# Electron-hole-pair damping of an excited state of a molecule adsorbed on a metal surface

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We present a theory of the lifetime of a vibrational excited state of a molecule adsorbed on a metal surface due to creation of electron-hole pairs at the surface. Our formulation treats the dynamical response of the electron gas at the surface exactly in the random-phase approximation. The Lang-Kohn electron density profile at the surface is used. The molecule is modeled as a two-level system whose dynamic dipole moment is enhanced relative to its gas-phase value by the adsorption process. Explicit results are given for the C–O stretch vibration for CO adsorbed on Cu(100). The calculated value of the lifetime accounts for the order of magnitude of the experimental lifetime. A comparison is made with previous theoretical work. We consider the dependence of the transition rate on the diffusivity of the electron density profile at the surface by comparing the transition rates obtained with use of the Lang-Kohn and infinite-barrier-model profiles.

## **INTRODUCTION**

Improvements in the experimental techniques (infrared spectroscopy) have recently produced the first few measurements<sup>1-4</sup> of the intrinsic linewidths of vibrational excited states of molecules adsorbed on a metal surface. Thus a comparison of the relative importance of the various mechanisms available for the relaxation of excited states of adsorbed molecules is a timely exercise. Clearly, a meaningful theoretical statement about the relevance of a given decay mechanism (coupling to phonons, electronhole pairs, etc.) can only be made via detailed computation of the lifetime of the molecular excited state for a model that accounts as fully as possible for the physics of the coupled system.

For frequencies less than twice the maximum phonon frequency of the substrate, Ariyasu *et al.*<sup>5</sup> have recently given detailed results for the magnitude and temperature dependence of vibrational linewidths for several adsorbate-substrate systems due to two-phonon emission processes. This mechanism (mediated by anharmonicity in the molecule—substrate bond) gives sizable linewidths, and in the case of the C—Ni stretch vibration for CO adsorbed on Ni it yields a value of the linewidth in excellent agreement with experiment (the theoretical<sup>5</sup> and experimental<sup>4</sup> values are 13.9 and 15.1 cm<sup>-1</sup>, respectively).

For frequencies several times higher than twice the maximum phonon frequency of the substrate, relaxation by creation of electron-hole pairs (EHP) at the metal surface is expected to dominate over multiphonon emission processes. It is this regime that we consider in this paper.

The purpose of this paper is twofold. First, we present a calculation of the lifetime of an excited state of an adsorbed molecule due to the excitation of EHP at the surface in which the screening response of the EHP is treated exactly in the random-phase approximation (RPA),<sup>6</sup> and with the use of a realistic electron density profile at the surface, namely the Lang-Kohn profile.<sup>7</sup> Second, for the commonly studied case of the C–O stretch vibration for CO adsorbed on a copper surface, we correlate the results obtained in the present work with previous theoretical work<sup>8-12</sup> and with experiment.<sup>1</sup> This comparison is important in view of the statement made at the outset, and because of the rather large spread in the calculated values of the lifetime.<sup>8-12</sup> In light of our results, some statements made about the damping mechanism considered in this paper appear unwarranted.<sup>10,11</sup>

The damping of a vibration of an adsorbed *atom* due to its coupling to the EHP at the surface is briefly considered in an appendix. In it we present results for the lifetime of the vibration of an H atom perpendicular to the surface of a nearly-free-electron metal.

## TRANSITION RATE

We consider a vibrational excited state of a molecule,  $|B\rangle$ , which has an allowed dipolar transition to the ground state  $|A\rangle$ , with matrix element

$$\vec{\mathbf{p}} \equiv \langle A \mid \vec{\mathbf{p}}_{\rm op} \mid B \rangle , \qquad (1)$$

where  $\vec{p}_{op}$  is the dipole-moment operator. As shown schematically in Fig. 1, the molecule is embedded in the tail region of the electron density profile  $n_0(z)$  (z denotes the coordinate normal to the surface). If the molecule is



FIG. 1. The physical system considered in the present work (schematic).

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physisorbed on the surface, one has that  $p \equiv |\vec{p}| = p_0$ , where  $p_0$  is the gas-phase value of the dipole moment. If the molecule is *chemisorbed*, it is found experimentally that  $p > p_0$ . For example, for the C–O stretch mode of CO adsorbed on Cu(100), Ryberg<sup>1</sup> has determined that  $p=2.5p_0$ . The explanation of this enhancement of the dynamic dipole moment with chemisorption is thought to be as follows.<sup>1,11</sup> From the fact that the frequency of the C-O stretch mode is shifted downward with adsorption, one concludes that the shifted and broadened antibonding  $2\pi^*$  orbital of the gas phase is partially occupied, i.e., the orbital straddles the Fermi level of the substrate. When the molecule vibrates this broadened orbital oscillates up and down in energy about the Fermi edge, and this gives rise to an oscillatory transfer of charge between the substrate and the molecule, which in turn enhances the dipole moment.

We take the phenomenological viewpoint that the adsorption process is accounted for by this enhancement of the dipole moment; its experimental value is used in the numerical calculations. The Hamiltonian for the molecule-surface interaction is then given by

$$\hat{H}_{\rm int} = -e \int d^3x \hat{n}(\vec{x}) \phi_{\rm dip}(\vec{x}) , \qquad (2)$$

where e is the magnitude of the electron charge,  $\hat{n}(\vec{x})$  is the density operator for the substrate electrons, and

$$\phi_{\rm dip}(\vec{x}) = \frac{\vec{p} \cdot (\vec{x} - \vec{x}_1)}{|\vec{x} - \vec{x}_1|^3}, \qquad (3)$$

where  $\vec{x}_1$  is the position of the center of mass of the molecule.

We denote by  $|I\rangle$  and  $|F\rangle$  two eigenstates of the Hamiltonian for the *interacting* electron gas, with  $E_I$  and  $E_F$  the corresponding energies. We consider an event in which the molecule undergoes a transition described by the matrix element given by Eq. (1) while the electron system undergoes a transition from the state  $|I\rangle$  to the state  $|F\rangle$ . From the golden rule of perturbation theory we have that the probability for such an event is given by

$$P(B; I \to A; F) = \frac{2\pi}{\hbar} |\langle F | \hat{H}_{int} | I \rangle |^{2} \delta(E_{F} - E_{I} - \hbar\omega) , \qquad (4)$$

where  $\hbar \omega$  is the energy of the molecular excited state  $|B\rangle$  relative to the ground state  $|A\rangle$ .

The transition rate  $\Gamma_{BA}(\omega)$  is obtained by summing Eq. (4) over all final states  $|F\rangle$  and over all initial states  $|I\rangle$ ,

the latter weighted with the usual statistical factor that gives the probability that the substrate is initially in the state  $|I\rangle$ . Formally, we have

$$\Gamma_{BA}(\omega) = Z^{-1} \sum_{F,I} e^{-\beta(E_I - \mu N)} P(B; I \to A; F) , \qquad (5)$$

where  $\mu$  is the chemical potential, N is the number of electrons, Z is the partition function, and  $\beta = 1/k_B T$ . (The limit T=0 K is taken at the end.) Proceeding in a standard way (the central steps in the derivation are outlined in Appendix A), we arrive at the result that

$$\Gamma_{BA}(\omega) = -\frac{2e^2}{\hbar} \\ \times \int d^3x \int d^3x' \phi^*_{dip}(\vec{x}) \operatorname{Im} \chi(\vec{x}, \vec{x}\,' | \, \omega + i\eta) \\ \times \phi_{dip}(\vec{x}\,') , \qquad (6)$$

where we have introduced the density response function  $\chi(\vec{x}, \vec{x}' | \omega + i\eta)$ , giving the electron density response to an external longitudinal field<sup>6,13</sup> (in the present case, the dipole potential). We note that  $\Gamma_{BA}(\omega)$  depends on the position of the molecule through the dependence on  $\vec{x}_1$  of the dipole potential  $\phi_{dip}(\vec{x})$  given by Eq. (3).

Equation (6) is a general result for the transition (or damping) rate associated with the coupling Hamiltonian given by Eq. (2). We note that Eq. (6) could also be the basis for the study of a higher-frequency transition involving an *electronic* excited state of the molecule. In that case Eq. (6) treats the surface-plasmon decay channel on the same footing with the EHP channel.

## **RESULTS AND DISCUSSION**

In the present work the transition rate  $\Gamma_{BA}(\omega)$  is obtained using the jellium model for the substrate periodic background. This is a good approximation for a nearlyfree-electron substrate such as aluminum. It is also a reasonable approximation for the case of CO adsorbed on a copper surface, since for the C–O stretch mode one has that  $\hbar\omega = 0.25$  eV, and the copper *d* bands lie 2 eV below the Fermi level. The use of the jellium model allows us to introduce the reduced density response function<sup>6,13</sup>  $\chi(q_{\parallel}, \omega | z, z')$ , defined as the two-dimensional (2D) Fourier transform of  $\chi(\vec{x}, \vec{x}' | \omega)$  (here  $q_{\parallel}$  is a 2D wave vector in the plane of the surface). The transition rate  $\Gamma_{BA}(\omega)$  is given in terms of  $\chi(q_{\parallel}, \omega | z, z')$  by the equation

$$\Gamma_{BA}(\omega) = -\frac{4\pi e^2}{\hbar} p_z^2 \int_0^\infty dq_{||} q_{||} \int_0^d dz \int_0^d dz' \Lambda(q_{||} | z - z_1) \Lambda(q_{||} | z' - z_1) \operatorname{Im} \chi(q_{||}; \omega + i\eta | z, z') ,$$
(7)

where we have made the definition

$$\Lambda(q_{||}|z-z_1) = e^{-q_{||}|z-z_1|} \operatorname{sgn}(z-z_1) .$$
(8)

In Eq. (7) we have set  $\vec{x}_1 = (0,0,z_1)$  and  $\vec{p} = (0,0,p_z)$ , i.e., the molecule has been placed on the z axis and its di-

pole moment has been directed normal to the surface. [Both infrared spectroscopy (IRS) and near-specular electron-energy-loss spectroscopy probe only the vibrational motion of the adsorbate normal to the surface.] The domain of integration of the spatial integrals in Eq. (7) is the metal interior. The length d will be defined shortly. Note that a finite imaginary part of

 $\chi(q_{||};\omega+i\eta | z,z')$  ( $\eta$  is a positive infinitesimal) corresponds to the excitation of electron-hole pairs at the surface.<sup>14</sup>

The transition rate  $\Gamma_{BA}(\omega)$  was computed with use of the density response function  $\chi(q_{\parallel}; \omega | z, z')$  obtained recently by the present author<sup>6</sup> within the RPA. In Ref. 6 the RPA integral equation for  $\chi(q_{\parallel};\omega \mid zz')$  is solved for a substrate of finite thickness (denoted by a) using a double-cosine Fourier-series representation for  $\chi(q_{\parallel};\omega \mid z,z')$ . In this representation the spatial integrals in Eq. (7) are elementary. The thickness d introduced in Eq. (7) is given by  $d = a + 2z_0$ , where  $z_0$  is the distance from each edge of the jellium slab to the point where the electron density profile  $n_0(z)$  is assumed to vanish.<sup>6,13</sup> The value of  $z_0$  must be chosen large enough that the physical results are insensitive to the actual value used. (We note that the computer time increases rather rapidly<sup>13</sup> with  $z_0$ .) In the present problem the choice  $z_0 \sim 1.5 a_0$  is adequate,  $a_0$  being the lattice constant of the substrate. Similarly, the thickness a must be sufficiently large that the results for  $\Gamma_{BA}(\omega)$  correspond to the usual experimental situation in which the molecule is adsorbed on a thick (semi-infinite) substrate. For frequencies in the electronvolt range and below it was found that one needs a > 15atomic layers.15

The basic input used in the computation of the kernel of the integral equation for the response function is the set of self-consistent wave functions and energy eigenvalues obtained solving the Kohn-Sham-Lang ground-state problem.<sup>7</sup> This problem was solved according to the scheme given in Ref. 13. Note that the molecule is thus embedded in the Lang-Kohn electron density profile at the surface. Below we shall also give results obtained for a simpler model of the ground state in which the electrons are confined solely by infinite potential walls placed at a distance  $z_0 = 3\pi/8k_F$  from the jellium edges ( $k_F$  being the Fermi wave vector). The corresponding (non-self-consistent) wave functions are simply sine waves. This is the infinite-barrier model<sup>16</sup> (IBM), which has been used in the present context by Persson and Persson.<sup>8</sup> In fact, a comparison of the transition rates obtained with the Lang-Kohn and IBM density profiles serves as a separate motivation for the present work, in view of the recent interest in the subject of boundary effects on electron scattering, transition rates, and optical absorption in both planar<sup>17</sup> and spherical<sup>18</sup> geometries.

For definiteness, let us consider the C–O stretch mode of CO adsorbed on Cu(100). For this system the experimental parameters needed by our formulation are known: one has that  $p_z = 0.25$  D,  $\hbar\omega = 0.25$  eV (both quantities are known from IRS work<sup>1</sup>), and the adsorption site (known from LEED measurements<sup>19</sup>) is located at  $z_1 = 1.6$  Å outside the jellium edge. In our numerical calculations, carried out as outlined above, we used a jellium substrate with the bulk density of Cu and a thickness equal to 15 atomic layers of Cu in the (100) direction. For the present system we obtained a lifetime

$$\tau \equiv \frac{1}{\Gamma_{\rm BA}} = 9 \times 10^{-12} \text{ sec} . \tag{9}$$

The physical significance of this result is better analyzed by placing it in the context of previous theories<sup>8-12</sup> and experiment.<sup>1</sup> This is done in Table I, which we now comment on. Persson and Persson<sup>8</sup> carried out an IBM calculation of the lifetime, and obtained  $\tau = 100 \times 10^{-12}$  sec. Since these authors used the gasphase value of the dipole moment, using the adsorptionenhanced value ( $p=2.5p_0$ ) would give  $\tau = 16 \times 10^{-12}$  sec. Kozhushner *et al.*<sup>9</sup> report an approximate calculation of  $\tau$ for a finite-step model of the surface. They obtain  $\tau \cong 20 \times 10^{-12}$  sec. Apell<sup>10</sup> gives an estimate of  $\tau$  using a smooth potential barrier at the surface. He suggests that  $\tau \cong 5 \times 10^{-12}$  sec.

The above three papers share the spirit of the present work in that they deal with the *dynamical* screening of a vibrating dipole by the electron gas at the surface. The work of Persson and Hellsing<sup>12</sup> is an *ab initio* calculation of the EHP mechanism along a different approach. Persson and Hellsing express the damping rate as an in-

Author	Method	Lifetime $\times 10^{-12}$ sec
B. Persson		
M. Persson	IBM	100
( <b>Ref.</b> 8)		
Kozhushner et al.	Finite-step	20
(Ref. 9)	barrier	
Apell	Smooth barrier	5
( <b>Ref.</b> 10)		
M. Persson		
Hellsing	Embedding	6.6
( <b>Ref.</b> 12)		
Ryberg	Experimental	1.3
( <b>Ref.</b> 1)	IRS	
Present	BBA IBM	19
work	Lang-Kohn	9

TABLE I. Lifetime of the C-O stretch vibration of CO adsorbed on a copper surface.

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tegral over the derivative of the *static* one-electron potential of density-functional theory with respect to the vibrating coordinate. This potential is computed using the embedding approach to chemisorption,<sup>20</sup> which incorporates the adsorbate self-consistently with the continuum of electron states of the substrate. The value of  $\tau$  they obtain is  $\tau = 6.6 \times 10^{-12}$  sec, which, while of the same order of magnitude as the experimental value,<sup>1</sup> differs from it by a factor of 5. In spite of the *ab initio* nature of the calculation of Ref. 12, one should bear in mind that from the point of view of the electron gas it is basically a groundstate calculation that is being applied to a rather highfrequency vibration of a light adsorbate. Thus one would expect that the work of Ref. 12 is susceptible to improvement.

Before turning back our attention to our result given by Eq. (9), we would like to single out for comment two important points in connection with the work just reviewed. (i) It is stated in Ref. 11 that the EHP mechanism considered in the present paper gives rise to a damping rate that is so small as to be irrelevant. This statement obviously originates in the value  $\tau = 100 \times 10^{-12}$  sec quoted above.<sup>8</sup> It is then argued that only a calculation such as the embedding calculation of Ref. 12 gives a value of  $\tau$ within the order of magnitude of the experimental value.<sup>21</sup> (ii) It is stated in Ref. 10 that the transition rate is enhanced by a factor of  $\sim 10$  when the Lang-Kohn density profile is used instead of the IBM profile. This statement seems to originate in earlier work of Feibelman<sup>17</sup> in the limit that  $z_1 \gg z_0$ . Note that if the assertion of Ref. 10 were true, from the result for  $\tau$  of Ref. 8 (scaled down, as indicated above, by the use of the adsorption-enhanced dipole moment), one would obtain  $\tau = 1.6 \times 10^{-12}$  sec, in almost perfect agreement with the experimental lifetime.

We now address the above two points in the light of our results. Contrary to (i), the value of the lifetime of the C–O stretch mode for CO adsorbed on Cu given by Eq. (9) is of the same order of magnitude as the experimental value.<sup>1</sup> It is, moreover, quite close to the value obtained in the more elaborate calculation of Ref. 12 (both theoretical values of  $\tau$  differ by a factor of 1.3). Thus the model of the EHP mechanism of damping adopted in the present paper is qualitatively relevant. We address (ii) by noting that the counterpart of Eq. (9) obtained from Eq. (7) using the IBM in the computation of  $\chi(q_{\parallel};\omega | z,z')$  is

$$\tau(\text{IBM}) = 19 \times 10^{-12} \text{ sec}$$
 (10)

Thus, in the present case the damping rate associated with the Lang-Kohn profile [Eq. (9)] is enhanced by a factor of ~2 (and not 10, as argued in Ref. 10) relative to the IBM damping rate. We note that the value of this enhancement of  $\Gamma_{BA}$  (which is due to the increased diffusivity associated with the Lang-Kohn profile) depends on the distance  $z_1$  between the molecule and the surface; the enhancement is found to slowly increase with  $z_1$ . Furthermore, for a fixed value of  $z_1$  the enhancement depends on the substrate. For example, we find that for aluminum the enhancement factor is ~4 (for  $z_1 = 1.6$  Å). This is illustrated in Fig. 2, where we have plotted  $\Gamma_{BA}(\omega)$ 



FIG. 2. Transition (or damping) rate  $\Gamma_{BA}(\omega)$  [Eq. (7)] as function of the energy of the vibrational excited state, for copper and aluminum substrates. For each substrate we show the results obtained using both the IBM and the self-consistent Lang-Kohn electron density profiles at the surface. (We have set  $p_z=0.25$  D and  $z_1=1.6$  Å outside the jellium edge.)

as function of frequency for both Cu and Al substrates. (We have taken  $p_z = 0.25$  D and  $z_1 = 1.6$  Å in both cases.) For each substrate the computation was carried out for both the IBM and self-consistent Lang-Kohn profiles. Note the linear frequency dependence of the damping rate. Damping rates for other values of  $p_z$  can be simply read off Fig. 2 by scaling the dipole moment. The results given in Fig. 2 should be useful for a qualitative comparison with damping rates due to phonon emission for frequencies for which this mechanism becomes competitive.<sup>5</sup>

In conclusion, we have shown that the EHP mechanism considered in this paper provides an important decay channel for a vibrational mode of an adsorbed light molecule. Whether better *quantitative* agreement with experiment can be achieved within the present model by including in the response function  $\chi$  the effects of (a) collisons,<sup>22</sup> (b) exchange and correlation (they are absent in the RPA), and (c) periodic ionic structure of the substrate, is at the present time a matter of conjecture.

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#### APPENDIX A: DERIVATION OF EQ. (6)

Substituting Eq. (4) in Eq. (5), we have

$$\Gamma_{BA}(\omega) = \frac{e^2}{\hbar^2} \int d^3x \int d^3x' \phi^*_{dip}(\vec{x}) D(\vec{x}, \vec{x}' \mid \omega) \phi_{dip}(\vec{x}') ,$$
(A1)

where we have made the definition

$$D(\vec{\mathbf{x}}, \vec{\mathbf{x}}' | \omega) = 2\pi \hbar Z^{-1} \sum_{I,F} e^{-\beta(E_I - \mu N)} \times \langle I | \hat{n}(\vec{\mathbf{x}}) | F \rangle \langle F | \hat{n}(\vec{\mathbf{x}}') | I \rangle$$

$$\times \delta(E_F - E_I - \hbar\omega) . \qquad (A2)$$

With the usual trick of introducing the representation

$$\delta(E_F - E_I - \hbar\omega) = \int_{-\infty}^{+\infty} \frac{dt}{2\pi} e^{-i(E_F - E_I - \hbar\omega)t}, \quad (A3)$$

and defining Heisenberg operators according to the equation

$$\hat{n}(\vec{\mathbf{x}}t) = e^{i\hat{H}t/\hbar}\hat{n}(\vec{\mathbf{x}})e^{-i\hat{H}t/\hbar}, \qquad (A4)$$

where  $\hat{H}$  is the many-body Hamiltonian for the interacting electron system at the metal surface, we can recast Eq. (A2) as

$$D(\vec{\mathbf{x}}, \vec{\mathbf{x}}' | \omega) = \int_{-\infty}^{+\infty} dt \, e^{i\omega t} \langle \, \hat{n}(\vec{\mathbf{x}}, t) \hat{n}(\vec{\mathbf{x}}, 0) \, \rangle \,, \quad (A5)$$

where the angular brackets denote a thermal average.

Now the fluctuation-dissipation theorem<sup>23</sup> relates the density-density correlation function (A5) to the exact density response function  $\chi(\vec{x}, \vec{x}' | \omega)$  according to the equation

$$D(\vec{\mathbf{x}}, \vec{\mathbf{x}}' | \omega) = -\frac{2\hbar}{1 - e^{-\beta\hbar\omega}} \operatorname{Im} \chi(\vec{\mathbf{x}}, \vec{\mathbf{x}}' | \omega + i0^{+}).$$
(A6)

Substituting Eq. (A6) in Eq. (A1) and taking the limit T=0 K yields the result for the transition rate  $\Gamma_{BA}(\omega)$  given by Eq. (6) of the text. For completeness we recall that  $\chi(\vec{x}, \vec{x}' | \omega)$  is the frequency-Fourier transform of the retarded density response function, defined by the equation

$$\chi(\vec{\mathbf{x}}, \vec{\mathbf{x}}' | t - t') = -(i/\hbar)\Theta(t - t') \langle [\hat{n}(\vec{\mathbf{x}}, t), \hat{n}(\vec{\mathbf{x}}', t')] \rangle ,$$
(A7)

where  $\Theta(t)$  is the unit step function.

### APPENDIX B: DAMPING OF A VIBRATIONAL MODE OF AN ADSORBED ATOM

Equation (6) can also be used to study the damping of a vibration of an adsorbed *atom* due to the creation of EHP at the surface. As an example, in this Appendix we present results obtained using Eq. (7) for the case of the vibration of a hydrogen atom normal to the surface of a nearly-free-electron substrate. Hjelmberg<sup>24</sup> has given a detailed calculation of the three parameters that are needed in our computation: the *induced* dipole moment normal to the jellium surface, the vibrational frequency, and the position of the adsorption site.<sup>25</sup> He considered three substrates with the bulk density of Al, Mg, and Na, respectively.

The results of our calculation of the lifetime are listed in Table II. Since there are no experimental data for H chemisorbed on a simple metal, we compare our results with the theoretical results of Persson and Hellsing.<sup>12</sup> Both calculations agree extremely well for sodium, moderately well for magnetism, and rather poorly for aluminum. From the qualitative point of view, the main difference between both sets of results is that the  $r_s$ dependence of the lifetime is reversed ( $r_s$  is the density parameter, which in the jellium model completely characterizes the substrate). The fact that our theory yields

$$\tau(\mathbf{Al}) > \tau(\mathbf{Mg}) > \tau(\mathbf{Na}) \tag{B1}$$

is explained by the facts that

$$p_z(A1) < p_z(Mg) < p_z(Na)$$
 (B2)

and

$$z_1(A1) > z_1(Mg) > z_1(Na)$$
 (B3)

The combined effects of (B2) and (B3) overcompensate for the fact that for given values of  $p_z$  and  $z_1$  the lifetime  $\tau$  decreases with  $r_s$ .

Their limited practical interest notwithstanding, it is unfortunate that no experimental results are available for the simple chemisorption systems considered in this Appendix. A lifetime experiment performed on a simplemetal substrate could prove useful in settling the issue addressed here, namely the basic physics of the EHP damping mechanism.

TABLE II. Lifetime of the perpendicular vibration of a hydrogen atom chemisorbed on a simplemetal surface. The parameters used in the computation are taken from the embedding calculation of Hjelmberg (Ref. 24).

Substrate				Lifetime $\times 10^{-12}$ sec	
	$ p_z $ (D)	$\omega$ (eV)	$z_1$ (Å)	Present work	Ref. 12
Al $(r_s = 2.07)$	0.28	0.15	0.423	4	0.5
Mg $(r_s = 2.65)$	0.46	0.14	0.265	2	0.8
Na $(r_s = 3.99)$	1.25	0.05	0.106	1	1.2

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- <sup>14</sup>For  $\omega \ge \omega_p / \sqrt{2}$  ( $\omega_p$  being the plasma frequency of the substrate), the surface-plasmon channel also contributes to  $\text{Im}\chi(q_{\parallel};\omega+i\eta \mid z,z')$ .
- <sup>15</sup>This statement has to be qualitified. For  $\hbar\omega \gtrsim 1 \text{ eV}$ , but  $\hbar\omega < \hbar\omega_p$ , the computed lifetime converges rapidly as function of the jellium thickness *a*. In that case even a nine-layer film is "thick enough." However, at lower frequencies  $\tau$  shows an oscillatory dependence on the thickness (with amplitude of oscillation  $\sim 5\%$  for  $\hbar\omega = 0.25 \text{ eV}$ ) in the range of thicknesses considered (up to 23 atomic layers). This behavior of  $\tau$  must reflect a frequency dependence of the surface screening length. The results given in Eqs. (9) and (10) give the lifetime for a half-space problem to  $\sim 5\%$  accuracy.

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- <sup>20</sup>O. Gunnarsson and H. Hjelmberg, Phys. Scr. 11, 97 (1975).
- <sup>21</sup>Another possibility, suggested in Ref. 11, is based on the explicit calculation of the damping rate due to the dynamic charge transfer that takes place during the adsorbate vibration. Since this mechanism (implicitly taken into account by our use of an adsorption-enhanced dipole moment) has not yet received a truly quantitative treatment, we will not refer to it any further in this paper.
- <sup>22</sup>While the effect of collisions can be properly included as discussed by K. S. Yi and J. J. Quinn [Phys. Rev. B 27, 1184 (1983)], as an exploratory exercise we replaced the positive infinitesimal  $\eta$  in the argument of  $\chi$  in Eq. (7) by an appropriate bulk collision frequency. The change in the computed lifetime  $\tau$  is small. [Instead of (9) one obtains  $\tau = 8 \times 10^{-12}$  sec.]
- <sup>23</sup>See, e.g., S. Doniach and E. H. Sondheimer, Green's Functions for Solid State Physicists (Benjamin, Reading, 1974), Appendix B.
- <sup>24</sup>H. Hjelmberg, Phys. Scr. 18, 481 (1978).
- <sup>25</sup>We note that the values of  $P_z$  given in Table II have been read off Fig. 5 of Ref. 24 for the *static* dipole moment. We have not estimated a dynamic dipole moment from the slope of the curves. Nonetheless the slopes can be seen to be in agreement with the inequalitities given by Eq. (B2). The results for  $\tau$ given in Table II can be simply scaled to take into account a more accurate value of the dynamic dipole moment.