

Experimental Investigation of β_1 -H on W(100) Using High-Resolution Electron-Energy-Loss Spectroscopy: Bond Distances, Scattering Mechanisms, and Impact-Scattering Selection Rules

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High-resolution electron-energy-loss studies of β_1 -H and β_1 -D on W(100) are reported for experimental conditions under which the first-order diffracted beam emerges from the crystal. A new vibrational mode is observed and assigned to the asymmetric stretch mode of β_1 -H. The results yield an independent new determination of the H-W bond distance. The impact-energy dependence of the new asymmetric stretch mode does not agree with theoretical predictions related to cross sections and selection rules that govern them.

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The chemisorption of hydrogen on tungsten is one of the most thoroughly studied systems of surface science. Hydrogen is chemically active and adsorbs on most surfaces, and is also one of the simplest adsorbates. Therefore, hydrogen represents an attractive model adsorbate for studying general trends and underlying mechanisms in chemisorption. The W(100) surface is also of particular interest because of its intrinsic properties and its interaction with H. The clean W(100) surface undergoes a structural phase transition upon cooling below room temperature,¹⁻³ and hydrogen chemisorbed on it at room temperature produces at least two distinct surface structures.^{4,5} One structure associated with low H coverage (β_2 phase) yields a $c(2 \times 2)$ low-energy electron-diffraction (LEED) pattern, and a second structure associated with saturated H coverage (β_1 phase) yields a (1×1) LEED pattern. Thermal-desorption studies⁶ have established that the β_1 phase has two hydrogen atoms per unit cell, and surface-vibrational experiments⁷⁻⁹ have shown that the atoms are bridge bonded along the short bridge site.

High-resolution electron-energy-loss spectroscopy (EELS) is rapidly being developed into one of the most useful scattering-based spectroscopic methods for studying the properties of surfaces.¹⁰ The broadly recognized importance of this technique has stimulated considerable interest in understanding the scattering mechanisms^{7,11-13} responsible for EELS as well as the selection rules^{14,15} which govern them. As a result of its simplicity the H/W(100) system is an attractive model system for studying both theoretically¹³ and experimentally⁷ the mechanisms responsible for losses observed in inelastic electron scattering from surfaces.

The present paper presents a study of the saturated coverage (β_1 phase) of H and D on W(100) using EELS. We demonstrate the application of a novel technique for observing parallel vibrations in specular scattering geometry and use it to observe for the first

time the asymmetric stretch mode of β_1 -H on W(100). This mode permits reevaluation of the height of the H atoms above the W(100) surface previously obtained by Willis.¹⁶ Our results also raise interesting new questions regarding the application of selection rules which govern electron inelastic-scattering cross sections for surface adsorbates.

Our experiments were performed with use of an EELS spectrometer which has been described previously.¹⁷ The sample manipulator provided access to LEED optics and cylindrical-mirror Auger optics which were used to check crystalline order and mirror-plane alignment and to determine the presence of surface adsorbates (except H and D). The W(100) crystals ($\frac{3}{8}$ in. diam by 0.030 in. thick) were spark cut after alignment to $\pm 1^\circ$ by x-ray Laue techniques. The surface was prepared by polishing to a mirror finish and was cleaned *in situ* by standard procedures which included annealing in oxygen and repeated flashes to 2800°C.

Figure 1 displays a series of EELS spectra for β_1 -H on W(100) taken in specular geometry along the [010] crystal direction and for several impact energies. The electron impact energy is defined here as the monochromator pass energy plus the voltage difference between the exit slit and the W(100) sample. By use of the diffraction condition and the bulk lattice constant of W ($a = 3.16 \text{ \AA}$), the $(0\bar{1})$ beam is predicted to emerge parallel to the [010] crystal direction at $E_{\text{inc}} = 4.32 \text{ eV}$ when the incident angle is $\theta_I = 60^\circ$. The data in Fig. 1 span this energy and clearly exhibit three hydrogen loss peaks which correspond to the symmetric stretch mode $\nu_{\text{sym}} = 130 \text{ meV}$, the new asymmetric stretch mode $\nu_{\text{asy}} = 118 \text{ meV}$, and the wag mode $\nu_{\text{wag}} = 80 \text{ meV}$. The asymmetric-stretch-mode loss peak is most apparent at $E_{\text{inc}} = 4.3 \text{ eV}$ where (as discussed later) the elastic peak and 130-meV peaks are suppressed. At other energies, the asymmetric stretch mode is less apparent in specular geometry but can still be seen as a small shoulder on the low-energy

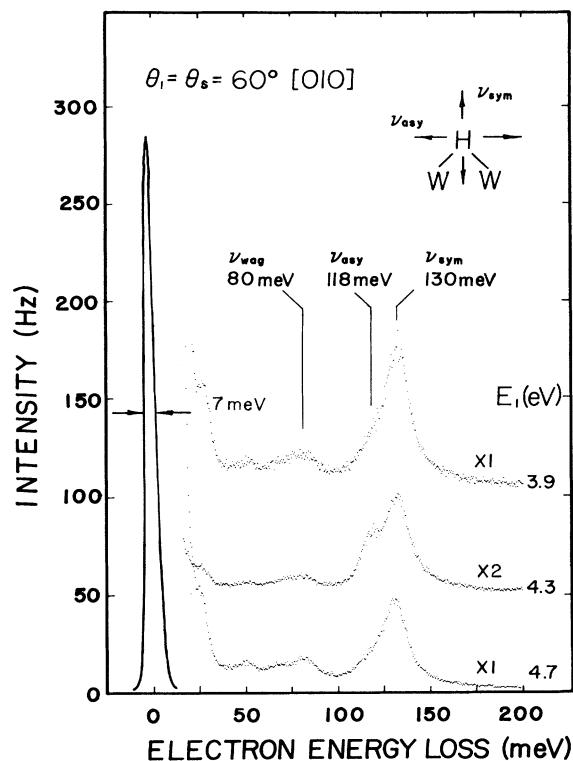


FIG. 1. EELS spectra for β_1 -H on W(100) for three incident energies E_i . The baseline for each spectrum is shifted 50 Hz. Inset, illustration of bridge-bonded hydrogen in a [010] plane showing the symmetric stretch and asymmetric stretch vibrations.

side of the 130-meV peak. The 118-meV peak is readily observed in off-specular geometry provided energy resolution of 6–8 meV is used. Previous EELS studies⁷ of β_1 -H on W(100) have suggested that $\nu_{\text{asy}} = 160$ meV. However, these results were obtained with 30-meV energy resolution and the 118-meV peak was not resolved in either specular or off-specular scattering geometry spectra. The 160-meV peak, which was also observed in some of our data (not shown) for β_1 -H on W(100), is an overtone of the 80-meV wag mode as suggested previously.¹⁸

Figure 2 displays a set of specular and off-specular data for β_1 -D on W(100) along the [010] crystal direction. These spectra exhibit the corresponding three peaks shifted down in energy by $\sqrt{2}$ as a result of the higher mass of the deuterium atoms. Previous studies^{7,16} of the angle dependence of the 80- and 130-meV loss peaks confirm that the 130-meV loss peak is due primarily to dipole scattering and that the 80-meV peak is due to impact scattering. Corresponding angle-dependent data for the 118-meV loss peak, shown in Fig. 2, establish that it is due to the impact-scattering mechanism. The “clean” spectrum was sig-

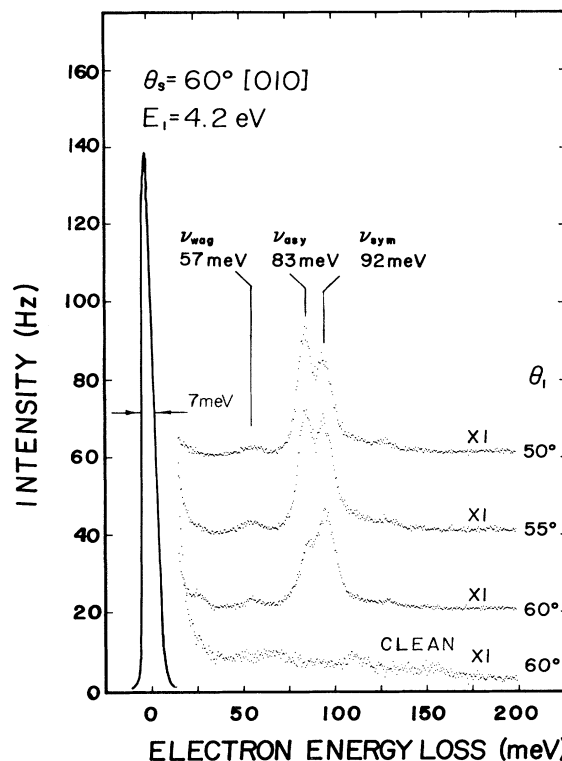


FIG. 2. EELS spectra for β_1 -D on W(100). The baseline for each spectrum is shifted 20 Hz. Incidence energy, E_i , and scattering angle, θ_s , are fixed; incident angle, θ_i , is varied. Clean spectrum was taken after desorbing the deuterium (refer to text).

nal averaged 90 min after gently annealing the crystal to desorb the deuterium. Small loss peaks near 70 meV due to CO and O and at 155 and 110 meV due to the low-coverage β_2 phase of H and D are evident. These peaks originate from residual gas adsorption from the 2×10^{-11} -Torr background pressure in the chamber.

Figures 1 and 2 exhibit an additional vibrational loss peak, at 26 meV, which has not been reported previously.¹⁹ This peak is produced by dipole scattering, on the basis of the angle dependence of its strength shown in Fig. 2, and is associated with the tungsten surface since its energy does not depend on whether H or D is present on the surface. The peak is not observed on clean W(100) at room temperature, but appears and vanishes with temperature similar to the $c(2 \times 2)$ reconstruction.

A classical model based on the harmonic approximation of a bridge-bonded atom^{10,16} leads to the result $\nu_{\text{asy}}/\nu_{\text{sym}} = \tan(\alpha/2)$, where α is the included angle between central forces. Our new asymmetric-mode energy changes the previous estimate¹⁶ of α from 100° to 84° . With the assumption that the β_1 -H-stabilized

W(100) surface has a W-W distance equal to the bulk value (3.16 Å), the corrected height of H above the surface plane (d_{\perp}) is 1.74 Å. This height is not in particularly good agreement with a recent estimate²⁰ based on LEED ($d_{\perp} = 1.17$ Å).

One could question the applicability of this classical model of vibrational modes and the value of d_{\perp} obtained from it in view of recent effective-medium calculations^{21,22} of the ground-state properties of H on transition-metal surfaces. These calculations suggest that the H atoms on W(100), and on other transition-metal surfaces, are delocalized and that the vibrational modes cannot be adequately described within the harmonic approximation. In particular, the calculated contours of constant potential energy in the plane of the surface for adsorbed H are noncircular, and contours perpendicular to the surface suggest that parallel-mode excitations will have substantial perpendicular components. Thus, assignment of "parallel" and "perpendicular" modes might not be legitimate in which case the above model calculation becomes questionable.

On the other hand, objections to the classical model are generally refuted by experimental facts: Neutron-scattering studies have failed to provide strong evidence of delocalized hydrogen.²³ Also, even though the intrinsic linewidth of the hydrogen vibrational levels established by our data²⁴ (13 meV) and infrared results²⁵ (11 meV) is broad enough to suggest some anharmonicity, recent lattice calculations²⁶ have demonstrated that even in cases where there is substantial anharmonicity, like rare-gas atoms on graphite, the modes are decoupled. On the basis of these results, our simple model calculation probably yields a fairly accurate bond height for β_1 -H on W(100).

We now consider the question of impact-scattering selection rules and the violation of these rules. Application of the selection rules¹⁴ to β_1 -H on W(100) results in the prediction that neither parallel mode ($\nu_{asy} = 118$ meV, $\nu_{wag} = 80$ meV) should be observed in an EELS spectrum taken in specular geometry along a [010] or [001] crystal direction except possibly under the conditions associated with LEED beam emergence from the crystal.¹⁵ In this case, the selection rule can, in principle, break down because one of the assumptions (time-reversal symmetry) is no longer valid.

Figure 3 illustrates the impact-energy dependence of the elastic peak intensity and the loss intensities for all three adsorbate modes. The incident beam intensity (target current) was observed to be constant within $\sim 10\%$ over the energy range represented; in addition, the lens voltages of the optics changed very little. The areas under the loss peaks can therefore be regarded as representative of the relative scattering cross sections. Gaussian curve fitting was used to obtain the areas of the resolved doublet corresponding to ν_{sym} and ν_{asy} .

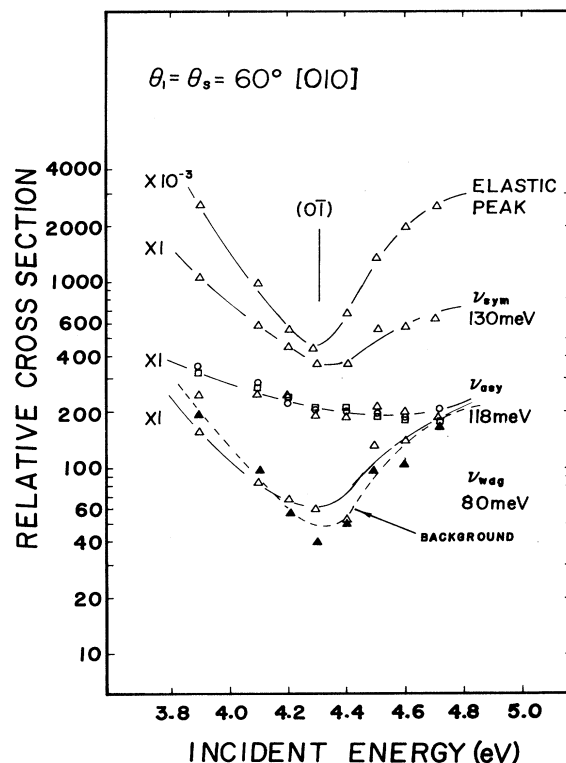


FIG. 3. Relative scattering cross sections for β_1 -H on W(100) (refer to text). Dashed line illustrates the energy dependence of the background under the 80-meV peak. The incident energy at which the (01) beam emerges is shown.

The relative counting rates have been accurately preserved in the figure and from the relative cross sections it is clear that a choice of E_i and θ_i to yield beam-emergence conditions greatly reduces the scattering intensity of the elastic and 130-meV dipole loss peaks.

The reduced data in Fig. 3 (as well as the corresponding raw data) show clearly that the asymmetric mode can be observed in specular scattering geometry under LEED beam-emergence conditions, in agreement with the prediction of the selection-rule violation. However, the EELS data also clearly show that the energy dependence of the asymmetric-stretch-mode cross section does not agree with the predictions based on multiple-scattering calculations.¹⁴ We have observed similar results for $\theta_1 = \theta_s = 48^\circ$; in this case, the minima in the elastic-scattering cross section occurs at 4.5 eV, and the (01) beam emerges at 4.96 eV. If there were a strict selection rule which applied in the present situation, one would expect the cross section for the parallel modes to decrease rapidly on either side of the beam emergent energy.²⁷

There are several possibilities which could explain the fact that effects of the selection rule are not ob-

served: The H atoms could be in sites of lower symmetry than required for the selection rule to be valid (i.e., not in a true bridge site); at low impact energies, the assumption that $k_i = k_f$ could be sufficiently inaccurate that the selection rule breaks down; the azimuthal alignment of our sample ($\sim 1^\circ$) might not be precise enough. An additional possible explanation could be based on the delocalized model²¹ of the H adsorption in which the "parallel" and perpendicular vibrations are coupled to some extent. However, the appearance of a perpendicular vibrational component at the *same* frequency as a parallel vibration given the symmetry of the system is difficult to explain on the basis of a simple model. Clearly, additional experimental work will be required to assess thoroughly the practicality of the selection rules.

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