Nonadiabatic Adsorbate Vibrational Damping and Surface Electronic Structure: H on W(001)

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Recent infrared-absorption measurements of the vibrations of hydrogen adsorbed on W(001) have provided unambiguous evidence for electronic damping of atomic vibrations on metallic surfaces. This is a simple example of nonadiabatic coupling of a discrete state to a continuum. We describe here selection rules and other criteria for nonadiabatic electronic damping of adsorbate vibrations and report the observation and characterization, using angle-resolved photoemission, of a surface resonance close to the Fermi level on H-saturated W(001) which satisfies these criteria.

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Determining the coupling between electrons and atomic vibrations of adsorbates and surfaces is of crucial importance in understanding energy transfer within the adsorbate-surface complex. Of particular interest is characterization of nonadiabatic processes within the complex since these govern damping of the atomic vibrations. This subject is of widespread interest since damping of vibrations via substrate electrons is a textbook example of the interaction of discrete states with a continuum. Recent infrared- (ir-) absorption measurements by Chabal of the vibrational modes of hydrogen adsorbed on W(001) have provided the first direct evidence for electron-hole damping of atomic vibrations on metallic surfaces.[1] It is deduced that the electrons responsible for the damping most likely reside in narrow surface states or resonances near the Fermi level (E_F).[1] We report here the direct observation, using high-resolution angle-resolved photoemission spectroscopy, of two hydrogen-induced surface resonances at E_F on the (H saturated) W(001)-2H surface. One of these resonances is ideally suited to couple to various hydrogen vibrational modes, but its symmetry is not that predicted by the ir measurements.[1] We propose an alternative vibrational-mode assignment which is supported by recent theoretical work.[2] Furthermore, the selection rules for the coupling of atomic vibrations to surface electronic states are clarified in the context of our photoemission results, and a discussion of the general problem of nonadiabatic coupling processes is presented.

In the ir spectra for W(001)-2H, only one absorption line (at 157.5 meV) shows the Fano-like asymmetry that is characteristic of electronic damping of a vibrational mode.[3] As was shown by Langreth,[3] the asymmetry arises from the interaction between the discrete atomic vibration of the H and a continuum of electron-hole pairs at E_F. The goal of this study was first to investigate the electronic structure of W(001)-2H using photoemission spectroscopy in order to characterize both the symmetry and the density of states of H-induced surface states near E_F, and then to use this information to understand more fully the nonadiabatic coupling of the atoms and electrons. The experiments to be discussed here were performed on beam line U4A at the National Synchrotron Light Source. The typical energy and angular resolutions used were less than 100 meV and 1°, respectively.[4] The tungsten crystal was cleaned by repeated cycles of annealing to 1100 K in O_2 and flashing to 2500 K. The H-saturated W(001) surface was obtained by exposing a clean W(001) surface to 10 L (1 L=1 langmuir$=1\times10^{-6}$ Torr sec) of H_2 at room temperature. All data presented here were taken with light incident at 45° to the sample normal.

Figure 1 shows photoemission spectra taken with 42-eV photons from the clean and the H-saturated W(001) surface. Both the light and the detector are in the (100) mirror plane of the surface, and the angle of the detector is such that states that exist at the $\bar{X}$ point in the surface Brillouin zone (SBZ) are being measured; the $\bar{X}$ point is defined in Fig. 1 and has $k_{\parallel}=1.0$ Å^{-1}. A well-defined emission feature approximately 0.2 eV below E_F is visible in the spectrum from the H-saturated surface. By moving the detector out of the mirror plane, the symmetry of these states can be determined; the H-induced feature is found to be predominantly even with respect to the (100) mirror plane. [Unless otherwise noted, the

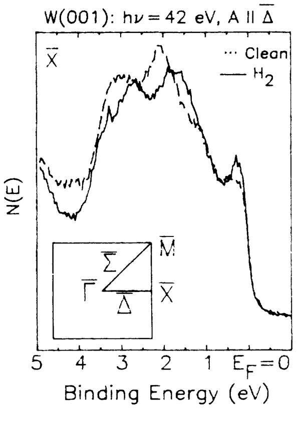

FIG. 1. Photoemission spectra taken with 42-eV photons from both the clean and H-saturated W(001) surface at the $\bar{X}$ point in the surface Brillouin zone ($k_{\parallel}=1.0$ Å^{-1}).

terms even and odd will refer to symmetry with respect to the (100) mirror plane throughout the rest of this paper.] The calculations of Papaconstantopoulos[5] for bulk W reveal that close to E_F at the $\bar{X}$ point there exists a band of even states but no odd states. Since the feature observed at $\bar{X}$ is of even symmetry, it is, in fact, a surface resonance; i.e., a two-dimensional state that overlaps bulk, three-dimensional states in both energy and momentum parallel to the surface. We will refer to the origin of the even emission feature seen at $\bar{X}$ on the H-saturated W(001) surface as the $\bar{X}$ resonance. That this resonance is indeed a two-dimensional state was verified by noting first its absence on the clean W(001) surface (Fig. 1), and more significantly by observing no dispersion of this feature as the photon energy was varied.[6] Dispersion with photon energy would indicate a dependence on the component of momentum perpendicular to the surface, which in turn indicates a three-dimensional state.[6] The intensity of the feature changed significantly with photon energy, being most intense at approximately 42 eV. Thus, a well-defined extrinsic resonance close to E_F is observed; however, its ability to couple nonadiabatically to atomic vibrations remains to be shown.

A significant requirement for effective nonadiabatic coupling between an electronic state and an atomic vibration is that there be a large density of electron states close to E_F. For example, Zhang and Langreth have recently published a comprehensive theory for nonadiabatic coupling in the W(001)-2H system which relies on a δ-function density of states (DOS) at E_F for the filled electronic levels.[2] Clearly, a δ-function DOS is not a physical reality. However, a two-dimensional state possesses a different type of discontinuity: In a two-dimensional periodic system the DOS is actually a constant ($=4\pi m^*/h^2$ for a free electron) close to the band edge, and is thus a step function. The two-dimensional DOS can be determined by measuring the two-dimensional dispersion of the state. Figure 2 shows the photoemission spectra obtained with 42-eV photons from both the clean and the H-saturated W(001) surface as the detector is moved to sample different parts of the surface Brillouin zone along the $\bar{\Delta}$ line around $\bar{X}$. The $\bar{X}$ resonance is seen to display only slight dispersion. It appears from above E_F at approximately $k_{\parallel}=0.5$ Å^{-1}, disperses slightly to reach a maximum binding energy of <0.2 eV at $\bar{X}$, and then moves above E_F in the second zone. As can be seen in Fig. 2, a large bulk feature moves close to E_F near $\bar{X}$ and swamps emission from the H-induced feature. This bulk feature disperses away from E_F in the second zone and the H-induced peak is again easily seen until it disperses above E_F. Based on the measured band minimum of 0.2 eV, it is clear that the two-dimensional DOS for the $\bar{X}$ resonance is large with respect to the total DOS at E_F of W; the height of this step function for the $\bar{X}$ resonance is approximately 2.0/eV atom(W), whereas the bulk density of states at E_F for W is 0.42/eV atom.[5] Note also that in this case the requirement of a large DOS close to E_F constrains the band minimum (or maximum) of the initial electronic state to be within E_v of E_F, where E_v is the energy of the vibration being damped, and also forces the band itself to be rather flat. A flat band indicates slow electrons, which are required to introduce the nonadiabaticity into the system.

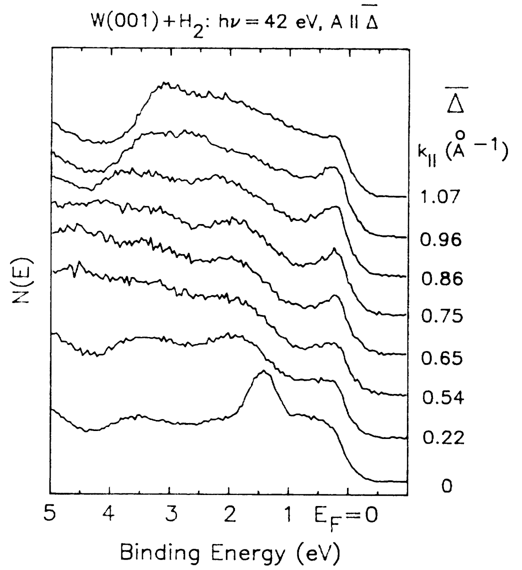

FIG. 2. Photoemission spectra from W(001)-2H taken with 42-eV photons incident parallel to the (001) mirror plane. The detector was also in the (001) plane, and set at angles corresponding to the $k_{\parallel}$ vectors shown.

The initial state of the system in the vibrational-damping problem consists of a hydrogen atom in an excited vibrational state and an occupied hydrogen-induced electronic surface resonance just below E_F. The final state is a hydrogen atom in the vibrational ground state and an occupied bulk electron state just above E_F. The transition from the initial to the final electron state is explicitly interband in the absence of free-carrier scattering.[2] The vibrational wave vector q is zero for an infrared excitation, and must conserve $k_{\parallel}$ in the electronic transition (i.e., the electronic transition is vertical in parallel momentum). Intraband transitions were considered previously to play a role in the damping,[1] but these are clearly forbidden for vertical transitions. Transitions from one surface state to another are also forbidden since, due to spin-orbit interactions, no two bands can come close enough in energy to allow the transition to occur. The atomic vibration and the initial and final electronic states have to satisfy a simple selection rule in order that coupling occur. Specifically, if a mode is even (odd) with respect to a mirror plane of the surface, then the product of the initial and final electronic states must be even (odd) for the coupling to be nonzero. Quite generally then, the initial electronic state has to satisfy two main criteria for a strong breakdown of vibrational adiabaticity to occur; it has to satisfy the selection rule detailed above and have a large DOS close to E_F. We have shown that the $\bar{X}$ resonance satisfies the second of these criteria, but to test the first requires that we discuss specifically the details of the experiment of Chabal.[1]

There exists a basic ambiguity about the identification of the lone vibrational mode that is observed by Chabal[1] to display electronic damping.[2] There are three zone-center acoustic vibrational modes for this system: the symmetric stretch, the asymmetric stretch, and the wag mode;[7,8] the first is a H vibration perpendicular to the surface, and the latter two are parallel to the surface. All these modes have been measured using electron energy-loss spectroscopy (EELS); the symmetric stretch is observed at 130 meV, the asymmetric stretch at 160 meV, and the wag at 80 meV.[7,8] The 157.5-meV absorption in the grazing-incidence ir spectra was not assigned to the asymmetric stretch since, being parallel to the surface, this mode is not dipole allowed;[1] instead, it was assigned to the first overtone of the wag mode, which has a component perpendicular to the surface.[9] This assignment leads to a paradox since it implies that the overtone of the wag should also be visible in dipole EELS; only the symmetric stretch at 130 meV is in fact seen.[7,8] A resolution was offered by Reutt, Chabal, and Christman,[10] who proposed that the overtone of the wag mode couples strongly to the small parallel component of the electric field in the grazing-incidence ir experiment. Since the parallel component of the electric field is strictly zero in the dipole EELS experiment, the mode would thus remain unobserved in EELS. However, Zhang and Langreth[2] have pointed out that this coupling to the parallel field is only allowed if the surface has no reflection symmetry (i.e., is disordered). Furthermore, if the parallel electric field is a significant factor, then the asymmetric stretch should also be visible in the ir spectra, with no surface disorder required. Thus the possibility exists that the mode at 157.5 meV is the asymmetric stretch and indeed the large intensity of the mode at 157.5 meV relative to that of the symmetric stretch at 130 meV favors the identification of this mode as a fundamental rather than an overtone.[2]

One significant difference between the wag and asymmetric stretch modes is that the former is of odd symmetry and the latter even. From the selection rule discussed above, it is clear that for nonadiabatic coupling to occur, the final electronic state is required to be of the same symmetry as the initial state for an even vibration, and to be of opposite symmetry if the vibration is odd. Thus if the $\bar{X}$ resonance is the initial state in the damping transition and is even, then the final bulk state must be odd if the vibration is odd (wag), and even if the vibration even (asymmetric stretch). There are no bulk states of odd symmetry with respect to the (001) mirror plane close to E_F at $\bar{X}$. Thus the vibration is constrained to be even with respect to (001) if it is to couple to the $\bar{X}$ resonance (and by default the initial state must be a resonance rather than a state). Consequently, the $\bar{X}$ resonance can be responsible for the electronic damping of the 157.5-meV mode only if that mode is identified as the asymmetric stretch. Thus, based on the ideal nature of the $\bar{X}$ resonance described here and the acknowledged ambiguity in the assignment by Chabal[1] of the 157.5-meV mode to the overtone of the wag, we propose that this mode be assigned instead to the asymmetric stretch, observed at 160 meV in EELS.[7,8]

A second H-induced resonance close to E_F was also observed. With the crystal oriented with the light incident in the (110) mirror plane ($\bar{\Sigma}$ direction), a feature 0.5 eV below E_F was visible in the normal-emission spectrum ($k_{\parallel}=0$, $\bar{\Gamma}$ point). This feature dispersed towards E_F along the $\bar{\Sigma}$ direction, crossing at approximately 0.33 Å^{-1}. It does not lie in a projected bulk band gap and is thus a resonance. The binding energy at $\bar{\Gamma}$ of this resonance (0.5 eV) is over 3 times the energy of the 157.5-meV vibration. The density of states is considerably less than that of the $\bar{X}$ resonance, and the dispersion is greater, indicating much faster electrons at E_F than in the $\bar{X}$ resonance. The $\bar{\Gamma}$ resonance is predominantly odd and calculations indicate that there exist even bulk states close to E_F at $\bar{\Gamma}$.[5] Thus this resonance has the correct symmetry (and available final states) to couple with the wag mode (since the wag mode is odd), but fails to satisfy the other criteria for effective interaction with a vibrational model. Consequently, while states exist near E_F of correct symmetry to couple to both the wag and the asymmetric stretch, the latter display many more of the characteristics necessary to interact with adsorbate vibrations. Assignment of the 157.5-meV mode to the asymmetric stretch remains logical.

To summarize, we have studied the H-saturated W(001) surface using photoemission spectroscopy in order, first, to characterize the nature of H-induced surface states close to E_F and, second, to use this knowledge of the electronic structure to understand more fully nonadiabatic electronic damping of adsorbate vibrations. Such damping has been unambiguously identified by Chabal in this system using ir spectroscopy.[1] The criteria for a filled electronic state to participate in the strong breakdown of vibrational adiabaticity were identified as, first, a symmetry that allows it to couple both to the vibration and to empty electronic states in the bulk continuum, and, second, the possession of a large DOS close to E_F. We have identified a hydrogen-induced surface resonance within 0.2 eV of E_F at the $\bar{X}$ point in the surface Brillouin zone that satisfies these criteria. However, the vibrational mode observed to be damped in the ir spectra must be assigned to the asymmetric stretch to couple to this state. This assignment is in agreement with a recent theory of nonadiabatic coupling in this system,[2] but is not the assignment originally made by Chabal.[1]

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