Direct Infrared Photodesorption of Physisorbed H$_2$

M. Hassel, K. Svensson, M. Persson, and S. Andersson

Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden
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Blackbody radiation induced desorption rates of H$_2$ and D$_2$ physisorbed on a Cu(510) surface were determined via electron-energy-loss measurements. Intense dipole-excited vibrational transitions to high-lying bound levels in the physisorption well indicate the possibility of direct infrared photodesorption. We have calculated rates for such a mechanism from spectroscopic data for H$_2$ adsorbed on the (100)-like terraces and find excellent agreement with the experimental results. [S0031-9007(98)05576-8]

Although photons in the infrared spectral range can induce desorption of adsorbed molecules, bond-selective photodesorption via resonant laser excitation of specific vibrational modes of an adsorbate-substrate system is, in general, prevented by fast vibrational deexcitation and weak vibration-translation coupling [1,2]. The large amount of energy that lasers can feed into the vibrational modes is instead transferred within the system resulting in indiscriminant thermal desorption [1,3].

Infrared photons can also excite substrate phonons which may induce desorption of weakly adsorbed species via single-phonon annihilation. It has been suggested [4,5] that this process could be responsible for thermal radiation induced desorption of molecular hydrogen from liquid-helium cooled substrates. Early observations [6] of unexpectedly large hydrogen desorption rates from cryopumping surfaces were attributed to the incident room-temperature blackbody radiation originating from the vacuum chamber walls. Later experiments [4,5,7] confirmed these observations and provided further evidence for a nonthermal origin of the desorption process. Specifically, it was found [5] that the velocity distribution of HD molecules desorbed from a LiF(100) surface by infrared radiation was nonthermal, and the desorption efficiency increased with increasing wavelength of the photons. The desorption was attributed to single phonons created in a cascade following optical absorption.

An alternative route has been discussed by Pearlstine and McClelland [8]; *direct infrared photodesorption* of adsorbed hydrogen molecules from the lowest bound vibrational level in the physisorption well to unbound continuum states. In this Letter, we present direct evidence of such a desorption process from measured and calculated rates of blackbody radiation induced desorption of H$_2$ physi-sorbed on a Cu(510) surface. The desorption rate is substantial because the shallow physisorption well contains only a few bound states and the dipole moment of the molecule-surface bond is a strongly nonlinear function of displacement. Our spectroscopic measurements reveal, for example, intense dipole-excited transitions to bound levels close to the continuum. We find that di-rect infrared photodesorption rates calculated with the use of the spectroscopic data agree in an excellent way with our measurements for H$_2$ adsorbed on the terraces of the Cu(510) surface. Larger rates measured for step-adsorbed H$_2$ relate qualitatively to larger dipole activity of the vibrational motion.

The experiments reported here were performed in an ultrahigh vacuum chamber operating at a base pressure of 3×10^{-11} Torr. The x-ray aligned ($<0.2°$) and polished Cu(510) specimen was cleaned in the ultrahigh vacuum chamber by standard methods involving argon-ion bombardment and annealing cycles. Using helium as a cryogen, the specimen could be cooled to temperatures below 10 K, and it was heated resistively. Substrate surface properties and subsequent hydrogen adsorptions were monitored by low-energy electron diffraction (LEED), high-resolution electron-energy-loss spectroscopy (EELS), work function measurements, and mass spectroscopy. The clean Cu(510) surface produced the expected LEED pattern, with split spots in the [1$\bar{5}$0] direction, corresponding to an average surface topology with (100)-like terraces of five atomic rows width separated by (110)-like steps. We have used two different methods to determine rates of desorption of H$_2$ and D$_2$ caused by background blackbody radiation. One method relies on vibrational loss intensity measurements using EELS and the other on retarding field measurements of the adsorbate-induced work function change [9] performed in a small side chamber whose wall temperature can be varied during the experiment.

Our electron-energy-loss measurements show that the hydrogen physisorption on Cu(510) proceeds in two characteristic stages; the step sites are occupied first and further adsorption populates the terraces. This behavior is nicely illustrated in Fig. 1, which displays EEL spectra where (a) primarily the steps (*S*) and (b) both steps (*S*) and terraces (*T*) are covered with adsorbed H$_2$. The loss peaks at 9.0, 15.4, and 21.3 meV that grew in (b) are due to H$_2$ populating the (100)-like terraces. These peaks nearly coincide with the $0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$ vibrational transitions in the H$_2$-Cu(100) physisorption well, observed at 8.9, 15.3, and 20.5 meV [10], and the molecule evidently experiences almost
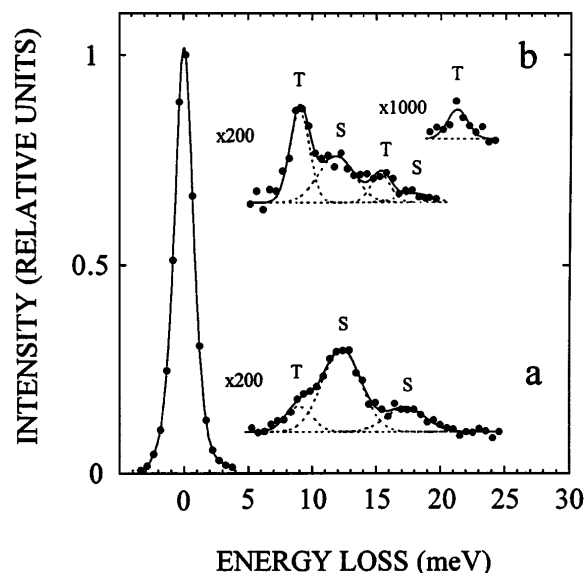
FIG. 1. Electron-energy-loss spectra from H_2 adsorbed on Cu(510) at 9 K for initial gas exposures of (a) 0.7 L and (b) 1.6 L (1 L = 1 × 10^{-6} Torr sec). The spectra are measured in the specular direction for a 1 eV electron beam incident at 48° from the surface normal. A smooth background has been subtracted, and the dashed curves indicate the decomposition of the spectra in step (S) and terrace (T) related features.

FIG. 2. (a) Measured H_2 (●) and D_2 (○) pressures P_b required to maintain a fixed adsorbate coverage and (b) measured intensities of the $0 \rightarrow 1$ vibrational transitions for H_2 adsorbed at step (●) and terrace (○) sites. The data were obtained for different initial gas exposures $P_e t$ of the Cu(510) surface at a background temperature of 296 K.

identical physisorption potentials in these two cases. Larger binding energy for H_2 adsorbed at the steps results in larger $0 \rightarrow 1$ and $0 \rightarrow 2$ vibrational energies, 12 and 18 meV, respectively. All of the vibrational excitations observed in Fig. 1 are dipole excited, and the intense overtones in the spectra are caused by a strongly nonlinear dipole moment function, a behavior which resembles our previous observations for H_2 adsorbed on Cu(100) [10]. We note that the dipole active $0 \rightarrow 3$ transition for H_2 adsorbed on the terraces is quite close to the continuum limit around 25 meV.

Desorption of H_2 due to background blackbody radiation is a pronounced effect, and we obtained the spectra shown in Fig. 1 by applying an H_2 pressure in order to maintain a fixed H_2 coverage. With the vacuum chamber at room temperature (296 K), a pressure of 4×10^{-9} Torr is required to keep the steps saturated with adsorbed molecules. This pressure is independent of the substrate temperature below 14 K, but depends on the temperature of the surrounding walls of the vacuum chamber. At a wall temperature of 240 K, the applied pressure is about a factor of 2 lower. The specimen temperature is unaffected by the changing radiation load. These observations are consistent with related findings for a number of H_2 physisorption systems [4–7]; the desorption is evidently nonthermal and induced by the infrared radiation emitted from the walls.

Both step- and terrace-adsorbed molecules are desorbed by the thermal radiation. This can be seen in Fig. 2, where we have plotted the applied pressure P_b and the intensities of the $0 \rightarrow 1$ vibrational transitions for adsorbed H_2 versus the initial gas exposure $P_e \cdot t$, with the vacuum chamber
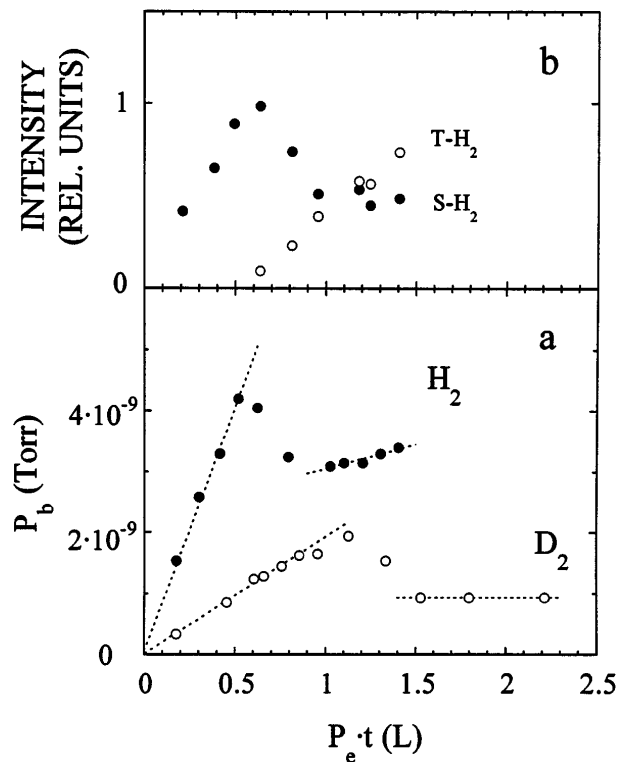
at room temperature [11]. The intensities are proportional to the population of molecules, and the plot in Fig. 2(b) shows how the steps are occupied first and that further adsorption populates the terraces with a concomitant redistribution among the two kinds of adsorbed molecules. The pressure data for H_2 in Fig. 2(a) reflects this behavior with a linear increase as the steps become populated, terminating with slower increase when the adsorbate fills the terraces. At this stage, the steps are filled, and the slow increase in P_b reflects desorption from the terraces.

We have determined desorption rates for step- and terrace-adsorbed molecules by simply measuring the decay of the $0 \rightarrow 1$ vibrational peak intensity with time. It is straightforward to employ this method for step-adsorbed molecules, and Fig. 3 shows such measurements with the chamber at room temperature. The initial gas exposures were 0.5 and 1.0 L (1 L = 1 × 10^{-6} Torr sec) for H_2 and D_2, respectively [12]. The intensity decays in an exponential fashion with time, $I(t) = I(0)e^{-t/\tau}$, where τ is the mean lifetime of an adsorbed molecule, and we obtain rates $1/\tau$, 7×10^{-3} s^{-1} for H_2, and 2×10^{-3} s^{-1} for D_2. Terrace-adsorbed molecules diffuse easily to unoccupied step sites and photodesorb. This means that desorption rates for such molecules are not readily measured from spectra similar to those in Fig. 1. H_2 adsorption at the steps can be prevented, however, via preadsorption
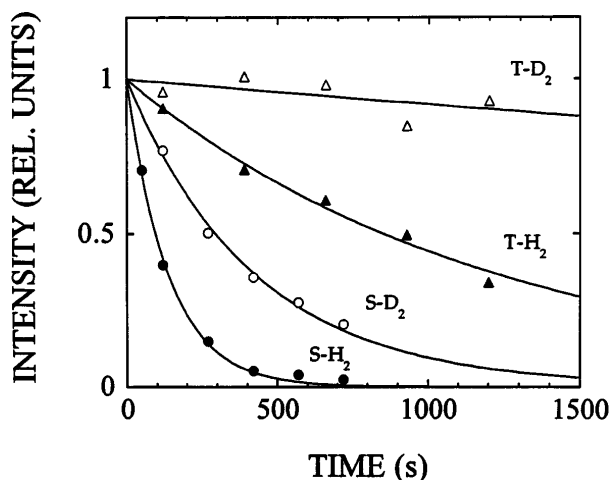
FIG. 3. Decay of the $0 \rightarrow 1$ vibrational peak intensity with time for step adsorbed H_2 (●), D_2 (○), and terrace-adsorbed H_2 (▲), D_2 (△) at a background temperature of 296 K. The solid curves represent fitted exponential decays.

of a suitable inert adsorbate. We found that N_2 serves this purpose well [13]; the molecules adsorb stably at the steps, prevent step adsorption of H_2, and affect the subsequent H_2 adsorption on the terraces only marginally as judged from the EEL spectra. The $0 \rightarrow 1$ vibrational transition is observed around 9 and 7 meV for H_2 and D_2, respectively. The peak intensity decays with a long time constant as can be seen in Fig. 3. The corresponding desorption rate is 8×10^{-4} s^{-1} for H_2 and around an order of magnitude lower for D_2. Our measurements do not permit a more precise determination for D_2 because of influence from the ambient gas.

Desorption rates can also be obtained from the pressure data in Fig. 2(a). We have performed such measurements at different background temperatures in the small side chamber. The linear increase of the vibrational intensities when the steps as well as the terraces are populated [see Fig. 2(b)] indicates that the sticking coefficient remains constant in these ranges of exposure. The mean lifetime τ then has a simple identification; adsorption and desorption rates are equal in the stationary situation and $P_b\tau$ is just the gas exposure required to produce the specific adsorbate density in the absence of desorption. Normally, we dose at a much higher pressure P_e during a short time t to achieve this density. This means that $P_b = (1/\tau)P_e t$ and the rates $1/\tau$ for molecules desorbing from the steps can consequently be determined from the initial slopes in Fig. 2(a). We find rates 8×10^{-3} s^{-1} and 2×10^{-3} s^{-1} for H_2 and D_2, respectively, values that agree very well with the corresponding rates obtained from the spectroscopic measurements.

The population of step-adsorbed H_2 remains constant in the exposure range $1-1.4$ L [see Fig. 2(b)]. The increase in P_b in this exposure range then corresponds to H_2 desorption from the terraces. From the slope, we obtain the rate 8×10^{-4} s^{-1} with the chamber at room temperature confirming the rate we measured from the decay of the

$0 \rightarrow 1$ vibrational intensity. The rate decreases to 5×10^{-4} s^{-1} when the background temperature is lowered to 210 K and increases to 15×10^{-4} s^{-1} at a temperature of 370 K. The desorption rate for terrace-adsorbed D_2 is so low that we are unable to measure it.

We will concentrate our discussion on H_2 desorption from the (100)-like terraces. Our spectroscopic measurements reveal intense dipole-excited vibrational transitions to high-lying bound levels in the physisorption well. This indicates the possibility of direct transitions to continuum states via absorption of single photons with energies $\hbar\omega$, larger than the threshold energy E_{th} for desorption, resulting in direct infrared photodesorption as discussed by Pearlstine and McClelland [8]. The rate of single-photon absorption from background blackbody radiation at a temperature T is directly related to the well-known result for the reverse process, spontaneous photon emission [14] and is given by

$$W = \frac{8}{3\hbar c^3} \int_{E_{th}}^{\infty} n(\omega)\omega^3 C(\omega)\,d\omega, \quad (1)$$

where $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose-Einstein distribution function. $C(\omega)$ is the Fourier transform of the dipole-dipole correlation function, which at zero substrate temperature can be expressed as

$$C(\omega) = \sum_n |\langle 0|\mu_{ad}|n\rangle|^2 \delta(\omega - (E_n - E_0)/\hbar). \quad (2)$$

Here, $|0\rangle$ is the ground state of the molecule-surface system with energy E_0, $|n\rangle$ are excited states with energies E_n, and μ_{ad} is the perpendicular component of the adsorbate dipole moment.

The interaction of hydrogen molecules with low-index copper surfaces has a relatively simple nature. Molecular beam scattering experiments reveal [15] that the adsorbed molecule rotates freely, its lateral motion is free particle-like, and its motion perpendicular to the surface is governed by a one-dimensional potential $V_0(z)$, where z is the distance from the molecular center to the surface. Absorption of a photon with $\hbar\omega > E_{th}$ will, hence, result in a vertical transition between the ground state and a continuum state of $V_0(z)$ in which the lateral momentum is conserved. Readsorption of the molecule in such a continuum state is dominated by energy transfer to substrate phonons. We know from sticking measurements that the probability for such an event is less than 20% for a light particle such as H_2 [15]. W should, accordingly, be a good measure of the direct photodesorption rate for this system.

Our measurements of the dipole-excited bound level spectrum of terrace-adsorbed hydrogen molecules enables us to construct an accurate model for μ_{ad}. The matrix elements $|\langle 0|\mu_{ad}|n\rangle|$ were extracted from $C(\omega)$ which was calculated in the time domain via propagation of a wave packet in the physisorption potential. Previously, we noted that H_2 experiences nearly identical physisorption potentials on the (100)-like terraces of Cu(510) and on Cu(100), and we have used the well-characterized

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H_2-Cu(100) potential [15] in our calculations. We used a simple functional form for μ_{ad} as shown in Table I, and adjusted the parameters so that our calculations accurately reproduce the measured dipole matrix elements for the $0 \to 1$, $0 \to 2$, and $0 \to 3$ vibrational transitions. From $C(\omega)$ and Eq. (1), we then obtain, for terrace-adsorbed H_2, the desorption rates 4×10^{-4}, 8×10^{-4}, and 12×10^{-4} s^{-1} at the blackbody temperatures 210, 296, and 370 K, respectively. These rates are in excellent agreement with the corresponding measured values 5×10^{-4}, 8×10^{-4}, and 15×10^{-4} s^{-1}, and we conclude that our experimental observations are consistent with a direct infrared photodesorption mechanism. The calculated rate for D_2, 9×10^{-5} s^{-1} at 296 K, is about an order of magnitude smaller than for H_2 which explains the experimental difficulty to determine a precise D_2 desorption rate. The strong isotope dependence derives from the sensitivity with respect to particle mass of the dipole matrix elements for transitions with energies much larger than the fundamental vibrational energy.

We measure a much larger photodesorption rate for H_2 adsorbed at steps than at terraces, 7×10^{-3} s^{-1} versus 8×10^{-4} s^{-1} at 296 K background blackbody radiation. This difference is striking and only partly accounted for by the larger dipole activity of the step-adsorbed H_2. The effect is interesting and deserves further attention.

The infrared radiation can also excite phonons at the metal surface [16] and the adsorbed molecules may subsequently be desorbed via single-phonon annihilation [4,5]. The rate of absorption of photons with $\hbar\omega > E_{th}$ by substrate phonons at the Cu(510) surface can be directly calculated from their cross section for dipole excitation as measured by electron-energy-loss spectroscopy [16]. We find that this rate is 2×10^{-5} s^{-1} per surface unit cell at a blackbody temperature of 296 K. These high frequency phonons are, however, weakly coupled to the translational coordinate of the physisorbed molecule and the resulting phonon-induced desorption rate is several orders of magnitude smaller than the direct photodesorption rate [17].

In summary, we have shown that direct infrared photodesorption of an adsorbate can be an effective process for light and weakly bound species such as physisorbed H_2 as suggested from previous theoretical considerations. Our observation of intense dipole-excited transitions to bound levels close to the continuum and the excellent agreement we find between measured and calculated rates of photodesorption caused by blackbody radiation, for H_2 adsorbed on the terraces of a Cu(510) surface, provide compelling evidence for this mechanism. The observation of a much larger photodesorption rate for H_2 adsorbed at step sites than at terrace sites is interesting and deserves further attention. We believe that direct infrared photodesorption could be effective also for other light physisorbates, in particular, at intentionally introduced low-coordinated adsorption sites.

TABLE I. Dipole matrix elements, $\mu_n = |\langle 0|\mu_{ad}|n\rangle|$, for the $0 \to n$ vibrational transitions of H_2 physisorbed on the terraces of Cu(510). The measured values were evaluated from the vibrational intensities (see Ref. [10]). The calculated values are derived with the use of the dipole function, $\mu_{ad} = \mu_0 \exp[-\beta(z - z_0)]$, where $\beta = 1.5a_0^{-1}$, $\mu_0 = 0.0342$ D, and z_0 is the position of the potential energy minimum; in units of debye (D).

n	Measured	Calculated
1	0.021	0.021
2	0.015	0.014
3	0.0086	0.0091

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