Electronic Damping of Adsorbate Vibrations on Metal Surfaces

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First-principles calculations of the vibrational lifetime of atomic and molecular hydrogen adsorbed on metal surfaces due to excitation of electron-hole pairs in the substrate are reported. The calculated electronic contribution to the vibrational linewidth compares favorably with experimental observations. A correlation is demonstrated between enhanced damping rate and the passage of an adsorbate-induced resonance through the Fermi level.

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Energy relaxation of an excited adsorbate is an important phenomenon in chemical reactions and other dynamical processes at surfaces. The electron-hole pair is a characteristic elementary excitation of metal substrates. A matter of controversy, in particular addressed in the context of sticking,[1] is the extent to which this type of excitation provides an important channel for energy transfer.

In recent years it has been possible by infrared reflection spectroscopy and related techniques to resolve the inherent linewidth of vibrational resonances of adsorbed species on metal surfaces.[2-4] Qualitative arguments have been put forth that broadening of the observed high-frequency vibrational modes, i.e., modes with a frequency above the bulk phonon band, should be dominated by energy transfer to electron-hole pairs instead of phonons.[5,6]

In this Letter we report the first *ab initio* calculations of the electronic mechanism for lifetime broadening of vibrationally excited adsorbates.[7] With applications to the hydrogen atom and molecule chemisorbed on free-electron-like metal surfaces we show that electronic damping is important, giving lifetimes typically of the order 10^{-13}–10^{-12} s. Calculated linewidths compare favorably with observed ones. Enhanced damping rates are shown to correlate with adsorbate-induced resonant electron states near the Fermi level. In addition, contact is made with a simple phase-shift formula for vibrational lifetimes, which should be useful for estimates of lifetimes of other adsorbates.

The electronic mechanism for lifetime broadening has earlier been treated in a few different models. The linewidth of the stretch mode of CO adsorbed on Cu(100), measured to be 0.5 meV,[4] has been shown not to be accounted for in a physisorption model but to be well accounted for in a Newns-Andersson–type model for the electronic structure of the chemisorbed molecule.[8] The calculation of Brivio and Grimley[9] gives a valuable first estimate, which would, however, benefit from the addition of screening of the field from the vibrating proton and of a more elaborate description of the electrons.

We have adopted the formalism for calculating broadening of vibrational modes developed in the field of electron-phonon interactions in metals.[10] In technical terms, the density-density response kernel that constitutes the self-energy of the vibrational mode is calculated to the lowest order in the screened ion-electron interaction. The electronic ground state is then treated in the density-functional scheme with the local-density approximation for the exchange-correlation potential. For weak nonadiabatic coupling the line shape of the vibrational resonance is a Lorentzian, and the mode is consequently lifetime broadened with a full width at half maximum Γ. In the quasistatic regime the following expression can be derived for the broadening[11]:

$$\Gamma = \frac{2\pi\hbar^2}{M} \sum_{\substack{\vec{k}',\vec{k} \\ \epsilon_{\vec{k}'}=\epsilon_{\vec{k}}=\epsilon_F}} \left| \int d^3x\, \psi_{\vec{k}'}(\vec{x}) \frac{\partial V}{\partial Q}(\vec{x}) \psi_{\vec{k}}(\vec{x}) \right|^2 . \tag{1}$$

The one-electron wave function $\psi_{\vec{k}}(\vec{x})$ with wave vector $\vec{k}$ and energy $\epsilon_{\vec{k}}$ and the derivative of the total one-electron potential $\partial V/\partial Q(\vec{x})$ with respect to the vibrational coordinate Q are ground-state quantities. The factor 2 comes from spin degeneracy.

Already from Eq. (1) several general physical conclusions can be drawn that should be useful in the experimental verifications of the electronic damping mechanism. The most prominent features are the dependence of Eq. (1) on the reduced mass M of the vibrational mode and the absence of the vibrational frequency. This introduces an isotope effect, as has been observed experimentally for methoxide adsorbed on copper.[5]

A striking fact is that no Bose-Einstein distribution factors for thermally activated electron-hole pairs appear in Eq. (1), causing a negligible temperature dependence of the broadening. This behavior should be quite different from the rather strong temperature dependence expected for the broadening due to multiphonon processes, in analogy with results for impurity-mode broadening in solids.[12]

In addition to a light mass M, a large matrix element in Eq. (1) will also enhance the damping rate. The strength of the coupling $\partial V/\partial Q$ depends sensitively on the character of the field that perturbs the electrons, e.g., the range being more extended for a dipole than for a quadrupole field, and on the effectiveness of the screening by the conduction electrons. The latter certainly limits the range of the field from the vibrating nuclei. Therefore the local electronic structure should influence the magnitude of the matrix element. For instance, an adsorbate-induced resonance at the Fermi energy causes locally a large amplitude of the wave functions in the matrix element and should consequently be favorable for strong damping.

The lifetime broadening has been evaluated from expression (1) with ground-state quantities calculated in the embedding scheme of Gunnarsson and Hjelmberg.[13] This scheme is based on the fact that the screening by the conduction electrons effectively limits the range of the perturbation by the adsorbate. For this reason the perturbed quantities, e.g., the one-electron potential, are expanded in a finite basis set of localized functions $|n\rangle$ centered on the adsorbate. To account for the continuous spectrum of one-electron states and the screening properties of the substrate, the semi-infinite jellium model has been used.

Within the embedding scheme, Eq. (1) can be reexpressed in the following way[11]:

$$\Gamma = (2\pi\hbar^2/M)\operatorname{Tr}\{WW\}, \qquad (2)$$

where

$$\langle n|W|n'\rangle = \textstyle\sum_m \langle n|\rho(\epsilon_F)|m\rangle\langle m|\partial V/\partial Q|n'\rangle.$$

Here Tr stands for the trace over the finite basis set, $\langle n|\rho(\epsilon_F)|m\rangle$ is the total one-electron density of states at the Fermi energy, and $\langle m|\partial V/\partial Q|n\rangle$ is the derivative of the one-electron potential projected on the local basis functions.

A general expression for the damping rate of a vibrating atom in a homogeneous electron gas can be derived from Eq. (1),[11]

$$\Gamma_{\text{hom}} = \frac{3\hbar^2}{Mr_s^{\,2}}\left(\frac{4}{9\pi}\right)^{1/3} \sum_{l=0}^{\infty}(l+1)\sin^2(\delta_{l+1}-\delta_l), \qquad (3)$$

where δ_l are scattering phase shifts at the Fermi energy ϵ_F and r_s is the electron density parameter $(4\pi r_s^{\,3}/3 = 1/n)$. This expression is closely related to the Gaspari-Gyorffy formula for the electron-phonon coupling constant[14] and related expressions for the stopping power of atoms[15] and the impurity resistivity.[16] The full drawn curve in Fig. 1 gives Γ_{hom} for hydrogen in jellium for different r_s values from Eq. (3) using phase-shift data.[17] The calculated values from Eq. (2) for hydrogen located far inside the jellium surface are also depicted in Fig. 1. As Eqs. (2) and (3) have a sensitive dependence on the details of the potential and as the approach of Ref. 17 differs from the present one, the agreement should be considered good enough to demonstrate that the embedding scheme is appropriate for calculating vibrational lifetimes.

With this method we have studied two adsorbates, the hydrogen molecule and atom, chemisorbed on jellium surfaces representing free-

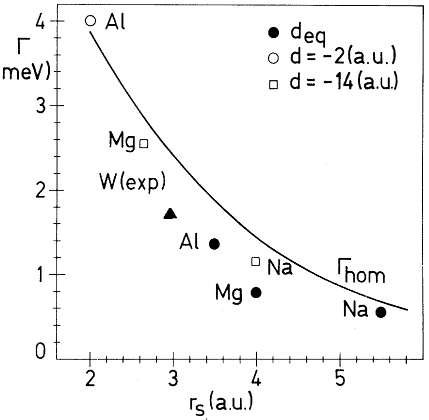

FIG. 1. Damping rate Γ for the vibration of a hydrogen atom perpendicular to a jellium surface as a function of the local electron density parameter r_s. The solid line is the result for the homogeneous electron gas [Eq. (3)]. Indicated points are calculated within the embedding scheme [Eq. (2)], except for the triangle which is an experimental observation for H/W(100) (Ref. 2) with an effective r_s value assigned according to Ref. 21. The parameter d is the distance between the proton and the jellium edge.

electron–like metal surfaces, such as Al, Mg, and Na. The adsorbate-induced electronic structures behave qualitatively differently in the two cases. Upon approach to the metal surface the antibonding orbital $2\sigma^*$ of the free-hydrogen molecule is shifted downward and broadened into a resonance when overlapping with the substrate conduction band.[18] For a hydrogen atom immersed in a homogeneous electron gas of metallic densities, a bound state exists just below the bottom of the conduction band.[19] The electronic structure for the hydrogen atom adsorbed in the surface region can be interpreted in terms of a bound state just below the local band bottom, defined by the one-electron potential, which is broadened into a resonance when interacting with the substrate conduction band.[20]

We have calculated the lifetime broadening of the stretch mode in the hydrogen molecule chemisorbed on the jellium surface in the geometry shown in Fig. 2(a). The broadening shows a strong variation with the distance d from the jellium edge, which at first sight correlates with the variation of the electron density in the surface region, as understood from comparing Figs. 2(a) and 2(b). There is a dramatic increase in the damping rate when the hydrogen molecule is forced inside the jellium edge, however, particularly in the case of Na. This behavior can be understood physically from the fact that the dominant contribution to the field $\partial V/\partial Q(x)$ comes from a region close to the hydrogen molecule. Thus according to Eq. (1), the damping rate is sensitive to the local electronic structure at the Fermi level. Figure 2(c) shows schematically how the antibonding resonance crosses the Fermi level further inside the jellium edge in Na than that in Mg, which correlates well with the strong enhancement in the damping rate. This correlation, anticipated in Ref. 8, means that damping of adsorbate vibrations should be added to the list of phenomena for which the passage of an antibonding adsorbate resonance through the Fermi level is a key concept, other such phenomena being shifts in adsorbate vibrational frequency, bond breaking, and sticking.[1]

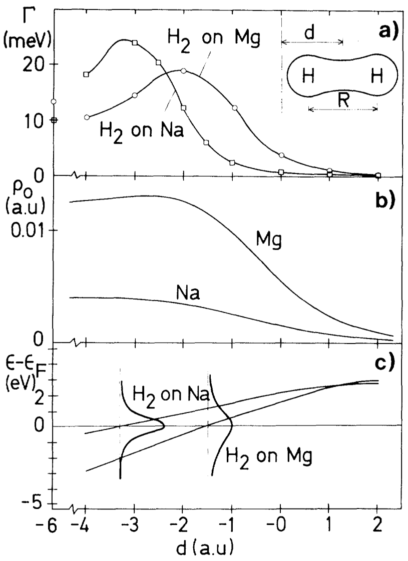

FIG. 2. (a) Damping rate Γ for the hydrogen molecule as a function of the distance d from the jellium edge of jellium surfaces representing Na and Mg, respectively. The configuration of the hydrogen molecule used in the calculation is also depicted ($R = 1.4$ a.u.). (b) The free-surface electron density profiles of Na and Mg in the jellium model. (c) The position of the adsorbate-induced resonance $2\sigma^*$ for the hydrogen molecule as a function of the distance d from the jellium edge and the corresponding width when crossing the Fermi level.

Lacking experimental data for molecularly adsorbed hydrogen we have to limit ourselves to a rough comparison with existing data for CO on Cu(100), based on some similarities in the electronic structure.[18] Scaling the value for the damping rate of the vibrating hydrogen molecule [H_2 on Mg for $d = 1$ a.u. in Fig. 2(a)] according to the mass ratio would give the value 0.1 meV for the broadening of the stretch mode. This is of the same order of magnitude as the experimentally observed linewidth 0.5 meV.[4]

For the hydrogen atom we have calculated the lifetime broadening of the vibrational mode normal to the surface. The results are shown in Fig. 1 both for the equilibrium positions on three different jellium surfaces[20] and for some other positions. The r_s values chosen correspond to the local densities of the free surface at the position of the proton. A striking fact is the fair agreement between the calculated values in the surface region and the results from the homogeneous electron gas. This correlation can be understood from the similarities in the electronic structure and effectiveness of the screening. Hence Eq. (3), with the use of phase-shift data,[17] can in a simple way provide useful estimates of vibrational lifetimes of a large number of adsorbates. The calculated values and the inferred correlation with Γ_{hom} agree well with the experimentally observed linewidth (2.3 meV) of the vibrational mode of H on W(100).[2] The r_s value has been chosen in accordance to an effective medium scheme recently developed by Nørskov.[21] The linewidth observed for hydrogen vibrational modes in CH_3O on Cu(100) have a similar size (2 meV).[3]

In conclusion, *ab initio* calculations of the lifetime broadening of vibrational modes of light adsorbates on metal substrates have shown the electron-hole pair mechanism to give an important contribution to the experimental linewidth. The damping rate is shown to correlate with the local density of the conduction electrons, for systems with undramatic electron structure near the Fermi level. This suggests a simple method for estimates for other adsorbates. Adsorbates inducing resonant electron states at the Fermi level relating to the vibrational mode should have an enhanced damping rate.

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