Recombinative Desorption of Vibrationally Excited $D_2(v''=1)$ from Clean Pd(100)

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Recombinative desorption of D_2 from clean Pd(100) was studied with rotational-state selectivity by using resonantly enhanced two-photon ionization. The amount of vibrationally excited D_2 molecules increased exponentially with the surface temperature T_s, associated with an activation energy, in addition to that for desorption of $D_2(v''=0)$, of 210 ± 60 meV, considerably less than the vibrational energy of free D_2 molecules. This activation energy can be accounted for by a temporary trapping of D_2 in a molecular chemisorption state with a softened D—D bond, in qualitative agreement with a recently proposed model.

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The interaction of molecular hydrogen with metal surfaces is often regarded as a model for more complicated systems. Theoretical studies of the adsorption process on jellium[1-4] and cluster[5] substrates proposed a physisorption well followed by a molecular chemisorption state. In this precursor state the molecules are thought to be dynamically trapped and highly mobile along the surface. After surmounting an energy barrier the molecule finally adsorbs in a dissociative state. These barriers show various heights on different substrates which range from being larger than room-temperature thermal energy to not existent.

The adsorption of hydrogen in the physisorption well has been observed by Avouris, Schmeisser, and Demuth[6] and Andersson and Harris[7] at low temperatures on Ag and Cu substrates, respectively. On both metals the barriers for crossing to more tightly bound adsorption states are known to be high (e.g., Cu, $E_b \sim 0.2$ eV, Ref. 8) compared to transition-metal surfaces. The physisorption potentials show well depths between 32 and 55 meV for a variety of metal surfaces, as determined with HD molecular-beam scattering.[9] In this potential the hydrogen molecule was observed to behave as a free rotor with energy levels unchanged from the gas-phase values.[6,7] First evidence for molecular adsorption in a chemisorption state has been recently reported by Martensson, Nyberg, and Andersson.[10] They observed electron energy losses on the hydrogen-saturated stepped Ni(510) surface, which were attributed to internal vibrations of a molecularly adsorbed species, with high-resolution electron-energy-loss spectroscopy. Although these energies— 398 meV and 286 meV for H_2 and D_2, respectively— differed markedly from the vibrational energies of free hydrogen molecules (516 meV and 371 meV, respectively), the frequency shift upon isotopic substitution showed the expected behavior. This energy shift may be rationalized by a softening of the hydrogen bond in the chemisorption state. Such a bond softening has very recently been proposed by Müller[5] in a cluster calculation of potential energies for hydrogen approaching a Pt(111) surface. The lowest-energy state was found at a H_2—Pt distance of 3.0 bohrs with a much weakened H—H bond. An even softer potential was calculated at a distance of 3.5 bohrs. The shape of the H_2 interatomic potential changed drastically upon approach to the Pt surface. In this Letter we want to report first experimental results which may give evidence for a temporary adsorption of D_2 molecules in a chemisorption state during recombinative desorption from a clean Pd(100) surface, where dissociative chemisorption is known to be nonactivated.[11]

A detailed description of the experimental setup will be given elsewhere.[12] Briefly, the experiments are performed in an ultrahigh-vacuum system with a base pressure of less than 2×10^{-10} mbar. The chamber is equipped with low-energy electron diffraction and Auger electron spectroscopy. The experiments reported here are carried out with carefully cleaned surfaces. This has been verified and cleanliness has been established before and after each individual laser ionization spectrum. Internal state distributions for recombinative hydrogen desorption from Pd(100) partially covered with S atoms will be reported elsewhere (Ref. 12). The deuterium atoms are supplied to the clean Pd(100) surface by permeation through the bulk crystal. The probe is radiatively heated and experiments are performed at surface temperature T_s in the range $325 \leq T_s \leq 740$ K. At these temperatures the desorption flux is limited by permeation. From the kinetic parameters the deuterium atom density on the surface is estimated to be in the 10^{-3} monolayer range.

The desorption flux is crossed at a distance of 25 mm from the Pd surface by a tunable vacuum-ultraviolet (VUV) laser beam. The VUV radiation at wavelengths around 106 nm is generated by nonresonant frequency tripling of the output of a pulsed, tunable ultraviolet (UV) laser ($\lambda \sim 318$ nm, pulse energy 5 mJ, pulse duration 5 ns) in Xe gas. At the location of the desorption flux about 5×10^9 VUV photons per pulse are available. The VUV beam excites D_2 molecules in the $B\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ Lyman system with rovibrational-state selection. Absorption of a second photon from the fundamental UV laser beam leads to ionization of only the electronically excited molecules [(1+1) resonantly enhanced multiphoton ionization (REMPI)]. These resonantly produced photoions are detected by a microchannel plate detector. The output of the microchannel plate is measured by a counting electronic and transferred to a microprocessor. The signal is normalized to the VUV laser intensity, determined separately from the UV laser by an ionization cell placed behind the interaction region. Since the desorption flux is continuous, a background arises from molecules which after equilibrating at the vacuum chamber walls reappear in the interaction region. This background, determined separately at each surface temperature by pointing the desorption flux in a way that only background molecules can reach the interaction region, amounted to about 20% of the heights of $v''=0,J''$ lines and was not detectable for $v''=1,J''$ lines, as expected.

Figure 1 shows a typical ionization spectrum of D_2 at $T_s=677$ K for a wavelength scan from 106.2 to 106.7 nm. Rotational lines of the $v'=4 \leftarrow v''=0$ Lyman band are clearly resolved and identified. From the line heights rotational-state populations can be deduced after the relative ionization probabilities of the $B\,^1\Sigma_u^+(v',J')$ states have been determined.[12-14] Also lines of the $v'=7 \leftarrow v''=1$ Lyman band can be recognized in Fig. 1 which originate from vibrationally excited D_2 molecules. An absolute value for the amount of vibrational excitation was obtained in a separate experiment using VUV laser-induced fluorescence.[12] This detection scheme is about 1 to 2 orders of magnitude less sensitive than (1+1) REMPI, and therefore was used only for this calibration. After taking the Franck-Condon factors for absorption and fluorescence and the wavelength dependence of the photomultiplier (EMR 542-G) properly into account we arrived at a vibrational population of $N_{v''=1}=(1.5 \pm 0.3)\%$ for D_2 desorption at $T_s=677$ K from clean Pd(100). This is about 9 times as much as would be expected for molecules in thermal equilibrium with the surface temperature. Vibrationally excited H_2 molecules are not observed within the current sensitivity limit of the detection system.

The intensities of the lines originating from vibrationally excited molecules show a pronounced temperature dependence when compared to those of the $v''=0$ state. An exponential increase of the relative intensities, $I(v''=1)/I(v''=0)$, with surface temperature is observed. The important parameter is the ratio of flux intensities of vibrationally excited to ground-state molecules. In a preliminary experiment we therefore measured the velocity distribution in rovibrational quantum states. Within the experimental uncertainties these distributions are Maxwellian at T_s, and are independent of the specific rovibrational state; in particular $D_2(v''=1)$

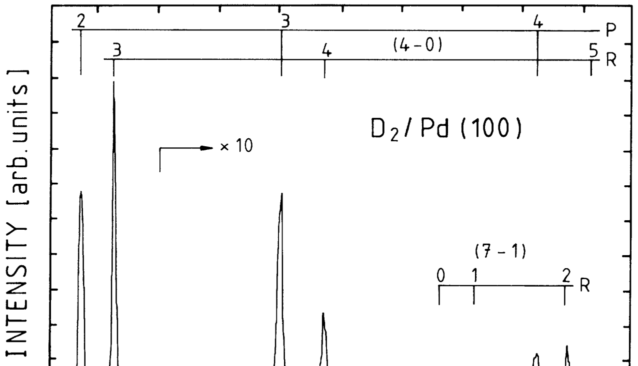

FIG. 1. (1+1) REMPI spectrum of D_2 desorbing from Pd(100) with the VUV laser tuned from 106.2 to 106.7 nm. The spectrum displayed is normalized to the VUV laser intensity. The signal was averaged over fifty laser pulses at each wavelength setting. $T_s=677$ K.

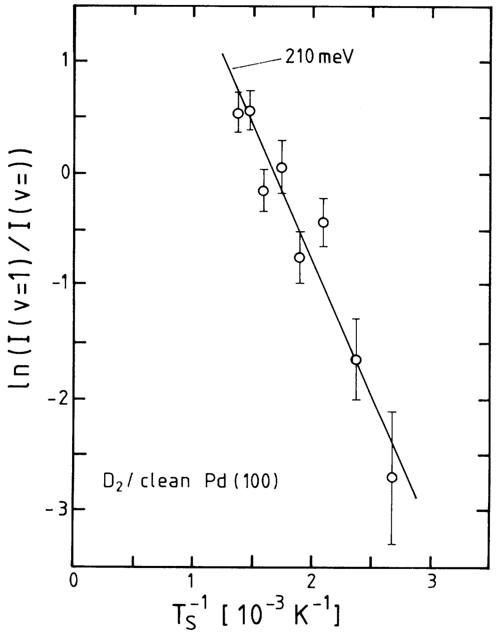

FIG. 2. Arrhenius plot of the relative vibrational line intensities, $I(v''=1)/I(v''=0)$.

molecules show the same velocity as ground-state molecules. With regard to the flux angular distribution, which has not yet been measured state specifically, one only has to assume independence of T_s of these distributions for molecules in $v''=1$ and $v''=0$.

Figure 2 shows the logarithm of the relative intensities $\ln[I(v''=1)/I(v''=0)]$, plotted versus the inverse surface temperature T_s^{-1}. Good agreement with an Arrhenius-type behavior can be seen. From the slope of the straight line, which represents a least-squares fit to the experimental data, we deduce an activation energy of $E_a = 210 \pm 60$ meV. Since the ratio of the populations in $v''=1$ and $v''=0$ is plotted, this activation energy has to be supplied in addition to that for desorption of the vibrational ground state, which is unknown. Thus more energy is necessary to desorb vibrationally excited molecules than ground-state deuterium molecules from a Pd(100) surface.

First, we discuss models proposed to explain earlier observations of vibrational excitation in desorbing molecules. Then, arguments will be presented which support a model which accounts for the temperature dependence and the low activation energy for $D_2(v''=1)$ desorption observed. The fraction of vibrationally excited molecules measured in this experiment is considerably lower than what has been found in hydrogen desorption from single-crystal copper surfaces.[14] At $T_s = 850$ K, Kubiak, Sitz, and Zare determined the vibrational population to be $(5.2 \pm 1.4)\%$ and $(24 \pm 20)\%$ for H_2 and D_2 desorption from Cu(110), respectively. Hydrogen desorption from a copper surface has to proceed via a barrier of about 170–220 meV.[8] Recently Harris, Rahman, and Yang performed classical trajectory calculations of the H_2 and D_2 recombination on copper using a realistic potential.[15] The recombination occurred on a ridge separating the dissociative adsorption potential from the associative desorption potential. This ridge had a minimum of about 1 eV at a hydrogen atom separation of 1.63 bohrs. Most recombination processes thus take place at a distance larger than the gas-phase equilibrium separation of 1.4 bohrs for D_2, causing the desorbing molecules to vibrate. Variation of the surface temperature, which represents an energy small compared to the minimum height of the ridge, should not have a great influence on the vibrational population of the desorbing molecules, in agreement with the experimental findings of Kubiak, Sitz, and Zare.[14] The vibrational excitation in this system is thus probably determined by the dynamics on the potential surfaces.

Another model proposed for vibrational excitation of desorbing molecules invokes the formation of a temporary negative-ion state.[16] Upon leaving, the electron jumps back to the surface in a fast process, leaving the molecule at an equilibrium bond length of the negative-ion state. Since this bond length is generally greater than that of the neutral molecule, a vibrationally excited state is formed. The net probability of the harpooning mechanism is found to be proportional to $\exp[-E_{\text{vib}}/kT_s]$. Thus, in an Arrhenius plot the activation energy should be equal to the vibrational excitation energy, in accordance with observations in NO scattering from a Ag(111) surface.[17] In positive molecular-ion beam scattering with low glancing angle of incidence, negative ions leaving the surface have been observed.[18] However, for H_2^+ scattering no such negative-ion formation, which could be related to a harpooning mechanism, was found: The H_2^- ion is lying energetically much higher than the H_2 molecule and thus this process is unfavorable.

The vibrational excitation observed in the present experiment cannot be explained by either model, since no barrier exists for D_2 desorption from clean Pd(100) and the additional activation energy for $D_2(v''=1)$ desorption observed here is much lower than the vibrational spacing. Very recently, a cluster calculation by Müller[5] suggested a considerable softening of the hydrogen bond as the molecule approaches a Pt(111) surface. At a molecule-surface distance of 3.0 to 3.5 bohrs a minimum of the total potential energy was found, forming a molecular chemisorption state, which for Pt has a calculated well depth of about 110 meV (Ref. 5) as compared to the depth of the physisorption potential of 55 meV (Ref. 9). In this adsorption state the D—D bond softens in a way that, compared to the gas-phase value, the zero-point energy is lowered by about 90 meV. As a result of the very anharmonic shape of this interatomic potential the energy of the $v''=1$ state is lowered even more from the gas-phase value than the $v''=0$ state. This behavior is shown schematically in Fig. 3. The right-hand side depicts the energy levels of the lowest two vibrational states, $v''=0$ and $v''=1$, of free D_2 molecules in the gas

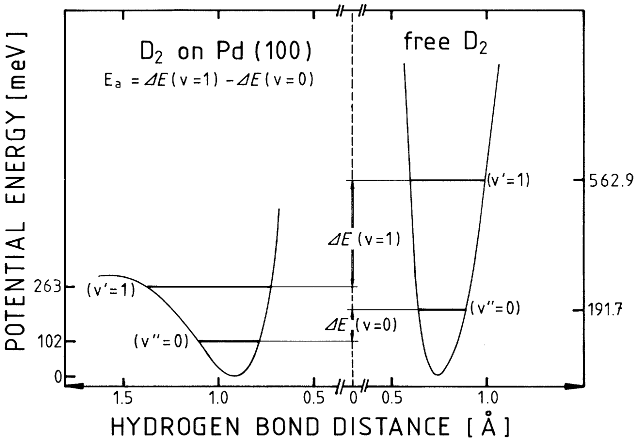

FIG. 3. Schematic diagram of the energy levels of free (right-hand side) and chemisorbed (left-hand side) deuterium molecules. The internal energy levels of chemisorbed H_2 would be at 140 meV ($v''=0$) and about 320 meV ($v''=1$).

phase and the left-hand side denotes those of the chemisorbed species. The actual level shift of the $v''=0$ state is not known experimentally, and we thus use the value calculated by Müller for H_2-Pt(111),[5] $\Delta E(v''=0)=90$ meV. The activation energy $E_a=210$ meV measured in this experiment represents the difference between the lowering of the zero-point energy and the lowering of the $v''=1$ state: $E_a=\Delta E(v''=1)-\Delta E(v''=0)$. In the molecular chemisorption state the vibrationally excited D_2 molecules are thus more strongly bound than the groundstate molecules.

According to the intramolecular hydrogen potential calculated for H_2-Pt at a distance of $z_{H_2\text{-Pt}}=3.5$ bohrs the energy levels of chemisorbed H_2 are at 140 meV for $v''=0$ and at about 320 meV for the vibrationally excited state.[5] The chemisorption state thus does not support a stable $v''=1$ state of H_2. These molecules ought to dissociate at this distance, in accordance with the lack of observation in this experiment.

In conclusion, we have presented data which might give evidence for a molecular chemisorption state of hydrogen on Pd(100). The proposed mechanism for vibrational excitation is purely thermal. Whether other processes contribute to this excitation and/or a deviation from Boltzmann's law takes place can only be decided when the intramolecular hydrogen potential is known for the adsorption on Pd(100). In conjunction with a theoretical calculation of the hydrogen approach on a Pd(100) surface, the experimental data presented will give a basis to characterize this adsorption state and the internal binding of the molecule with sufficient accuracy.

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