Two-Dimensional Quantum Rotation of Adsorbed H_2

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We report experimental and theoretical evidence of H_2 adsorbed in a confined quantum rotor state on a stepped copper surface. Rotational transitions of step-adsorbed para-H_2 and ortho-H_2 observed in electron-energy-loss measurements occur close to the energies expected for an ideal 2D rotor. Dramatic enrichment of adsorbed ortho-H_2 is observed at elevated surface temperatures and hydrogen background pressures. Calculations reveal a molecule residing above a step atom and confined to rotate in a two-dimensional manner.

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Recently, spirited attention has been directed to rotorlike states of single molecules adsorbed on metal surfaces, stimulated by ideas regarding molecular-based mechanical and memory devices. Experimental visualization using scanning tunneling microscopy has been reported, concerning, for example, supramolecular bearings formed by large organic molecules on a copper surface [1] and tunneling-current-controlled rotation of small molecules adsorbed on platinum [2] and copper surfaces [3]. Confined metal dimer rotation on a close-packed metal surface has been theoretically predicted [4]. The rotary motion, driven either by thermal energy or inelastic electron tunneling is in these cases restricted by energy barriers and is diffusive.

Free rotary motion confined to two dimensions (2D rotor) is also conceivable, at least for weakly adsorbed light molecules such as hydrogen. For example, the mechanism of preferential adsorption of metastable orthohydrogen species was long ago [5] suggested to be associated with a 2D rotor adsorption state [6]. Enrichment occurs readily on activated alumina. Silvera and Nielsen [7] observed, using inelastic neutron scattering, that the rotational spectrum of hydrogen adsorbed on alumina powder at low temperatures was greatly distorted from that of the free molecule. They found that their observations were more consistent with an axially constrained rotor state. In the extreme limit the confining potential will in this case lead to a loss of two rotational degrees of freedom and the molecule can only vibrate against the surface. Whereas hydrogen molecules physisorbed on flat crystal surfaces [8–10] experience only weak rotational hindering, for local adsorption at low-coordinated surface sites such as adatoms or step atoms, a much stronger hindering may be conceived.

In this Letter we present electron-energy-loss measurements and density functional calculations, which provide evidence of hydrogen adsorbed as a confined rotor on a stepped copper surface. Our measurements reveal, for step-adsorbed molecules, rotational transitions of parahydrogen (p-H_2) and orthohydrogen (o-H_2) at energies close to the values expected for an ideal 2D rotor. This adsorption state is readily identified in total energy calculations and corresponds to a molecule residing above a single atom at the step edge in an axially symmetric orientational potential barrier, which confines the molecule to rotate in a two-dimensional manner. Our measurements also reveal preferential adsorption of o-H_2 at elevated surface temperatures and hydrogen background pressures creating an inverted population with almost exclusively adsorbed o-H_2. At low temperatures and pressures ortho-para conversion proceeds at a sufficient rate to exclude any substantial concentration of adsorbed o-H_2.

The measurements reported here were performed in an ultrahigh-vacuum chamber operating in the low 10^{-11} Torr range. Substrate surface properties and subsequent hydrogen adsorption were monitored by low-energy electron diffraction, work-function measurements, and high resolution electron-energy-loss spectroscopy (EELS). Further details concerning the preparation of the stepped Cu(510) specimen and experimental procedure are presented elsewhere [11]. Our measurements focus on adsorption at the steps and such hydrogen coverages that terrace adsorption is negligible [12].

Hydrogen adsorption on Cu(510) proceeds in two stages; the steps are occupied first and further adsorption populates the terraces. Our spectroscopic measurements reveal that terrace adsorption closely resembles hydrogen physisorption on a flat Cu(100) surface [11]. The adsorbed molecule rotates as a weakly perturbed 3D rotor, a characteristic feature of H_2 physisorption on flat crystal surfaces [8–10]. Step-adsorbed molecules, on the other hand, exhibit new and exciting properties, nicely illustrated by a set of spectra displayed in Fig. 1. These data were taken for off-specular scattering at different specimen temperatures and such background pressures of hydrogen that the coverage of step-adsorbed molecules is kept constant while the terraces remain uncovered. The features observed in the three spectra can be described briefly as follows: (i) All observed modes are excited by short-range inelastic electron scattering. They can tentatively be assigned to rotational transitions involving H_2 adsorbed in two different rotor states resembling ideal 2D

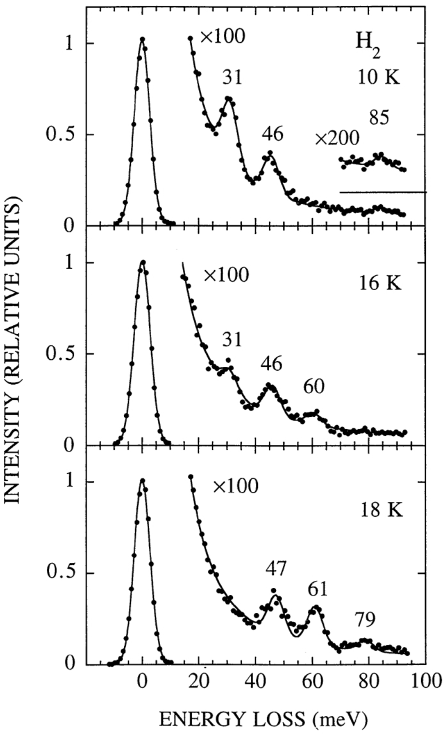

FIG. 1. Electron-energy-loss spectra from H_2 adsorbed at the Cu(510) steps at different substrate temperatures. The H_2 coverage is kept constant by means of an applied H_2 pressure in the range 4×10^{-9} to 1.5×10^{-6} Torr. The spectra are measured 6° off specular for an angle of incidence 48° and an energy 3 eV of the incident electron beam.

and 3D rotors. (ii) At low specimen temperature only p-H_2 is observed with $0 \rightarrow 2$ rotational transitions at 31 and 46 meV for the 2D and 3D rotor states. The corresponding energies [6] for the ideal rotors are $4B = 29.4$ meV and $6B = 44.1$ meV. (iii) At higher temperatures and background pressures also o-H_2 is detected. At 18 K o-H_2 has almost completely replaced p-H_2 in the 2D rotor state now characterized by a $1 \rightarrow 3$ rotational transition around 61 meV. A small concentration of o-H_2 also appears in the 3D rotor state with a $1 \rightarrow 3$ transition around 79 meV. The related energies for the ideal rotors are $8B = 58.8$ meV and $10B = 73.5$ meV.

The two kinds of adsorbed molecules must occupy different sites at the step. We suggest, in accordance with previous considerations concerning physisorption at stepped surfaces [13], that the 3D rotor state corresponds to adsorption at the lower edge of the step where the molecule experiences attraction to the terrace as well as to the step. Only a small population of o-H_2 is observed in this state even at the highest pressure. For normal hydrogen, we expect the $1 \rightarrow 3$ peak to be more intense than the $0 \rightarrow 2$ peak. The low concentration of o-H_2 in the 3D rotor state is most likely due to ortho-para conversion [14]. The other adsorption state at the step, which we simply call a 2D rotor state, is the focus of our attention. Density functional calculations discussed below reveal that this state corresponds to H_2 weakly bonded to a single atom at the step edge.

At low temperature and hydrogen background pressure only p-H_2 is observed in this adsorption state. This is presumably due to ortho-para conversion, but other factors related, for example, to the sticking dynamics [15] may also influence the relative population of adsorbed ortho and para species. At higher temperatures and pressures, orthoenrichment occurs at a sufficiently high rate to create an inverted population with almost exclusively adsorbed o-H_2. This transformation is due to the different energy levels of the ortho and para species. The gas-phase levels are 0 and $2B$ for the $j = 0$ and $j = 1$ rotational states, respectively. For an adsorbed ideal 2D rotor the corresponding energies are $-\epsilon_0$ and $-\epsilon_0 + B$ where $-\epsilon_0$ is the lowest lying bound level in the adsorption well. Para and ortho molecules will accordingly experience different desorption energies and the desorption rate for p-H_2 will for this reason be a factor $\exp(B/kT)$ larger than for o-H_2. At a substrate temperature $T = 18$ K the difference in rates is ~ 100 and o-H_2 may hence be efficiently enriched at temperatures in this range.

The two adsorption states at the step have a similar low binding energy ~ 40 meV, but are bonded to the surface by different mechanisms. Spectra obtained in the energy range of the internal H-H vibration reveal the difference. When the surface is completely covered with H_2 the 2D rotor state is depleted and the fundamental H-H vibration of the 3D rotor state is observed at 514 meV. When only the steps are covered, as shown in Fig. 2, this mode is observed at 510 meV. These energies are close to the corresponding gas phase value, 516 meV, an observation which taken together with the weakly hindered 3D rotational motion is characteristic for

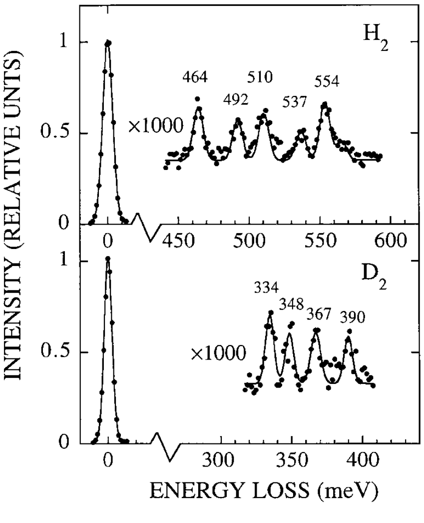

FIG. 2. Electron-energy-loss spectra from H_2 and D_2 adsorbed at the Cu(510) steps at 10 K. Applied $H_2(D_2)$ pressure is $4 \times 10^{-9} (2 \times 10^{-9})$ Torr, otherwise conditions as in Fig. 1.

physisorbed H_2. In contrast the 2D rotor state shows a dramatic lowering, to 464 meV, of the H-H vibration and a confined rotational motion. For D_2 the corresponding energies are 334 and 367 meV for the 2D and 3D rotor states, respectively. The gas-phase value is 371 meV. The other spectral features in Fig. 2 derive from vibration-rotation combinations like the 2D rotor satellites at 492 (H_2) and 348 meV (D_2). We will discuss these features in relation to the calculations presented below.

Assignment of some of the measured spectral features in terms of rotational transitions of H_2 adsorbed in a 2D rotor state is highly suggestive and is corroborated by theoretical calculations. Knowledge about adsorption geometry and nature of the adsorption state, properties inaccessible to the experiment, is provided by our total energy calculations based on density functional theory [16]. Possible H_2 adsorption states at the Cu(510) step were explored by a search for local energy minima. The deepest potential well was identified for a molecule coordinated to a single step atom in a configuration shown in Fig. 3. Confinement of the light hydrogen molecule in this narrow, 99 meV deep potential well results in an unusually large zero-point energy of 107 meV [18]. A compensating decrease of the internal H-H vibration zero-point energy gives a net adsorption energy around 24 meV. This adsorption state has some peculiar properties; the small binding energy is typical for physisorption while the short H_2-Cu equilibrium distance of ~1.8 Å, a dramatic decrease of the internal vibration energy, and an elongation of the H-H distance are characteristic for chemisorption. In this situation of a weak chemical bond, the inadequacy of our model [16] to describe the van der Waals interaction should not pose a problem, but inaccuracies in the long-range part of the molecule-surface interaction are to be expected.

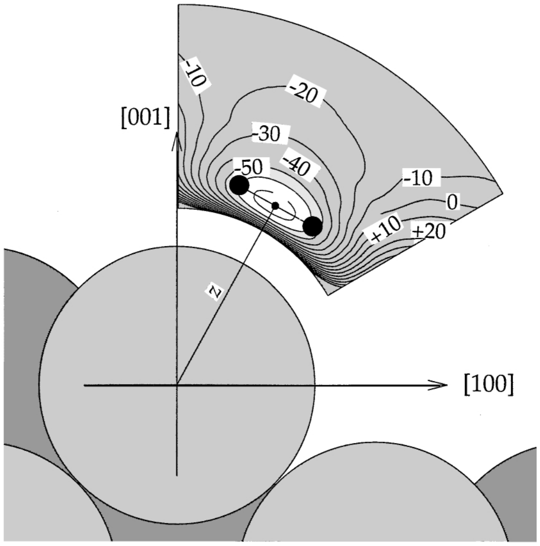

FIG. 3. Calculated adsorption geometry and confining potential of the 2D rotor state of H_2 adsorbed at the Cu(510) steps. The molecular axis is found to be perpendicular to the direction, $\hat{z}$, from the center of the step atom to the molecular center. The 2D section of the potential energy surface has been determined using the calculated gas-phase value for the H-H bond distance. Relaxing this distance to its equilibrium value for the adsorbed molecule shortens the H_2-Cu distance, z, from 1.89 to 1.81 Å and increases the well depth by 24 meV. The energy contours are in meV.

We have used the results of the total energy calculations to construct a reduced 3D potential energy surface (PES), $V(z, r, \theta)$, which depends on the center of mass coordinate z, the H-H distance r, and the polar angle θ between the molecular axis and the $\hat{z}$ direction [19]. The PES varies only weakly with the azimuthal angle for rotations around the $\hat{z}$ axis. This dependence can be neglected with a most important consequence; the z component of the angular momentum, $J_z = \hbar m_j$, is conserved. Coupling of the fast internal vibration to the slow external motions of the molecule is treated via an adiabatic PES, $U_\nu(z, \theta)$, associated with the internal vibrational eigenstate ν [20]. The $\nu = 0 \rightarrow 1$ transition energy of the adsorbed molecule is determined directly from the energy difference between the ground states of $U_\nu(z, \theta)$ for $\nu = 0$ and 1. For H_2 and D_2 these energies have decreased by 78 and 55 meV from the calculated gas-phase values. Similar large adsorption-induced shifts, 52 and 37 meV, are indeed observed in the experiment.

In the calculations, we have identified a set of 2D rotorlike states, whose origin has a simple explanation, which is evident from Fig. 4. Around the equilibrium position $z_{\mathrm{eq}} = 1.8$ Å (for $\nu = 0$), the potential causes a strong confinement in the $\theta = \pi/2$ orientation. The ground state for each m_j is sufficiently localized in this respect so that the m_j-dependent part of the Hamiltonian,

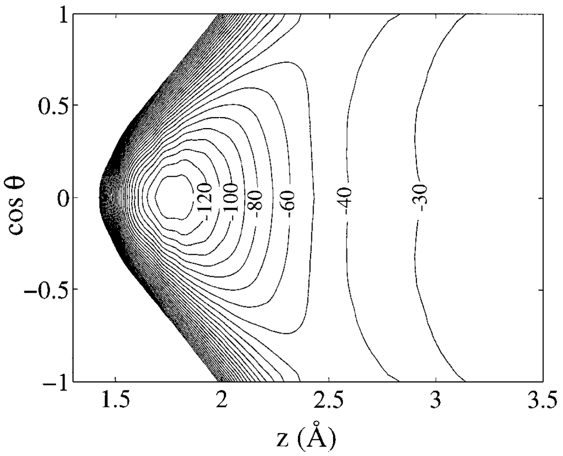

FIG. 4. Calculated vibrationally adiabatic potential energy surface, $U_\nu(z, \theta)$, of the 2D rotor state of H_2. The internal H-H vibration is in its ground state $\nu = 0$. θ is the polar angle for the molecular axis with respect to the H_2-Cu bond direction $\hat{z}$ and z is the corresponding distance. Note that this potential includes the change in zero-point energy of the adsorbed molecule. The energy contours are in meV.

$\hbar^2 m_j^2/[2\sin^2\theta I_\nu(z,\theta)]$, where $I_\nu(z,\theta)$ is the moment of inertia, results in an energy level sequence that is closely given by the 2D rotor result, $B_\nu m_j^2 = \hbar^2 m_j^2/[2I_\nu(z_{\mathrm{eq}}, \pi/2)]$. For H_2 in the vibrational ground state, $\nu = 0$, the $m_j = 0 \rightarrow 2$ and $1 \rightarrow 3$ transitions are found at 29 and 57 meV in good agreement with the measured energies 31 and 61 meV [21]. In the vibrationally excited $\nu = 1$ state the $m_j = 0 \rightarrow 2$ transitions for H_2 and D_2 are found at 24 and 13 meV, respectively. These energies also agree well with the measured relative loss energies 28 and 14 meV for the satellite peaks to the $\nu = 0 \rightarrow 1$ losses for H_2 and D_2.

In conclusion, we have from a combination of electron-energy-loss measurements and density functional calculations identified a 2D rotor state of hydrogen adsorbed at a single step atom on a stepped copper surface. The 2D character of the rotational motion and the associated energy spectrum provide a key ingredient for preferential adsorption of orthohydrogen on this surface. These metastable species form, along the steps, one-dimensional arrays of confined quantum rotors also in the ground state. Other unusual and unexpected features of this hydrogen adsorption state give new insight in the special physical and chemical conditions prevalent at low-coordinated adsorption sites. In particular, the short copper-hydrogen distance and the strongly perturbed molecular bond suggest the formation of a surface chemical bond but the binding energy is low and in the range for physical adsorption.

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[18] This result was obtained from the calculated vibrational energies for the molecular motion in the well using the harmonic approximation.

[19] We have kept only the z component of the center of mass motion since the z dependence of the PES is much more anharmonic than the x and y dependencies as shown by the calculated section in Fig. 3.

[20] $U_\nu(\theta, z)$ was obtained by solving numerically the radial part of the Schrödinger equation for the molecule in $V(r, \theta, z)$ for fixed θ and z. Eigenenergies and eigenstates of $U_\nu(\theta, z)$ were determined by a diagonalization of the Hamiltonian in a product basis of spherical harmonics and plane waves. Changes in the moment of inertia $I_\nu(\theta, z)$ due to the varying H-H equilibrium distance with θ and z are accounted for in the Hamiltonian.

[21] A feature at 85 meV in the measured H_2 spectrum (see top panel in Fig. 1) may be identified with a transition to an excited state of m_j. Such states were found at 65 and 74 meV in the calculations.