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Electronic Damping of Hydrogen Vibration on the W(100) Surface

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The first observation of the overtone infrared absorption of the wagging mode of H on W(100) at saturation coverage is reported. This measurement provides the first unambiguous evidence for electron-hole-pair coupling of an adsorbate vibration on a metal substrate.

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One of the most important problems in surface physics is to understand the mechanisms responsible for energy transfer between an adsorbate and a surface. On metal surfaces, a mechanism which has received recent attention is the excitation of electron-hole pairs.[1,2] Experimentally, evidence has been looked for in the linewidth of adsorbate internal vibrational modes[3] but no solid conclusions could be drawn as several different mechanisms can contribute to the linewidth.[2] Very recently, a rigorous analysis of the electron-hole damping of vibrational modes pointed out that this mechanism necessarily produced an asymmetric line shape, arising from the phase lag associated with the electronic tunneling.[4] This work shows that it is the line shape, and not the linewidth, that can give unambiguous evidence of whether or not electron-hole-pair production is an effective energy-transfer mechanism. For well-ordered overlayers with negligible inhomogeneous broadening, all other mechanisms such as dephasing, phonon damping, and diffusion would give symmetrical line shapes.

I report here the first unambiguous evidence for a strong electron-hole damping of the vibrational mode of an atom on a metallic surface. By use of high-resolution ($2\ \mathrm{cm}^{-1}$) infrared spectroscopy, the highly asymmetric line shape of the overtone of the wagging mode of H (and D) on W(100) at saturation coverage is measured for the first time. This mode has not been seen with electron energy-loss spectroscopy (EELS)[5,6] because its low resolution, typically $50\ \mathrm{cm}^{-1}$, hinders the detection of the sharp derivative-like structure. This line shape is well accounted for by the nonadiabatic process of electron-hole-pair creation. In contrast, the line shape of the symmetric stretching mode does not exhibit such an asymmetry. A mechanism accounting for the strong and weak couplings of the wag and stretch motions, respectively, to the electron-hole-pair continuum of the W(100)-$p(1\times1)$H system is suggested.

The present experiment uses a single grazing-incidence (85°) reflection. Changes in reflectivity of less than 10^{-4} can be observed over the range $700\text{–}3000\ \mathrm{cm}^{-1}$ with a nominal resolution of $4\ \mathrm{cm}^{-1}$ in about 5 min. These attributes make it possible to study the line shapes—involving *long tails*—of the weak vibrations[7] of both H and D on the reactive W(100) surface. The experimental apparatus has been described elsewhere.[8] The sample is cleaned by repeated baking at 1475 K in 10^{-7} Torr of O_2 (>10 h) and flashing in vacuum to 2150 K by means of electron-bombardment heating. The Auger spectrum shows that less than 1% monolayer of C and O contamination accumulates during the measurement ($\frac{1}{2}$ h) at the working pressure of 3×10^{-11} Torr. The LEED patterns can be monitored during the ir measurement without moving the sample. All of the various reconstructions previously reported[9] for increasing H coverage are observed before the saturation phase, characterized by a 1×1 pattern, is established.

A number of experiments have established that the W(100) surface, when saturated with H, is unreconstructed with two H per W atom,[10,11] located at the bridge sites.[5] Very recent high-resolution ($60\ \mathrm{cm}^{-1}$) EELS data have established that the three normal modes are at $645\ \mathrm{cm}^{-1}$ (wag), $950\ \mathrm{cm}^{-1}$ (asymmetric stretch), and $1060\ \mathrm{cm}^{-1}$ (symmetric stretch).[6] Symmetry considerations dictate that, of the fundamental modes, only the symmetric stretch should be infrared active. However, the *first overtone* of the wagging mode is allowed.[12]

The data, shown in Fig. 1, are obtained by subtracting the reflectivity of the clean W(100)-$(\sqrt{2}\times\sqrt{2})R45°$ surface from that of the H- (or D-) saturated surface and taking the ratio of this difference to the clean-surface reflectivity. Variations in the broadband reflectivity over the range investigated ($700\text{–}3000\ \mathrm{cm}^{-1}$) are observed as the H coverage increases, and have been attributed to the changes in the W surface reconstruction.[13,14] The frequency dependence of these nonvibrational changes is established by measuring the reflectivity of the D-saturated surface in the region of the W_2-H vibrational spectrum ($1000\text{–}1300\ \mathrm{cm}^{-1}$) and vice versa. The results show that a linear background can be used in the region of the W_2-H (or W_2-D) vibrational spectrum.

The vibrational spectra are characterized by two well-defined features: a mode at $1070\ \mathrm{cm}^{-1}$ for H ($767\ \mathrm{cm}^{-1}$ for D) and a highly asymmetric line at $1270\ \mathrm{cm}^{-1}$ for H ($915\ \mathrm{cm}^{-1}$ for D). The former is due to the symmetric stretch vibration (ν_1) which has been measured before.[14] I focus here on the asymmetric line which has not been previously observed. I

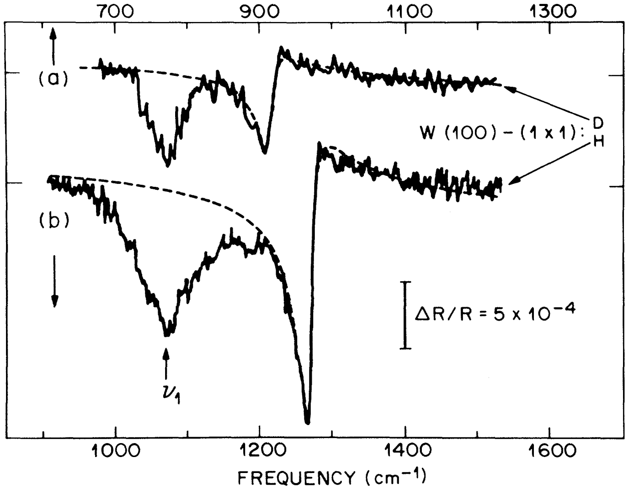

FIG. 1. Vibrational spectra (unsmoothed) of D and H on W(100) at saturation [10 L, where 1 langmuir (L) $=10^{-6}$ Torr sec]. The resolution is (a) 4 cm^{-1} and (b) 2 cm^{-1}. A linear background subtraction was used to remove the broad nonvibrational absorption. The dashed lines are the fits using the line shape given in Eq. (1) to calculate $\Delta R/R$ (parameters listed in Table I).

TABLE I. Damping parameters for H and D on W(100).

	ω_r (cm^{-1})	γ (cm^{-1})	$\omega_r\tau$
H	1270	26	0.44
D	915	22	0.46

first show that the line shape arises from electronic damping and then present evidence for the assignment of this line to the overtone of the wagging mode.

Langreth has shown[4] that the line shape of the vibrational mode which arises from a electron-hole-pair decay process is

$$L(\omega)=4\left(\frac{\omega_r}{\omega}\right)\left(\frac{\mu_1^2}{\gamma}\right)\frac{(1-\omega\tau x)^2}{(1+x^2)}, \qquad (1)$$

where $x=(\omega^2-\omega_r^2)/\gamma\omega$. Here ω_r is the fully renormalized Born-Oppenheimer vibration frequency, ω the probing radiation frequency, and μ_1 the real part of the net dynamic dipole moment. γ and $\omega\tau$ are the width and the phase delay associated with the electronic damping. The quantities ω_r, γ, and τ are parameters which contain all the physics of the process. These parameters, given in Table I, are a result of a least-squares fit of the entire experimental line shape as shown in Fig. 1 (dashed curves). The quantity $\omega_r\tau$ corresponds to the asymmetry parameter of the profile.

Briefly, electronic damping will occur if there exists a relatively narrow band of surface states or resonances which can couple to the adsorbate vibration. The oscillation of this band about E_F produces electron-hole pairs. The strength and response time of this coupling are measured by γ and τ, respectively. In the small-ω limit, the theory predicts no temperature or isotopic dependence of these parameters. I have therefore measured the spectra for both H and D over the range 100–400 K and found no effect on the line shape. The vibrational lifetime remains $\gtrsim 0.5$ ps ($\gamma \lesssim 25$ cm^{-1}), where the inequality indicates that some inhomogeneous broadening cannot be ruled out. In fact, inhomogeneous broadening could produce some asymmetry in the line. However, the characteristic Fano line shape, with a "negative" part digging into the continuum, unambiguously rules out inhomogeneous broadening as the *dominant* mechanism. There does appear to be a small isotopic dependence. The deuterium data are best fitted with values larger than those predicted in the small-ω limit,[1,4] i.e., $\frac{1}{2}\gamma(\mathrm{H})$ and $(\frac{1}{2}\sqrt{2})\omega_r\tau(\mathrm{H})$, as shown in Table I. This will be addressed shortly.

As the resolution is decreased (>4 cm^{-1}), the line shape is altered. At typical EELS resoltions (50–150 cm^{-1}), the asymmetric line becomes much smaller than the ν_1 line. This fact explains why previous EELS studies[5,6,15] have not detected this mode when using specular scattering geometry. However, in the off-specular geometry for which the ν_1-mode scattering intensity is drastically reduced, a weak shoulder at 160 meV has been observed[16] and can be attributed to the mode discussed here.

I now turn to the nature of this mode. The asymmetric stretch can be ruled out since recent EELS work has determined it to be at 950 cm^{-1} with no dipole character.[6] The wagging mode ($\nu_2 \approx 645$ cm^{-1}), on the other hand, does have an allowed overtone which should occur at twice the frequency. In fact, the measured frequency, $2\nu_2 = 1270$ cm^{-1}, can be accounted for with a reasonable anharmonicity ($x_e = 1.5\times10^{-2}$). A test for this assignment consists in determining the mode wave number as a function of isotopic mixture, i.e., H and D coadsorption at saturation coverage. Any adsorbate-adsorbate dynamical coupling will give rise to a frequency shift as a function of H concentration.[17,18] In Fig. 2, the wave numbers of ν_1 and $2\nu_2$ are plotted for both H and D. As the H concentration is increased, a large *negative* shift (≈ 30 cm^{-1}) is observed for $2\nu_2(\mathrm{H})$. In contrast, a weaker *positive* shift (≈ 20 cm^{-1}) is measured for $\nu_1(\mathrm{H})$. Correspondingly smaller shifts are found for the deuterium modes. The dashed lines in Fig. 2 represent the shift due purely to dipole-dipole interaction, calculated by performing the lattice sum,[19]$_0$ U, with a tungsten-hydrogen distance[20] $d_\perp \approx 1.6$ Å, and assuming that the effective charge of the wagging mode is the same as that of the stretching mode, $e^*/e = 0.053$, as measured by infrared spectroscopy.[14] Although the

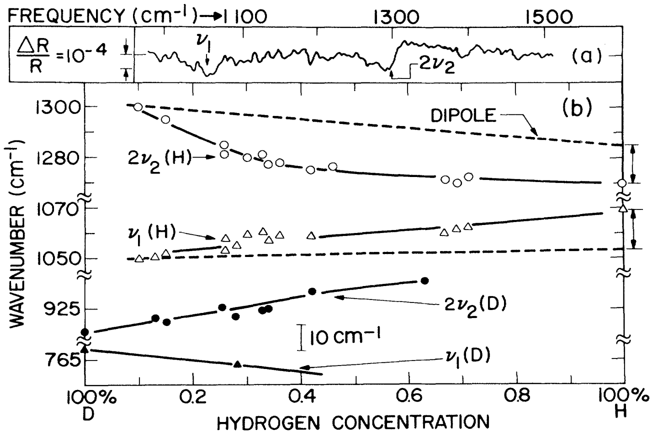

FIG. 2. (a) Example of unsmoothed data for 10% H concentration at 4-cm^{-1} resolution (unsmoothed). Note that the line shape of $2\nu_2$ is well fitted with use of the parameters of Table I. (b) Wave numbers of ν_1 and $2\nu_2$ for both H and D as a function of H concentration, determined from the area of the ν_1(H) line. The parameters calculated for the dipole contribution (dashed lines) are $U = -0.9$ Å^{-3} and $\alpha_v = 0.026$ Å^{-3} for $2\nu_2$ and $U = +0.8$ Å^{-3} and $\alpha_v = 0.01$ Å^{-3} for ν_1 (see Refs. 17 and 19). The solid lines are a guide to the eye.

dipole interaction does not account for the total observed shift, the *sign* of the shift is significant. Positive shifts are typical for vibrational modes *perpendicular* to the surface and have been observed for dipole[17] and nondipole interactions mediated by the metal electrons.[18] A negative shift has only been observed for vibrational modes *parallel* to the surface.[19] The complete shift of $2\nu_2$ could be accounted for by a slightly larger effective charge, $e^*_{\mathrm{wag}} \approx 1.4 e^*_{\mathrm{stretch}}$. However, for lack of an exact knowledge of e^*_{wag}, the results plotted in Fig. 2 indicate that, if the e^*'s are comparable, then both $2\nu_2$ and ν_1 have an additional shift (double-ended arrows, ≈ 16 cm^{-1}) which arises from nondipole dynamical interactions, with again a negative shift for the parallel mode. The fact that the asymmetric line occurs at twice the wagging-mode frequency *and* displays a negative shift, characteristic of *parallel* vibrations, establishes that it is the overtone of the wagging mode.

The reason that the overtone is so strong comes precisely from its interaction with the electron-hole-pair continuum. This is formally similar to the enhanced phonon absorption measured in valence-fluctuation compounds,[21] which arises from a coupling to the resonant electronic level associated with valence fluctuations. In the case of the W(100) surface, the most likely candidates for the resonant level are surface states. The requirement for these states to damp effectively only the wagging vibration by production of electron-hole pairs is that they lie in the vicinity of the Fermi level and that they couple to the wag motion and not to the stretch motion. Self-consistent calculations for the clean unreconstructed[22] and H-saturated[23] W(100) surface do show bands of states which are not significantly altered upon H adsorption (e.g., with d_{xy} symmetry) and which cross or lie at E_{F}. Such states could then couple to the wag motion because that motion *breaks the symmetry* of the tungsten-hydrogen surface layer. The stretch motion, on the other hand, does not break any symmetry and is strongly coupled only to the bonding states which are localized well below E_{F}.[23] The probability for the stretching mode to excite electron-hole pairs is therefore negligible.

The small isotopic dependence may be the result of a sharp density of surface states with a peak at E_{F}. The broadband reflectivity is found to decrease (i.e., the absorption increases) with ω compared to that of the clean reconstructed surface in the range investigated. In particular, the broadband absorption in the W_2-D overtone region is twice as large as in the W_2-H overtone region. If this broadband absorption arises from the surface states to which the wagging mode can couple, then an increased coupling would result for deuterium. The small-ω limit used by Langreth[4] would not be as good an approximation for such a sharp density of states.

In conclusion, this work shows that electronic damping can affect vibrational modes quite differently depending on the particular symmetry of the electronic structure and of the vibrational mode. Electronic damping may, in general, be stronger for parallel vibrations of adsorbates than for perpendicular vibrations such as an adsorbate *internal* stretch. The present data will hopefully motivate detailed self-consistent calculations of the H-phonon-electron coupling. Alone, they dramatically demonstrate the need for high resolution (≈ 1 cm^{-1}) in the study of adsorbate-metal vibrational modes.

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