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# Molecular-orbital calculations of the lifetimes of the vibrational modes of CO on Cu(100)

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A nonempirical molecular-orbital theory of the relaxation of excited vibrations at metal surfaces by energy transfer to conduction electrons is described. With use of *ab initio* calculations on cluster models of the adsorbate-surface system, the lifetimes of all four local modes of CO on Cu(100) are obtained. The calculated lifetimes are in qualitative agreement with experiment, and can be understood in terms of simple orbital interpretations of the nonadiabatic vibrational relaxation mechanisms.

Advances in time-resolved spectroscopy permit real-time measurements of lifetimes of excited vibrations at surfaces.[1-4] Infrared line shapes also provide valuable information on vibrational relaxation.[5-7] Relaxation occurs by anharmonic coupling to phonons on nonmetals, while on metals nonadiabatic energy transfer to the conduction electrons contributes. For the four modes of CO on Cu(100), real-time experiments yield a 2-ps lifetime for the CO stretch,[4] and surprisingly, a similar lifetime is inferred for the frustrated rotation[7] from its Fano line shape.[8] The lifetime of the in-plane frustrated translation has been estimated as 40 ps (Ref. 9) from surface-resistivity data. The CO-Cu stretch lifetime is not known, but that of the CO-Pt(111) stretch is greater than 10 ps.[6] An empirical charge-transfer model[10] accounts for relaxation of the CO stretch and is supported by density-functional calculations.[11] No calculations are available for the other modes. In this paper we describe a molecular-orbital theory of nonadiabatic vibrational relaxation on metal surfaces which we apply to give a unified picture of the lifetimes of *all* modes of CO on Cu(100).

In our model the initial state is the product of the ground electronic state (a single determinant[12]) and the excited $v=1$ state of a local vibration (a harmonic oscillator). The final state is the product of the $v=0$ state with an excited electronic state (the original determinant with a single occupied orbital replaced by a virtual orbital which is a vibrational quantum higher in energy[13]). The rate of relaxation $\Gamma$ into this manifold of final states is given by the Fermi golden rule, with the perturbation being the nuclear kinetic-energy operator. Our derivation circumvents the possible vanishing[14] of the Hartree-Fock density of states (DOS) at the Fermi level $\varepsilon_F$ by imposing a physically correct smooth form. The result is[15]

$$\Gamma=\frac{1}{\tau}=\pi\hbar\,\mathrm{Tr}[\mathbf{P}(\varepsilon_F^-)\mathbf{G}\,\mathbf{P}(\varepsilon_F^+)\mathbf{G}]\ . \tag{1}$$

All matrices are in the local atomic-orbital (AO) basis.[12] $\mathbf{P}(\varepsilon_F)$ is the local DOS (LDOS) at $\varepsilon_F$ ($-$ and $+$ imply transitions from below to above $\varepsilon_F$). $\mathbf{G}$ is a coupling matrix, consisting of Hamiltonian ($\mathbf{H}$) and overlap ($\mathbf{S}$) derivatives with respect to the normal coordinate $Q$ for the excited vibrational mode:

$$\mathbf{G}=\mathbf{H}^Q-\varepsilon_F\mathbf{S}^Q\ . \tag{2}$$

Vibrational relaxation is spatially localized as $\mathbf{G}$ contains derivatives that can only be nonzero near the adsorbate. The electronic transition involves a very small energy change, and so only the electronic structure in the vicinity of $\varepsilon_F$ is relevant. A similar result is obtained quite differently within density-functional theory.[16]

To evaluate Eq. (1) formally requires a Hartree-Fock calculation on the adsorbate plus semi-infinite metal surface. However, the chemisorption bond and relaxation process are both spatially localized. We therefore extract[15] $\mathbf{G}$ and $\mathbf{P}(\varepsilon_F)$ from *ab initio* Hartree-Fock cluster calculations, which have proven useful for describing the bonding of CO on Cu(100).[17] $\mathbf{H}^Q$ and $\mathbf{S}^Q$ are directly obtained, and $\varepsilon_F$ is set to the highest occupied level of the cluster, yielding $\mathbf{G}$. For $\mathbf{P}(\varepsilon_F^-)$ and $\mathbf{P}(\varepsilon_F^+)$, we smear the density due to the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital of each symmetry type over an appropriate energy range $\Delta E$ (their separation plus half of the next spacings). This is reasonable for metals with wide flat conduction bands, such as Cu. To a good approximation (neglecting overlap), the relaxation rate in terms of nonadiabatic couplings between cluster orbitals is

$$\Gamma=4\pi\hbar\sum_I\sum_J(\Delta E_I\Delta E_J)^{-1}(\varepsilon_{\mathrm{LUMO}(I)}-\varepsilon_{\mathrm{HOMO}(J)})^2\times\left\langle \mathrm{LUMO}_I\left|\frac{\partial}{\partial Q}\right|\mathrm{HOMO}_J\right\rangle^2\ , \tag{3}$$

where the sums are over irreducible representations of the cluster point group.

We apply the method to study the lifetimes of the modes of CO on Cu(100), using a $\mathrm{Cu_6CO}$ cluster, consisting of one surface atom, four second-layer atoms, and one third-layer atom. Full details of the calculations are given elsewhere.[15,18] The C and O positions are varied (subject to frozen Cu atoms), giving an optimized geometry and normal modes that are in reasonable agreement with experiment.[7,17] The calculated frequencies, atomic displacements, and lifetimes for each of the four local modes are summarized in Table I. The CO stretch and frustrated rotation relax rapidly, while the frustrated

TABLE I. Calculations of the frequencies $\omega$, relative Cartesian displacements $Q$, and lifetimes $\tau$ of the four modes of CO on Cu(100). From left to right in the table, the modes are the in-plane frustrated translation ($E$), the in-plane frustrated rotation ($E$), the normal frustrated translation ($A_1$), and the CO stretch ($A_1$).

| $x\uparrow \; \rightarrow z$ | $\text{Cu-}\overset{\uparrow}{\text{C}}\text{-}\overset{\uparrow}{\text{O}}$ | $\text{Cu-}\underset{\downarrow}{\text{C}}\text{-}\overset{\uparrow}{\text{O}}$ | $\text{Cu}\leftrightarrow\text{C-O}$ | $\text{Cu-C}\leftrightarrow\text{O}$ |
|---|---|---|---|---|
| ω(calc) | $15.4\text{cm}^{-1}$ | $288\text{cm}^{-1}$ | $247\text{cm}^{-1}$ | $2304\text{cm}^{-1}$ |
| Q(calc) | $x_C=0.126$<br>$x_O=0.225$ | $x_C=0.259$<br>$x_O=-.110$ | $z_C=0.188$<br>$z_O=0.189$ | $z_C=0.219$<br>$z_O=-.163$ |
| τ(calc) | 108ps | 2.3ps | 82ps | 3.3ps |
| ω(expt) [7] | - | $285\text{cm}^{-1}$ | $345\text{cm}^{-1}$ | $2085\text{cm}^{-1}$ |
| τ(expt)[a] | 40ps | >1ps | >10ps | 2ps |

[a] For citations and discussion, see text.

translations have considerably longer lifetimes, in qualitative agreement with experiment. The use of a larger (10- and 14-atom) Cu clusters does not change the distinction between modes with short and long lifetimes, although the calculated lifetimes can change by a factor of 2 or 3.[15] These results suggest that our model contains the essential physical features needed to describe the vibrational relaxation and that it is therefore an appropriate basis for discussing the nature of the relaxation processes.

As an adsorbate molecule vibrates, adiabatic changes in the electron-density distribution occur as a result of changes in the shape of occupied orbitals. *Nonadiabatic* transitions from an occupied orbital will be to unoccupied orbitals (of the correct energy) which look most like the desired *adiabatic* changes. These adiabatic changes are given as the derivative of the occupied orbital with respect to the normal coordinate, and thus based on Eq. (3), we analyze the lifetimes by comparing cluster LUMO's with HOMO derivatives for each mode. The three occupied "conduction-band" orbitals in the $Cu_6CO$ cluster are of $A_1$ and $E$ symmetry, as are the lowest unoccupied conduction-band orbitals. Contour plots of these orbitals in the vicinity of the adsorbate are shown in Fig. 1. The $A_1$ HOMO and LUMO derive partly from the occupied $5\sigma$ orbital of free CO (a nonbonding orbital centered on C). The $E$ HOMO and LUMO in the vicinity of CO derive largely from the unoccupied $2\pi^*$ orbital of free CO. Upon adsorption it broadens into a resonance whose tail dips below the Fermi level,[10] causing the metal-to-adsorbate charge-transfer characteristic of the chemisorption bond.[17] Indeed, the diffuse Cu-C $\pi$ bond is evident in the $E$ HOMO.

Derivatives of the HOMO's of Fig. 1 with respect to the in-plane frustrated translation and frustrated rotation are shown in Fig. 2. Their symmetry properties follow from the direct product of the orbital symmetry ($A_1$ or $E$) with the symmetry of the modes ($E$). The $A_1$ derivatives have $E$ symmetry, while the $E$ derivatives have a large $A_1$ component. Inspection of Fig. 2 shows that the

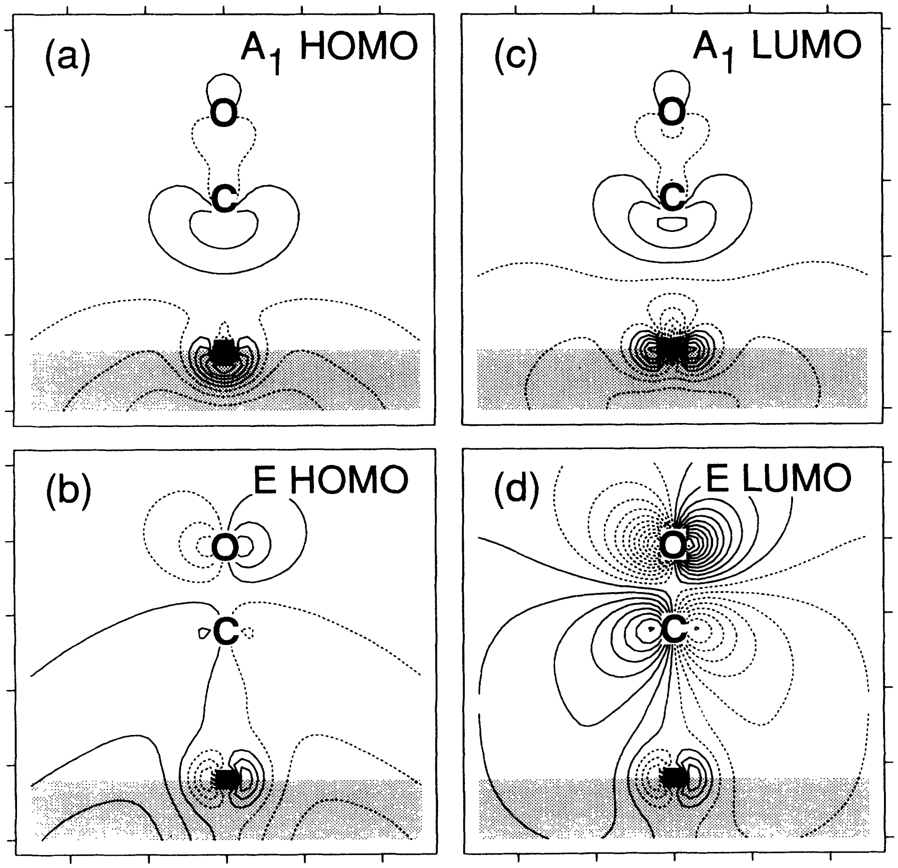

FIG. 1. Contour plot of the $Cu_6CO$ highest occupied molecular orbitals (HOMO's) of (a) $A_1$ and (b) $E$ symmetry and lowest unoccupied orbitals (LUMO's) of (c) $A_1$ and (d) $E$ symmetry. These orbitals represent local contributions to the conduction band. The contours are ±0.01, ±0.03, ±0.05, etc. Tick marks are in 1-Å steps. The surface-layer Cu atom is marked with a square, and the surface region is shaded.

derivatives are largely due to the HOMO's of Fig. 1 *following* the nuclear displacements of each mode. Displacing either normal coordinate breaks the $C_{4v}$ cluster symmetry so that orbitals of different symmetry dynamically mix during vibration if the broken-symmetry HOMO is expanded in terms of $C_{4v}$ orbitals. Hence nonadiabatic transitions which excite (or scatter[19]) an electron from an occupied orbital of $A_1$ symmetry to an unoccupied $E$ orbital or vice versa can relax these parallel modes.

Two features of the C and O displacements for the frustrated rotation cause it to relax far faster than the in-plane frustrated translation: the greater motion of C relative to O and the opposing direction of atomic motion (see Table I). Since the $A_1$ HOMO has more amplitude at C than O, its derivative with respect to the frustrated rotation in Fig. 2(c) is much stronger than Fig. 2(a). The nodal structure of Fig. 2(c) also overlaps better with the $E$ LUMO in Fig. 1(d) because of the opposing atomic motion. The $E$ HOMO involves the diffuse Cu-C bond, and so its derivative with respect to the frustrated rotation in Fig. 2(d) has much greater amplitude between adsorbate and surface than Fig. 2(b), leading to excellent overlap with the surface component of the $A_1$ LUMO. In other words, C displacement causes a delocalized electron-density shift as the chemisorption bond follows the atomic motion, making nonadiabatic transitions more probable for the frustrated rotation than the frustrated translation.

In Fig. 3 we plot derivatives of the HOMO's with respect to the two perpendicular modes: the CO and Cu-C stretches. These modes are of $A_1$ symmetry, and so they couple orbitals of like symmetry. The rapid relaxation of the CO stretch follows from the strong resemblance of the $E$ HOMO derivative in Fig. 3(d) to the $E$ LUMO in Fig. 1(d). The change of the $E$ HOMO with vibration leads to charge transfer from metal to adsorbate as the CO bond stretches. This is due to lowering of the $2\pi^*$ energy level of free CO as the bond stretches and confirms the standard empirical model[10] for relaxation of this mode. The $\pi^*$ character of the adiabatic charge flow is evident in Fig. 3(d), and unlike the in-plane modes, the derivative is inconsistent with the HOMO simply following the atomic motion.

The relaxation process for the Cu-CO stretch is slower than for the CO stretch, but similar in that it is also driven by changes in the extent of charge transfer between adsorbate and surface during vibration. Thus the derivative of the $E$ HOMO in Fig. 3(b) is inconsistent with orbital following. Just as stretching the CO bond affects charge transfer to the adsorbate by shifting the $2\pi^*$ resonance, reducing the Cu-CO distance broadens the resonance and increases the extent of charge transfer. The faster relaxation of the CO stretch relative to the Cu-CO stretch is due to both larger adiabatic charge fluctuations for that mode and better overlap with the low-lying unoccupied orbitals.

In conclusion, we have described a nonempirical theory of vibrational relaxation via nonadiabatic cou-

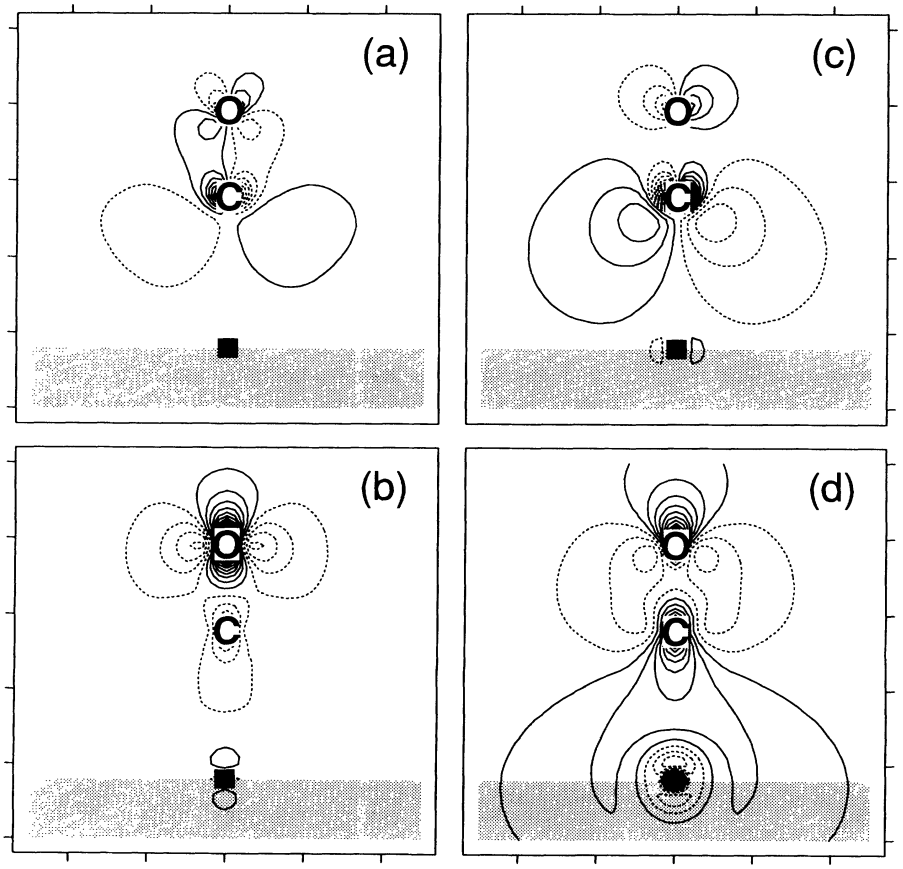

FIG. 2. Derivative of the cluster HOMO's of Fig. 1 with respect to the normal coordinates of $E$ symmetry. The derivatives of the $A_1$ and $E$ HOMO's with respect to the in-plane frustrated translation are shown in (a) and (b), while derivatives with respect to the frustrated rotation are given in (c) and (d). The contours are spaced by 0.006 $\text{Å}^{-1}\,\text{amu}^{-1/2}$; other details are as for Fig. 1.

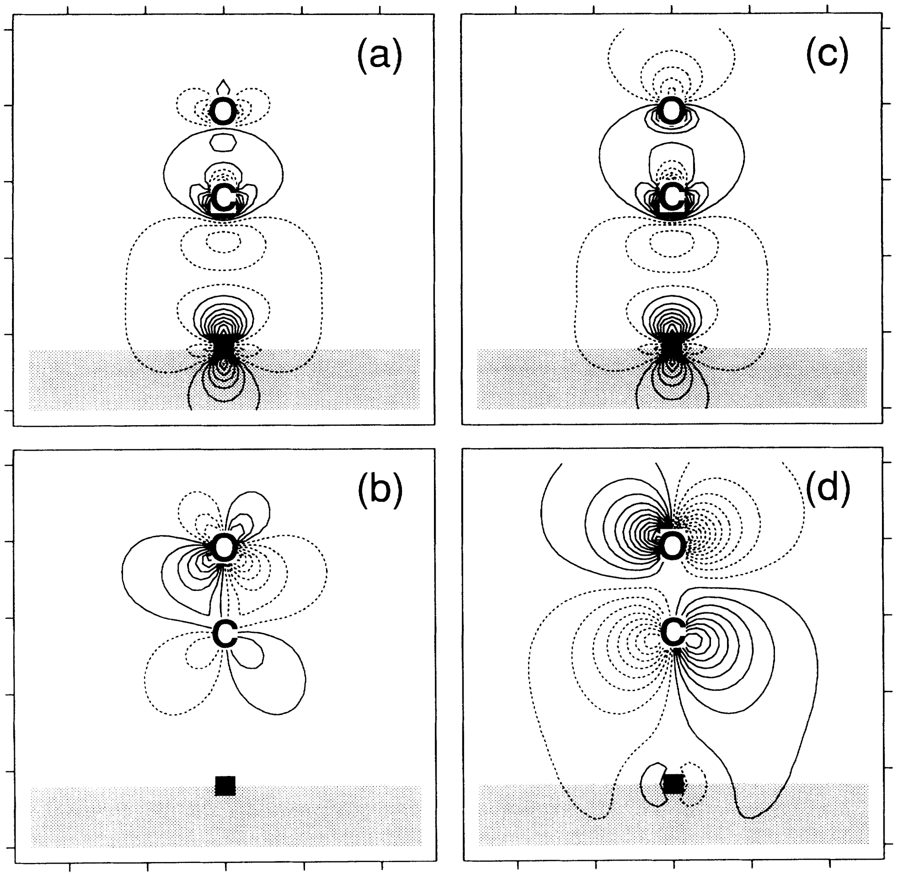

FIG. 3. Derivative of the $A_1$ and $E$ HOMO's with respect to the normal coordinates for the normal frustrated translation [panels (a) and (b)] and the CO stretch [panels (c) and (d)] in the format of Fig. 2.

pling, which can be evaluated with *ab initio* Hartree-Fock cluster calculations. For CO on Cu(100), we report a set of calculations of the lifetime of all modes. Our orbital model enables us to explain the lifetimes in physical terms, such as extent of charge rearrangement with vibration and the nature of the chemisorption interaction. We plan extensions of this model to treat vibrational excitation of adsorbates scattering from hot surfaces and the effect of femtosecond electronic excitation of conduction electrons on adsorbed species.

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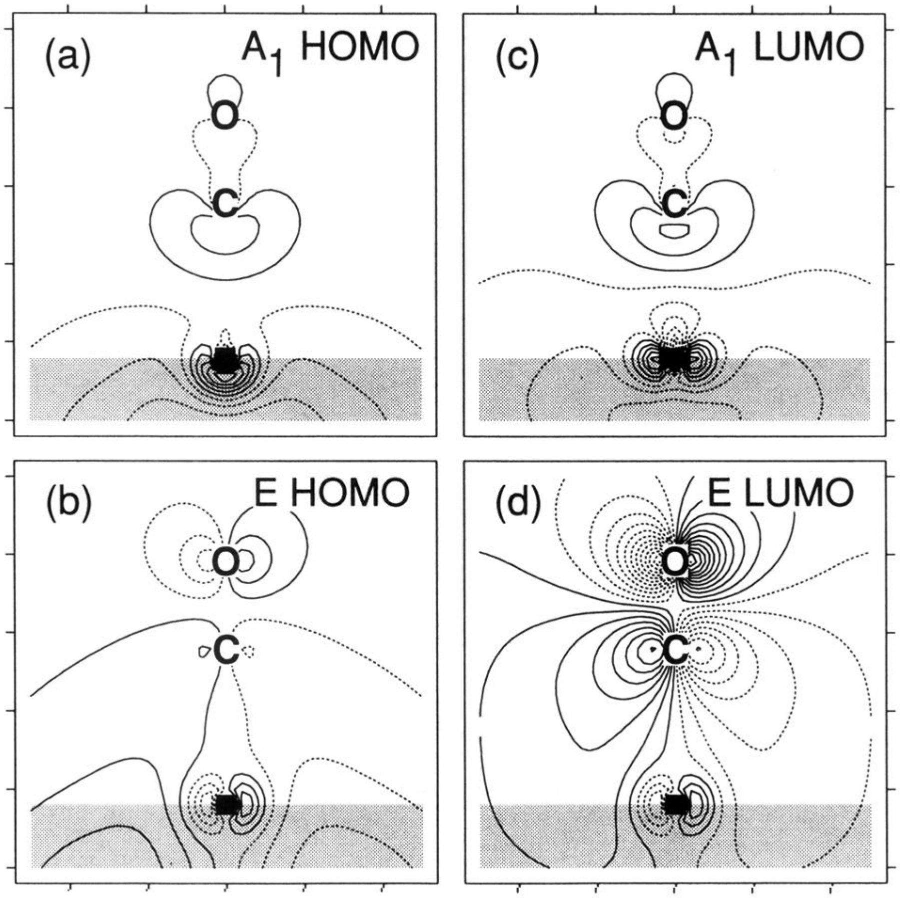

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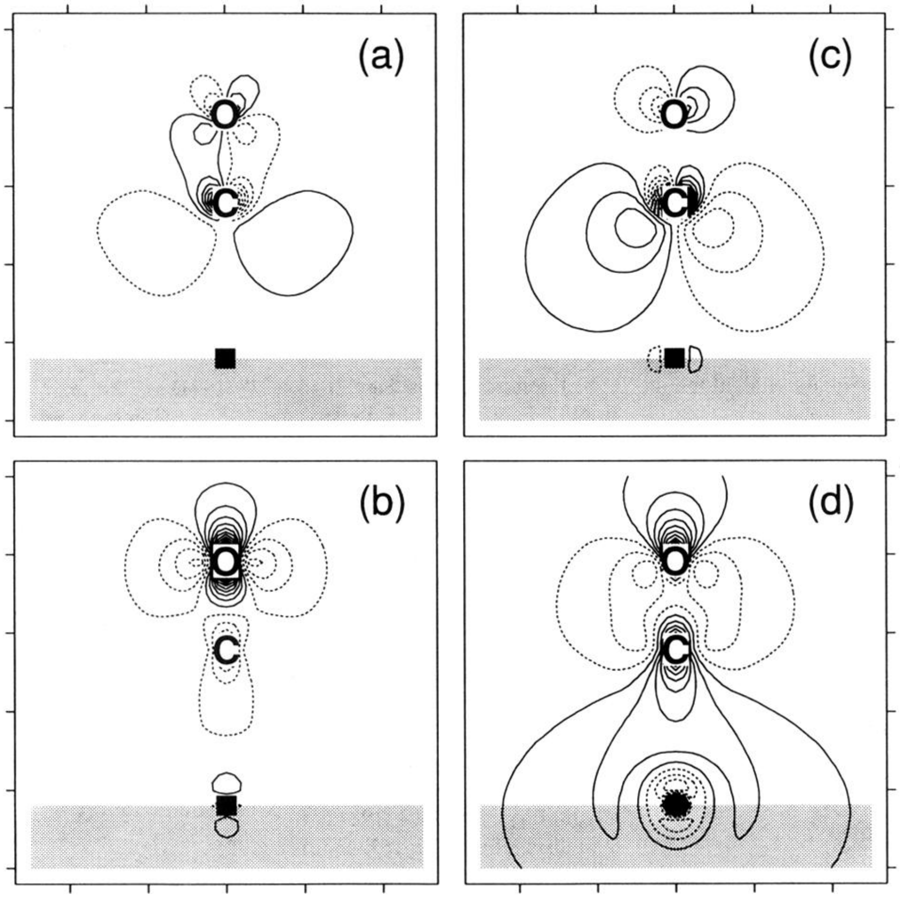

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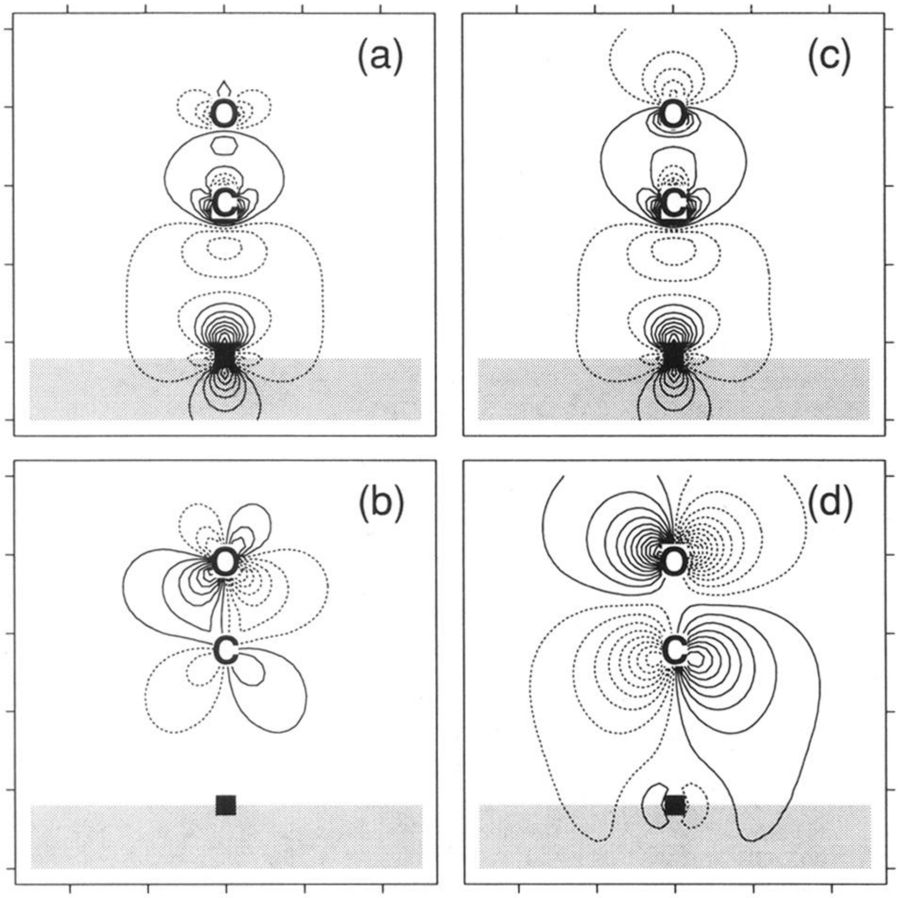

FIG. 3. Derivative of the $A_1$ and $E$ HOMO's with respect to the normal coordinates for the normal frustrated translation [panels (a) and (b)] and the CO stretch [panels (c) and (d)] in the format of Fig. 2.