or study the wavelength dependence.

In our experiments, a freshly cleaved $1.0 \times 1.0 \times 0.5$ -cm³ LiF crystal was mounted with a crushed indium wire seal to a cryostat so that five sides contacted liquid helium while the cleaved (100) surface faced a vacuum of 3×10^{-10} Torr within a 10-K cold shield. Crystal temperatures were computed from the helium vapor pressure. Except as noted, either optical grade crystals from Harshaw or ultrapure samples supplied by G. Schmidt of Cornell University were used, and these gave identical results. Since the crystal mount permitted baking out the crystal only to 40°C, the LiF surface probably was contaminated with about 0.01 monolayer of H⁺ and OH⁻.⁹ To minimize the detector background, the HD isotope ($\geq 99.9\%$ hydrogen isotopes with $\geq 97\%$ HD) was used, dosed from a 2-mm-i.d. tube near the crystal. A doubly differentially pumped electron-bombardment ionizer was situated 22 cm away, followed by a mass spectrometer detector and ion counter. ir radiation was generated by a 1650-K blackbody emitter and sent through filters and a chopper wheel before entering the vacuum chamber and impinging on the vac-

uum side of the crystal. The data presented here were reproducibly obtained in about a dozen "runs" with several crystals over a period of six months.

In the present paper only photodesorption results corresponding to photons absorbed by the solid ($\geq 6 \mu\text{m}$) are discussed. This mechanism is very different from proposed single-photon-induced desorption initiated by direct absorption by an intramolecular vibration¹⁰ or by a gas-surface bond.¹¹ Ir-induced desorption signals in the transparent region of LiF were also observed and will be described in a future paper containing complete experimental details and results.¹²

The steady-state desorption signal from a 2.5-K crystal at low HD dosages (< 1 monolayer) was measured as a function of the total incident ir flux from the 1650-K unfiltered blackbody radiator. Seven neutral density filters ranging in transmission from 100% to 2.2% were mounted together on the chopper wheel so that each illuminated the crystal for 7 ms. At full load the sample absorbs 0.01 W; this was estimated from the measured He boiloff and the LiF optical properties.¹³ The maximum desorption rate is 0.001 monolayer/s. Over a total counting time of 3000 s, the noise level found in this experiment is equivalent to a standard deviation σ of 0.6%, which agrees with a shot-noise prediction based on the counting rate, which is principally background. Four of the seven measured desorption intensities fall within $\pm \sigma$ of a straight line directly proportional to the incident light intensity, while all the data fall within $\pm 2\sigma$ of this line. This result and other data between 1.5 and 4.2 K indicate that at low HD coverage the desorption is absolutely linear in ir intensity.

The time-of-flight (TOF) spectra of Fig. 1 were recorded by an increase of the chopper speed so that the photodiode-measured slit function was 0.7 ms wide. For comparison, Maxwell-Boltzmann TOF distributions were convoluted with the slit function. The low-coverage

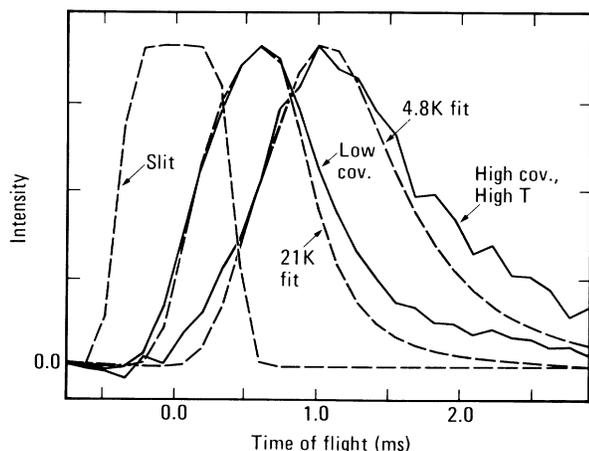


FIG. 1. Time-of-flight spectra. Solid lines, experimental data; dashed lines, ir slit function and Maxwell-Boltzmann fits.

spectrum shown was recorded at 1.5 K, and was best fitted by a 21-K curve; identical spectra and intensities were measured at crystal temperatures up to 4.2 K, and, aside from an overall proportionality, the TOF curves were independent of light intensity. Here the 21-K temperature is presented as merely a convenient single parameter with which to describe the measured distribution, and we are not implying that the distribution is strictly Boltzmann. The exact shape of the TOF curve is distorted by a tail present at times > 1 ms, which we attribute to desorbing HD building up in the radiation-shielded area and effusing out. The rising edge and peak were found to be independent of pumping conductance from this area, and so we chose this part of the data to fit with the Maxwell-Boltzmann curves. The TOF data can alternatively be characterized by the average translation energy of the desorbed molecules. Even if the entire TOF curve displayed (including the long-time tail) is used to calculate the average energy, the value found is the same as that of a Maxwell-Boltzmann distribution at 14 K. Thus by any measure, the molecules are desorbing with energies an order of magnitude higher than that given by the surface temperature.

Below the monolayer regime, the signal at low crystal temperature (< 3.5 K) increases linearly with dosage, but at large doses, the signal begins to decrease until it disappears altogether after about 5–10 monolayers. If this same crystal with its multilayers of HD is raised to 4.2 K, photodesorption occurs, but at about $\frac{1}{5}$ the total intensity and at a much slower velocity, as shown in Fig. 1. We will refer to this high-temperature, high-coverage signal as Signal 2 to distinguish it from the low-coverage signal described above (Signal 1). The early part of the TOF spectrum of Signal 2 (Fig. 1) is best fitted by a 4.8-K Maxwell-Boltzmann distribution, while the average energy of the desorbing molecules is that of a 4.0-K distribution. All observations concerning the signal as a function of temperature and dosage are independent of the order in which HD dosings and temperature changes are applied to the crystal.

To study the wavelength dependence of Signal 1, we compared the magnitude of the continuous desorption signal obtained with use of several different bandpass filters. For each filter, we determined the total power absorbed by the crystal by the formula

$$W = \int [1 - R(\lambda)] (1 - e^{-a(\lambda)d}) I(\lambda) T(\lambda) d\lambda,$$

where R is the reflectivity, a is the absorption coefficient measured for a 7-K crystal,¹³ d is the crystal thickness, $I(\lambda)$ is the ir blackbody-radiation curve, and $T(\lambda)$ is the fractional transmittance of the filter. The normalized desorption rates at low coverage were computed by our dividing the observed signal levels by W and are displayed in Fig. 2. The desorption efficiency is found to increase steadily with increasing wavelength.

For Signal 1 we estimate that the desorption efficiency

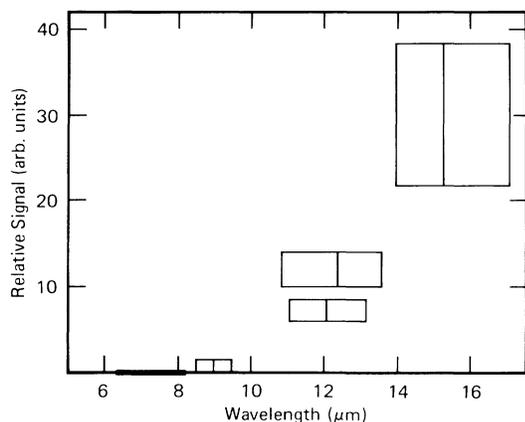


FIG. 2. Photodesorption Signal 1 vs λ . Each measurement is represented by a rectangle, with a height representing ± 1 standard deviation and width representing the λ range containing $\frac{2}{3}$ of the incident power, with $\frac{1}{6}$ of the power extending beyond each edge. The vertical line represents the average λ .

at ≈ 1 monolayer coverage is, within a factor of 3, 4×10^{-5} molecules per photon at $15 \mu\text{m}$, which is the wavelength of maximum signal. We use here the detector efficiency calibrated with an effusive HD source and we assume a cosine angular distribution for desorption.

Signal 1 is consistent with a model of single-phonon desorption of HD from LiF. The ir radiation, absorbed in the bulk, creates high-energy phonons which desorb HD at high translational energies. As this model requires, the process is strictly linear in the light intensity. Varying the surface temperature between 1.5 and 4.2 K does not increase the desorption intensity or translational energy and indicates occupation of, and desorption from, the ground state of the HD/LiF potential. The linearity (non-Arrhenius behavior) and temperature independence are compelling evidence against the possibility that the ir load is simply raising the temperature of the surface of the crystal (perhaps to 21 K), thereby causing desorption.

The coverage dependence of the signal removes any possibility of a thermal effect. If Signal 1 at low T were due to thermal desorption, then adding multilayers of HD would vastly increase the signal, since the sublimation energy of HD (10 meV) is much smaller than the desorption energy of HD on LiF ($E_d = 30$ meV).¹⁴ In the He-sapphire system, Goodstein *et al.* indeed see a multilayer He thermal-desorption signal ($E_d = 2.6$ meV) grow in to be 20 times larger than the single-phonon He-sapphire signal ($E_d = 6$ meV).⁵ In our experiment, the quenching of the desorption process by multilayers of HD probably occurs through reflection or absorption of the high-energy phonons impinging on the surface. Since the optical method we use for generating high-energy phonons produces a very small temperature increase in the low-energy phonon background, thermal

desorption even for HD multilayers is negligible for crystal temperatures below 3.5 K.

We can calculate the heat rise of the LiF-crystal surface directly from known thermal properties. From the measured thermal resistivity of Harshaw LiF samples like ours at 2.5 K,¹⁵ and with the assumption of the extreme case in which the entire 0.01-W ir-radiation load is absorbed directly at the surface, the temperature rise across the LiF crystal will be 0.03 K. From the heat capacity and thermal conductivity of LiF, its time constant for heating is found to be $\approx 20 \mu\text{s}$, so that the thermal properties reach a steady state during the relatively long 1-ms radiation pulses. An additional temperature gradient arises from the well-documented Kapitza resistance of the He-LiF interface.¹⁶ If we scale this resistance by T^3 to account for the LiF heat capacity, the temperature rise across the He interface will be 0.02 K at the maximum ir load for a 2.5-K crystal. The LiF surface will thus at most rise to 2.55 K. At this temperature, HD has a vapor pressure $< 10^{-16}$ Torr, and so thermal desorption from either HD multilayers or adsorbed HD is negligible and cannot explain our results. Note also that, since the optical-absorption depth is ≤ 0.1 cm for $\lambda > 10.5 \mu\text{m}$, the path length for thermal conduction to the back of the crystal is fixed in this wavelength range, and the efficiency per unit absorbed power of a thermal process would be independent of wavelength, contrary to observation.

Signal 2, at high coverages and high temperature, seems indeed to be thermal desorption. It is observed only when the crystal is warm enough so that HD has an appreciable vapor pressure (3.3×10^{-9} Torr at 4.2 K), so that the added radiation need only slightly perturb the crystal temperature to generate a detectable signal. From the HD vapor pressure and the size of the observed signal, we compute that the needed temperature rise is only 0.005 K. This agrees within a factor of 2 with the rise calculated by the heat-transfer considerations outlined above, but starting at 4.2 K.

The desorption process that we observe must begin with multiphonon desorption, since the phonon spectrum of LiF cuts off below the energy corresponding to $15 \mu\text{m}$.¹⁷ These optically created phonons eventually decay to other lower-energy phonons, until the completely thermalized energy is conducted away from the surface. While optical phonons are extremely short lived, some of the lowest-branch near-zone-edge transverse acoustical phonons which are created in the cascade process may exist for 10^{-4} to 10^{-9} s,¹⁸ a sufficient length of time for some of them to propagate from where they are created in the bulk to the surface, where an individual phonon may cause desorption from the lowest HD bound state. The distance a phonon can travel to the surface is further reduced by elastic scattering off of the mixed isotopes of Li, which is estimated to occur every 10^{-11} s.¹⁹ A high absorption coefficient insures that many phonons

will be created close enough to the surface to survive and cause desorption, and this explains the sharply increasing desorption signal versus wavelength in Fig. 2. The low intensity of the incident radiation insures that the actual density of high-energy phonons is quite low and therefore we see no nonlinear effects indicating multiple-quantum desorption processes or interactions between phonons created by different photons. In a future paper,¹² we will present the details of a semiquantitative model based on this mechanism, which explains the desorption rate, wavelength dependence, and velocity distribution reported here.

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