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Observation of Rotational Transitions for H_2, D_2, and HD Adsorbed on Cu(100)

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Energy losses observed when low-energy electrons were scattered from a Cu(100) surface exposed at $T \sim 15$ K to H_2 (and D_2, HD) lie close to rotational and rotational-vibrational transitions (H_2, D_2) of the free molecules. Both o- and p-H_2 and -D_2 physisorb on the surface, with negligible conversion on the time scale of the experiment. The relative populations were different from those characteristic of the adsorbing gas, suggesting a j-dependent sticking coefficient.

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In recent years, electron energy-loss spectroscopy (ELS) has emerged as a powerful probe of the vibrational excitations of adsorbed molecules, thus providing a most important source of new information about them. From measured vibrational frequencies it is relatively straightforward to draw conclusions about, e.g., molecular or dissociative adsorption and possible adsorption geometries. In this Letter we demonstrate that rotational and combined rotational-vibrational transitions of H_2 and D_2 adsorbed weakly on the well-characterized Cu(100) surface can be resolved,[1] and give information about the adsorption state previously inaccessible to any technique.

The system chosen is particularly suited to a study of rotational excitations. There is strong evidence that the ground state of H_2 on Cu(100) corresponds to atomic chemisorption and that the dissociation is activated.[2] The activation barrier might separate physisorption and chemisorption regions. Alternatively, it may cause H_2 to be trapped in a molecular "precursor" of the type recently proposed for the Mg(0001) surface.[3] The two types of adsorption give rise to similar vibration frequencies but completely different rotational spectra. For weak physisorption, one expects transitions of a perturbed three-dimensional rotator, while the molecular precursor would show the spectrum of a strongly hindered, or even confined rotator. Examples of each type have been seen in neutron scattering, for H_2 on Grafoil[4] and on activated alumina,[5] respectively.

In the neutron scattering experiments no attempt was made to adsorb rotationally excited molecules (o-H_2, p-D_2), or to measure relative populations and conversion rates. These quantities are of importance because the mechanism of ortho-para conversion at surfaces is still not understood in detail. They can be estimated directly from the ELS intensities once the relative cross sections for the $j = 0 \rightarrow 2$ and $j = 1 \rightarrow 3$ transitions are known.

The measurements reported in this Letter were obtained with use of a high-resolution spectrometer (optimum resolution 3 meV) that has been described elsewhere.[6] Analyzer and specimen can be rotated so that angles of incidence and detection can be varied independently. The specimen is mounted on a precision manipulator and is cooled by He gas that flows through a pair of copper tubes attached to the specimen support via two short copper braids. Following standard procedures the Cu(100) surface was cleaned, initially by argon-ion bombardment and annealing, and between successive gas exposures by heating first to 950 K, cooling, then reheating to 300 K before the final cooling to the required sample temperature estimated to be about 12 K. The crystal was then dosed with 0.5–10 L [1 langmuir (L) $=1\times10^{-6}$ Torr sec] of H_2 (and D_2, HD) and spectral data were taken under an ambient pressure of 8×10^{-11} Torr. The measurement time was 5–15 min and only minute traces of background contaminants (CO, H_2O) were observed in the spectra.

Figures 1 and 2 summarize a set of ELS spectra taken for specular scattering at an incident angle of 50°. The spectra of clean Cu(100) at T ~25 and ~ 12 K (Fig. 1) show that a strong 28-meV loss grows at low temperature. This we attribute to an intrinsic excitation of the Cu(100) surface, presumably related to the copper phonon spectrum.[7] Also shown in Fig. 1 are spectra for 1-L and 5-L H_2 exposures at a substrate temperature of 12 K. In addition to the substrate peak two new loss peaks at 45 and 72 meV are found to grow and saturate. These energies are very close to the rotational transitions $j=0\rightarrow2$ (44 meV) and $j=1\rightarrow3$ (73.5 meV) of gaseous H_2.[8] Spectra observed for adsorbed D_2 and HD show analogous peaks at 22 and 37 meV for D_2 and at 33 meV for HD (Fig. 1). These coincide with the observed gas-phase transitions $j=0\rightarrow2$ (22 meV), $j=1\rightarrow3$ (37 meV) for D_2, and $j=0\rightarrow2$ (33 meV) for HD.[8] Final confirmation that these loss peaks originate from rotational transitions of the adsorbed molecules is the observation of combined rotational-vibrational excitations of adsorbed H_2 and D_2 (Fig. 2). These data were taken with use of 3-eV incident-energy electrons at resolutions of 8 and 6 meV, respectively. There are three high-energy-loss peaks, at 518, 560, and 587 meV for H_2 and 372, 393, and 407 meV for D_2. The gas-phase $\nu=0\rightarrow1$, $j=0\rightarrow2$, and $j=1\rightarrow3$ excitations lie at 516, 557, and 585 for H_2 and 371, 392, and 407 meV for D_2.[8] While the elastic line

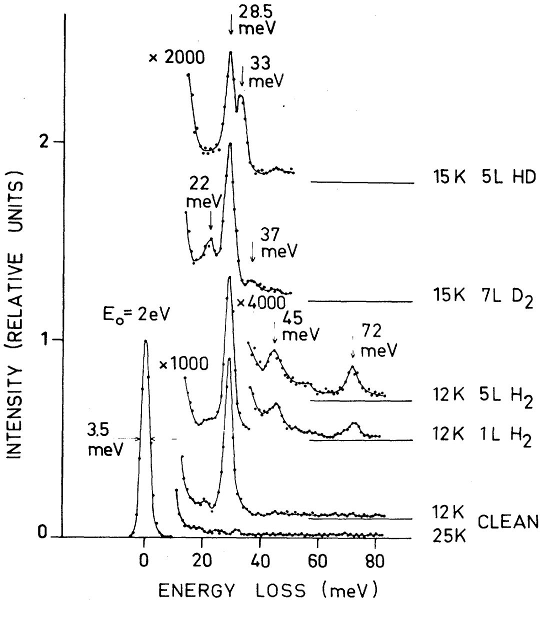

FIG. 1. Electron energy-loss spectra from H_2, D_2, and HD adsorbed on Cu(100) at low temperatures (1 L $=1\times10^{-6}$ Torr sec). The spectra are measured in the specular direction for an angle of incidence 50° and an energy 2 eV of the incident electron beam.

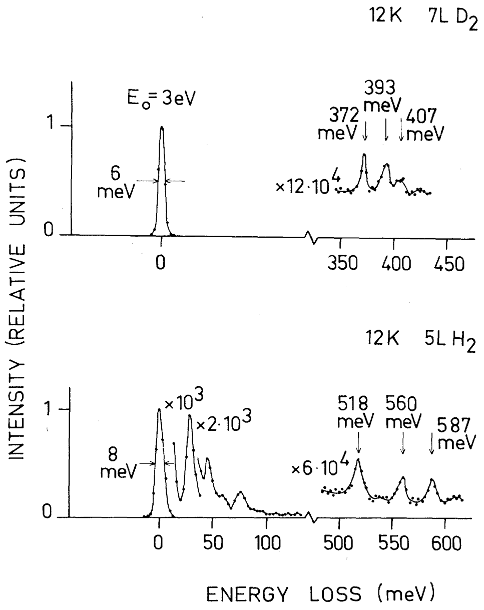

FIG. 2. Electron energy-loss spectra from H_2 and D_2 adsorbed on Cu(100). Electron energy 3 eV; conditions as in Fig. 1.

and the intrinsic Cu(100) 28-meV peak fell rapidly in intensity away from specular, the rotational peaks persisted, as one expects for a short-range scattering mechanism.

Under the assumption of differential cross sections similar to those measured for scattering from gas-phase molecules,[9] the observed loss intensities imply a saturation H_2 density $\sim 10^{15}$ molecules/cm^2. This number corresponds to a reasonably dense monolayer[4] and rules out the possibility that we are observing molecules adsorbed at steps or defects. The fact that the rotational spectrum maintains the same form, growing smoothly from small exposures to saturation, taken together with the value for the density, is evidence that the excited molecules are adsorbed and not condensed in a thick layer on the surface.

Because the energy of the surface-molecule system depends on the molecular bond distance, r, and on the orientation of the axis with respect to the surface $\hat{r} = (\theta, \varphi)$, it is at first sight surprising that the rotational-vibration excitations of adsorbed molecules coincide with those of free molecules. Since for metastable "precursors" the energy barrier against free rotation is ~ 0.5 eV,[10] the H_2 must be physisorbed, which means that an energy barrier separates regions of chemisorption and physisorption.[3,10] It remains to explain why the internal excitations of physisorbed H_2 are so little affected by the surface potential, e.g., why the $(2j+1)$-fold degeneracy of the rotational multiplets is not lifted. This we do with the aid of a simple model calculation.

Physically, the activation barrier arises because at large distances the H_2 $1\sigma_g$ shell behaves like an inert core to which the band wave functions, $|k\rangle$, must orthogonalize.[11] Crudely, the repulsion resulting from this orthogonalization, V_R, is proportional to the overlap sum $\sum_{\vec{k}} |\langle k| \times |1\sigma_g\rangle|^2$. Asymptotically this gives

$$V_R(Z, r, \theta) \sim C \exp(-2k_\varphi Z) \times \left(1 + \frac{r^2 k_\varphi^2}{12}\left[1 + 2P_2(\cos\theta)\right]\right), \quad (1)$$

where Z is the normal distance of the molecular center of mass from the surface, $k_\varphi \equiv (2m\varphi/\hbar^2)^{1/2}$ is the decay constant of a Fermi-surface Bloch function (φ is the work function and m is the electron mass), and P_2 is a Legendre polynomial. Equation (1) gives $\sim 17\%$ anisotropy between parallel and perpendicular orientations. If we choose $C \sim 0.5$ a.u., then (1) matches smoothly at $Z = 3$ a.u. to the jellium potentials.[10] The attractive interaction has the usual van der Waals form, $V_{\text{vW}}(Z, r, \theta) = -C_{\text{vW}}(r, \theta)/(Z - Z_{\text{vW}})$.[3] The constants C_{vW} and Z_{vW} are taken from calculations for He on Cu,[12] and C_{vW} scaled with the static polarizability. This gives, e.g., $\langle C_{\text{vW}}(r_0, \theta)\rangle_\Omega \sim 0.2$ a.u., where r_0 is the H_2 equilibrium separation and $\langle \cdots \rangle_\Omega$ denotes an angular average. The r dependence of C_{vW} arises from that of the H_2 polarizability, and the θ dependence[13] leads to an anisotropy in V_{vW} of $\sim 7\%$. The averaged potential $V_0(Z) = \langle V_R(Z, r_0, \theta) + V_{\text{vW}}(Z, r_0, \theta)\rangle_\Omega$ gives a physisorption well with ground-state energy $\epsilon_0 = -14$ meV, and wave function $\Psi_0(Z)$ that is nonvanishing for $Z \sim 7$–10 a.u. above the top layer of ions.

The excitation energies can now be determined via perturbation theory. In zeroth order, the center-of-mass and the relative motions are completely decoupled and the rotational-vibrational energies have their free molecular values. These are perturbed by $\Delta V(Z, r, \theta) = V_R + V_{\text{vW}} - V_0$, which leads to shifts of the pure rotation energies of $\Delta\epsilon_j^m = \langle \Psi_0 U_0 \chi_j^m | \Delta V | \chi_j^m U_0 \Psi_0 \rangle$, where U_0 refers to the vibrational ground state of H_2 and χ_j^m is a spherical harmonic. These shifts and the perturbations of the rotational-vibrational energies are easily calculated and are ~ 0.1 meV. The smallness of the shifts is in part due to a cancellation between V_{vW} and V_R. Whereas V_{vW} favors an expanded molecule oriented perpendicular to the surface, V_R shows the opposite tendency. The shifts depend sensitively on the surface potential which we have estimated only crudely. For this reason, different potentials might give splittings substantially larger (~ 1 meV) than estimated above which might be the reason why the rotational loss peaks are somewhat broader (~ 1 meV) than the elastic line or the 28-meV substrate loss peak.

The observations and interpretation detailed above show that both ortho and para H_2 and D_2 physisorb on Cu(100) at low temperature. No change in the relative intensity $R = I_{1\to 3}/I_{0\to 2}$ was detected on the time scale of the experiment, indicating a rate of conversion smaller than $\sim 1\%$/min. However, the measured value of $R_{H_2} \sim 1.0$ (Figs. 1 and 2), does not agree with a simple estimate involving gas-phase populations and cross-section ratios. Under the assumption that the cross sections, σ, are related as in the gas phase,[9] $\sigma_{1\text{-}3}/\sigma_{0\text{-}2} \sim 0.7$, this value of R_{H_2} implies a population ratio, P, for physisorbed orthohydrogen and parahydrogen of $P_{H_2} \sim 1.4$. A j-independent sticking coefficient, however, gives $P_{H_2}=3$, reflecting the ortho-para ratio in the adsorbing gas ($T=298$ K).[14] Since the electronic structures of physisorbed and gas-phase molecules are similar, this discrepancy seems too great to be attributed to differences in the cross sections, and is more likely due to a j-dependent sticking coefficient. Such a dependence can arise in several ways. One interesting possibility is that trapping occurs mainly via conversion of center-of-mass into rotational kinetic energy. The trapping probability, t_j, then depends on the number of incident molecules with translational energy $\epsilon \geqslant \Delta\epsilon_{j\rightarrow j+2}$, i.e., roughly, $t_j \sim n_j \exp(-\Delta\epsilon_{j\rightarrow j+2}/kT)$, where n_j are the rotational populations in the gas. This gives $P_{H_2}\sim 1.7$ and $P_{D_2}\sim 0.4$, in reasonable agreement with the observed values $P_{H_2}\sim 1.4$ and $P_{D_2}\sim 0.3$.

In conclusion, we have reported observation by ELS of rotational transitions of H_2, D_2, and HD adsorbed on a Cu(100) surface at low temperature. The transition energies lie very close to the gas-phase values. This is compatible with physisorption of the molecules. These observations establish that an activation barrier separates physisorption and chemisorption regions on Cu(100), that the ortho-para conversion rate for physisorbed H_2 is less than 1%/min, and suggest that the sticking coefficient is j dependent.

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