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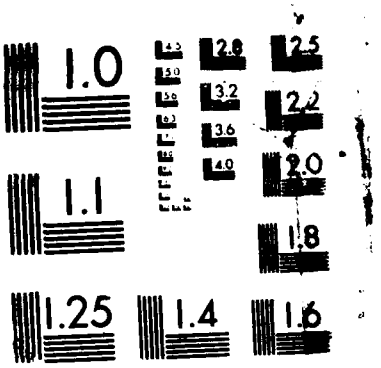

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Coupling of Vibrational Modes of Adsorbates: Application to Field Induced Shifts for CO and CN on Cu(100)

by

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We have studied the coupling of the metal-ligand and the intra-molecular ligand stretching vibrations for CO and CN chemisorbed on Cu(100) using potential energy surfaces obtained with *ab initio* cluster model wave functions. When there is no applied electric field, approximate internal coordinate modes for these vibrations and the fully coupled normal modes give essentially the same results, showing that their coupling is small. In the presence of an applied field,

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the coupling is important for CN. The origin of the coupling is shown to arise from the large field induced changes in the metal-ligand distance for the ionic bond between metal and CN. The present calculations also confirm the mechanism of the field induced changes in the bond lengths and vibrational frequencies for both chemisorbed CO and CN as a Stark effect. Chemical changes are shown to be small.

Keywords:

COUPLING OF VIBRATIONAL MODES OF ADSORBATES: APPLICATION TO FIELD INDUCED SHIFTS FOR CO AND CN ON Cu(100)

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ABSTRACT: We have studied the coupling of the metal-ligand and the intra-molecular ligand stretching vibrations with *ab initio* cluster model wavefunctions. When there is no applied electric field, uncoupled internal coordinate modes and the fully coupled normal modes give essentially the same results. In the presence of an applied field, the coupling is important for CN. The coupling is shown to arise from the large field induced changes in the metal-ligand distance for the ionic bond between metal and CN. The mechanism of the field induced changes in the bond lengths and vibrational frequencies as a Stark effect is confirmed; chemical changes are shown to be small.

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A theoretical analysis of the effect of an electric field on the vibrational frequencies, ω, of CO and CN chemisorbed on a Cu(100) surface was presented in a previous paper.[1] Far and away the largest contribution to the field induced shift was a Stark effect. The nature of the metal-ligand bond, covalent for chemisorbed CO and ionic for CN, leads to quite different Stark mechanisms. These conclusions were based on *ab initio*, molecular orbital, MO, self-consistent field, SCF, wavefunctions for clusters.

When the internuclear axis of the adsorbed ligand is normal to the surface there are two A_1 symmetry stretching modes which are infrared active.[2] The intra-molecular ligand stretch is denoted L, L = C-O or C-N, and the surface-adsorbate frustrated translation is denoted ML, ML = Cu-CO or Cu-CN. The notations ω(L), ω(ML), r(L), and r(ML) are for the L and ML frequencies and bond distances. For both CO and CN, ω(L) and ω(ML) have quite different values;[3] ω(L) is ~2000 cm^{-1} and ω(ML) is ~200 cm^{-1}. In our earlier work,[1] we formed L and ML internal modes, treated as approximate normal modes, with no coupling of these modes. For the internal modes, the field induced shift in ω(CN) was much smaller than the shift in ω(CO). This is not consistent with experimental evidence where the field induced shifts for CO[4] and CN[5] are similar. The coupling of the L and ML internal modes may be important for CN. Rough estimates[1] supported this conjecture. In the present paper, results for normal modes where the coupling is explicitly included show that the coupling is important for CN. Furthermore, the coupling is shown to be directly related to the nature of the adsorbate-substrate bond. An applied electric field substantially changes the equilibrium Cu-CN distance from the field free value because chemisorbed CN is ionic,[1] CN^-. When this change of Cu-CN distance is taken into account in the definition of the L internal mode, the internal and the normal mode ω(L) have almost the same field induced shifts. The coupling is not important for CO because the field does not significantly change the Cu-CO distance for the covalent metal-CO bond. The shifts in ω(L) and ω(ML) are largely Stark effects even when the coupling of the L and ML modes is taken explicitly into account.

The outline of our paper is as follows. We describe briefly the details of the chemisorption geometry, and cluster models that we have used. Then we present our results for the equilibrium geometries and normal modes. We show that the field induced shifts in ω(CN) are smaller than but comparable to those for ω(CO) and we analyze the origin of the coupling for the L and ML modes.

We study CO and CN at an on top site of a cluster chosen to model Cu(100); the molecular axis of the ligand is normal to the surface with the C atom closest to the surface. This adsorption geometry is supported by strong evidence for CO/Cu(100) and CO on other metals.[6] For CN, the linear geometry that we have used is generally accepted for electrochemical environments.[5a,7] A uniform electric field is applied normal to the surface to simulate the field applied in Lambert's[8] ultra-high vacuum experiments and that which exists in electrochemical cells.[1,4,5] The cluster used here has 14 Cu atoms, five in the first and third layers and four in the middle layer; the metal atoms are fixed at their positions for bulk fcc Cu. The ligand is added above the central atom of the first layer. The potential surface for the motion of the ligand atoms is obtained from SCF cluster wavefunctions. Details of the computational approach, including choice of cluster geometry, the core-electron Cu pseudopotential and, the basis sets are discussed for $Cu_{14}CO$ in Ref. 9; the same approach is used for $Cu_{14}CN$. The cluster calculations for CN/Cu(100) are performed for $Cu_{14}CN^-$. This is done for computational convenience; $Cu_{14}CN^-$, isoelectronic to $Cu_{14}CO$, is also a closed shell system.[9] When CN is chemisorbed on Cu, it is CN^- regardless of the total charge on the cluster used to model the adsorption;[1,10].

The energies on the SCF potential surface for the variation of the ligand geometry are denoted E_{SCF} (F,Q); F is the magnitude of an electric field normal to the surface and Q represents the ligand coordinates. The SCF variational solution is obtained with the Hamiltonian, H(F),

$$H(F) = H(0) + \mathbf{F} \cdot \Sigma_i \mathbf{r}_i - \mathbf{F} \cdot \Sigma_i \mathbf{R}_i ; \qquad (1)$$

$H(0)$ is the usual $F = 0$ Hamiltonian and $\underline{r}_i(\underline{R}_i)$ are the electron (nuclear) coordinates. The sign of F is such that $F < 0$ attracts electrons from the surface toward the ligand. The first order perturbation theory energy, $E_P(F,Q)$ is

$$E_P(F,Q) = E_{SCF}(0,Q) - \underline{\mu}(0,Q) \cdot \underline{F}; \qquad (2)$$

$\underline{\mu}(0,Q)$ is the dipole moment for $F = 0$.

The difference in $E_P(F,Q)$ and $E_{SCF}(0,Q)$ is a Stark effect;[8] it does not include any chemical changes which the field may cause. We refer to the equilibrium bond distances, r_e, and ω for the $E_P(F,Q)$ surface as Stark values. The fully variational SCF values of r_e and ω obtained from the $E_{SCF}(F,Q)$ potential surface do include the effect of chemical changes due to the field. Hence, the differences between the SCF values of r_e and ω and the Stark values are caused by field induced chemical changes and provide a measure of the importance of these changes.

The $r_e(ML)$, $r_e(M)$, $\omega(ML)$, and $\omega(L)$ are determined in two ways. In the first, we use internal coordinates which we believe are good approximations to the normal modes. The internal coordinate calculation starts from bond distances $r^0(ML) = r(Cu\text{-}C)$ and $r^0(L) = r(C\text{-}O)$ or $r(C\text{-}N)$; normally, these r^0 are chosen close to r_e. For the ligand stretch internal coordinate, the position of the ligand center of mass is fixed and the C-O (or C-N) bond distance is varied. For the metal-ligand stretch, the ligand distance is fixed and the metal-ligand distance is varied. For these internal modes, the r_e and the harmonic approximation vibrational frequency are obtained from a polynomial fit; they are denoted by the the superscript I. This approach is equivalent to taking particular one-dimensional cuts of the full two-dimensional potential surface. It neglects the coupling of the two internal modes, which is expected to be small[11] because $\omega(ML)$ and $\omega(L)$ are an order of magnitude different. In the second approach, this coupling is explicitly considered; the full two-dimensional potential surface for the r(Cu-C) and r(Cu-O) [or r(Cu-N)] bond distances is used. The r_e and the normal mode

ω are determined[12] from a two-dimensional polynomial fit and denoted by the superscript N. The specific notations for the r_e and ω are $r_e^I(ML)$, $r_e^I(L)$, $\omega^I(ML)$, and $\omega^I(L)$ for the internal coordinates and $r_e^N(ML)$, $r_e^N(L)$, $\omega^N(ML)$, and $\omega^N(L)$ for the normal coordinates.

For the internal modes, a fourth degree polynomial is fit to the energies of five points about the equilibrium along the internal coordinate. For the coupled, normal modes, a two-dimensional polynomial to fourth degree in the positions of both ligand atoms is fit to the energies of 25 points about the equilibrium positions. The absolute SCF values for ω are not in close agreement with experiment;[13] the SCF ω are typically too large by ~10% and inclusion of electron correlation effects is required to obtain more accurate values. Although the absolute values of the SCF ω are in error, the changes in the $\omega^I(CO)$ due to an electric field are similar for SCF cluster energies[1] and for cluster energies for wavefunctions which include correlation.[14] This similarity of the SCF shifts and the shifts obtained with more accurate, correlated, wavefunctions should be general.

In Table I, we give the equilibrium geometries for $Cu_{14}CO$ and $Cu_{14}CN^-$ for $F = 0$ and $F = \pm 0.01$ a.u. $= 5.2 \times 10^7$ V/cm; this field is comparable to the fields at the electrode surface of an electrochemical cell when a potential of ~1V is applied.[15] These $r_e^N(ML)$ and $r_e^N(L)$ are obtained from the coupled two-dimensional polynomial fit. For $F = \pm 0.01$ a.u., we give both the fully variational SCF and the Stark values. When the field is applied, the Stark r_e are very similar to the SCF values; the largest difference is ~1% for the $r_e^N(ML)$ for $Cu_{14}CO$.

The largest field induced change in bond distance is for r_e^N(Cu-C) for CN/Cu(100). This occurs because chemisorbed CN is negatively charged[1] and repelled or attracted depending on the sign of the field, F. For $F = -0.01$ a.u., the ion CN^- is pulled away from the surface leading to a large increase in r_e; similarly, $F = +0.01$ a.u. pushes the ion toward the surface. We show later that these large changes in r_e(Cu-C) are important

for understanding the coupling between the ML and L modes for CN/Cu(100). The field induced changes in r_e^N(Cu-C) for CO/Cu(100) are quite small. The computed r_e(Cu-C) = 3.95 bohrs is larger than the value of 3.6 ± 0.2 bohrs[6] given by low energy electron diffraction, LEED, for CO/Cu(100). When the π portion of the Cu-CO interaction in Cu_5CO is correlated,[16,17] the predicted value is r_e(Cu-C) = 3.69 bohrs which is in close agreement with the LEED value. For the Cu_5CO cluster,[16] the SCF r_e = 3.90 bohrs. Thus the SCF value for the Cu-CO r_e is ~0.2 bohrs too large because the SCF somewhat underestimates the magnitude of the Cu to CO 2π back-donation.[17,18] The Stark changes in r_e^N(Cu-C) are very small, ~0.1%, because the π back-donation leads to a dative covalent bond.[1,9] The SCF changes in r_e^N(Cu-C) of $Cu_{14}CO$ for F = $\pm$ 0.01 a.u. are slightly larger than the Stark changes because the electric field leads to a small, but not entirely negligible, change in the metal-CO chemical bond. Overall, the absolute values of the r_e and the changes induced by the electric field for $Cu_{14}CO$ and $Cu_{14}CN^-$ are similar to the values obtained[1] with a Cu_{10} cluster.

The Stark and the normal mode frequencies for F = 0, and $\pm$0.01 a.u. are given in Table II. The Stark and the fully variational SCF shifts in ω are very similar, especially when the shifts are not very small. For the field induced shift in the ML stretch for CO/Cu(100), the SCF and Stark shifts do not agree as well but both are very small. The agreement between the SCF and Stark ω^N and the agreement for the r_e^N noted earlier provide further strong evidence[1] that chemical effects are small for these properties. A second important conclusion from Table II is that the field induced shifts in ω^N(L) are of similar magnitude for both CO/Cu(100) and CN/Cu(100). The field induced shifts in ω_e^N(CO) for F = $\pm$0.01 a.u. are only a factor of ~2 larger than those in ω^N(CN). Previously,[1] the shifts in the CN stretch internal mode, ω^I(CN), had been found to be much smaller than the shifts in ω^I(CO). For $Cu_{10}CO$ and $Cu_{10}CN^-$, the ω^I(CN) shift for F = +0.01 (−0.01) a.u. was smaller by a factor of 5(13) than the ω^I(CO) shift.[1] For the ML stretches, we find that the field induced shift in ω^N(Cu-CN)

is large, comparable in magnitude, to ω^N(CN). This is consistent with surface enhanced Raman spectra, SERS, of the ML and L frequencies for CN adsorbed on an electrode.[5(b),19] The large shift in ω^N(Cu-CN) is due to the large derivative of the dipole moment for the frustrated translation of CN with respect to the surface.[1] The derivative is large because adsorbed CN is ionic.[1,10] On the other hand, the shift in ω^N(Cu-CO) is quite small, consistent with the fact that the dipole moment derivative for the frustrated translation of CO is small.[1] Finally, we note that there is some asymmetry for the shifts of both the Stark and SCF frequencies between F = +0.01 and −0.01 a.u.; this may be a real effect or it may be an artifact related to the size of the Cu_{14} cluster.

A key conclusion about the field induced shifts in the ligand stretch frequencies is that the magnitudes of the shifts for CO and CN are comparable when the fully coupled normal modes are considered. This result is consistent with experimental measurements[4,5] of shifts of ω(L) for CO and CN as a function of the voltage across the electrodes of an electrochemical cell. For CO on Pt electrodes[4] and for CN on Cu, Ag and Au electrodes,[5] very similar shifts were found. The fact that we find the shifts in ω^N(CN) to be somewhat smaller than those in ω^N(CO) may be related to the size of the Cu_{14} cluster.

We compare, in Table III, the ω(L) and ω(ML) obtained for the internal and the normal coordinates in order to establish the origin of the coupling which is important for CN. Included in Table III are the r_e obtained in both ways. We consider first the results for $Cu_{14}CO$ and $Cu_{14}CN^-$ when there is no external field, F = 0. The starting points for these F = 0 internal mode calculations are very close to the equilibrium geometry; thus, it is not surprising that the r_e determined in both ways are nearly identical. Moreover, the ω^I and the ω^N are also nearly identical; the largest difference is 3 cm^{-1}. Clearly, the internal modes are good approximations to the normal modes; the coupling of the ML and L internal modes is very small. This is consistent with the large difference of the ω for the two modes. In Table III, we also compare the internal and normal mode results for CN/Cu(100) for F = ±0.01a.u.; the r_e and ω are the fully

variational SCF results for $Cu_{14}CN^-$. The internal mode analysis is made from two different starting points. The first starting point, r_0(Cu-C) = 3.90 and r_0(C-N) = 2.20 bohrs is very close to the r_e for no applied field, F = 0. In this case, the ω^I(CN) and r_e^I(CN) for F = $\pm$0.01 are very close to the values, either ω^I and r_e^I or ω^N and r_e^N, for F = 0. The field induced shifts for this choice of starting point for the internal mode are much smaller than the shifts for the normal mode values. The small differences between the values of ω^I and r_e^I, for F = 0 and those for F = $\pm$0.01 for the the $Cu_{14}CN$ cluster are quite similar to the internal mode results for the $Cu_{10}CN$ cluster obtained previously.[1] However, we must identify the reason why the electric field induced shifts in the coupled, normal mode, ω^N(CN), are so much larger, see Table II, than those for the internal mode.

The simplest form of coupling of the L and ML modes is to carry out the internal mode analysis near the r_e(Cu-C) and r_e(C-N) when the field is applied. This is our second starting point for the internal mode analysis. The results for this starting point are very close to the fully coupled normal mode results; in particular, the ω^I(CN) are quite close to the normal mode ω^N(CN). In other words, the key aspect of the coupling of the ML and L modes is the change in the equilibrium ML distance due to the applied field.

When r^0(Cu-C) is decreased from 3.90 to 3.75 bohrs in the F = $-$0.01 case, the internal mode frequency increases by 21 cm^{-1}; when r^0(Cu-C) is increased from 3.90 to 4.30 bohrs in the F = +0.01 case, this frequency decreases by 40 cm^{-1}. Clearly, there is a monotonic relationship between the distance of CN from the surface and the stretch frequency of the CN! This relationship occurs because the adsorbed ligand is stretching against the surface charge density, a "wall" which resists, with some degree of hardness, the ligand stretch. For the adsorption geometry that we have used, the 5σ lone pair of CO or CN is directed toward the surface. As the ligand is stretched along the internal coordinate, the 5σ lone pair overlaps and penetrates the surface charge to a greater extent. The largely non-bonding[20,21] penetration by the ligand σ charge leads to an

increase in ω(L); the increase due to this repulsion has been examined in detail for CO[22,23] and CN[23] and found to be large. This explains the need to take account of the field induced changes in r_e(ML). The change in r_e(ML) is large for CN and must be included; it is small for CO and may be neglected.

We summarize by stressing that our present normal mode analysis has shown conclusively that the coupling of the L and ML modes is responsible for the magnitude of the field induced changes in the CN stretch frequency. However, this coupling has a clear and direct origin in the ionic nature of the Cu-CN bond. Because CN is ionic, the applied electric field changes the equilibrium Cu-CN bond distance by a substantial amount. The ligand stretch frequency depends on the distance of the lone pair CN or CO ligands from the surface; the nearer the ligand is to the surface, the greater the surface barrier is to the ligand stretch motion. When this field induced change in r_e(Cu-CN) is taken into account in selecting the starting point for the internal coordinate ligand motion, the internal mode and normal mode ω are very similar. The electric field has an almost negligible effect on r_e(Cu-CO) for the covalent metal-CO bond. The field induced changes in r_e and ω for both ML and L modes are dominantly Stark effects, whatever chemical changes an applied electric field causes make only minor contributions to these properties. Although our calculations have been performed specifically for a Cu surface, we expect the features that we have stressed above to apply to CO and CN chemisorbed on other metal surfaces as well.

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TABLE I

Equilibrium bond distances, $r_e^N(ML)$ and $r_e^N(L)$ in bohrs; both SCF and Stark values are given.

F		$Cu_{14}CO$		$Cu_{14}CN^-$	
		r_e^N(C-O)	r_e^N(Cu-C)	r_e^N(C-N)	r_e^N(Cu-C)
0	SCF	2.140	3.952	2.190	3.920
+0.01	Stark	2.120	3.947	2.181	3.753
	SCF	2.121	3.971	2.182	3.753
−0.01	Stark	2.162	3.956	2.201	4.289
	SCF	2.163	3.999	2.202	4.287

TABLE II

The normal mode vibrational frequencies, ω^N(ML) and ω^N(L) in cm^{-1}, and the differences between the values for F = 0 and F = ±0.01a.u., $\Delta\omega$, are given.

F		$Cu_{14}CO$		$Cu_{14}CN^-$	
		ω^N(C-O)/$\Delta\omega$	ω^N(Cu-C)/$\Delta\omega$	ω^N(C-N)/$\Delta\omega$	ω^N(Cu-C)/$\Delta\omega$
0	SCF	2155/---	184/---	2284/---	260/---
+0.01	Stark	2259/+104	186/+2	2331/+47	325/+66
	SCF	2258/+103	180/−4	2325/+41	325/+65
−0.01	Stark	2037/−118	185/+1	2232/−52	141/−118
	SCF	2035/−120	172/−12	2227/−57	142/−118

TABLE III

Normal- and internal-mode SCF r_e, in bohr, and ω , in cm^{-1}. For the internal modes, the starting values of the bond distances, r^0(Cu-C) and r^0(L), are given.

Ligand	F(a.u.)	Mode	r^0(Cu-C)	r^0(L)	ω(L)	ω(ML)	r_e(L)	r_e(ML)
CO	0	Internal	3.95	2.15	2155	186	2.140	3.944
		Normal	----	----	2155	184	2.140	3.952
CN	0	Internal	3.90	2.20	2287	261	2.190	3.920
		Normal	----	----	2284	260	2.190	3.920
CN	+0.01	Internal	3.90	2.20	2296	328	2.188	3.753
		Internal	3.75	2.20	2317	328	2.182	3.753
		Normal	----	----	2325	325	2.182	3.753
CN	−0.01	Internal	3.90	2.20	2266	143	2.193	4.286
		Internal	4.30	2.20	2226	143	2.202	4.286
		Normal	----	----	2227	142	2.202	4.287

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