Coupling Between Adsorbate Vibrations and an Electronic Surface State

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We report direct angle-resolved photoemission measurements of the coupling between the symmetric stretch vibrational mode of adsorbed hydrogen and a surface band on W(110). This coupling is manifested by the surface band being split into two branches at a binding energy comparable to the vibrational mode energy, as confirmed by observation of a dramatic hydrogen/deuterium isotope effect. The electron-phonon coupling parameter λ is found to be significantly larger than that for bulk W, and to be closely related to the degree of surface localization of the surface state wave function.

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The coupling between electrons and atomic and molecular vibrations at surfaces is of crucial importance for understanding energy transfer within the adsorbate-surface complex. Of particular interest is the characterization of nonadiabatic processes since these contribute to the dampening of adsorbate vibrations and thus are key to controlling surface reaction mechanisms. Despite this importance, quantitative, direct measurements of the two coupled components, the adsorbate vibrational mode and the underlying electronic continuum, with adequate resolution and sensitivity are rare [1,2]. While the phonon side of the problem is now well studied [3], there has been to date little or no work to directly see the effect of adsorbate phonons on electronic states.

Here we report measurements for hydrogen and deuterium adsorbed onto the tungsten (110) surface in which we directly observe the manifestation of strong electron-phonon coupling (EPC) between adsorbate optical phonon modes and an intrinsic surface electronic state. This coupling was confirmed through observation of a pronounced isotope effect. Additionally, using these data, we estimate the EPC parameter λ. In fact, we find a greatly enhanced EPC effect compared to the clean surface, which is a consequence of both the dramatically increased electronic localization to the surface attendant upon H adsorption, and also the creation of additional phonon modes intrinsic to H. We discuss the role such coupling might play in surface chemical reactions and also speculate upon other exotic surface physical phenomena that might arise.

The electron-phonon coupling (EPC) interaction has recently been studied for clean metal surfaces [4–9] with high-resolution angle-resolved photoemission, an ideal probe for measuring the complete energy and momentum dependence of interactions between electrons and other excitations. These studies demonstrate that the important parameters of the EPC can be extracted from photoemission experiments in favorable cases. The situation reported here (adsorbate on metal substrate) is particularly interesting because, by engineering such a system, we can modify its parameters so as to vary the EPC and thereby the low energy properties of the surface.

We chose H on W(110) for study because it has already been shown from scattering measurements to have a significant electron-phonon coupling at the surface [10], and because of the variety of well-characterized surface states [11–13]. Samples were prepared and measurements conducted in the same apparatus as in Ref. [12] at beam line 7.0 of the Advanced Light Source. Here we present results only for the saturated surface where one H or D atom is adsorbed per surface W atom. Angle-resolved photoemission was conducted using 100.0 eV photons at temperature ~150 K and pressure 5×10^{-11} T.

Figure 1(a) shows a schematic of the Fermi contours, and 1(b) shows the associated electronic bands of the relevant surface states, S_1, S_2, induced by H or D on W, as well as a bulk state B, taken from Ref. [12]. We have recently shown that the two surface state bands (S_1 and S_2) are derived from a single surface band that has been split by the spin-orbit interaction due to the breaking of inversion symmetry at the surface [13]. Moreover, bands S_1 and S_2 are coupled over limited regions of their associated Fermi

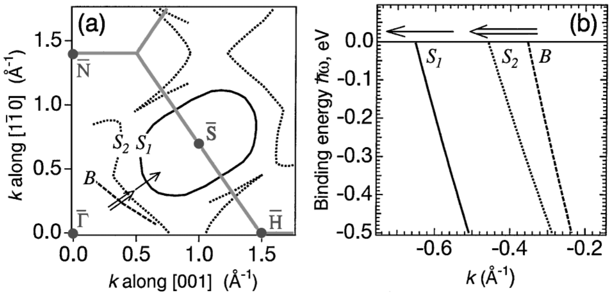

FIG. 1. Electronic states for one monolayer H on W(110) at photon energy 100 eV. (a) Fermi contours in the 2-dimensional k plane. The grey lines are the surface Brillouin zone boundary. (b) Schematic of single-particle bands. The arrow ⟶ is the path taken for Figs. 2(a) and 2(b), and the arrow ⇒ is the path taken for Fig. 2(c).

contours to drive a pronounced phonon (Kohn) anomaly on this surface [10,12].

Figure 2(a) shows photoemission data of the S_1 surface state for various in-plane momenta k along the line $\overline{\Gamma \mathrm{S}}$ of the surface Brillouin zone, as indicated by the arrow (→) in Fig. 1. Normally in photoemission, a measured valence band acquired for a particular momentum k exhibits a single peak at the final state photohole energy, since the bands are single valued with respect to k, as indicated in Fig. 1(b). At the higher binding energies shown in Fig. 2(a), this is observed. But near E_F, the state S_1 in Fig. 2(a) is clearly structured, with (at least) two separate branches apparently trading intensity as a function of momentum. As indicated by the vertical dashed line, this mixing occurs on an energy scale comparable to the measured symmetric stretch hydrogen vibrational mode energy on this surface of $\hbar\omega_0^\mathrm{H} = 161$ meV [14]. We have found similar behavior for band S_1 over its entire Fermi contour, even where it is not nested with band S_2. This splitting therefore appears to be unrelated to the Kohn anomalies observed on this surface [10,12]. For the same reason, our results cannot be explained in terms of a reconstruction of the (1×1) surface.

Such a splitting of a single-particle band immediately suggests a many-body explanation. The energy scale at which the splitting is observed suggests that the electron-phonon interaction is involved, and that the relevant vibrational mode is the symmetric hydrogen stretch. A simple understanding emerges: two branches are observed because of the distinct characters of the photohole above and below the phonon frequency. For energies greater than $\hbar\omega_0$ from E_F, the photohole has sufficient energy to decay by creation of a phonon. For energies closer to E_F, the photohole has insufficient energy to decay into phonons, but instead it is dressed with a cloud of virtual phonons, which renormalize the velocity (or effective mass) compared to the undressed, single-particle state. This causes the branch near E_F to have a measurably different slope from the branch below, as observed in the figure and examined more closely below.

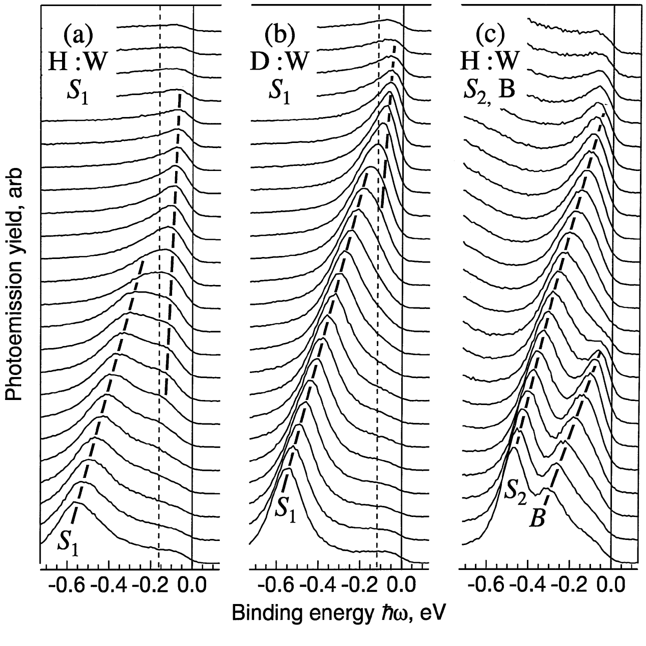

FIG. 2. Bottom to top, a series of photoemission spectra for increasing k along the arrows (→, ⇒) indicated in Fig. 1(a) The S_1 surface state (along →) for H on W. The splitting of the band near energy $\hbar\omega_0^\mathrm{H}$ (dashed line) is clearly visible. (b) The same state S_1 for D on W. By substituting D for H, the oscillator energy shifts to $\hbar\omega_0^\mathrm{D} \approx \hbar\omega_0^\mathrm{H}/\sqrt{2}$ (dashed line). (c) Bulk (B) and S_2 states (along ⇒) for H on W. No splitting near E_F is evident.

To further test this qualitative picture, we performed two variations on the experiment in Fig. 2(a). First, we replaced hydrogen by deuterium. Since there should be no difference in the chemical interaction with the metal, the undressed single-particle electronic bands have exactly the same dispersion relations. The only significant difference is due to the doubling of the nuclear mass, which implies that adsorbate vibrational energy should be reduced by $\sim\sqrt{2}$. This is indeed observed in Fig. 2(b). Careful examination shows a similar splitting behavior, now occurring near the measured deuterium symmetric stretching mode energy of $\hbar\omega_0^\mathrm{D} = 117$ meV [14]. The splitting appears first about halfway up the panel as a buildup of intensity just below E_F, then as a noticeable widening of the overall peak, and eventually as a sharpening again as the peak crosses E_F. Analytical modeling of these systematic changes in line shape was successful only when using two peaks in the vicinity of $\hbar\omega_0^\mathrm{D}$.

In addition to this reduced energy scale of the EPC, we find a markedly increased sharpness of the state compared to the case for hydrogen. This is a further consequence of the vibrational mode energy difference, as will be shown below. Second, we considered the crossings of the S_2 and B bands. These states have wave functions that sample the surface layer to a lesser degree than state S_1 [12], so we expect that they would exhibit smaller perturbation due to the coupling to a vibrational mode that is highly surface localized. Indeed, no splitting of these bands can be resolved, as shown in Fig. 2(c). That S_2 is sharper than S_1, approaching the width of the bulk state, is a further indication of the weakened EPC. It is very unusual for a surface state to have a larger linewidth than the bulk state from which it is derived, though this is clearly seen to be the case for S_1 and B in Fig. 2.

The linewidth trends may be understood as follows. The observed ω- and k-dependent photoemission spectra are approximately given by the photohole's spectral function [6,7,9]:

$$A(k,\omega) = \frac{|\mathrm{Im}\Sigma(k,\omega)|}{[\hbar\omega - \varepsilon_k - \mathrm{Re}\Sigma(k,\omega)]^2 + \mathrm{Im}\Sigma(k,\omega)^2}\,. \tag{1}$$

Here $\hbar\omega$ is the measured hole binding energy, $\varepsilon_k \propto k$ is the undressed hole energy as a function of k, and $\Sigma(k,\omega)$ is the complex many-body self-energy function. Essentially, $\mathrm{Re}\Sigma(k,\omega)$ is related to altered energies and $\mathrm{Im}\Sigma(k,\omega)$ increases the linewidth due to many-body interactions. Although $\Sigma(k,\omega)$ has additional contributions from electron-electron and electron-impurity scattering, these contribute only a few tens of meV or less to $\Sigma(k,\omega)$, a negligible contribution compared to the EPC contribution for our system.

Consider the interaction between the photohole and a single vibrational mode oscillating at frequency ω_0. While the situation is actually more complicated due to the presence of other surface and bulk vibrational modes, these occur at lower energy and their contributions appear to be small. Furthermore, we neglect the vibrational coupling between adsorbate atoms; this is a reasonable assumption for both H and D since their optical phonon bands show little momentum dependence [14]. Far below E_F, the photohole decays by creating a phonon quantum of energy $\hbar\omega_0$. In a detailed treatment for a δ-function-like phonon density of states, we find

$$\mathrm{Im}\Sigma(\omega \to -\infty, k) = \hbar\omega_0\lambda\pi/2\,, \tag{2}$$

where λ is the dimensionless electron-phonon coupling constant, which also appears in treatments of conventional superconductivity [15]. Consider the effect of adsorbate mass on state S_1. Provided that λ remains the same upon going from H to D, Eq. (2) predicts the linewidths should be reduced by $\sim\sqrt{2}$, which is approximately observed. Now consider the different behaviors of states S_1 and S_2 for constant adsorbate mass. While in normal calculations λ is an isotropically averaged quantity, here things are complicated by the varying degree of spatial overlap between the electronic wave function and the surface phonons. Consequently, the surface band S_2, which lies closer to the bulk band continuum and therefore has a greater degree of penetration into the bulk, should have a smaller coupling strength λ than state S_1. This explains the fact that the state S_2 appears much sharper [Fig. 2(c)] than state S_1 [Fig. 2(a)], even though the relevant phonon vibrational frequency ω_0 is the same for both bands.

We now estimate the EPC parameter λ from our data. The parameter λ impacts both the real and imaginary part of the electron-phonon self-energy, and thus can be determined in different ways. First, previous studies that focused on coupling to acoustic phonon states have estimated λ using the temperature dependence of the photoemission linewidth, which reflects $\mathrm{Im}\Sigma(k,\omega)$ [4,5]. This approach fails here because the adsorbate optical phonon energy is large and there is a negligible thermal excitation of the phonons at our temperature range. Indeed, the measured linewidths at 150 and 300 K are nearly identical. Second, we can apply Eq. (2) assuming $\omega_0^\mathrm{H} = 161$ meV. The observed linewidth of ~0.25 eV at high binding energy in Fig. 2(a) implies $\lambda \sim 0.5$, which is larger than the Fermi-surface-averaged value for bulk tungsten of 0.2 [16]. Third, $\mathrm{Re}\Sigma(k,\omega)$ renormalizes the hole velocity near E_F, $\hbar^{-1}\nabla_k\varepsilon_k$, by the factor $(1 + \lambda)$ [15]. Figure 3 shows intensity maps of the data from Figs. 2(a) and 2(b) together with the best-fit peak positions derived from least-squares fitting of the data in Fig. 3 to two peaks. The slopes of the branches near and far from E_F were extracted, and, equating their ratio with $(1 + \lambda)$, we find that $\lambda = 1.4 \pm 0.1$ and $\lambda \sim 0.8$ for band S_1 in the presence of H and D, respectively. As indicated by the horizontal dashed lines, these fits confirm that the dominant effect occurs at an energy scale very close to $\hbar\omega_0$ for the two cases. The discrepancy between the H and D coupling parameters might be due to the increased uncertainty in fitting the deuterium data or to the large anharmonicity of the potential well of the pseudo-three-fold adsorption site. For band S_2 in the presence of hydrogen, a small kink in the dispersion rate could be observed upon close examination of the spectra; from this we can roughly estimate $\lambda \sim 0.1$ for this band. No deviations or splitting could be observed for the bulk band B, or for the surface states S_1 and S_2 on the clean surface.

The estimates of λ for S_1 based on $\mathrm{Re}\Sigma(k,\omega)$ and $\mathrm{Im}\Sigma(k,\omega)$ are seen to be inconsistent. Moreover, fitting the raw spectra in Fig. 2 to spectral functions calculated using this simplified model have failed since the width of the peak at large ω and the modified dispersion at small ω cannot be simultaneously modeled with a single value for λ. This reflects directly the different values of λ deduced separately above. An interesting possible explanation is that the EPC strength is strongly ω dependent. This could result, for example, from the fact that the separation of the state S_1 from the bulk continuum [delineated by state B in Fig. 1] decreases as the band falls below E_F. The state becomes correspondingly less surface localized, and the coupling to adsorbate vibrations would then decrease, as was the case for S_2. We caution, however, that there are systematic problems with these estimates of λ. Equation (2) is based upon a very simplified representation of the phonon density of states and also neglects the different coupling strengths between various surface vibrational

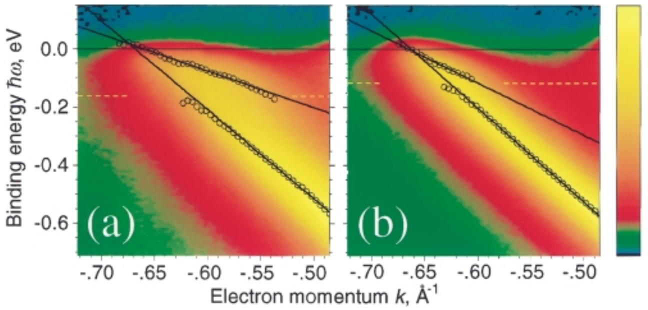

FIG. 3 (color). Intensity maps of band S_1 in the presence of (a) hydrogen and (b) deuterium. Also shown are the fitted positions to the two peaks (circles) and the best-fit lines through these data, as well as the known hydrogen and deuterium symmetric stretch vibrational energies ω_0 (horizontal dashed lines). From the slopes of these fitted lines one can derive the electron-phonon coupling parameters λ as discussed in the text.

modes and the hole state. For similar reasons, fitting the spectra to two peaks is also not technically correct since every prominent feature in the phonon density of states will lead to structure in $\mathrm{Re}\Sigma(k,\omega)$ and thus will split the spectral function into two branches.

Despite these uncertainties in how best to model our results, the data in Fig. 2 provide a kind of information that is directly relevant to surface chemical and physical processes. The basis for the strong EPC which we reported is the extreme sensitivity of the W(110) surface states' Fermi wave vectors k_F (and hence electronic occupation) to the density of H adsorbed [12]. Vibrational oscillations of the surface adlayer should therefore induce an oscillation in the Fermi surface dimensions, yielding low energy electron excitations near the Fermi level E_F [17]. While the exact details of the dynamic electronic response are very difficult to calculate for real surfaces, we expect that for sufficiently large vibrational energy scales, the electronic manifold lags the phonon motion, leading to dissipative forces. The imaginary part of the self-energy measures the rate at which energy is transferred from vibrational to electronic manifolds, and vice versa. For this system, the characteristic time, given by the inverse linewidth at large hole energy, is several femtoseconds, certainly very fast for a typical kinetic step in a thermal chemical reaction. To our knowledge, this is the first time angle-resolved valence band photoemission has been used to measure such information for an adsorbate system.

Another important implication of our results is the intriguing possibility of two-dimensional superconductivity, consisting of Cooper pairs confined to the surface, whose attraction is mediated by the adsorbate optical phonons. While this was predicted up to a critical temperature $T_c = 70$ K for the clean surface of Be [8], no superconducting energy gap at that surface has thus far been detected, down to temperatures as low as 12 K [7].

In contrast, the hydrogenated W(110) surface has an unusual combination of both a sizable coupling constant $\lambda \geq 0.5$ together with a larger phonon energy scale $\sim$161 meV, both larger than bulk tungsten, which might conceivably also lead to a surface superconducting at significantly higher T_c than for bulk W. This is reminiscent of the exceptional case of Pd, which remarkably goes from a nonsuperconductor to a superconductor with $T_c = 10$ K upon formation of bulk PdH [18]. The situation for H on W is especially unusual because for most systems, including hydrogen optical modes, λ and the phonon energy scale are inversely related [15], which is why conventional superconductivity is limited to such low T_c's. The reason for the enhancement of T_c for PdH is due to an anomalously low H optical vibrational frequency ($\hbar\omega \sim 40$ meV) [19]; no such enhancement was seen for other metal hydrides [20,21].

Using our measured electron-phonon coupling parameter, we can estimate a remarkable value of T_c in excess of 50 K in the strong-coupling limit [15]. This estimate of T_c for H on W is probably too high, due to suppression of T_c of a superconducting film near a nonsuperconducting substrate; however, this might be offset by the reduced coupling between surface and bulk electronic states [8].

To summarize, we reported the large electron-phonon coupling for H/W(110). We confirmed the effect by measuring the energy shift upon substitution of D for H, and by comparing the strength of the effect for bands with different degrees of surface localization. These results are an important aspect of energy dissipation of adsorbates by excitations of electrons in metal substrates, which should impact surface chemistry and kinetics.

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