Vibrational Spectra of Atomic H and D on Cu(110): Evidence for H Quantum Delocalization

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The vibrational spectra of H on Cu(110) measured with high-resolution energy-loss spectroscopy at very low coverage strongly support the predicted "protonic" band structure. Localization is observed for increasing coverage. A simple model qualitatively describes the coverage dependence of the spectra.

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On several metallic surfaces the flatness of the hydrogen-substrate potential allows efficient tunneling of single chemisorbed hydrogen atoms between adjacent adsorption sites [1-6]. Diffusion due to tunneling has been observed on W(110) [1], while evidence for a delocalized H wave function has been obtained by ion scattering on W(211) [2]. If the corrugation of the periodic H-substrate potential is small, the vibrational properties of the overlayer are substantially modified and, in the low coverage limit, the H motion on the surface is conveniently described in terms of "protonic" two-dimensional energy bands (fully delocalized H atoms) instead of small vibrations around the equilibrium position [3,4]. Such energy bands have been computed in the single-atom limit for H on Ni(100), Ni(111), and Ni(110) [3]. The results show that the bandwidth of the ground state is a few meV, but that of the excited states can be of the order of several tens of meV, and that this effect should be stronger on the (110) surface, where in addition H propagation is closely one dimensional, being restricted to a single $[1\bar{1}0]$ trough. For increasing coverage the strong short-range H-H interaction is expected to introduce substantial correlation effects limiting the mobility and therefore to modify the single-atom band structure, resulting, at saturation coverage, in complete localization and negligible bandwidth [3].

In this Letter we show that the vibrational spectra of H on unreconstructed Cu(110) show a strong coverage dependence, which is well accounted for by the picture described above, providing spectroscopic evidence for the gradual transition from quantum delocalized to localized adsorbed atoms as the coverage is increased. Both delocalization and its visibility in the H vibrational spectra are maximized in this system by its one-dimensional nature. In the two-dimensional case of H on Rh(111) Mate and Somorjai [5] found that the H vibrational bands are wide even at full coverage, that the energy of the lowest excited band does not decrease by a factor $\sqrt{2}$ in the deuterium spectra, and that the linewidth of the observed bands depends strongly on the energy of the exciting electrons, contrary to the theoretical predictions. Studies of coverage-dependent H vibrational spectra for H/Ni(100) [7] did not provide evidence for delocalization, consistently with the small bandwidth computed for the H levels on this surface [3].

We have found instead that for H on Cu(110) the width of the dipole active A_1^2 H band [3] decreases from ~30 to ~8 meV when the coverage θ is increased from 0.01 monolayer (ML) to 0.3 ML. The θ dependence of the shape and the width of this band can be well described by a simple model accounting for the interaction between the highly mobile vibrationally excited H atom and the remaining, slowly moving, H atoms thermally populating the ground-state band. H and D vibrational spectra were taken by high-resolution electron-energy-loss spectroscopy (HREELS) using a ELS 22 spectrometer. We limited the energy resolution to 7-8 meV yielding a good signal-to-noise ratio for coverage as low as 0.01 ML. Our spectra, measured in the specular geometry (scattering plane along $[1\bar{1}0]$) with a primary energy of 2.5 eV, correspond to dipole-allowed transitions. Dissociative hydrogen adsorption was obtained by vibrationally exciting hydrogen molecules with a carefully outgassed W filament heated at 1550 K and placed 5 cm away from the sample surface [8]. During dosing the sample temperature T was 110 K. The only contaminants we could detect by HREELS were CO and H_2O. The maximum CO coverage was less than 0.03 ML at the highest H exposure and decreased linearly with the H dose. Impurity contamination was checked by exposing the sample to H with the filament off and to the filament without H at pressures and for time periods comparable to those used for the H dosing. In both cases the H_2O peak (84-97 meV) had an intensity less than 1×10^{-5} of the elastic peak. This peak reached an intensity of 3×10^{-5} after ~90 min. This intensity is about $\frac{1}{3}$ of that of the 90-meV peak in our H $\theta=0.01$ ML spectrum (see Fig. 1) and corresponds to $\theta_{H_2O}\cong3\times10^{-4}$. Therefore we restricted our acquisition time to within 90 min. The H_2O peak contribution cannot affect our results in an appreciable way for $\theta_H\geq0.01$ because of its weakness. The H and D coverages were measured by thermal

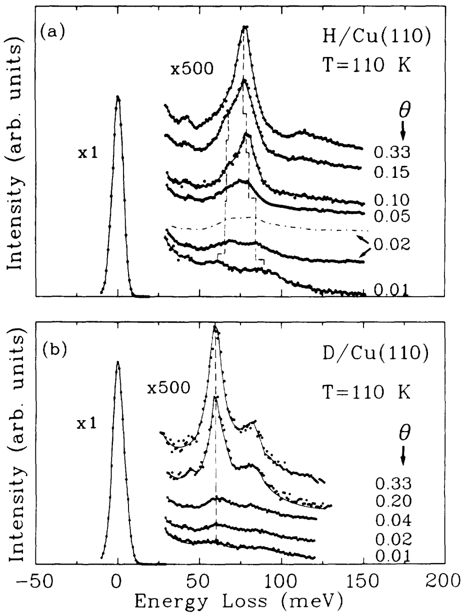

FIG. 1. HREELS spectra of (a) H and (b) D on Cu(110). The spectra are normalized to the elastic peak intensity. The H dash-dotted line spectrum is taken 10° off specular. The scaling factor for each spectrum is 500 except for the H $\theta=0.01$ one (scaling factor 1000) and the $\theta=0.02$ (scaling factor 50) off-specular one.

desorption spectroscopy (TDS). The saturation coverage of H on Cu(110) is estimated to be 0.5 ML [9] at 190 K. The coverage θ is defined here as the number of H atoms for each Cu first-layer atom [10]. A sharp (1×3) LEED pattern is best observed at ~0.3 ML and is visible for $0.15<\theta<0.35$ ML at $T<140$ K. We assume this pattern to correspond to chains of H atoms which are spaced by the Cu-Cu lattice parameter along the $[1\bar{1}0]$ troughs separated by two Cu rows in the [001] direction [11] ($\theta=0.33$). No extra spots or streaks are seen for $\theta<0.15$ ML, as also observed by Hayden, Lackey, and Schott [11]. This suggests that H forms, for $\theta<0.15$ ML, a disperse lattice-gas-like phase rather than, for example, dense chains separated by more and more Cu rows as θ decreases (staging). At higher coverages the (1×3) extra spots evolve into a broad and streaked (1×2) pattern. Since the TDS and HREELS spectra show that at $\theta\geq0.35$ ML more than one adsorption site is occupied [12], in the following we will discuss only the data obtained for $\theta<0.35$ ML at 110 K. For $T>140$ K a (1×2) reconstruction takes place, drastically modifying the vibrational spectra [12].

Figures 1(a) and 1(b) show, respectively, the HREELS spectra of H and D as a function of coverage. At 0.33 ML [(1×3) LEED pattern] the main features of the spectrum are very similar to those observed on Ni(110)(2×1) [13], and we therefore attribute the peaks at 79 and 118 meV to vibrations of H in the pseudothreefold site, polarized within the $(1\bar{1}0)$ mirror plane, essentially parallel and perpendicular to the surface, respectively [13]. The third H vibration along $[1\bar{1}0]$ is silent in the specular geometry [13] even if, as in our case, the scattering plane contains the $[1\bar{1}0]$ direction. The small peak at 41 meV is due to CO contamination. With decreasing coverage, the 79-meV peak broadens, while a shoulder develops on the low-energy side, and finally it splits into two components of comparable intensity, whose separation reaches 28 meV at 0.01 ML, independent of the primary electron energy. The 118-meV peak also broadens and cannot be resolved for coverages lower than 0.15 ML.

In contrast to this, the D vibrational spectra [Fig. 1(b)] are much less θ dependent, showing only a change in the relative intensity of the two main structures and a slight broadening. The energies of the two peaks, 58 and 80 meV, are a factor of 1.4 (within 10%) lower than those of the H peaks, as expected. The D data rule out the interpretation of the evolution of the low-coverage H spectra in terms of adsorption in more than one site or in a site close to a defect or an impurity. If this were the case, the 58-meV D peak should also split into two components at low θ, one at 47 meV and the other at 63 meV, which should be easily resolved. Moreover adsorption on a surface intentionally enriched with defects by ion bombardment yields narrow H energy-loss peaks at 50 and 71 meV (32 and 58 meV for D). Substantial contribution of contaminants to our spectra is ruled out by the clear difference of the H and D spectra for $\theta\geq0.02$ ML. No evidence for contaminants is found comparing the H spectra taken in off-specular conditions (see, as an example, the dash-dotted line in Fig. 1) to the specular ones.

The H spectra have been fitted with Gaussian or Lorentzian line shapes convoluted with a Gaussian representing our experimental resolution. Up to $\theta=0.25$ the results of the fitting are univocal since the two components of the 79-meV peak are clearly observed in the spectra. The energies of these components, as determined by the fitting, are plotted in Fig. 2(a) as a function of coverage [14]. Their energy splitting is strongly θ dependent for $\theta<0.1$, while it remains essentially constant above this value. The 0.33-ML spectrum is well fitted by a single Doniach-Šunjić (DS) line shape similarly to the H loss peak on Ni(110) [13]. For $\theta\geq0.25$, fittings of comparable quality are obtained using two Lorentzian peaks or a single strongly asymmetric DS. The results of the former fitting procedure are reported in Fig. 2(a). The 58-meV peak in the D spectra can be fitted with a single component. Its full width at half maximum (FWHM) is shown in Fig. 2(b).

Therefore the starting point for a discussion of the $\theta=0.01$ spectrum is the energy-band calculation by Puska and co-workers [3] which shows that on Ni(110) the motion of a single H atom may be described in terms of one-dimensional bands. Preliminary calculations show

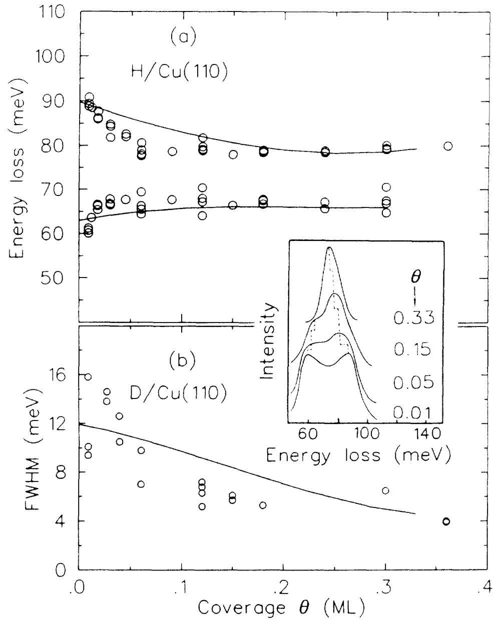

FIG. 2. (a) Comparison of the energy position of the two components of the H 79-meV peak as determined from the experimental data (circles) and from the calculations (solid line) at 110 K. Inset: The calculated density of states of the A_1^2 band for different coverages (see text). (b) Comparison of the experimental (circles) and calculated (solid line) FWHM of the D 58-meV peak.

that the H band structure on Cu(110) is quite similar [12]. The intensities of both H losses are strongly peaked in the specular direction and do not show resonances as a function of the primary electron energy. Therefore they correspond to dipole-allowed excitations and have to be associated to transitions from the ground-state A_1^0 band to other A_1 bands. The first of these bands is predicted to lie ∼20 meV above the A_1^0 band. Preliminary calculations show that the wave functions of the A_1^1 band have a nodal plane essentially normal to the surface (similar to that of the A_1^1 state of Fig. 9 in Ref. [3]) therefore the dipole moment for transitions to this band has only a small component normal to the surface [12]. It is not observable in our spectra because it is probably masked by the 20-meV resonance of the clean Cu(110) surface [15]. The A_1^2 band extends from ∼45 to 90 meV above the A_1^0 band. Its wave functions have a larger "perpendicular" character, similar to that of the A_1^2 band on Ni (100) and (110) [3]. This implies a larger A_1^0-A_1^2 vertical dipole matrix element. Since the A_1^0 band is only a few meV wide and the system is quasi one dimensional, the joint density of states of the $A_1^0 \rightarrow A_1^2$ transitions should have two singularities at energies close to the extrema of the A_1^2 band. This prediction is consistent with the energetic position of the observed peaks (60 and 90 meV). The third band A_1^3, which extends from 75 to 140 meV, can be associated with the 118-meV peak. Our data show that its matrix element is a factor of 10 lower than that of the 79-meV band and this may be the reason why it is no longer visible when it broadens at low coverages.

In order to explain the apparent narrowing of the A_1^2 band signified by the gradual collapse of the two H peaks for increasing coverage we use a model which takes into account the possibility for an excited H atom to hop to the neighbor sites in the same trough and the repulsion for other ground-state H atoms thermally occupying that site. Reference [3] shows that the overlap of wave functions belonging to different troughs is always negligible, that the bandwidth of the excited A_1^2 state is an order of magnitude larger than that of the ground state, and that the wave functions of the excited states are much more spread out in the unit cell than the ground-state one. Therefore we assume that (a) the interaction between H atoms belonging to different troughs and the hopping probability between adjacent troughs are negligible; (b) quantum hopping for an H atom in the ground state is negligible relative to that of the excited states; (c) the repulsion of two H atoms in the ground state is such that only one H can occupy a certain site, but (d) because of the larger extension of its wave function, an H atom in the excited state can share a site with another atom in the ground state, spending a finite repulsion energy U; and (e) there is also a weak nearest-neighbor repulsion, as indicated by a slight upward shift of the main peak of Fig. 1(a), with respect to the average energies of the low-coverage peaks for increasing coverage. The one-dimensional model Hamiltonian for the excited H atom is thus

$$H = E\sum_i n_i^1 + t_1\sum_{ij} c_j^{\dagger 1} c_i^1 + U\sum_i n_i^1 n_i^0 + V\sum_{ij} n_i^1 n_j^0 , \qquad (1)$$

where the indexes 1, 0, i, and j refer to the excited state, the ground state, the sites in the linear chain, and the nearest neighbors of site i, respectively, t_1 is the hopping energy for the H atom in the excited state, E is the on-site excitation energy, $c_i^\dagger$ (c_i) is the creation (destruction) operator for the site i, and $n_j^1 = c_j^{\dagger 1} c_j^1$.

The eigenvalues of this model Hamiltonian were numerically evaluated for a finite chain ($N=20$) assuming that the atoms in the ground state are randomly distributed along the trough, i.e., that quantum correlation effects are negligible at the temperature (110 K) at which the spectra were measured. As a further approximation, justified by the smallness of V, we replaced the last term in (1) with $2Vn_i^1$ when both neighbors of i are occupied, and zero otherwise. The resulting densities of states of the A_1^2 band, averaged over the spatial atom distribution and convoluted with a Gaussian, mimicking our experimental resolution and the intrinsic linewidth ($\Gamma = 12$ meV), are shown in the inset of Fig. 2. The parameters used in the calculation were $t_1 = 9$ meV, $U > 70$ meV, $E = 75$ meV, and $2V = 5.5$ meV [16]. Since the bandwidth of the excited band is much larger than that (<4

meV) of the ground-state band [3], which is also narrower than k_BT, the computed densities of states closely correspond to the imaginary part of the dielectric function $\varepsilon_2(\omega)$ calculated with a constant dipole matrix element. The energy-loss spectra are quite similar to $\varepsilon_2(E)$ if, as in our case, the substrate dielectric function is large and the H dynamic dipole moment is small [12].

The calculated spectra generally consist, before broadening, of three peaks. The first and third peaks correspond to excited atoms which remain mobile, since they have one or both neighboring sites empty. These peaks dominate at low θ, where their energy is $E \pm 2t_1$, and shift gradually to $E \pm t_1$ at large θ where their intensity vanishes. The second peak, at $E+2V$, is that of a totally localized excited atom. It becomes dominant at large θ. After broadening, the calculated H spectra show only two main peaks whose energy positions and relative intensities closely follow the corresponding experimental values (see inset of Fig. 2). The peak energies of the two main components are compared in Fig. 2 with those of our data, showing a fairly good agreement except for very small θ. The same model fits the D spectra with $t_1=2.5$ meV and $V=0$ meV. The computed FWHM is shown in Fig. 2(b). We tried to improve this model by taking into account the coexistence of (1×3) islands and a "gas" phase as suggested by the (1×3) LEED pattern for $\theta > 0.15$ ML and considering, for $\theta > 0.15$ ML, a linear combination of the (1×3) saturation spectrum and of the 0.15-ML gas-phase spectrum, with the weight of the former increasing with coverage. The resulting spectra are not appreciably different; in particular, the "fast" peak shrinking at small θ is not explained. We speculate that this additional effect might be due to the tendency of low-density H atoms to clump together. This effect has not been included in our simple picture, and ought to be considered in a more detailed theory. We expect that in the low-coverage limit, at $T=0$ K, only the low-energy peak in the HREELS spectra survives because it corresponds to a transition from the bottom of the A_1^0 band. Preliminary data show that at lower temperatures the intensity of the low-energy component of the H 79-meV peak increases with respect to the higher-energy one.

In conclusion, our study provides important direct spectroscopic evidence for delocalization of low-density H atoms, on a metallic surface, and strongly supports the protonic band structure calculated by Puska and coworkers [3].

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[16] The value of t_1 is determined by the experimental bandwidth at $\theta \rightarrow 0$ ($4t_1=36$ meV before convolution). The lower limit for U develops from the following: (a) For U less than 70 meV a peak at energy $E+U$ should be visible in the HREEL spectra with an intensity larger than 1% of the 79-meV H peak, and (b) the calculated spectra do not depend on U for $U > 70$ meV.