Electron-Induced Desorption of Physisorbed H$_2$ via Resonance Vibrational Excitation

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We show by electron energy-loss measurements that desorption of physisorbed H$_2$ and D$_2$ induced by low-energy electrons takes place with large cross sections, predominantly via resonance excitation of the molecule-surface vibrational mode. The observed H$_2$, D$_2$ cross-section ratio supports a picture where rotation-translation conversion of the resonance excited $j = 0 \rightarrow 2$ rotational transition contributes to the desorption of H$_2$, while this channel is energetically closed for D$_2$.

Weakly adsorbed atoms and molecules are easily desorbed by thermal excitation but may also desorb via more state selective nonthermal processes involving incident radiation like photons and electrons. Infrared photons, for example, can desorb light physisorbed species via direct excitation of the adparticle from the lowest bound vibrational level of the adsorption well to unbound continuum states [1] as observed for physisorbed H$_2$ [2] and He [3]. Such dipole active transitions may also be induced by electrons, but electron stimulated desorption is in general discussed in terms of an initial electronic excitation either via a Frank-Condon transition to an antibonding state of the adsorbate-substrate system [4,5] or a core-hole excitation with an Auger transition [6].

A mechanism proposed by Antoniewicz [7], and of particular relevance at the relatively large adsorbate-substrate distances of physisorption systems, involves ionization of the adparticle by the incident electron and subsequent acceleration of the ion towards the surface by the attractive image interaction. The ionization cross section and its dependence on the incident electron energy puts an upper limit to the efficiency of this process and provides a simple test of the applicability of the model in specific cases [8].

In this Letter we present experimental evidence for desorption of physisorbed H$_2$ and D$_2$ induced by 1–3 eV electrons, too low in energy to permit ionization of the molecular valence level. Hence the Antoniewicz mechanism for desorption of physisorbed species is not operating since this model requires ionization as the initial step. However, these low-energy electrons form a short-lived negative ion state involving the H$_2$ σ_u shape resonance centered around 3 eV incident electron energy for physisorbed H$_2$ [9]. An additional attractive interaction of image potential character will then be turned on just as in the Antoniewicz model [7,10]. Gadzuk [11] has pointed out that this attractive force will cause enhanced excitation of the molecule-surface bonding mode. We find that this

mechanism gives a reasonable estimate of the measured electron energy-loss spectroscopy (EELS) short-range scattering cross sections for excitation of the H$_2$-Cu(100) vibrational mode. Extrapolation of the measured cross sections for vibrational transitions in the potential well to energies above the desorption threshold gives estimates of the cross sections for bound-free transitions that are in very good agreement with the measured cross sections for electron-induced desorption of H$_2$ and D$_2$ physisorbed on the Cu(100) surface. We also find that the cross-section ratio for H$_2$ and D$_2$ indicates that rotation-translation conversion of the resonance excited $j = 0 \rightarrow 2$ rotational transition contributes significantly to the desorption of H$_2$ while this channel is energetically closed for D$_2$. Desorption can also occur via dipole excited bound-free transitions, but we find that the cross section for this process is much smaller than for the resonance excitation mechanism.

The experiments reported here were performed in an ultrahigh-vacuum equipment, operating at a base pressure in the low 10^{-11} Torr range. Substrate surface properties and subsequent hydrogen adsorptions were monitored by low-energy electron diffraction, work function measurements, and high-resolution EELS. The specimen was cleaned *in situ* by standard methods involving argon-ion bombardment and heating cycles and could be cooled to temperatures below 10 K using helium as a cryogen and it was heated resistively. Prior to hydrogen adsorption the specimen was flash heated to 900 K and rapidly cooled to 10 K. The EELS and electron-induced desorption measurements were obtained for uncompressed physisorbed hydrogen monolayers of a density $n_s = 0.7 \times 10^{15}$ molecules/cm^2 [12]. The adsorbate density was routinely monitored by work function measurements using the low-energy electron diffraction electron gun in retarding field mode. This electron gun was also used in the electron-induced desorption measurements operating at low electron energies, 1–3 eV relative to the specimen vacuum

level, and beam currents in the range 10–100 nA. EELS spectra were obtained for 3 eV incident electrons at an energy resolution around 2 meV. Spectra have been recorded for specular as well as off-specular scattering conditions in order to obtain cross sections for both dipole and short-range resonance inelastic scattering processes.

Photoemission measurements from a monolayer of H_2 physisorbed on Cu(100) show that the occupied H_2 $1\sigma_g$ level is located about 9 eV below the Fermi level of the Cu (100) substrate [13]. Incident electrons with a kinetic energy in the range 1–3 eV above the vacuum level, i.e., around 5.5–7.5 eV above the Fermi level, can accordingly not ionize the physisorbed molecule. Ionization is the initial step in the Antoniewicz model for electron-induced desorption of physisorbed adparticles, and this model is in this respect not adequate in our case. However, another charged state and its concomitant image attraction may be of vital importance. The low-energy electrons trap temporarily in the σ_u shape resonance of the H_2 molecule, forming a short-lived ($\sim 10^{-15}$ s) H_2^- state of profound importance in e-H_2 scattering [9,14]. A physisorbed molecule will, during the life of the negative ion state, experience an additional image attraction, $-e^2/4z$, and accelerate towards the surface resulting, as discussed by Gadzuk [11], in excitations of molecule-surface modes whose displacements have a component in the z direction. Hence, we expect that transitions among the vibrational levels of the H_2-Cu(100) physisorption potential well may occur via this mechanism. From Eq. (8) in Ref. [11], it is straightforward to evaluate the no-loss probability per event, P_0, for a molecular mass $M = 2$, vibrational energy $\hbar\omega_1 = 8.9$ meV, and potential minimum 2.4 Å outside the surface representing H_2 on Cu(100). For a resonance lifetime of 10^{-15} s we obtain $P_0 = 0.95$, which means that a sizable fraction of the e-H_2 scattering events will result in excitation of the H_2-Cu(100) vibrational modes. The elastic e-H_2 gas phase scattering cross section is $\sim 14 \times 10^{-16}$ cm^2 for 3 eV incident electrons [14], which gives an estimated cross section of $\sim 0.7 \times 10^{-16}$ cm^2 for excitation of the H_2-Cu(100) modes.

The EELS measurements provide detailed information about the transition probabilities from the ground vibrational state to higher lying vibrational levels in the physisorption well involving the $\nu = 0 \to 1$, $0 \to 2$, and $0 \to 3$ transitions at 8.9, 15.3, and 20.0 meV as shown in the off-specular spectrum displayed in Fig. 1(a). The incident electron energy is 3 eV and the instrumental angular resolution is 1.4° full width at half maximum of the elastic angular distribution. The short-range off-specular differential scattering cross section, $d\sigma/d\Omega$, for the vibrational excitation can be obtained from the relation [15]

$$I_{0\to\nu}/I_{00} = \frac{n_s}{R\cos\alpha} \int_\Omega \frac{d\sigma}{d\Omega} d\Omega, \tag{1}$$

where $I_{0\to\nu}$ is the vibrational loss intensity, I_{00} is the specular elastic intensity, n_s is the number of adsorbed
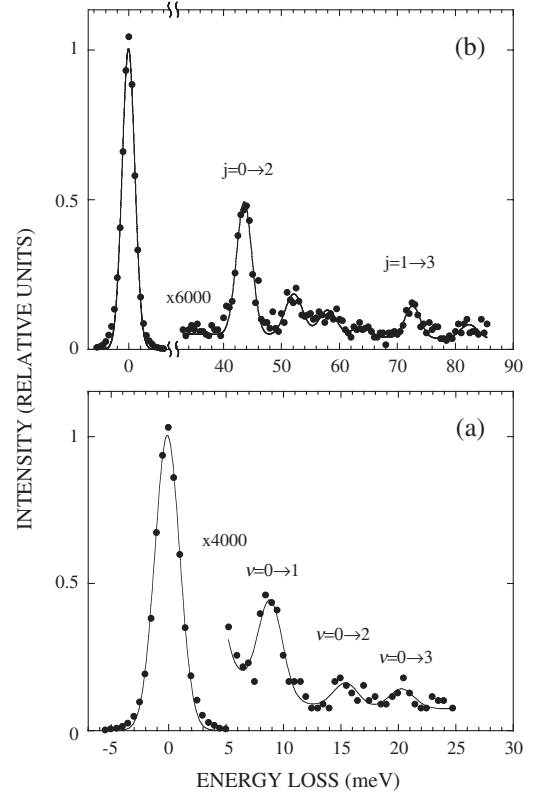

FIG. 1. EELS spectra of a H_2 monolayer adsorbed on Cu(100) at about 10 K. (a) the H_2-surface vibrational regime and (b) the H_2 rotational, rotational-vibrational regime at a background H_2 pressure of 4×10^{-8} Torr. EELS conditions: 3 eV incident beam energy, 48° angle of incidence, around 5° off-specular detection, elastic peak in specular detection.

molecules per unit area, R is the electron reflectivity, α is the angle of incidence relative to the surface normal, and Ω is the solid angle of detection. Values for the $\nu = 0 \to 1$, $0 \to 2$, and $0 \to 3$ transitions are listed in Table I together with the corresponding data for D_2. The $\nu = 0 \to 3$ transition is only a few meV below the threshold for bound-free transitions and $d\sigma/d\Omega$ remains substantial which indicates that electron-induced desorption via such transitions will occur. Assuming that the angular distribution is isotropic we obtain a cross section of 2.4×10^{-16} cm^2 for the $\nu = 0 \to 1$ H_2-Cu(100) transition which is somewhat

TABLE I. Measured short-range off-specular differential scattering cross sections, in 10^{-18} cm^2 sr^{-1}, for the $\nu = 0 \to 1$, $0 \to 2$, $0 \to 3$ molecule-surface vibrational transitions of H_2 and D_2 in the physisorption potential well on Cu(100) (transition energies, $\hbar\omega$, are given in meV).

	$\hbar\omega$		$d\sigma/d\Omega$	
$\nu \to \nu'$	H_2	D_2	H_2	D_2
$0 \to 1$	8.9	7.1	19	16
$0 \to 2$	15.3	12.7	4.6	3.4
$0 \to 3$	20.0	17.0	3.7	2.7

larger than the theoretical estimate derived above. However, we note that the sum of cross sections for bound-bound and bound-free transitions (see below) is $\sim 8 \times 10^{-16}$ cm^2, which is an order of magnitude larger than the theoretical estimate.

We have no *a priori* knowledge about how the transition probability decreases with increasing ν and in the continuum range. In order to obtain estimates of the cross sections for bound-free transitions, we have used numerical fits to the measured $\nu = 0 \to 1$, $0 \to 2$, and $0 \to 3$ cross sections versus transition energy, $\Delta \epsilon$, in meV. An inverse power law $d\sigma/d\Omega = 1.8 \times 10^{-15} \Delta \epsilon^{-2.1}$ cm^2 sr^{-1} fits the H$_2$ data satisfactorily and gives a differential cross section, $d\sigma/d\Omega = 3.7 \times 10^{-17}$ cm^2 sr^{-1}, for transitions from the ground state level at -25.5 meV [16] to the continuum states above the threshold energy $\epsilon_t = 25.5$ meV. The corresponding data for D$_2$ give for $\epsilon_t = 27.1$ meV, $d\sigma/d\Omega = 1.8 \times 10^{-17}$ cm^2 sr^{-1}. Assuming that the angular distributions are isotropic we obtain cross sections $\sigma = 4.7 \times 10^{-16}$ cm^2 and $\sigma = 2.3 \times 10^{-16}$ cm^2 for bound-free transitions of H$_2$ and D$_2$, respectively. Readsorption of the molecule in such a continuum state is given by energy transfer to the substrate phonons and the surrounding molecules. The probability for such an event is known from sticking measurements [12] and is around 0.5 for H$_2$ and D$_2$ on Cu(100). Correcting our cross sections for this effect gives $\sigma = 2.4 \times 10^{-16}$ cm^2 and $\sigma = 1.2 \times 10^{-16}$ cm^2 for electron-induced desorption of H$_2$ and D$_2$, respectively.

The spectral regime involving rotational and combined rotational molecule-surface vibrational modes is also of interest in this context; the cross sections are quite large and the $j = 0 \to 2$ rotational energy for H$_2$ is 44 meV which is large enough to permit desorption of H$_2$ via rotation-translation energy conversion which we believe is a more efficient process than rotational decay via two-phonon processes. However, for D$_2$ the $j = 0 \to 2$ rotational energy of 22 meV is less than $\epsilon_t = 27.1$ meV and this desorption channel is closed. Figure 1(b) shows this spectral regime for H$_2$. The $j = 0 \to 2$ rotational peak at 44 meV dominates the spectrum while the $j = 1 \to 3$ rotational peak at 73 meV is quite weak due to ortho-para conversion at surface defect sites [17].

The measured differential cross section for the $j = 0 \to 2$ rotational transition is 1.7×10^{-17} cm^2 sr^{-1} [18] at the resonance maximum around 3 eV impact energy, somewhat larger than the value 1.3×10^{-17} cm^2 sr^{-1} observed for e-H$_2$ scattering in the gas phase [19,20]. Assuming that the angular distribution is isotropic gives a cross section of 2.2×10^{-16} cm^2. If the probability for rotation-translation conversion is 1 and for readsorption 0.5 (as given above), then the $j = 0 \to 2$ rotational channel will contribute to the cross section for electron-induced desorption of H$_2$ by 1.1×10^{-16} cm^2 increasing the total cross section to $\sigma = 3.5 \times 10^{-16}$ cm^2 [21].

The specular EELS measurements show that vibrational excitations among the bound levels in the H$_2$-Cu(100) physisorption well are dipole active [22] which results in

direct infrared photodesorption of physisorbed H$_2$ [2]. Low-energy electrons can also cause desorption via dipole transitions to unbound continuum states. We have estimated the cross sections for this process using a dipole moment function obtained from the EELS intensity data [23] and obtain the dipole matrix elements $\mu_c = 0.0061$ and 0.0017 D for transitions to the continuum states of H$_2$ and D$_2$, respectively. It is straightforward to calculate the differential cross sections, $d\sigma/d\Omega$, from current dipole scattering theory. We assumed a reasonable transition energy of 30 meV, and integrated $d\sigma/d\Omega$ over a wide cone of half-angle 35° for 3 eV incident electrons which resulted in estimated cross sections for bound-free transitions of $\sigma_c \sim 3 \times 10^{-19}$ cm^2 for H$_2$ and $\sigma_c \sim 2 \times 10^{-20}$ cm^2 for D$_2$. The dipole excitation mechanism evidently results in much smaller cross sections than the resonance scattering process, and the isotope effect is large like in the direct infrared photodesorption case [2].

Electron-induced desorption rates were determined from the applied hydrogen pressure P required to maintain the full monolayer coverage for different electron beam current densities J. This condition was monitored via the electron reflectivity, which is sensitive to small changes of the coverage in the dense monolayer regime. Figure 2 shows P versus J data obtained for an electron beam energy around 3 eV and normal incidence. The data for both H$_2$ and D$_2$ fall on straight lines and desorption rates can be determined directly from the slopes. Influence from infrared photodesorption or thermal desorption will not affect the slope but only result in a rigid shift and offset of P from zero for $J = 0$. Since the measurements are performed at equilibrium, the hydrogen coverage and the sticking coefficient of the impinging molecules remain constant. The diffusion coefficient for dense hydrogen monolayers is small [24], $D \sim 1 \times 10^{-5}$ cm^{-2} at 10 K. The concentration gradient in our equilibrium measurements is also small and lateral diffusion of hydrogen over macroscopic distances is negligible. For 3 eV incident
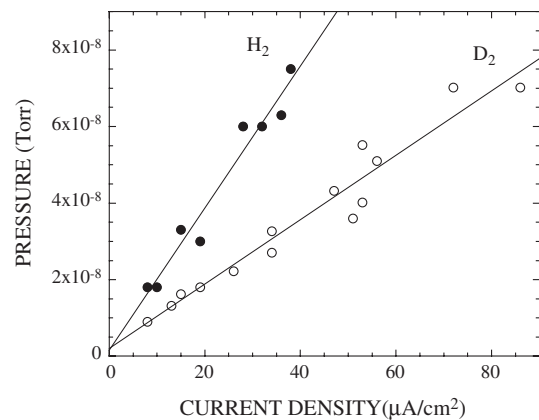

FIG. 2. Measured H$_2$ (●) and D$_2$ (○) pressures P required to maintain full monolayer coverage during electron irradiation of current density J. The electron beam hits the 10 K Cu(100) surface at normal incidence with 3 eV impact energy.

electrons, the adsorption system is reversible with respect to electron-induced desorption and adsorption from the gas phase, while at higher electron energies, around 10 eV, irreversible processes occur.

In order to obtain quantitative information about the cross section σ for electron-induced desorption, the lateral intensity distribution of the incident electron beam was determined by measuring the current to the sample while moving the sample edge across the beam. For the focus conditions used, we found that a central area of diameter $\phi \sim 0.40$ mm was quite homogeneous in intensity while an outer region of decreasing intensity corresponded to $\sim 20\%$ of the total beam intensity. The desorption rate will be largest for the central area of high current density and the measured equilibrium pressure will correspond to this rate. Assuming that the current density is homogeneous over the central beam area, adsorption and electron-induced desorption give at equilibrium

$$\frac{dn_s}{dt} = \nu S - n_s J \sigma = 0, \tag{2}$$

where ν is the impact rate of molecules from the gas phase, S is the sticking coefficient, and σ is the cross section for electron-induced desorption. Hence we have

$$\sigma = \frac{\nu S}{n_s J}. \tag{3}$$

From the slopes in Fig. 2, using the sticking coefficient, $S \sim 0.5$, for adsorption of H_2 and D_2 at the monolayer coverage, we obtain the cross sections, $\sigma = 3.1 \times 10^{-16}$ cm^2 (H_2) and $\sigma = 1.0 \times 10^{-16}$ cm^2 (D_2), for desorption induced by 3 eV incident electrons. These cross sections agree very well with the values $\sigma = 2.4 \times 10^{-16}$ cm^2 (H_2) $\sigma = 1.2 \times 10^{-16}$ cm^2 (D_2) estimated from the vibrational spectroscopy data. However, the isotope ratios differ significantly, 3.1 for the electron-induced desorption data and 2.0 for the vibrational spectroscopy data. Including the contribution from the H_2 $j = 0 \rightarrow 2$ rotational cross section increases the estimated H_2 desorption cross section to 3.5×10^{-16} cm^2, as discussed above, and gives an isotope ratio of 2.9 in much better agreement with the value 3.1 obtained from the desorption measurements.

In conclusion, we have found that desorption induced by low-energy electrons of physisorbed H_2 and D_2 occurs with large cross sections due to resonance excitation of vibrational transitions from the ground vibrational level in the physisorption potential well to unbound continuum states. The H_2 σ_u shape resonance, involved in this process, also yields large cross sections for excitation of the $j = 0 \rightarrow 2$ rotational transition which, as judged from the observed cross-section ratios, contributes significantly to the desorption of H_2, while this channel is closed for desorption of D_2. The desorption cross sections are large because of the additional image attraction turned on when the incident electron is temporarily trapped in the molecular shape resonance and because the shallow physisorption well contains only few bound states for light species like H_2. For heavier weakly adsorbed molecules, resonance excitation of internal vibrational modes and subsequent vibration-translation conversion may also result in electron-induced desorption. We believe that this class of resonance excited processes is of substantial interest to explore at the local molecular level encountered in STM experiments.

[1] K. A. Pearlstine and G. M. McClelland, Surf. Sci. **134**, 389 (1983).
[2] M. Hassel, K. Svensson, M. Persson, and S. Andersson, Phys. Rev. Lett. **80**, 2481 (1998).
[3] T. Niedermayer, H. Schlichting, D. Menzel, S. H. Payne, and H. J. Kreuzer, Phys. Rev. Lett. **89**, 126101 (2002).
[4] D. Menzel and R. Gomer, J. Chem. Phys. **41**, 3311 (1964).
[5] P. A. Redhead, Can. J. Phys. **42**, 886 (1964).
[6] P. J. Feibelman and M. L. Knotek, Phys. Rev. B **18**, 6531 (1978).
[7] P. R. Antoniewicz, Phys. Rev. B **21**, 3811 (1980).
[8] B. Xia and S. C. Fain, Jr., Phys. Rev. B **50**, 14 576 (1994).
[9] J. E. Demuth, D. Schmeisser, and Ph. Avouris, Phys. Rev. Lett. **47**, 1166 (1981).
[10] R. E. Walkup, Ph. Avouris, N. D. Lang, and R. Kawai, Phys. Rev. Lett. **63**, 1972 (1989).
[11] J. W. Gadzuk, Phys. Rev. B **31**, 6789 (1985).
[12] L. Wilzén, S. Andersson, and J. Harris, Surf. Sci. **205**, 387 (1988).
[13] W. Eberhardt, R. Cantor, F. Greuter, and E. W. Plummer, Solid State Commun. **42**, 799 (1982).
[14] N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980).
[15] J. W. Davenport, W. Ho, and J. R. Schrieffer, Phys. Rev. B **17**, 3115 (1978).
[16] S. Andersson, L. Wilzén, and M. Persson, Phys. Rev. B **38**, 2967 (1988).
[17] K. Svensson and S. Andersson, Phys. Rev. Lett. **98**, 096105 (2007).
[18] K. Svensson and S. Andersson, Surf. Sci. **392**, L40 (1997).
[19] F. Linder and H. Schmidt, Z. Naturforsch., A: Astrophys., Phys. Phys. Chem. **A26**, 1603 (1971).
[20] S. F. Wong and G. J. Schultz, Phys. Rev. Lett. **32**, 1089 (1974).
[21] Combined rotational-vibrational modes will add smaller contributions for both H_2 and D_2.
[22] K. Svensson and S. Andersson, Phys. Rev. Lett. **78**, 2016 (1997).
[23] M. Hassel, K. Svensson, J. Bellman, S. Andersson, and M. Persson, Phys. Rev. B **65**, 205402 (2002).
[24] M. Maruyama, M. Bienfait, F. C. Liu, Y. M. Liu, O. E. Vilches, and F. Rienford, Surf. Sci. **283**, 333 (1993).