Atomic Nature of the β States of Hydrogen on W(001)

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High-resolution electron-energy-loss spectroscopy is applied to detection of surface vibrations induced by adsorption of hydrogen on clean W(001). The two β states are resolved and a bending mode of the β_2 state is detected. Results of experiments with D_2 and HD compared with those of the calculated vibrational modes of their possible molecular configurations on W(001) constitute a decisive and conclusive proof of the atomic nature of these adsorbed species on W(001) for the whole range of coverage.

The interaction of hydrogen with the W(001)surface has been the subject of numerous studies, and well-documented articles have been published.¹⁻³ Until recently the experimental results have been discussed in terms of two models: In the first,⁴ adsorption consists of the sequential filling of an atomic β_2 state and a molecular β_1 state on the fourfold-symmetry sites; in the second model,⁵ atomic adsorption occurs on bridge sites and the two apparent binding states revealed by flash desorption may arise because of adsorbate-adsorbate interactions.⁶ Although none of these models completely accounts for all experimental results,¹⁻³ recent work seems to favor the purely atomic adsorption model.³ Vibration spectroscopy may be used to clarify adsorption-related problems⁷ and, at the time the present investigation was started, two works on localized vibrations of hydrogen on W(001) were published.^{8,9} However, some points remained unresolved: In the electron-energy-loss spectroscopy experiment⁸ only one state has been detected, perhaps because of too high target temperature during adsorption and of insufficient resolution; the inelastic field-emission experiment⁹ failed to detect any vibration for saturation at 300 K. The need for the re-examination of the vibrational spectrum of hydrogen on W(001) was therefore evident and motivated the present investigation. During the course of our work, the results of high-resolution (10 meV) electron-energy-loss spectroscopy on this system were published¹⁰; coverage dependence of the population of the β_2 and β_1 states was demonstrated, and different surface sites associated with the two phases identified; the atomic nature of the β_2 and especially the β_1 phase was assumed from the complete isotopic mixing between \boldsymbol{H}_2 and $\boldsymbol{D}_2.^{11}$ However, one of the authors who reported the isotopic-mixing experiment¹¹ stated³ later that "the question of atomic versus

molecular adsorption in the two hydrogen binding states revealed by flash desorption measurements has persisted." In order to remove this long-standing uncertainty about the nature of the β states, high-resolution and -sensitivity experiments have been performed, and we present in this Letter results which are thought to be direct demonstration of atomic adsorption in the two states.

The electron spectrometer used is a tandem of two 127°-deflection cylindrical monochromators.¹² Only minor modifications of the original version¹² allow achievement of high resolving power. The spectrometer is set to give a 7.5-meV overall resolution as measured by the full width at halfmaximum of the elastic specularly reflected beam. The incidence angle is 45° with respect to the target normal, and impact energies of 5 eV are used. The crystal is oriented so that the incidence plane contains the [001] crystal direction (azimuthal angle = 0°). Standard cleaning procedures are used with a base pressure of 2×10^{-11} Torr in the ultrahigh-vacuum system. Auger measurements of residual contamination are not possible in the present system but previous results on low-energy electron diffraction¹³ show good surface quality. After flashing, the crystal is allowed to cool until its temperature is lower than 350 K; it takes only approximately 1.5 min. Partial-pressure analysis indicates a total contamination by active gases no higher than $\sim 0.2\%$ of the hydrogen pressure used during the exposures. Coverages are calculated from the published data³ and from the exposures corrected for gauge sensitivity. Spectra are recorded in a few minutes; and if the statistical noise is too high, the experiment is repeated, and the spectra numerically added.

Figure 1 shows the sequence obtained for different hydrogen coverages. For $\theta < 0.5$, only one



FIG. 1. Energy-loss spectra of hydrogen on W(001) for various surface coverages.

peak at 159 ± 1 meV is seen, with a width of 10.5 meV, indicating a natural width of $\simeq 7.5$ meV. For $\theta = 2$, one peak is detected at 132 ± 1 meV, a natural width of $\simeq 14.7$ meV being estimated from the observed 16.5-meV width. Peak positions are in good agreement with the recently measured levels.¹⁰ There is no peak near 70 meV for $\theta = 2$, attributed previously to CO contamination,¹⁰ in agreement with the high purity observed during our H₂ exposures. Intermediate-coverage spectra show the conversion between β_2 and β_1 , which has been observed to be completely reversible, as reported in Ref. 10. A feature not previously detected is the growth of a low-intensity peak near 79 meV, for $\theta < 1.2$, followed by a decrease of its intensity for $\theta > 1.3$. This peak is reversible too; i.e., it may be obtained either by adsorption or by desorption from the saturated surface. This fact precludes it from being a contamination peak; instead, it is attributed to a bending mode of H in the β_2 state, and its decreasing intensity follows the population decrease of this state as the coverage increases. A bending-force constant for atomic hydrogen $k_s/l^2 \simeq 2.4 \times 10^4$ dyn/cm is calculated from this vibrational frequency, which is the right order of magnitude to be ex-



FIG. 2. Energy-loss spectra of HD on W(001) in the β_2 ($\theta = 0.39$) and β_1 ($\theta = 2$) phases.

pected for a bending-force constant. Coupling of a lateral mode with the surface can make this mode not exclusively lateral,⁷ so that it may be detected by energy-loss spectroscopy. The different electronic structures of the two β states may account for a too low bending cross section in the β_1 state to be detected in the present experiment.

Although a unique observed vibrational frequency is good evidence for atomic adsorption,¹⁴ it must be noted that the low dynamical moment associated with the molecular mode of an undissociated adsorbed homonuclear diatomic molecule may lead to a very small cross section¹⁴; so the absence of loss peak near 0.51 eV, verified in our case in agreement with previous results,¹⁰ is not an absolutely convincing evidence of the atomic nature of hydrogen adsorption. This question may be answered with the help of the spectra obtained with D₂ and HD.

 D_2 adsorption gives the same sequence of spectra as H_2 with single peaks for the β_2 and β_1 phases located, respectively, at 114 and 94.5 meV, in close agreement with the 2^{-1/2} shift which is, however, expected for either atomic or molecular adsorbed species. The results obtained with HD are displayed in Fig. 2. The important feature is that each phase shows now two peaks each being located at the same energy as the single peak associated with hydrogen and deuterium in the same phase. This strongly supports the atomic-adsorption point of view, except in the case



FIG. 3. Schematic configurations for molecular adsorption of hydrogen; circles are W atoms, and dots H or D atoms.

where accidental frequency equality occurs between the two modes detected with HD and the single modes observed for H_2 and D_2 . This eventuality has been studied by frequency calculations for the possible molecular adsorption configurations of Fig. 3. These models may be unrealistic for other physical reasons, but it will be shown that they can be excluded by vibrational analysis alone. Assuming infinite mass for the W atoms-a very good approximation for the system studied—all these models have two modes in the symmetrical configuration (H₂ or D₂ adsorption) which carry a nonzero dipole moment $(A_1 \text{ modes})$, which may be detected by electron-energy-loss spectroscopy.¹⁴ One of these modes is, however, mainly H-H or D-D stretching and, as noted before, may have a lower cross section. These models are therefore compatible with the detection of only one peak for H₂ or D₂ within the limits of sensitivity of our apparatus. For HD adsorption, models a, c, and e always possess one A_1 high-crosssection mode, but two peaks should be detected, corresponding to the bonding of the HD molecule either through the H or the D atom; symmetry is broken in models b and d, which implies that now more than one mode may be detected. Therefore, the models are compatible with the occurence of two peaks in the HD spectra.

The valence-force model, including "surfacebending-force constants," is applied to the five configurations. Simple analytical expressions are derived for all symmetrical models and computer solution of the secular equation is performed for models b and d in the unsymmetrical HD case. Vibrational frequencies are calculated for a range of reasonable values of the parameters: The stretching-force constant of adsorbed H₂ (or D₂ or HD) is varied between 2 and 6×10^5 dyn/cm, the nuclear H-H distances between 0.74 and 1.0 Å, the H-W distances between 1.5 and 2.5 Å, and the bending-force constants between $\frac{1}{20}$ and $\frac{1}{4}$ of the corresponding stretching constant. The results of such a calculation are shown in Fig. 4 for configuration d, where one sees that, for the chosen set of parameters, one of the HD modes lying in the energy range of interest has the same frequency as the D_2 mode in the β_1 phase. However, if the molecular model was valid, this set should give another frequency near 106 meV, in contrast to the observed 132-meV value. Simultaneous equality between the two HD modes and the H₂ and D₂ modes has never been found for a particular set of parameters—and this has been found true for all five configurations shown in Fig. 3, in the β_1 and β_2 phases. The ob-



FIG. 4. Vibrational frequency as a function of the H-W (or D-W) stretching-force constant for configuration d. Curves labeled "H-H sym" and "D-D sym" refer to the high-cross-section A_1 modes. Curves labeled "H-D" are two modes of the adsorbed HD molecule which are in the energy range of interest. The dots refer to our experimental values.

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served fact that the spectrum obtained with HD is simply the superposition of the spectra measured with H_2 and D_2 is, therefore, not the result of an accidental degeneracy. The very important conclusion to be drawn is that the molecular models are not valid and that the β_1 and β_2 phases of hydrogen on W(001) are of atomic nature.

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Anomalous Thermoelastic Behavior and Molecular Reorientations in Crystals

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We have derived a microscopic Hamiltonian that takes into account rotational-translational coupling in molecular crystals. This coupling leads to an effective orientational interaction among nonspherical molecules. It is responsible for an anomalous behavior of the elastic constants and of the transverse-acoustic phonons. The temperature behavior of c_{44} and c_{11} in KCN above the 168-K phase transition is explained.

In molecular liquids it is well established that there exists a dynamical coupling between translational and orientational modes.^{1,2} More recently, the importance of a static coupling between translation and rotation has been realized for molecular crystals and used to explain Rayleigh-Brillouin measurements.³ This coupling should also be responsible for the drastic thermoelastic anomalies (softening of elastic constants⁴) that have been found near some orientational phase transitions in molecular crystals. This effect was discovered by ultrasonic methods⁴ and confirmed by Brillouin scattering.⁵ It manifests itself also very clearly in recent neutron scattering experiments⁶ where one finds a softening of transverse-acoustic phonons. To our knowledge, there exists no microscopic theory that describes in a satisfactory way the static coupling between

translation and reorientation in solids. Also, the experiments⁴⁻⁶ have found so far no theoretical explanation. The purpose of this Letter is twofold: First, we want to derive from a realistic microscopic-force model a Hamiltonian that contains such a static coupling. Second, we will apply this Hamiltonian to explain the experiments⁴⁻⁶ and to clarify the situation near the orientational phase transition.

To be specific, our theory will be most closely related to M(XY) compounds, say KCN, but its generalization to other substances will be obvious. In the high-temperature phase $(T > T_c)$ = 168 K), KCN has a cubic structure where the linear (CN) ions are surrounded by an octahedral cage of the K^+ ions. The (CN)⁻ ions assume octahedral symmetry by reorienting among equivalent orientations.⁷ At T_c , there is a phase