

Bonding Geometry and H Vibrations on W(001)

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The bonding geometry, fundamental H vibrational frequencies, and dynamic dipole moments for the saturated H coverage phase on W(001) are calculated with the *ab initio* linear augmented plane wave method. All three mode frequencies agree well with experiment and support earlier electron-energy-loss spectroscopic mode assignments. The present results indicate that nearest-neighbor central-force-constant models at surfaces are inadequate for quantitative analysis of adsorbate vibrations.

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The electronic, vibrational, and structural properties of adsorbates are a subject of active interest in surface science. An extensively studied adsorbate-metal system is H on W(001).^{1,2} Although for low H coverages, H on W(001) is a complex system with multiple phases, the saturation H phase is particularly simple. At saturation (two H per surface W) the surface assumes a simple 1×1 structure with the W atoms forced into the bulklike positions and the H atoms occupying all the closed bridge sites between pairs of W atoms³ (see Fig. 1). This phase has been characterized through electron-energy-loss spectroscopy (EELS)⁴⁻⁶ and infrared^{7,8} measurements of the vibrational modes, and low-energy electron diffraction (LEED) studies^{1,2,9} of the structure. We present here *ab initio* calculations of the bonding geometry and the H vibrational modes with an aim to clarifying the different interpretations that have resulted from the EELS measurements. Generally, a few adsorbate-metal systems have been studied with *ab initio* calculations for stretching vibrations. The present work represents the first comprehensive study for several modes of different symmetries and the first calculations of the fundamental H vibrations on W(001).

With high-resolution infrared techniques, Chabal⁷ has observed the infrared-active symmetric stretch mode at 132.6 meV and the overtone of the wag mode at 157.4 meV that has a novel Fano line shape. EELS measurements have led to conflicting interpretations of other vibrational peaks and the H bonding geometry. In earlier work, Ho, Willis, and Plummer⁴ and Barnes and Willis⁵ assigned the peaks of the specular and off-specular EELS spectra to the symmetric stretch (SS), wag, and asymmetric stretch (AS) modes with the energies given in Table I. The mode displacements are shown in Fig. 1. A H bonding geometry of $d = 1.15 \pm 0.05 \text{ \AA}$ and $2\alpha \approx 108^\circ \pm 5^\circ$ was inferred⁵ from the assumption of a constant W—H chemical bond length (1.95 \AA). This interpretation is qualitatively consistent with a simple nearest-neighbor central-force-constant model which would predict that $\nu_{AS}/\nu_{SS} = \tan\alpha$, where 2α is the W—H—W bond angle (see Fig. 1). However, in the recent EELS measurements of Wood and Erskine⁶ a new peak at 118 meV was seen, in addition to the SS and wag mode peaks (see Table I). This new peak was assigned to the asymmetric stretch mode and interpreted with the simple force-constant model to imply that the H is much

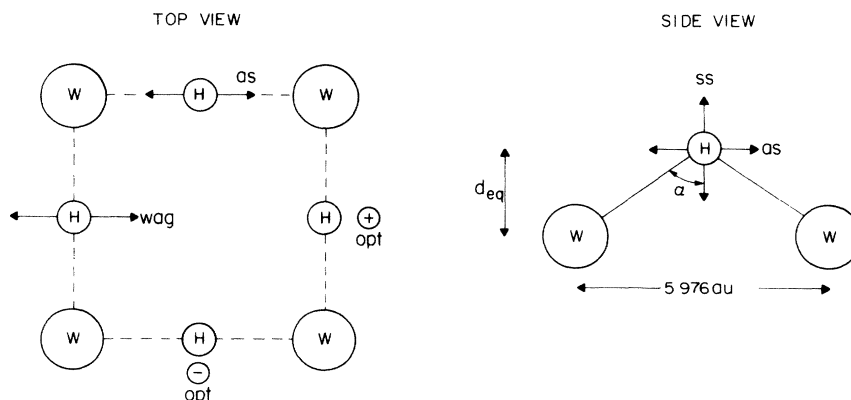


FIG. 1. Geometry of the saturated H coverage phase of the W(001) surface. H atoms occupy bridge sites in this 1×1 structure. Side and top views show the displacements for the zone-center symmetric stretch (SS), asymmetric stretch (AS), wag, and optic (opt) modes.

TABLE I. Experimentally measured energies of vibrational modes (in millielectronvolts) and present calculations.

Mode	Infrared ^a	EELS ^b	EELS ^c	Present theory
Wag		80	80	77
?		...	118	...
SS	132.6	130	130	141
Optic		...		150
Wag overtone	157.4			
AS		160		169

^aChabal (Ref. 7).

^bHo, Willis, and Plummer (Ref. 4); Barnes and Willis (Ref. 5).

^cWoods and Erskine (Ref. 6).

further away from the W; a distance $d \approx 1.74 \text{ \AA}$ with a bond angle $2\alpha \approx 84^\circ$ was suggested.⁶ This interpretation also differs from estimates of $d = 1.17 \text{ \AA}$ based on LEED I - V measurements.⁹

With a view to resolving these conflicting interpretations of the H vibrational modes and the bonding geometry, we perform *ab initio* frozen-phonon calculations for the H overlayer. The total energy and electronic charge density are calculated self-consistently with the linear augmented plane wave (LAPW) method, that has been demonstrated to describe accurately the properties of bulk tungsten,¹⁰ the clean W surface,^{11,12} and the electronic structure of H-saturated W(001).¹³ Real space is divided into muffin-tin, interstitial, and vacuum regions and the electronic wave functions are expanded in terms of muffin-tin orbitals, plane waves, and decaying numerical Laue functions in these three regions, respectively. There are no shape approximations to the potential or charge density in any of these regions. We utilize a frozen-core approximation, and include all relativistic effects except spin-orbit coupling.¹⁰

The W-H system is modeled by a four-layer W slab with two layers of H occupying closed bridge sites on either slab surface, and vacuum on both sides of the slab. We believe that the four-layer W thickness is sufficient to provide bulklike environments for the two inner-layer W atoms as well as to have the two outer W layers model surface atoms. Because of the small H-W mass ratio (0.0055), the motion of the H alone is an excellent approximation to the surface vibrations. We use an energy cutoff of 9.2 Ry for the interstitial plane waves leading to ≈ 360 LAPW's.

Our results for the equilibrium H position are displayed in Fig. 2 which plots the total energy as a function of the uniform displacement of the H atoms towards or away from the slab. A least-squares fit of a quadratic function through the calculated energies yields an equilibrium position of $d_{\text{eq}} = 2.02 \text{ a.u.}$ (1.07 \AA) corresponding to a W—H bond length of 1.91 \AA and a W—H—W bond angle of $2\alpha = 111.9^\circ$. The en-

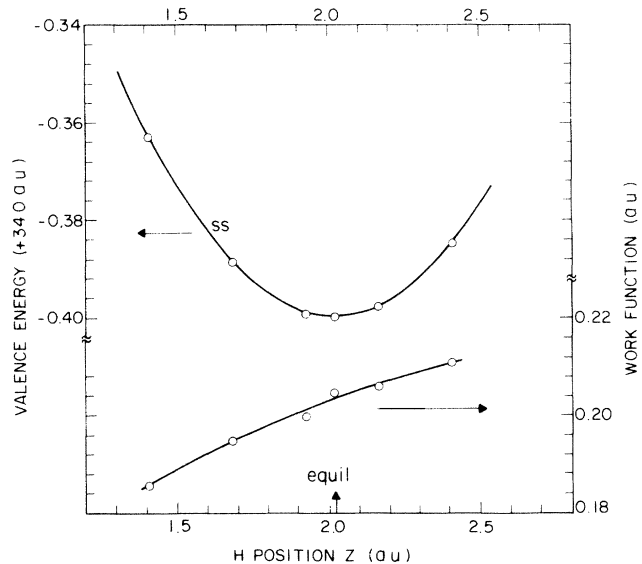


FIG. 2. Upper curve shows the total energy as a function of the symmetric-stretch-mode displacement with the calculated points and a quadratic fit (solid curve). Lower curve is the corresponding change in the surface work function.

ergy curve yields a frequency of 141 meV for the SS mode at the center of the surface Brillouin zone, which agrees well to $\approx 7\%$ with the experimentally measured value⁷ of 132.6 meV (from infrared measurement). The quadratic energy curve in Fig. 2 closely fits the calculated points to within an rms error of $\approx 1 \times 10^{-4}$ a.u. and a cubic fit produced values of d_{eq} and ν_{SS} that differed by less than 0.2%, indicating negligible anharmonicity. The equilibrium H—W bond length of 1.91 \AA is very similar to W—H bond lengths of bridged H in W cluster compounds (1.86 – 1.89 \AA),¹⁴ suggesting a simple local-chemical-bonding picture for the bonding geometry of the H overlayer on W.

Also displayed in Fig. 2 is the surface work function as a function of the H displacement, with the curve representing a quadratic fit. From the change in the surface dipole at d_{eq} , i.e., the slope at d_{eq} , we derived an effective charge of $e^*/e = 0.032$. This compares reasonably well with the experimental value⁷ of 0.053 ± 0.005 , allowing for uncertainties in the details of the dielectric model.⁷ At the equilibrium position, the computed work function of 5.6 eV compares very well with the experimental value of 5.5 eV.¹⁵

In the SS mode, the electronic properties of the slab change significantly as the H vibrates. The Fermi level lies in a minimum of the density of states that lies approximately between bonding and unfilled antibonding peaks in the density of states. As the H is displaced away from the surface, the charge transfer to the H decreases and the slab becomes more metallic. The charge density obtained is similar to that calculated ear-

lier¹³ and indicates screening of the W atoms by the dense H overlayer.

From the determined equilibrium geometry, displacements corresponding to zone-center AS and wag modes were examined (see Fig. 1), and the calculated total energies with quadratic fits are displayed in Fig. 3. Convergence and accuracy for these lower-symmetry distortions were similar to those in the SS calculation,¹⁶ and the soft wag mode was well described. We find frequencies of $\nu_{AS} = 169$ meV and $\nu_{wag} = 77$ meV which compare well with experiment (160 meV and 80 meV; see Table I). For both modes, quartic anharmonicity is small, changing the frequency by $\leq 1\%$. To minimize the possibility of systematic computational errors, the H atom was moved parallel to the surface, rather than in an arc, for the wag mode. The quartic correction to the energy from bond stretching is $\approx 2\%$ of the wag energy at the displacement of 0.35 a.u. Since the AS and wag modes have the same symmetry, the AS and wag motions depicted in Fig. 1 can, in principle, couple both dynamically and through a bilinear term in the harmonic energy function. The dynamic coupling is small because of the H/W mass ratio. We expect the bilinear term to be small since the related coupling in the optic mode is small as discussed below, and since both the wag and AS modes involve small charge transfers to the H. The frequencies from the diagonal quadratic terms differ by a factor of ≈ 2 , and so we expect the off-diagonal correc-

tions to the frequencies to be negligible.

The calculated ν_{AS} is clearly higher than ν_{SS} , which we believe casts serious doubt upon the interpretation of the 118-meV peak in the EELS spectrum of Woods and Erskine⁶ as the asymmetric stretch mode. The present calculations support the earlier EELS mode assignments,^{4,5} including 160 meV for the AS.

We have examined the possibility of the 118-meV EELS peak⁶ being due to the optic mode, where the displacements of the two H atoms in the unit cell are perpendicular to the surface but out of phase with each other, as shown in Fig. 1. This mode would constitute a zone-corner phonon for the H sublattice, but it is folded back to the center of the zone by the shorter reciprocal-lattice vector of the W substrate. The optic mode has not been discussed in previous work. Scattering from the optic mode would be weaker than for the other normal modes, since it is not dipole active and requires a two-step process including umklapp scattering from the substrate. Although we find all the other normal modes to be almost harmonic, there is a significant difference for the optic mode with the equilibrium energy somewhat lower than a harmonic curve fitted through the energies of the displaced points. The harmonic curve yields a frequency of 150 meV, which is clearly higher than the SS, and suggests that the optic mode cannot produce the 118-meV EELS peak.

From a quantum-mechanical viewpoint, the zero-point energy implies a ground-state level of $\frac{1}{2}h\nu$ in each of the calculated potential wells, where $h\nu$ is the calculated normal-mode energy. This leads to a rms z displacement between the two hydrogens of 0.31 a.u. for the optic mode. Anharmonicity over a small region near equilibrium for the optic mode will then have little effect on the frequency inferred above. Using the quadratic term from a quartic fit would lead to an unphysically high estimate of the frequency.

The present results provide one of the first tests for the validity of widely used force-constant models at surfaces. The simplest such model consists of a nearest-neighbor H-W spring. This model predicts that $\nu_{AS}/\nu_{SS} = \tan\alpha = 1.40$, for the determined bonding geometry, whereas the calculated ratio is 1.20. The stiffening of ν_{SS} , relative to ν_{AS} , may be accounted for by (i) bond-bending forces between the W-H bonds (since the AS keeps the W-H-W bond angle 2α fixed to lowest order), or (ii) an additional spring perpendicular to the surface, representing the interaction of H with the jelliumlike aspects of the surface. These spring models do not give stiffness to the wag mode, which must substantially come from bond-bending forces between W-H bonds on the W. We note that the difference between the calculated SS stiffness and the predicted value from the spring model is comparable to the wag stiffness, which supports the impor-

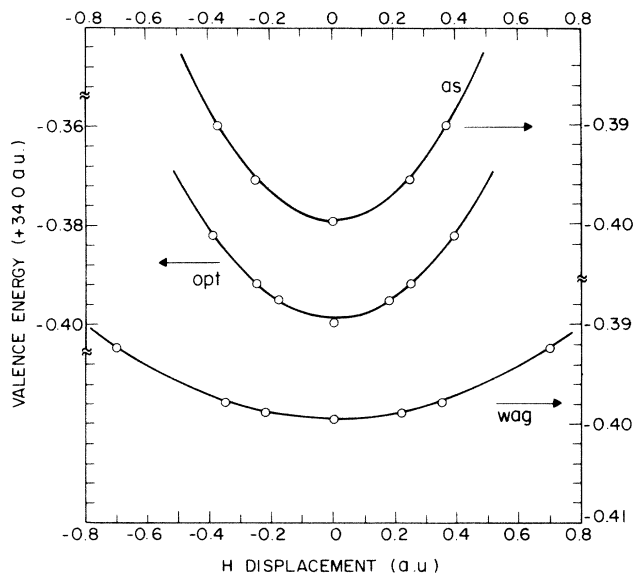


FIG. 3. Calculated total energies and quadratic energy fits for the asymmetric stretch, optic, and wag modes. Vertical energy scales for the optic mode and SS mode in Fig. 2 are enlarged by a factor of 2, since two H atoms per 1×1 cell are displaced in these modes. The curvature (or frequencies) for all modes can be compared directly. All three modes are symmetric about the equilibrium position.

tance of bond-bending interactions for the SS.

However, neither of these spring models, including an extension to next-neighbor springs, can account for the 9-meV difference between the calculated SS and optic frequencies. The direct dipolar coupling between the H would soften the optic mode relative to SS in contrast to the calculated stiffening. For the optic mode the calculated work function shows an *increase* of ≈ 0.004 a.u. over the range of displacement, in contrast to the slight *decrease* predicted by superposing work-function changes of the two H separately from Fig. 2. This indicates a complex charge-transfer process for the optic mode and an electronic interaction between the H mediated through the substrate, which can be responsible for the 9-meV optic-SS splitting.

Overall, simple force-constant models are deficient for the above reasons, although the trend of $\nu_{AS} > \nu_{SS}$ for the calculated geometry is qualitatively consistent with such models. The observed reversal of the SS and AS frequencies in the low-H-coverage regime ($\nu_{SS} = 155$ meV and $\nu_{AS} = 120$ meV)⁵ has been argued from simple force-constant models as due to "pinched" W atoms dimerizing in pairs, resulting in a large perpendicular H distance with $2\alpha < 90^\circ$.

For the wag and AS modes the work-function changes are less than ≈ 0.004 a.u. over the range of displacements considered. This suggests that the direct dipolar coupling of the wag overtone is small, and that the strong absorption seen in infrared measurements⁷ must be analyzed in conjunction with the coupled electronic absorption.

In conclusion, we have calculated the bonding geometry and fundamental vibrational frequencies for the saturated H coverage on W(001) and obtain results that are in good agreement with experiment and support the earlier EELS mode assignments.^{4,5} The present calculations suggest that the recently observed 118-meV EELS peak may not be one of the funda-

mental H vibration modes of the saturated surface.

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