

A FINITE CLUSTER APPROACH TO THE ELECTRON-HOLE PAIR DAMPING OF THE
ADSORBATE VIBRATION: CO ADSORBED ON Cu(100)

T.T. RANTALA¹, A. ROSÉN¹ and B. HELLSING²

¹Department of Physics, Chalmers University of Technology, S-412 96 Göteborg,
Sweden

²Department of Chemistry, University of California, Santa Barbara,
California 93106, USA

ABSTRACT

A finite cluster method is applied to describe the energy transfer from the adsorbate vibrations to the electron-hole pair excitations. For CO stretch vibration on Cu(100) surface a value of 0.5 meV is found for the consequent damping (corresponding to the lifetime of $1.3 \cdot 10^{-12}$ s) in an agreement with a recently measured vibrational line width. The mechanism behind the electron-hole pair excitations is found to be charge oscillations between the molecular $2\pi^*$ resonance and the substrate, caused by the molecular vibration. Cluster size effects have been found to be negligible.

INTRODUCTION

The mechanisms of heterogeneous catalysis on metals are of great interest within surface physics (ref.1). Essential steps in catalyzed reactions are those of energy transfer between different degrees of freedom of the adsorbate motion and other excitations in the system, since they often appear to be rate determining for the reactions (refs.1-4).

Energy dissipation, equivalent with damping or friction, of the adsorbate motions at the surface is caused by energy transfer from the adsorbate to the surface. This may be due to different mechanisms, for example, excitation of phonons (ref.5) and for metal substrates, in particular, excitation of electron-hole pairs (refs.6-13). Due to 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 (refs.12-15). This is for example the case for CO adsorbed on Cu(100), which is observed to give a large vibrational line width $\Gamma = 0.5$ meV as measured with IR spectroscopy (refs.14.15).

Up to now the electron-hole pair excitations in practical calculations have been treated within the jellium model and embedding scheme of Gunnarsson and Hjelmsberg (ref.16). For the first time we present an approach based on ab initio SCF finite cluster calculations and evaluate the electron-hole pair contribution to the damping Γ_Q obtained in terms of a recent theoretical approach (ref.11).

In order to treat small changes in the electron structure due to the molecular vibration we model the quasi-continuum of one electron levels at the Fermi energy by broadening the discrete one electron levels of the cluster in a self-consistent procedure. With the cluster approach we are able to exploit the proper description of the molecule-metal bond structure, including the substrate lattice structure with the adsorption site effects.

In the next two sections we describe the mechanism of the electron-hole pair damping and our finite cluster approach. Results and summary are given in the two last sections.

ELECTRON-HOLE PAIR DAMPING

CO adsorbed on Cu

During the adsorption of the CO molecule on a metal surface, the molecular valence electron levels interfere with metal valence electron levels, shift in energy and create new one electron levels, which form resonance structures. In the free molecule, the highest occupied σ levels interfere with the metal valence levels of the corresponding symmetry (a_1) forming a_1 resonances, which may be shifted and become therefore partly unoccupied leading to σ charge donation from the molecule to the metal Fermi sea. The lowest unoccupied level $2\pi^*$ of the free molecule interfere 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 gas phase, as experimentally observed (refs.14,17).

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 (refs.7-9). This is the case for CO adsorbed on metal surfaces, where the nature of the internal bond of the molecule is also strongly affected due to the adsorption (ref.18). A recent experiment by Ryberg (ref.15) shows a temperature independence of the vibrational line width of CO adsorbed on Cu(100), which indicates that phonons play a minor role for line broadening or damping. This also supports the picture of electronic mechanism as the main effect in the vibrational damping.

Charge transfer process

Resulting from the interference or the hybridization, the local density of electron states (LDOS) around ϵ_F is enhanced by metal a_1 (σ) and CO e (π) structures. When the molecule now vibrates, the position of the $2\pi^*$ resonance

relative to ϵ_F also oscillate according to its antibonding nature. Adiabatically this would mean large oscillation also in the occupation of the resonance, i.e. fluctuation of the charge between the molecular e and metal a_1 channels. 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. The charge balance of the whole system requires that there always must be more than one channel taking part into this charge transfer process.

The rate of exciting electron-hole pairs due to the charge transfer process is conveniently given in terms of the lifetime or the line width of the vibrational level. Starting from a Golden-Rule type expression for the probability of electron-hole pair excitations due to vibrational perturbation, in the quasi-static limit the vibrational line width

$$\Gamma_q = \frac{\pi \hbar^2}{2M} \sum_s \left(\frac{\partial n_s}{\partial Q} \right)^2, \quad (1)$$

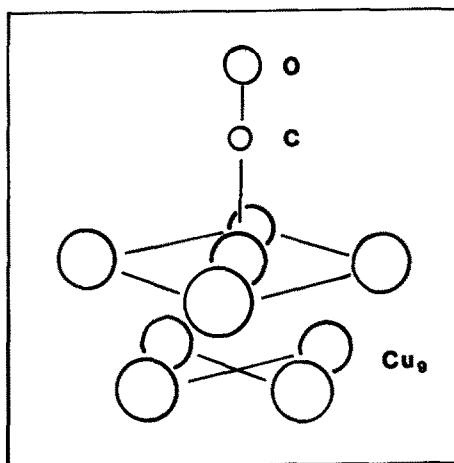
is obtained (ref.11), where the index s runs through the different symmetries of the one electron levels for the particular adsorbate-substrate system. M is the reduced mass relevant to the vibration, n_s is the adiabatic occupation of the symmetry channel s and Q is the normal coordinate of the vibration.

FINITE CLUSTER APPROACH

Calculation scheme

The cluster $\text{COCu}_9(100)$, which we use to describe the CO molecule at a top position on a Cu(100) surface is shown in Fig. 1 and the corresponding geometrical data is given in Table 1. The proper point group for the cluster is C_{4v} .

Fig. 1. The cluster COCu_9 modelling CO adsorbed in top position on a Cu(100) surface.



The molecular-cluster charge density and DOS are determined using an ab initio DVM-SCF cluster method (refs,19-22) within the local density approximation (LDA). The method is based on a linear combination of atomic orbitals (LCAO) principle, where the radial functions are given numerically as free atom wave functions for C, O and Cu (ref,20). Furthermore, we use additional free ion wave functions for C^{2+} , O^{2+} and Cu^{4+} (double basis) to improve the description of the bond.

The LDA potentials were chosen to be X_α (ref,23) with $\alpha = 0.7$ for comparison and the more sophisticated formulation by von Barth and Hedin (ref,24) for final calculations. Any noticeable dependence on the choice of the LDA potential was found neither in the electronic structure close to ϵ_F nor in the subsequent vibrational effects on it.

TABLE 1

Geoemtrical data in atomic units (1au=0.53Å) used in computations for $COCu_9$ in Fig. 1.

Atoms	Distance	Vibration amplitude
Cu - Cu	4.82 ^a	0.000
Cu - C	3.59 ^b	± 0.032
C - O	2.17 ^b	$\pm 0.056^c$

^aobtained from the bulk lattice constant $a = 6.82$ au.

^bfrom ref.25.

^cchosen to be large enough to achieve numerical stability.

Quasi-continuum of one electron levels

An embedding of the cluster into the infinite surface leads to the hybridization of the cluster one electron levels with the host one electron levels, and hence to the quasi-continuum of valence electron energies, which is related to the continuous low energy spectrum of the electron-hole pairs. To the cluster electron structure the hybridization can be introduced simply by broadening the discrete one electron levels to some reasonable line shape. Rigorously this shape should be determined by Green's function technique (refs.16,26), for example. We have adopted, however, a simple Lorentzian line shape, 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 was applied but for the levels further below ϵ_F the level width was diminished being essentially zero at $\epsilon = \pm 5$ eV, i.e. $\gamma(\pm 5eV) \approx 0$ eV.

It should be noticed that the broadening introduced above is not directly

involved with the shape of the $2\pi^*$ resonance, which is determined by the hybridization between the adsorbate CO levels and the cluster levels.

The broadening procedure together with the conditions of conserving the number of electrons was applied during the iterations to determine ϵ_F and the occupations of the levels self-consistently. We sum up the resulting one electron levels within each symmetry and obtain the symmetry resolved local density of states (SDOS) for the adsorbate-substrate system, i.e. $n_s(\epsilon)$ for each symmetry s , separately. Further, integrations over the occupied SDOS give the occupations n_s for the relevant symmetry channels s .

RESULTS

Cluster electronic structure

For comparison the calculations were performed also for the bare substrate cluster $\text{Cu}_9(100)$, i.e. without the adsorbate. The one electron levels near ϵ_F for both of the clusters are shown in Figs. 2 and 3 for the symmetry channels of interest, i.e. for a_1 and e , respectively. The remaining channels in C_{4v} symmetry, a_2 , b_1 and b_2 do not respond to the vibration essentially and are not shown. The Fermi levels referred to the vacuum level are -4.88 eV and -4.75 eV for COCu_9 and Cu_9 clusters, respectively. Note that the "DOS" curves sketched in Figs. 2 and 3 are obtained by broadening each level to the same width of $\gamma = 2$ eV, which is not the broadening used in the calculations, where the width γ depends on the energy ϵ explicitly, i.e. $\gamma = \gamma(\epsilon)$.

The obtained structure is in qualitative agreement with experiments (ref.27) and previous discussions (ref.13) of the subject. Number of the cluster levels in the combined system has increased, as expected, due to the 4σ , 5σ , 1π and $2\pi^*$ hybridization. Mulliken analysis, or a projection of the cluster levels onto the basis set, reveals that the three lowest of them have retained a large contribution from their molecular origin, and are so labelled in Figs. 2 and 3. An enhancement of DOS corresponding to the $2\pi^*$ resonance is also clearly seen in Fig. 3 but there is no single level to point out due to the stronger hybridization. Instead, the three levels next higher to ϵ_F get, according to Mulliken analysis, appreciable contributions from C and O centered atomic basis functions.

Level broadening

Different level widths for the broadening procedure from $\gamma(\epsilon_F) = 0.5$ eV to 4 eV was 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 $\Gamma(\epsilon_F) = 4$ eV the damping is decreased by 0.1 meV and for $\Gamma(\epsilon_F) = 1$ eV it is increased by 0.2 meV. The weakness of the dependency, which we find, is probably explained by the self-consistency of our calculations, which seems to cancel the effects from changing $\gamma(\epsilon_F)$, by adjusting the one electron levels around ϵ_F .

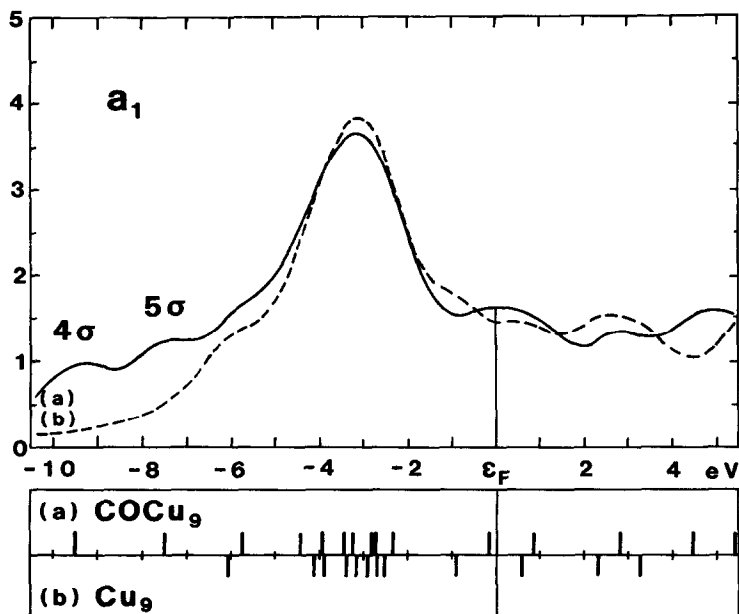


Fig. 2. The SCF one electron levels of a_1 symmetry (lower panel) for the clusters (a) $\text{COCu}_9(100)\text{top}$ and (b) $\text{Cu}_9(100)$. The (a) solid and (b) dashed "DOS" curves (upper panel) are drawn by broadening each of the levels to the same Lorentzian shape and width of 2 eV. Note that this is not the level broadening procedure used in calculations.

We have chosen to use $\gamma(\epsilon_F) = 2$ eV for the following reasons. The $\gamma(\epsilon_F) = 4$ eV obviously overestimates hybridization due to embedding and in this case even 1π contributes, however resulting in almost the same value $\Gamma_q \approx 0.4$ meV, as we obtain for $\gamma(\epsilon_F) = 2$ eV. For $\gamma(\epsilon_F) = 1$ eV, on the other hand, the remaining discreteness in a_1 DOS is behind the increasing tendency of Γ_q and the resulting value of $\Gamma_q \approx 0.7$ meV.

Charge transfer process

The derivatives in Eq. (1) are obtained numerically from three separate SCF calculations for the occupations n_s using different bond lengths for the CO molecule with a fixed center of mass, see Table 1, applying the level broadening procedure described in previous section. Numerically stable derivatives were obtained for $\Delta d_{\text{C-O}} = 0.056$ au, resulting in an average value of $\Gamma_q = 0.5$ meV. Slightly different values are obtained for contracting and stretching the molecule indicating a bond distance $d_{\text{C-O}}$ dependence for Γ_q of the order of $-0.1\text{meV}/0.04\text{au}$.

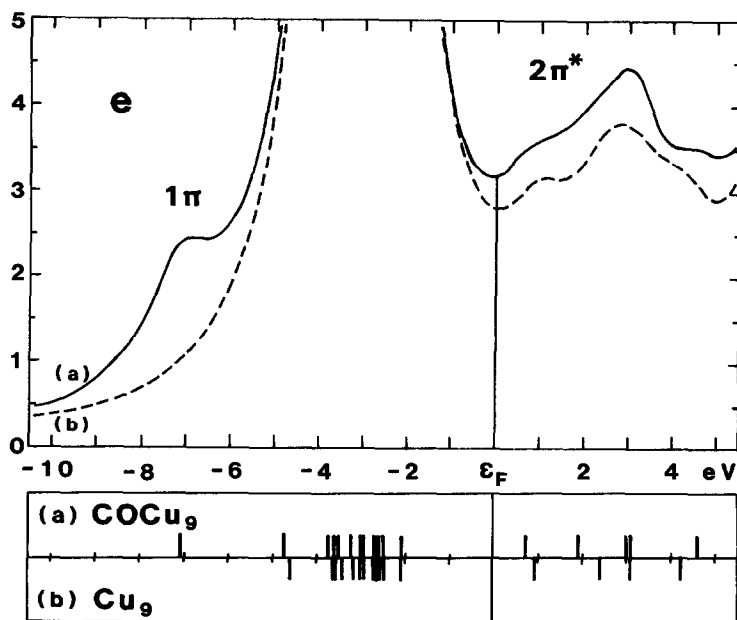


Fig. 3. The SCF one electron levels of e symmetry (lower panel) and the corresponding "DOS" (upper panel) for the clusters considered, see text in Fig. 2.

An analysis of the charge transfer process is shown in Table 2. The a_1 contribution to the charge transfer appears to be of same size as the e ($2\pi^*$) contribution. The levels of a_1 symmetry, which together contribute 98.5% to Δn_{a_1} , are the two next lower to ϵ_F and the two next higher to ϵ_F in Fig. 2. Mulliken analysis show that these levels are not very localized within the cluster. This may be an artifact arising from the finite cluster size and lacking screening from outside of the cluster and this will be further examined in studies of cluster size effects (ref.28) and dynamical dipole moment.

Instead, for the e symmetry in Fig. 3, the three levels having considerable molecular origin and located next higher to ϵ_F , contribute 99.8% to Δn_e . Even if these results might be slightly limited by our basis set, they support the picture of the charge fluctuation process, where the role of the $2\pi^*$ resonance is emphasized (ref.12). Though it should be noticed that due to the larger degeneracy of e channel, the a_1 channel formally contributes stronger to Γ_q than the e_x and e_y channels together. In Table 2, we see also that the a_2 , b_1 and b_2 channels of the point group C_{4v} contribute negligibly, which also means that the Cu d band is not much perturbed by the vibration.

TABLE 2

The charge transfer Δn_s between the independent channels s and the corresponding contributions Γ_q^s to the obtained damping $\Gamma_q = 0.5$ meV. The values of Δn_s correspond to stretching the C-O bond by 0.056 au.

s	a_1	a_2	b_1	b_2	e
Δn_s (in e)	-0.017	-0.000	-0.002	-0.001	0.020
Γ_q^s (in meV)	0.31	0.00	0.01	0.00	0.22

In more extensive studies (ref.28) the cluster size effects are found to be negligible for the numerical result of Γ_q compared to the uncertainties 0.2 meV and 0.1 meV arising from the choice of $\gamma(\epsilon_F)$ and C-O bond length, respectively.

SUMMARY AND CONCLUSIONS

Our finite cluster method appears to be able to reproduce the electron-hole pair contribution to the vibrational damping of the CO molecule on a Cu(100) surface. A simple procedure of broadening the cluster one electron levels to the Lorentzian lines and using them to form the electronic density of states appears to be adequate to model the quasi-continuum of the electronic energy spectrum or to describe the hybridization of the cluster one electron levels due to an embedding onto a large surface. Without any sophisticated and cluster dependent method to determine the width and the shape of the levels, the applied broadening procedure introduces the largest uncertainty to our approach.

Combined with a recent theory of a quasi-static description of electron-hole pairs (ref.11) we obtain $\Gamma_q = 0.5$ meV (corresponding to the lifetime $\tau = 1.3 \cdot 10^{-12}$ s for vibrational excitations) in a good agreement with a recent experimental value $\Gamma = 0.5$ meV for the corresponding vibrational line width (refs.14,15). The cluster size effects on the damping have been found to be negligible (ref.28).

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 $2\pi^*$ back donation. The $2\pi^*$ resonance is centered somewhat above ϵ_F , as seen in Fig. 3 and its role for the damping of the CO stretch vibrations is found to be essential as previously discussed (ref.12).

Our method, which takes fully 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. Further, the present success leads us to suggest that the finite cluster method might be applicable also for some other damping processes of the adsorbate motions at the metal surfaces originating from the electron-hole pair excitations.

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