

Electronic damping of adsorbate motion: CO vibration on the Cu(100) surface

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Cluster calculations have been applied to treat the electronic damping of adsorbate vibrations at a metal surface. Based on the broadening of the discrete one-electron energy levels of a finite cluster, buildup of a self-consistent quasicontinuum of electron energies at the Fermi level is shown to be possible. This is relevant to the description of the continuous low-energy spectrum of electron-hole pairs and application of a recent theoretical formulation. Using this approach we are able to evaluate the rate of electron-hole pair excitations induced by the vibrational motion, which lead to shorter lifetimes of the vibrational excitations, i.e., broadening of the vibrational levels, compared to those of a free molecule. For the linewidth of the C—O stretch-vibration level on the Cu(100) surface a value of 0.5 meV is obtained, corresponding to the lifetime of 1.3×10^{-12} s, in agreement with a recent experiment. The mechanism behind the electron-hole pair excitations is found to be localized charge oscillations between the molecular $2\pi^*$ resonance and the substrate, induced by the vibration. Cluster-size effects for this process were extensively examined and found to be negligible for the numerical result, which we obtain. For the C—Cu vibration mode our calculations predict electronic damping which is one order of magnitude less effective. We expect our approach to be applicable for the studies of adsorption-site effects and also for the evaluation of the electronic damping of other adsorbate motions.

I. INTRODUCTION

A deeper understanding of the mechanisms of the reactions catalyzed by metals is not only of fundamental theoretical interest within surface physics but also of great practical interest. As yet, a lot of experimental and theoretical research is therefore devoted to studies of the static as well as the dynamic properties of the substrate in the form of metal surfaces and the adsorbate in the form of atoms and molecules.¹⁻³ Essential phenomena appearing in these studies are the energy transfer between different degrees of freedom of the adsorbate motion and other excitations in the system, and the adsorbate-adsorbate interactions.^{4,5} These different types of energy exchanges determine to a large extent the adsorption, desorption, and the activation processes of the reactions and are of crucial importance since they often appear to be rate determining for the reactions. The sticking of the adsorbate onto a surface, for example, follows from the transfer of the adsorbate translational energy into some other degrees of freedom available in the system.

The energy dissipation, equivalent to damping of the adsorbate motion at the surface, is caused by energy transfer from the adsorbate to the surface. This may be due to different mechanisms, for example, the excitation of phonons⁶ and, for metal substrates in particular, the excitation of electron-hole pairs.⁷⁻¹³ Because of these processes the lifetime of the stretch vibrations of a molecule adsorbed on a metal surface is short compared to that of a free molecule. This is, for example, the case for CO adsorbed on Cu(100), which has a large vibrational linewidth $\Gamma=0.5$ meV as measured with ir spectroscopy.¹⁴ This should be compared with the linewidth for a free molecule $\Gamma_0=2 \times 10^{-11}$ meV. The excitation of phonons and

electron-hole pairs together with the adsorbate-adsorbate interactions determine also the adsorbate behavior in other dynamic processes such as sticking, rotation, and diffusion at surfaces, as studied, for example, in molecular-beam scattering at surfaces.³⁻⁵

The relative importance of the mechanisms for vibrational damping depends on the electronic structure, i.e., the nature of the bond between the adsorbate and the substrate. For chemically reactive adsorbates, where the electronic density of states (DOS) at the Fermi level (ϵ_F) is enhanced by the bond electrons, the electron-hole pair mechanism appears to be important.¹⁰⁻¹⁴ This is the case for CO adsorbed on metal surfaces,^{11,12,15-18} where the nature of the internal bond of the molecule is known to be strongly affected due to the adsorption. This picture has also been verified in molecular cluster calculations for chemisorbed CO on different Cu surfaces.¹⁶⁻¹⁸ As a result of the CO chemisorption on Cu the occupation of the molecular bonding and antibonding orbitals are changed due to hybridization with substrate electron levels resulting in resonances near ϵ_F . Because the occupations of these resonance structures are sensitive to the internal molecular bond distance, the molecular stretch vibration affects strongly the electronic structure at ϵ_F , which consequently excites electron-hole pairs with a high probability. Recent experiments by Ryberg¹⁴ on CO on a Cu(100) surface show also that the mechanism for the broadening of vibrational levels is temperature independent. This indicates that phonon excitation is not the main mechanism behind the observed broadening.

Up to now the electron-hole pair excitations in practical chemisorption calculations have been treated within the jellium model and embedding scheme of Gunnarsson and Hjelmberg.¹⁹ In this work we present an approach based

on *ab initio* self-consistent-field (SCF) finite-cluster calculations²⁰ and use it to evaluate the electron-hole pair contribution Γ_q to the damping Γ , where Γ_q is obtained in terms of a recent theoretical approach.^{10,11} Using a finite cluster we lose the inherent quasicontinuous energy spectrum of the metal valence electrons; however, we can model a continuum spectrum of one-electron levels by broadening the discrete one-electron levels of the cluster in a self-consistent procedure. Thus, we are able to treat small changes in the surface electron structure due to the molecular vibrations. In addition, with the cluster approach we exploit the proper description of the molecule-metal bond structure, including the substrate structure, as experimentally determined by low-energy electron diffraction,²¹ for example. Hence, our method should be specifically profitable in examining the adsorption site effects. As a first test of our approach we choose to study the damping of the adsorbate-molecule stretch vibration for CO chemisorbed on a Cu(100) surface,²⁰ where the electron-hole pair mechanism is expected to be dominant.¹²⁻¹⁴ We have in this work extended our studies to an analysis of the cluster size effects and to calculations of the influence of electron-hole pair excitations on the metal-carbon vibration.

In Sec. II we describe the mechanism of the electron-hole pair excitations and how the damping is evaluated. In Sec. III the calculation scheme is described and the model for the quasicontinuum of one-electron energies is explained. The results for the damping and cluster size effects are presented in Sec. IV. Summary and conclusions are given in Sec. V.

II. EXCITATION OF ELECTRON-HOLE PAIRS

During the adsorption of the CO molecule on a metal surface, the molecular valence-electron levels interfere with the metal valence electrons, shift in energy, and create new one-electron levels, which may form resonance structures. In a free CO molecule the occupied valence levels are 3σ , 4σ , 1π , and 5σ , with $2\pi^*$ and 6σ as the lowest unoccupied levels. The structures appearing in the adsorbed system CO/Cu(100) are characterized by C_{4v} symmetry; the nature of their molecular origin is as follows. In the free molecule, the highest occupied σ levels interfere with the metal valence levels of the corresponding symmetry (a_1) and form a_1 resonances. This is conventionally interpreted as σ charge donation from the molecule to the metal Fermi sea.¹⁵⁻¹⁷ The lowest unoccupied level $2\pi^*$ of the free molecule interferes with the metal valence levels of e symmetry, shifts downwards, and becomes partly occupied. This is conventionally interpreted as charge backdonation to the molecule. The occupation of the molecular antibonding $2\pi^*$ orbital weakens the molecular bond and thereby lowers the C-O stretch-vibration frequency compared to its value in the gas phase.^{14,22}

As a result of the interference of the hybridization, the local density of electron states (LDOS) around ϵ_F is mainly characterized by the metal and CO a_1 (σ) and e (π) structures.²⁰ When the molecule now vibrates, the position of the $2\pi^*$ resonance relative to ϵ_F also oscillates ac-

ording to its antibonding nature. Adiabatically this would mean a large oscillation also in the occupation number of the $2\pi^*$ resonance. For electrons, however, it takes time to reorganize as they do not follow the ion-core vibrations instantaneously. This implies the excitation of electron-hole pairs around the Fermi level.

Quantitatively the rate of exciting electron-hole pairs can be determined from a golden-rule-type expression, similarly as in the case of atom-surface scattering. Because the rate determines the lifetime of the vibrational excitation, it is convenient to write it in terms of the vibration-level linewidth Γ . In the quasistatic limit and one-electron approximation^{10,11} the linewidth can be expressed as

$$\Gamma_q = \frac{\pi\hbar^2}{M} \sum_{k,k'} \left| \left\langle k' \left| \frac{\partial V}{\partial Q} \right| k \right\rangle \right|^2 \delta(\epsilon_{k'} - \epsilon_F) \delta(\epsilon_k - \epsilon_F), \quad (1)$$

where M is the reduced mass of the vibration, k and k' label the one-electron levels (and spin m_s) with energies ϵ_k , and $\partial V/\partial Q$ is the perturbing potential due to the vibration.

The key quantity is the rate at which new one-electron levels are created or annihilated below ϵ_F during the adsorbate vibration, or more generally, during the motion in a coordinate Q . The linewidth can be given in terms of the consequent change in generalized scattering phase shifts of electrons at ϵ_F ,⁷ or equivalently, in terms of the change in the adiabatic occupation numbers $\partial n_L/\partial Q$,¹¹ i.e., in terms of the adiabatic charge transfer, in which case

$$\Gamma_q = \frac{\pi\hbar^2}{M} \sum_L \left(\frac{\partial n_L}{\partial Q} \right)^2. \quad (2)$$

The proper channels $L = (\eta, m_\eta, m_s)$ in LDOS are defined by the symmetry properties of the system. The index η runs through the different symmetries of the one-electron levels (the irreducible representations of the relevant point group), which in our case for C_{4v} are $\eta = a_1, a_2, b_1, b_2, e$, and m_η is the respective degeneracy (in the present case $m_\eta = 1$, except $m_e = 2$). The quantum number m_s is for the spin orientation.

It should be noted that the proper screening or the charge balance (Friedel sum rule)²³ requires that

$$\sum_L \frac{\partial n_L}{\partial Q} = 0. \quad (3)$$

Thereby the charge balance always requires that there must be more than one independent channel contributing to Eq. (1).

III. CALCULATION SCHEME

A. Linear-combination-of-atomic-orbitals cluster method

The cluster calculations presented in this work were carried out by an *ab initio* discrete-variational (DVM) SCF cluster method²⁴⁻²⁷ using the local density approximation (LDA) for the exchange-correlation potential.

This method is based on the linear-combination-of-atomic-orbitals (LCAO) principle and exploits the point group of the cluster symmetry for block diagonalization of the Hamiltonian as follows. The molecular charge density is expanded in terms of molecular orbitals, i.e., one-electron wave functions

$$\psi_i^\eta(\mathbf{r}) = \sum_j \chi_j^\eta(\mathbf{r}) C_{ji}^\eta, \quad (4)$$

where η labels the irreducible representations of the relevant point group and the "principal quantum number" i labels the levels consecutively within each η . The symmetry-adapted basis functions are given as

$$\chi_j^\eta(\mathbf{r}) = \sum_{v,n,l,m} W_{nlm}^{\eta j v} u_{nl}(r_v) Y_{lm}(\hat{\mathbf{r}}_v), \quad (5)$$

where $Y_{lm}(\hat{\mathbf{r}}_v)$ are spherical harmonics and $u_{nl}(r_v)$ are atomic radial wave functions located at nucleus v . The radial functions are given numerically as atomic wave functions for configurations $1s^2 2s^2 2p^2$ (C), $1s^2 2s^2 2p^4$ (O), and $\dots 3s^2 3p^6 3d^{10} 4s^1 4p^0$ (Cu). To improve the basis set for the description of the bond, additional wave functions for the free-ion configurations $2s^2 2p^0$ (C^{2+}), $2s^2 2p^2$ (O^{2+}), and $3d^7 4s^0 4p^0$ (Cu^{4+}) were used, except for the outermost Cu atoms in the largest cluster.

The Coulomb potential is determined using a multipole expansion of the molecular charge density as introduced by Delley and Ellis,²⁷ and matrix elements of the Hamiltonian and overlap matrices in the secular equation are evaluated by DVM.²⁵ For the exchange-correlation potential the parametrization of von Barth and Hedin²⁸ was used throughout the calculations. In order to test the sensitivity of the LDA potential form, the $X\alpha$ potential²⁹ with $\alpha=0.7$ was also tried, but without any essential changes in either the electronic structure at ϵ_F or the numerical results for the vibrational response.

B. Cluster geometry

The basic cluster is $COCu_9(100)_{top}$, which we use to describe the CO molecule at a top position of a Cu(100) surface, consists of a substrate Cu atom in the surface layer and all of the eight Cu atoms in the sphere of next-nearest neighbors of the fcc crystal structure. Hence, the total number of the surface layer atoms is five and the number of atoms in the second layer is four, see Fig. 1. The distance $d_{Cu-Cu}=4.82$ a.u. is obtained from the bulk lattice constant $a=6.82$ a.u. The CO molecule is terminally bonded with $d_{C-Cu}=3.59$ a.u. and $d_{C-O}=2.17$ a.u. as experimentally determined.²¹ The proper point group for the cluster is C_{4v} .

In order to study cluster size effects, the calculations were also performed for the clusters $COCu_{14}$, $COCu_5$, and $COCu_1$. For the largest cluster the substrate consists of a surface Cu atom and two next-nearest-neighbor spheres of eight and five Cu atoms of fcc structure, and for the $COCu_5$ cluster the substrate consists of five surface Cu atoms only. The substrate of the smallest cluster is a single Cu atom. All of these clusters describe a CO molecule adsorbed at a top position on a Cu(100) surface and were treated in C_{4v} symmetry.

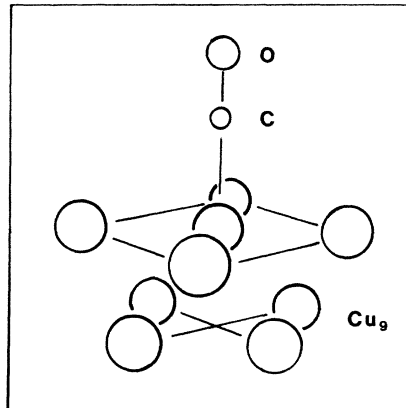


FIG. 1. Geometry of the $COCu_9(100)_{top}$ cluster, which was used to examine the level broadening procedure and the LDA potentials. The other clusters, which were used to examine the cluster size effects are simply obtained from the $COCu_9(100)_{top}$ cluster by adding or removing some outermost substrate Cu atoms.

C. Quasicontinuum of one-electron energies

The discrete one-electron energy spectrum of a finite cluster is not adequate to describe the response phenomena in the quasicontinuum of conduction-electron levels around ϵ_F , which relates to the continuous energy spectrum of electron-hole pair excitations. An embedding of such a cluster in the proper infinite system and the hybridization of the cluster one-electron levels with the host one-electron levels, on the other hand, forms the proper electron structure. This is introduced to the cluster electron structure by broadening the discrete one-electron levels to some reasonable line shape and width γ . Rigorously this shape should be determined by a Green's-function technique,^{19,30} for example.

We have adopted, however, a simple Lorentzian line shape $L(\gamma, \epsilon)$, which appears to be sufficient for our purpose. Furthermore, in order to introduce stronger hybridization for the levels near ϵ_F than for lower lying levels, such as Cu d electrons or localized core levels, the level width of $\gamma_{\epsilon_F}=2$ eV at ϵ_F is applied but for the levels further below ϵ_F the level width is diminished, to essentially zero at $\epsilon = \pm 5$ eV, i.e., $\gamma_\epsilon \approx 0$ eV for $\epsilon = \pm 5$ eV. This procedure appears to be able to describe the vibrational effects on the electron structure at ϵ_F in a way which is largely independent on the actual choice of the level width γ_{ϵ_F} , as described later. It should be noticed that this broadening is not directly involved with the shape of the $2\pi^*$ resonance, which in our case, is obtained from the hybridization between the adsorbate and cluster levels.²⁰

The broadening procedure using the energy-dependent level width γ_ϵ together with the condition of conserving the number of electrons is applied during the iterations to determine ϵ_F and the occupations of the levels self-consistently. Finally we sum up the resulting DOS's of the one-electron levels ϵ_i^η within each symmetry channel η and obtain the symmetry-resolved DOS (SDOS) for the cluster, i.e., the DOS is the following:

$$n_\eta(\epsilon) = \sum_i L(\gamma_{\epsilon_i^\eta}, \epsilon) \quad (6)$$

for each symmetry η , separately. The occupation number for each channel n_η is given by the occupations of the contributing single levels, or formally by the integral over the occupied DOS in Eq. (6). Finally, the derivatives in Eq. (2) are obtained numerically from three separate SCF calculations for different bond lengths and the degeneracies of the independent channels η to $L = (\eta, m_\eta, m_s)$.

Here we want to remark that our procedure differs from that used in Ref. 11 in choosing the channels L . In that specific case, H on jellium, with the calculated data from Ref. 11, for the equilibrium distance we would use $\delta n_\sigma = -0.047$ in their Eq. (12) resulting in $\Gamma_q^\sigma = 0.32$ meV, instead of using $\delta n_{\sigma_0}, \delta n_{\sigma_1}$, and δn_{σ_2} separately resulting in $\Gamma_q^\sigma = 0.64$ meV, which is reported in Ref. 11.

IV. RESULTS

A. Electronic damping Γ_q

The results for the electron structures of COCu₉ and Cu₉ clusters can be found in Ref. 20, and here we concentrate only on the vibrational response of the cluster electron structures. The derivatives in Eq. (2) were calculated as finite differences from the occupation numbers for the equilibrium, contracted, and stretched bond lengths, with the fixed center of mass of the CO molecule. Numerically stable values were obtained for $\Delta d_{C-O} = \pm 0.056$ a.u., resulting in an average value of $\Gamma_q = 0.5$ meV for the vibrational linewidth. Slightly different values were obtained by contracting and stretching the molecule indicating nonlinearity or a bond distance d_{C-O} dependence for Γ_q of the order of -0.1 meV/ Δd_{C-O} . The finite differences for the first and second derivatives of the occupation numbers are given in Table I.

Different linewidths for the broadening procedure of $\gamma_{\epsilon_F} = 0.5$ to 4 eV were applied and the consequent dependence of the damping Γ_q was determined. For $\gamma_{\epsilon_F} = 2$ eV we obtain $\Gamma_q = 0.5$ meV but for $\gamma_{\epsilon_F} = 1$ and 4 eV we obtain $\Gamma_q = 0.7$ and 0.4 meV, respectively. For $\gamma_{\epsilon_F} = 0.5$ eV

TABLE I. The first and second derivatives of the occupation numbers n_η for the independent channels η with respect to the normal coordinate of vibration Q (in atomic units). The given numbers are averages of the results of the two largest clusters COCu₁₄ and COCu₉.

η	$\frac{\partial n_\eta}{\partial Q}$	$\frac{\partial^2 n_\eta}{\partial Q^2}$
a_1	-0.29	0.5
a_2	0.00	0.1
b_1	-0.04	0.5
b_2	-0.02	0.4
e	0.35	-1.5

the SDOS loses its smoothness and is apparently composed of separated Lorentzian lines resulting in an appreciable increase of Γ_q . However, the damping Γ_q seems not to be strongly dependent on the actual choice of γ_{ϵ_F} if it only leads to smooth SDOS structure. This is obviously explained by the self-consistency of our calculations, which seems to lead to a cancellation of the linewidth effects by adjusting the energies ϵ_i^η and occupations n_i^η of the one-electron levels near ϵ_F . It should be noticed that the occupations n_i^η or n_η themselves do not directly contribute to the damping but it is only the change in the occupations $\partial n_\eta / \partial Q$ which contributes to Γ_q . We have chosen to use $\gamma_{\epsilon_F} = 2$ eV for the following reasons. Broadening of $\gamma_{\epsilon_F} = 4$ eV may overestimate the hybridization due to the embedding, however it has only a negligible effect of -0.1 meV on the value of Γ_q . In this case the decrement is traced back to the 1π contribution, which extends up to ϵ_F , although $\epsilon_{1\pi} = -7$ eV and $\gamma_{\epsilon_{1\pi}} = 0.5$ eV. For $\gamma_{\epsilon_F} = 1$ eV, on the other hand, the remaining discreteness in the a_1 DOS explains the increase of 0.2 meV of Γ_q . This number can also be considered as an order of uncertainty due to the level broadening procedure in the result $\Gamma_q = 0.5$ meV.

An analysis of the charge transfer processes between the independent channels is shown in Tables I and II together with the cluster size effects. The contributions

TABLE II. Cluster size effects; a comparison between the clusters examined. The adiabatic occupation changes Δn_η (in electrons) of each DOS, corresponding to a C—O bond stretch of $\Delta Q = 0.032$ a.u. (≈ 0.017 Å), and the corresponding contributions Γ_q^η (meV) to the damping Γ_q (meV). The differences between the vacuum level (ϵ_v) and the Fermi level (ϵ_F) are also given. It is emphasized that the level broadening procedure ($\gamma_{\epsilon_F} = 2$ eV) introduces an uncertainty of the order of 0.2 meV to Γ_q and the increased precision in this table is used to exhibit the cluster size effects only.

η	COCu ₁₄		COCu ₉		COCu ₅		COCu ₁	
	Δn_η	Γ_q^η	Δn_η	Γ_q^η	Δn_η	Γ_q^η	Δn_η	Γ_q^η
a_1	-0.009	0.25	-0.010	0.31	-0.009	0.27	-0.015	0.75
a_2	0.000	0.00	0.000	0.00	0.000	0.00		
b_1	-0.001	0.00	-0.001	0.01	-0.002	0.01	0.000	0.00
b_2	-0.001	0.00	-0.001	0.00	0.000	0.00	0.000	0.00
e	0.011	0.20	0.011	0.22	0.011	0.18	0.014	0.34
Γ_q (meV)	0.46		0.53		0.47		1.09	
$\epsilon_v - \epsilon_F$ (eV)	4.9		4.9		5.1		4.8	

from the a_1 and e channels appear to dominate in charge transfer, whereas the remaining three channels a_2 , b_1 , and b_2 do not essentially contribute. A Mulliken analysis further reveals²⁰ that the contributing one-electron levels, see Fig. 2, of a_1 symmetry are mostly Cu sp origin and the contributing e levels are to a significant extent of CO origin. The extent of localization of the substrate contribution remains to be examined by projecting the cluster charge on to the atomic basis functions²⁰ and in further studies of the dynamical dipole moment. Even if these results might be limited by our basis set or the finite size of the cluster, they confirm the picture of the charge-fluctuation process, where the role of $2\pi^*$ resonance is central,¹² and the fact that Cu d band is not much perturbed by the molecular vibration.

In Table II the occupation changes are converted to correspond to the classical turning point or the vibration "amplitude" $\Delta Q = 0.032$ a.u. in order to compare with the result of Persson and Persson,¹² where $\Delta n_{2\pi^*} = 0.03$ electrons and $\Gamma_q \approx 0.4$ meV. A comparison shows that their result, essentially the same as ours ($\Gamma \approx 0.5$ meV), is obtained by a 3 times as large charge transfer as ours but using only one independent channel π (e) and neglecting the others. Also, it should be noticed that such an independent-channel process is always too simple and even forbidden by Eq. (3). Furthermore, in the present case the larger degeneracy of the e channel ($m_e = 2$), leads to an even lesser contribution compared to the a_1 channel ($m_{a_1} = 1$), which therefore formally dominates for the damping.

We have studied also the C—Cu vibration mode using a similar procedure as for the stretch vibration. In this case the a_1 channel appears to dominate in the charge transfer, which is in accordance with the general picture of CO chemisorption on to the metal surface. The vibrational linewidth describing the damping, using the equilibrium C—O bond length, is only 0.06 meV. The small amount of damping in this case comes from the larger reduced mass of the vibration in question, while the charge transfer is of the same order of magnitude as for the stretch vibration.

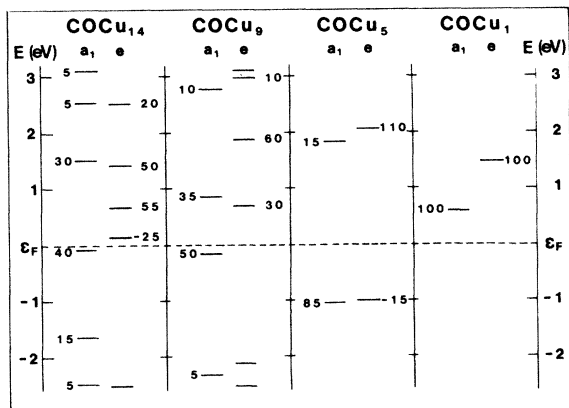


FIG. 2. For each cluster the one-electron levels near ϵ_F (aligned by common ϵ_F) for the symmetries a_1 and e , which give the main contributions to the charge transfer process. The contributions to the occupation change in Table II within each symmetry is given in percent (%).

B. Cluster size effects

To study the cluster size effects, calculations were performed in all four clusters COCu_{14} , COCu_9 , COCu_5 , and COCu_1 . For all of the three larger clusters considered, the charge transfer processes are the same. The e symmetry contributes 0.2 meV to Γ_q and the a_1 contributes about 0.3 meV, showing a good convergence in cluster size, see Table II. Also the Fermi level referred to the vacuum level converges well to a value of -4.9 eV.

The one-electron cluster levels which give the largest contributions to the occupation changes are shown in Fig. 2. It is clearly seen how the number of levels increases with the cluster size but the spread in energy remains constant. This again indicates the cluster-size-independent nature of the process we consider. For the present case the spread of the contributing levels appears to be larger for the a_1 channel compared to the e channel, which reflects the resonance nature of the contributing $2\pi^*$ or e DOS. The single e level for COCu_1 and the weighted average of the e levels for the two largest clusters in Fig. 2 may be used as an estimate for the location of the $2\pi^*$ resonance in energy. To reveal the shape of $2\pi^*$ resonance a projection of cluster levels onto the molecular CO levels should be done. Another alternative, which may lead to a slightly different result, is to compare the electron structures of the adsorbate-substrate system with that of the bare substrate.²⁰

The level broadening $\gamma_{\epsilon_F} = 2$ eV appears to be adequate even for the COCu_5 cluster but obviously a value smaller than 2 eV could be readily used for the largest cluster. Instead, for the smallest cluster $\gamma_{\epsilon_F} = 2$ eV generates a too discrete SDOS and this may partly explain the large deviations for the values for COCu_1 in Table II. The result for this cluster, which is however, of the correct order of magnitude supports the picture of localized substrate response to the molecular vibration.

We can conclude that the cluster size effects are negligible for the physical quantity Γ_q considered here. But on the other hand, the broadening procedure is more crucial, and has to be made with care. In particular, the a_1 contribution being more spread out may suffer from a too discrete SDOS structure.

V. SUMMARY AND CONCLUSIONS

The energy transfer from the C—O vibration to the electron-hole pair excitations of the Cu(100) substrate is studied using a SCF finite-cluster approach. Our method appears to be able to describe the strong changes at the Fermi level in the local density of states due to the CO vibration. Hence, we are able to evaluate the excitation rate of vibration-induced electron-hole pairs in the system in terms of a recent theoretical formulation.^{10,11} Because the energy transfer from the vibrations shortens the lifetime of the vibrational level, its linewidth can be used as a measure of the electron-hole pair contribution to the vibrational damping of the CO molecule on a Cu(100) surface.

The quasicontinuum of the electronic energy spectrum, typical for metals but not for a finite cluster, has to be added, however. A simple procedure of broadening the

one-electron levels in the cluster to Lorentzian lines and using them to describe the SCF electronic density of states appears to be adequate for this purpose. The broadening procedure can be thought to describe the hybridization of the one-electron levels in the cluster due to an embedding on to an infinite surface. Without any cluster-dependent method to determine the width and the shape of the lines the broadening procedure introduces the largest uncertainty to our approach.

Using the theory of a quasistatic description of electron-hole pair excitations^{10,11} we obtain $\Gamma_q = 0.5$ meV, corresponding to the lifetime $\tau = 1.3 \times 10^{-12}$ s for vibrational excitations, in good agreement with a recent experimental value $\Gamma = 0.5$ meV for the corresponding vibrational linewidth.¹⁴ We do not find noticeable cluster size effects on the damping, probably because of the localized nature of the vibrational effects. For the C—Cu vibration mode we obtain a linewidth, which is due to the larger reduced mass of vibration, an order of magnitude smaller than the one for the C—O stretch vibration.

Our results agree with the general view of the bond electron structure of the CO on a metal surface, in particular for the σ donation and $2\pi^*$ backdonation. The $2\pi^*$ resonance is centered somewhat above ϵ_F , is partly occupied and its role for the damping of the C—O stretch vi-

brations is found to be essential as previously discussed.¹² However, formally the substrate sp electrons give larger contribution to the damping than the $2\pi^*$ resonance itself.

Our method, which takes a full account of the local lattice structure of the substrate, should be well suited for the studies on the adsorption site effects in the electronic damping process. Furthermore, the present success leads us to suggest that the finite-cluster method might be applicable also for damping processes of some other adsorbate motions at the metal surfaces originating from the electron-hole pair excitations. The adsorbate-adsorbate interactions and the consequent effects on the molecular vibrations are more difficult to describe properly in a small cluster and therefore they require extensive calculations with larger clusters, which are, however, attainable¹⁸ within our cluster method.

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¹*Vibrations at Surfaces*, edited by R. Caudano *et al.* (Plenum, New York, 1982).

²*Many-Body Phenomena at Surfaces*, edited by D. Langreth and H. Suhl (Academic, Orlando, Florida, 1984).

³B. Kasemo and B. I. Lundqvist, *Comments At. Mol. Phys.* **14**, 229 (1984).

⁴B. Kasemo, in *Vibrations at Surfaces*, Ref. 1, p. 501, and references therein.

⁵J. W. Gadzuk and J. K. Nørskov, *J. Chem. Phys.* **81**, 2828 (1984).

⁶F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic, New York, 1976).

⁷K. Schönhammer and O. Gunnarsson, in *Many-Body Phenomena at Surfaces*, edited by D. Langreth and H. Suhl (Academic, Orlando, Florida, 1984).

⁸B. I. Lundqvist, O. Gunnarsson, H. Hjelmberg, and J. K. Nørskov, *Surf. Sci.* **89**, 196 (1979).

⁹B. Hellsing, M. Persson, and B. I. Lundqvist, *Surf. Sci.* **126**, 147 (1983).

¹⁰M. Persson and B. Hellsing, *Phys. Rev. Lett.* **49**, 662 (1982); and B. Hellsing and M. Persson, *Phys. Scr.* **29**, 360 (1984).

¹¹B. Hellsing, *Surf. Sci.* **152/153**, 826 (1985).

¹²B. N. J. Persson and M. Persson, *Solid State Commun.* **36**, 175 (1980).

¹³B. N. J. Persson and R. Ryberg, *Phys. Rev. Lett.* **48**, 549

(1982).

¹⁴R. Ryberg, *Surf. Sci.* **114**, 627 (1982); *Phys. Rev. B* **32**, 2671 (1985).

¹⁵G. Blyholder, *J. Phys. Chem.* **68**, 2772 (1964).

¹⁶D. Post and E. J. Baerends, *J. Chem. Phys.* **78**, 5663 (1983).

¹⁷K. Hermann, P. S. Bagus, and C. W. Bauschlicher, Jr., *Phys. Rev. B* **30**, 7313 (1984), and references therein.

¹⁸J. Paul and A. Rosén, *Phys. Rev. B* **26**, 4073 (1982).

¹⁹O. Gunnarsson and H. Hjelmberg, *Phys. Scr.* **11**, 97 (1975); H. Hjelmberg, *ibid.* **18**, 481 (1978).

²⁰T. T. Rantala, A. Rosén, and B. Hellsing, *J. Electron Spectrosc. Relat. Phenom.* **39**, 173 (1986).

²¹S. Andersson and J. B. Pendry, *Phys. Rev. Lett.* **43**, 363 (1979).

²²S. Andersson, *Solid State Commun.* **21**, 75 (1977).

²³J. Friedel, *Philos. Mag.* **43**, 153 (1952).

²⁴A. Rosén, D. E. Ellis, H. Adachi, and F. W. Averill, *J. Chem. Phys.* **65**, 3629 (1976).

²⁵D. E. Ellis and G. S. Painter, *Phys. Rev. B* **2**, 2887 (1970); and D. E. Ellis, *Int. J. Quantum Chem.* **11**, 35 (1968).

²⁶F. W. Averill and D. E. Ellis, *J. Chem. Phys.* **59**, 6412 (1973).

²⁷B. Delley and D. E. Ellis, *J. Chem. Phys.* **76**, 1949 (1982).

²⁸U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

²⁹J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974).

³⁰B. Lindgren and D. E. Ellis, *Phys. Rev. B* **26**, 636 (1982).