required to achieve stabilization. The basic result from the present work is that with rotation, a heavy-fluid–light-fluid interface can accelerate stably in the direction of the heavy fluid.

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Surface Sites of H on W(100)

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The surface vibrations of H adsorbed on W(100) at 300 K have been studied by electron-energy-loss spectroscopy. Two vibration modes corresponding to atomic hydrogen in two different sites have been found with the relative occupation depending on the total coverage. The single mode observed at high coverages is attributed to the occupation of bridge sites (β_1 hydrogen) while the mode observed at low coverages is associated with on-top sites (β_2 hydrogen).

Hydrogen on W(100) is one of the most extensively studied adsorption systems in surface science. Nevertheless the interpretation of the results is still very much disputed. On the question of whether hydrogen at room temperature adsorbs in one or two binding states no complete agreement has been obtained. Part of the results point towards atomic adsorption in a single site: the linear increase of the work function with coverage,[1] the linear decrease in the sticking coefficient,[2] and the complete isotopic mixing in desorption.[3] Photoemission spectroscopy shows that the electronic structures of hydrogen at low and high coverages are different; however, this does not provide a clear answer to the question of whether actually different sites are occupied.[4-6] The saturation coverage is two H atoms per surface atom, i.e., $\theta = 2$ ($= 2\times10^{15}$ atoms/cm^2), with a (1×1) low-energy electron diffraction (LEED) pattern.[1] For full coverage the occupation of bridge sites has been suggested.[1] However other structures would be consistent with the observations as well. Flash-desorption traces show two peaks β_1 and β_2, which reveal first- and second-order kinetics, respectively, and binding energies of 2.81 and 2.94 eV/atom. The population ratio in the two peaks is 2:1.[7] Originally the β_1 state observed at higher coverages was assumed to be molecular.[7] The isotopic mixing, however, requires atomic adsorption. The assumption of atomic adsorption on two different sites again is not consistent with a saturation coverage of $\theta = 2$, the (1×1) LEED pattern, and the 2:1 ratio of β_1 and β_2. The attempts to explain the two flash-desorption peaks by lateral interactions between equally adsorbed atoms[8,9] also failed to describe the ratio 2:1.

In this paper high-resolution electron-energy-loss spectra of the H-W surface vibrations are reported. Contrary to an earlier study[10] (with less resolution) two different surface vibrations corresponding to atomic hydrogen are observed. An analysis of the vibration losses at various coverages reveals that actually two different sites are occupied with the occupation numbers of the two sites depending on the total coverage.

The experiments were carried out in an (ultrahigh vacuum) electron spectrometer of the electrostatic deflector type, with improved background suppression which has been described recently.[11] The W(100) sample was cleaned by flashing in oxygen and in ultrahigh vacuum of 4×10^{-11} Torr following standard procedures. These procedures were checked with the particular sample subject to investigation using Auger analysis in a separate chamber. It was found that carbon and oxygen contaminations were less that 2% of a monolayer. The same upper limit to C and O contamination could be set *in situ* by comparing the loss spectrum of the nominally clean surface with spectra obtained after exposure to O_2 and CO.[12] The loss spectra were recorded at a primary energy of 5 eV, an angle of incidence of 75°, and a resolution of 10 meV.

A series of spectra obtained for different coverages is shown in Fig. 1. The coverages have been determined by integrating flash-desorption traces. The saturation coverage of 2×10^{15} atoms/cm^2 at $\theta=2$ was used for calibration.[2] At low coverages, $\theta<0.5$, a single surface vibration at 155 meV is observed. At coverages $\theta\geqslant0.5$ a second loss at 130 meV appears, and the 155-meV loss begins to disappear beyond $\theta>0.7$. For a surface covered by 2×10^{15} (H atoms)/cm^2 only the 130-meV vibration is observed. No vibration corresponding to molecular hydrogen (545 meV) was found. The small bump around 70 meV is due to a small CO contamination which could not be avoided since during H_2 exposure the CO partial pressure also rose. From a comparison to CO spectra[12] the coverage can be estimated to be ~ 2% of a monolayer! The technique has this particular high sensitivity to CO because of the comparably large dipole moment of adsorbed CO. The fact that the bump at 70 meV is not caused by hydrogen is also indicated by adsorption experiments with D_2 (Fig. 1), where only a single peak at $\hbar\omega=93$ meV and none at 50 meV is observed at full coverage. Here the 70-meV CO loss is not resolved.

The measured relative intensities of the two hydrogen losses versus θ are plotted in Fig. 2. In the intermediate range where the two losses exist simultaneously the intensities have been determined by unfolding the spectra graphically assuming a constant width for both peaks. Figure 2 shows that the intensity of the 155-meV loss is not proportional to θ but rather to θ^2. This effect is not fully understood. It has been suggested that the θ^2 dependence may result from coherent scattering from atoms adsorbed randomly on a periodic site structure.[13] It also appears from Fig. 2 that the last half of the monolayer of hydrogen does not significantly contribute to the inelastic cross section. This indicates a decrease in the average dynamic dipole moment per atom with increasing coverage, which is different from the behavior of the static dipole moment, i.e., the work function. In any case Fig. 2 shows that the intensities may be used as a qualitative measure of coverage only.

Spectra such as in Fig. 1 have been produced either by exposing a clean surface to an increasing dose of hydrogen or by partial desorption

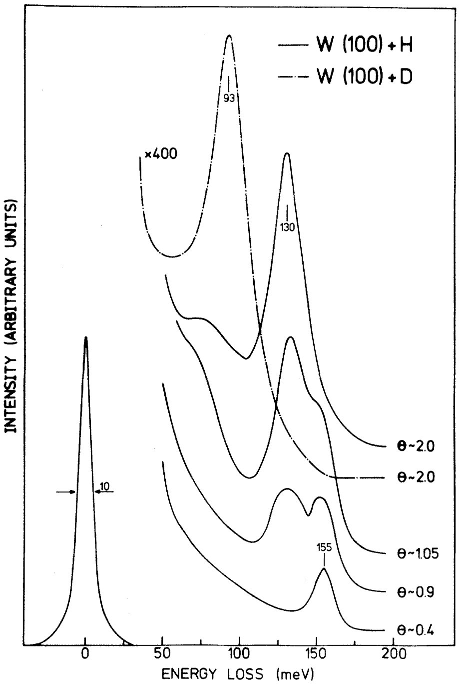

FIG. 1. Electron-energy-loss spectra of H and D on W(100). The two losses at 155 and 130 meV correspond to atomic hydrogen adsorbed in on-top and bridge sites, respectively. For deuterium the losses are shifted to lower energies by a factor $1/\sqrt{2}$.

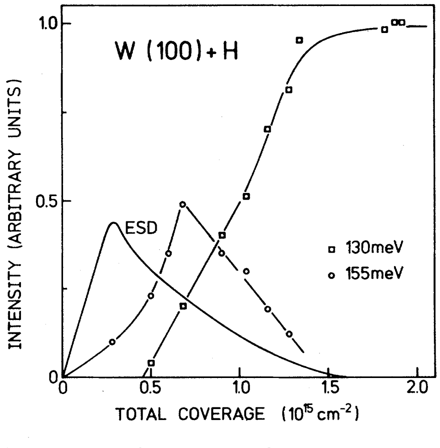

FIG. 2. Measured intensity of the two energy losses versus coverage. The intensity of electron-stimulated desorption (Ref. 2) is shown for comparison.

from a fully covered surface. They were completely reversible.

In electron-energy-loss spectroscopy only surface vibrations with a dipole component perpendicular to the surface have a considerabe cross section at low primary energies.[14] The geometry around an atom or molecule adsorbed on a surface defines a certain point-group symmetry. This symmetry determines the number of observable vibrations. A single vibration therefore is expected to appear in the loss spectrum for atomic adsorption in either one of the high-symmetry sites: on-top site, bridge site, or four-centered site. The spectra in Fig. 1 therefore show that at low coverage and at full coverage different single sites are occupied by atomic hydrogen, respectively. In the intermediate range both sites are occupied with the relative occupation depending reversibly on the total coverage as Fig. 2 shows. Since at full coverage a single site is occupied by atomic hydrogen and the bridge site is the only one that can accommodate 2×10^{15} atom/cm^2 in a single site, the spectra provide conclusive evidence that bridge sites only are occupied at saturation coverage (β_1 hydrogen).

In addition the observed energies of vibration contain information about the adsorption site: For an adsorbed atom in a position on top of a substrate atom the bond is concentrated on a single W atom and the force constant effective for a vibration normal to the surface will be comparatively high. Using a harmonic oscillator model the frequency for a H atom bound on top of a W atom is given by $\hbar\omega = 2\mathcal{R}(f/1836)^{1/2}$, with f the force constant in a.u. and $\mathcal{R} = 13.6$ eV. For an atom in the bridge position or in a fourfold coordination site the bond is shared between two or five W atoms, respectively. Under the assumption of a central nearest-neighbor force-constant model, the forces of the single adatom–surface-atom bond are only partially effective for a vibration perpendicular to the surface since the bonds have an angle $\alpha < 90°$ to the surface normal. The sum of the bond forces should be roughly equal for the three sites if the desorption energy is about equal. For a bridge site the frequency of vibration normal to the surface should then be of the order of $\hbar\omega \sim 2\mathcal{R}[(2\times f)/(2\times1836)]^{1/2} \times \cos\alpha$. For a fourfold site $\cos\alpha$ is negligibly small for the bond forces to the surface atoms leaving only the bond force to the nearest neighbor in the second layer effective. Thus one may estimate the frequency to be $\hbar\omega \sim 2\mathcal{R}[f/(5\times1836)]^{1/2}$. Therefore a relation $\omega_{\text{top}} > \omega_{\text{bridge}} > \omega_{\text{4fold}}$ should hold in agreement with actual observations for the W(100)+O system.[12] The higher frequency of vibration of 155 meV at low coverages therefore suggests the on-top site position for β_2 hydrogen.

Another very interesting aspect of the results is the clear demonstration of the coverage-dependent equilibrium between the occupation of the two absorption sites. The fact that this site conversion also works backwards after partial desorption has important consequences for the interpretation of flash-desorption traces. The ratio between the areas under the flash-desorption peaks β_1 and β_2 no longer represents the relative occupation of the two sites at full coverage but the ratio of the relative occupations integrated over the coverage. This ratio may be considerably different from the ratio of the maximum possible occupations of the two sites.

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