

<sup>12</sup>P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, p. 1.

<sup>13</sup>The difference in the propagation velocities between  $L$  and  $T$  phonons and geometric effects do not account for the observed difference in width.

## Observation of Nondipole Electron Impact Vibrational Excitations: H on W(100)

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High-resolution inelastic electron spectra have been measured for a saturated coverage of atomic hydrogen adsorbed on W(100). The fundamental modes corresponding to H occupying a  $C_{2v}$  point-group-symmetry bridge site plus an overtone ( $\nu = 0 \rightarrow 2$ ) of the intense symmetric stretch are resolved at angles off the specular direction. The intensity of these modes (normalized to the elastic peak) exhibits resonantlike behavior as a function of the impact energy.

Traditionally, high-resolution electron-energy-loss spectroscopy studies of the surface vibrations of chemisorbed atoms or molecules have been interpreted in terms of long-range dipole scattering.<sup>1-3</sup> The assumption of dipole scattering from an adsorbate on a metal surface leads to the following predictions: The inelastic intensity is strongly localized (within  $\sim \pm 2^\circ$ ) about the specularly reflected beam direction, and only those vibrational modes with a dynamic dipole moment perpendicular to the surface are excited.<sup>1-3</sup> The latter consequence of dipole scattering is referred to as the "surface dipole selection rule." It predicts that the relative intensities of the observed vibrational modes in electron scattering should be similar to those observed in an infrared absorption experiment.<sup>1</sup>

There is strong evidence supporting this dipole scattering model, especially for adsorption of atomic hydrogen on tungsten. The inelastic spectra for hydrogen adsorbed in all of the high-symmetry sites—on-top, bridge, or four-centered sites—exhibit only a single energy loss which is associated with the excitation of the stretching mode perpendicular to the surface.<sup>4</sup> All of these measurements were taken in the specular beam direction, where the dipole scattering cross section is the largest. In this Letter, we show that all of the fundamental modes relating to H occupying a  $C_{2v}$  point-group-symmetry bridge site [see

inset, Fig. 1(b)] can be observed when the measurements are made off the specularly reflected beam direction. The scattering mechanism is clearly nondipole as witnessed by the observation of modes which are forbidden by the "surface dipole selection rule," by the observation of an overtone mode and by the large momentum transfer associated with collection angles far from the specular direction.

Figure 1(a) shows a typical electron-energy-loss spectrum for hydrogen chemisorbed on W(100) at saturation coverage ( $\beta_1$  phase,  $2 \times 10^{15}$  atoms/cm<sup>2</sup>),<sup>5</sup> in the *specular direction* for an impact energy  $E_0 = 9.65$  eV and an angle of incidence  $\theta_i = 23^\circ$ .<sup>6</sup> A single loss at  $h\nu_1 = 130$  meV is observed and corresponds to the symmetric stretch vibration normal to the surface ( $A_1$  mode).<sup>7</sup> Previous measurements<sup>8,9</sup> have reported the single loss peak at 130 meV and much weaker loss peaks at 70 meV<sup>8</sup> and 79 meV.<sup>9</sup> The low-energy losses were attributed to CO contamination<sup>8</sup> or a "bending mode" of the  $\beta_2$  (low-coverage on-top site) H phase. In contrast to the spectrum shown in Fig. 1(a), taken in the specular direction, Fig. 1(b) shows that off the specular direction a multitude of modes are observed (80, 130, 160, and 260 meV). This spectrum was taken under the same incident-beam and hydrogen-adsorption conditions. The 160-meV peak is clearly resolved at other angles of incidence and collection.<sup>10</sup> All

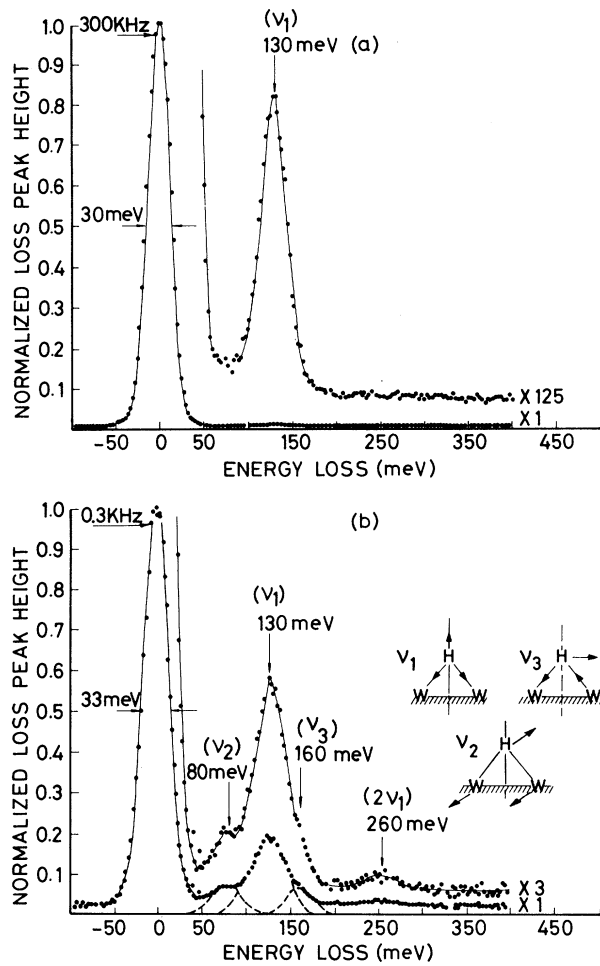


FIG. 1. Normalized electron energy-loss spectra for saturation coverage ( $\beta_1$  phase) of H chemisorbed on W(100) for  $\theta_i = 23^\circ$  incident angle and an impact energy  $E_0 = 9.65$  eV: (a) specular beam direction; (b)  $+17^\circ$  off the specular direction towards the surface. The elastic beam count rate (in kilohertz) and the energy resolution are indicated in the figure. The fundamental vibrational modes [inset Fig. 1(b)] correspond to bridge-site  $C_{2v}$ -symmetry bonding. The incident beam is along the [100] crystal direction.

of these modes shift down in frequency by  $\sim\sqrt{2}$  when deuterium is adsorbed<sup>10</sup> and they simultaneously disappear upon desorption of hydrogen. In addition, the spectrum changes for the on-top  $\beta_2$  phase of hydrogen adsorption; specifically there is a shift in the energy of the 130-meV loss to 155 meV and the 80-meV peak is absent.

The inset in Fig. 1(b) shows our tentative assignment of the observed modes. The 130- and the 260-meV loss peaks are the symmetric stretch and its overtone ( $v=0-2$ ), respectively. A simple spring model would predict that the 160-meV

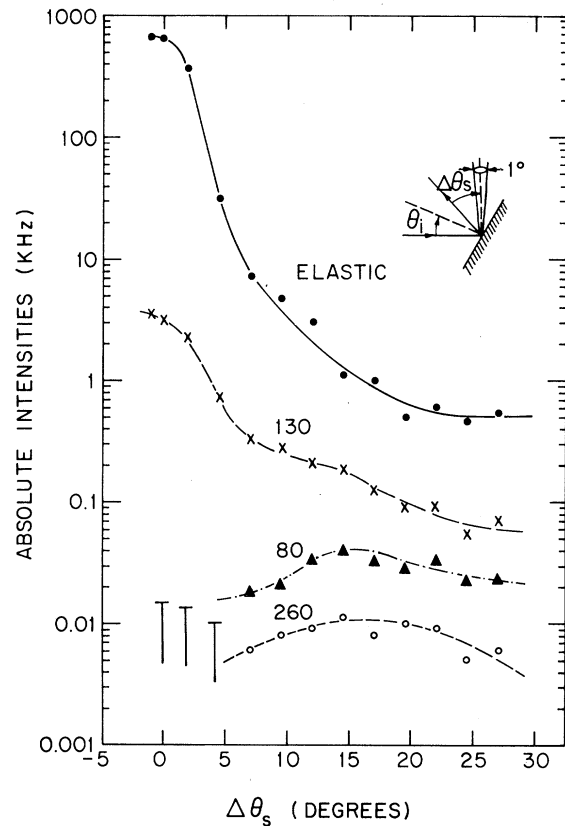


FIG. 2. Angle dependence of the absolute intensities as a function of the collection angle  $\Delta\theta_s$ . The scattering geometry is shown in the upper inset. The impact energy  $E_0 = 9.65$  eV and angle of incidence  $\theta_i = 23^\circ$ . The partial error bars for the data near the specular direction ( $\Delta\theta_s = 0^\circ$ ) for the 260-meV peak indicate the upper limit in intensity. [See Fig. 1(a) for the low signal-to-background ratio at 260 meV.]

mode is the asymmetric stretch and the 80-meV loss would then be associated with an out-of-plane bending.<sup>7</sup> The main feature shown in Fig. 1(b) is that all of the fundamental modes of the surface-molecule complex can be excited and observed when the measurement is made off the specular beam direction.

The magnitude of the elastic and inelastic signals are shown in Fig. 2 as a function of collection angle with respect to the specular direction ( $\Delta\theta_s$ ). The incident energy and angle, and the H coverage are the same as those in Fig. 1. The symmetric stretch mode observed at 130 meV has its largest intensity near the specular direction ( $\Delta\theta_s = 0$ ) and decreases by a factor of approximately 30 at  $\Delta\theta_s = +17^\circ$  [Fig. 1(b)]. This is the qualitative behavior that should be expected for a "surface-dipole-allowed" mode. However, the

intensity observed for this loss for angles greater than  $\Delta\theta_s \sim +7^\circ$  is too large for dipole scattering and is therefore determined by nondipole or short-range "impact" scattering at these large angles. The intensity variation of the 80-meV mode which is forbidden by the "surface dipole selection rule" clearly confirms a nondipole scattering mechanism; its intensity is maximum at large angles away from the specular direction ( $\Delta\theta_s \sim +15^\circ$ ), and shows no sign of peaking in the forward direction. Figure 2 also shows that the 260-meV overtone is excited by short-range "impact" scattering. The error bars in Fig. 2 are the determination of the upper limit to the signal strength of this mode near the specular direction. A relevant observation is that the corresponding infrared data on transition-metal-hydrogen complexes indicates that the ratio of the overtone to the primary loss is very small and is never observed because of interference from other absorption peaks.<sup>11</sup>

Figure 3 illustrates another feature of the inelastic electron scattering, i.e., resonantlike behavior. Here we have plotted the ratio of the loss signals to the quasielastic signal as a function of impact energy for the present collection geometry of  $\Delta\theta_s = +17^\circ$ .<sup>10</sup> This figure shows that all of the modes exhibit resonantlike behavior at an impact energy of  $\sim 10$  eV. This resonance behavior is very reminiscent of negative-ion resonances observed in gas-phase inelastic electron scattering.<sup>12,13</sup> It is tempting, therefore, to associate the present results with an analogous adsorbate-molecular-ion resonance, as recent calculations on oriented diatomic molecules would suggest.<sup>13</sup> However, our data on the incident angle dependence of resonant energy show complex dispersion behavior ( $10 < E_{\text{res}} < 4$ ) over a range  $23^\circ < \theta_i < 60^\circ$ .<sup>10</sup> This behavior is indicative of surface-band-structure effects, i.e., resonant enhancement due to beam threshold or surface states/resonances.<sup>14,15</sup>

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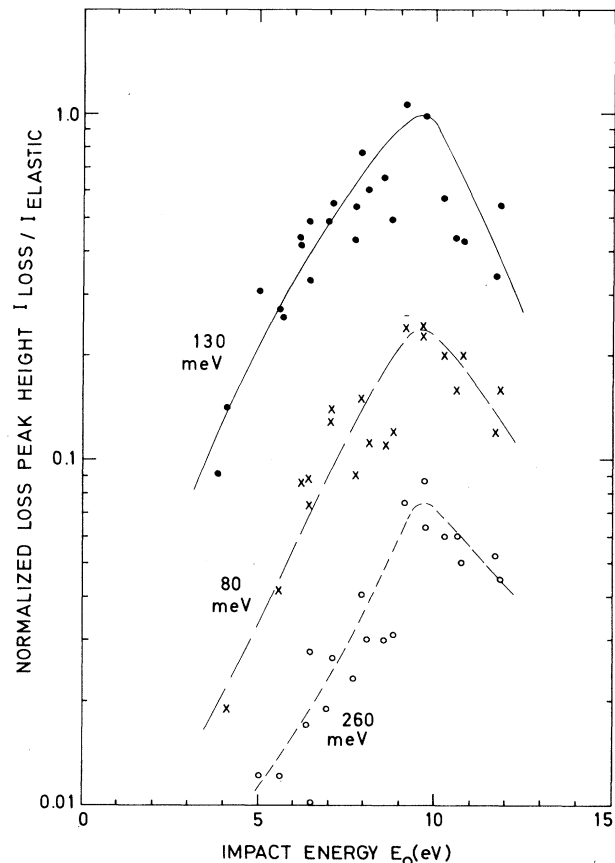


FIG. 3. Impact-energy dependence of loss peaks for a scattering angle  $\Delta\theta_s = +17^\circ$  from specular direction. Angle of incidence is  $\theta_i = 23^\circ$ . Relative  $I_{\text{loss}}/I_{\text{elastic}}$  intensity is normalized to unity at maximum for the 130-meV loss.

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<sup>6</sup>The experimental arrangement will be discussed in two longer papers. See M. R. Barnes and R. F. Willis, to be published; and W. Ho, R. F. Willis, and E. W. Plummer, to be published [a full report of the angle and impact-energy dependence of the differential vibrational cross sections of H on W(100) ( $\beta_1$ - and  $\beta_2$ -phase adsorption) is in preparation].

<sup>7</sup>The irreducible representations of the three normal vibrations of a nonlinear triatomic molecule,  $\Gamma_v = 2A_1 + B_2$ , correspond to two symmetric and one asymmetric modes [G. Herzberg, *Infrared and Raman Spectra*

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(Van Nostrand, Princeton, New Jersey, 1945)]. The corresponding *lattice* modes for H occupying a  $C_{2v}$  point-group bridge site on W(100) are equivalent to a motion of the H atom *perpendicular* to the surface ( $A_1$  symmetric stretch) and two *lateral* displacement modes ( $B_2$  asymmetric stretch and a second  $A_1$  out-of-plane "bending" mode). The latter two lateral modes are only resolved for off-specular scattering (see text).

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## Random Occupation of Adsorption Sites in the $c(2 \times 2)$ Structure of CO on Fe{001}

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A low-energy electron-diffraction intensity analysis of the Fe{001} $c(2 \times 2)$ -CO structure confirms the results of photoemission studies by other workers suggesting dissociation of the CO molecule. The data are fitted well by a model with random occupation of four-fold symmetrical sites by carbon and oxygen atoms in a  $c(2 \times 2)$  configuration, similar to that proposed earlier by Felter and Estrup and by Riwan, Guillot, and Paigne for Mo{001} $c(2 \times 2)$ -CO.

The adsorption of carbon monoxide on iron has been recently studied by photoemission with both polycrystalline<sup>1,2</sup> and single-crystalline<sup>3</sup> substrates. In both cases, the experimental results have indicated that the CO molecule dissociates upon adsorption. In addition, the work of Rhodin and Brucker<sup>3</sup> has shown that on Fe{001} the adsorbed layer is ordered and forms a  $c(2 \times 2)$  structure. We have also observed such a superstructure in our own adsorption experiments of CO on Fe{001}. We wish to report here the results of a LEED (low-energy electron-diffraction) intensity analysis of this structure, which reveals an atomic arrangement not heretofore confirmed on any other surface.

The experimental and theoretical details will be reported elsewhere. Here we will mention only that we have collected, for the purposes of structure analysis, a total of 23 LEED spectra: five at normal incidence, ten at polar angle  $\theta = 10^\circ$ , and eight at  $\theta = 20^\circ$ , all for an azimuth angle  $\varphi = 0^\circ$ . The intensity calculations were done with a computer program that includes in a single surface layer the three subplanes of carbon, oxygen,

and uppermost iron atoms, and calculates all multiple scatterings within this composite layer in the angular-momentum representation. The multiple scattering between this composite layer and the bulk layers is then computed in the plane-wave representation. Exploratory calculations were made with five phase shifts and 58 beams, while the final calculations for the best model were made with eight phase shifts and 58 beams for energies up to about 100 eV, 74 beams up to 150 eV, and 90 beams up to 200 eV.

Following the photoemission results, only structural models involving dissociated CO were tested. However, it was confirmed in the initial stages of the analyses that the model of CO molecules perpendicular to the surface with the C end does *not* produce agreement with experiment. Since a recent LEED analysis has established that oxygen chemisorbed on Fe{001} in a  $1 \times 1$  structure resides in the fourfold symmetrical hollows,<sup>4</sup> it was assumed that the latter would also be the adsorption sites for O in the Fe{001} $c(2 \times 2)$ -CO structure. Thus, the models to be tested involved 0.5 monolayer of O always in the four-