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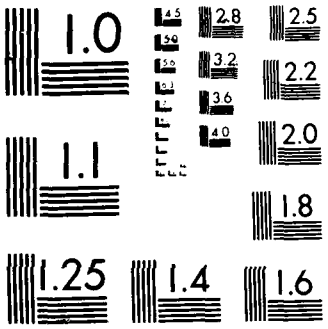

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Field Induced Vibrational Frequency Shifts of CO and CN Chemisorbed on Cu(100)

by

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Analysis of ab initio cluster wave functions show that the shifts in the vibrational frequencies of CO/Cu and CN/Cu due to an applied electric field arise dominantly from a Stark effect. The CN bonding is largely ionic while CO has a large contribution from a dative covalent π bond and consequently the Stark effect mechanisms significantly different.

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ABSTRACT: Analysis of ab initio cluster wave functions show that the shifts in the vibrational frequencies of CO/Cu and CN/Cu due to an applied electric field arise dominantly from a Stark effect. The CN bonding is largely ionic while CO has a dative covalent π bond. Consequently the Stark effect mechanisms are significantly different.

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Shifts of the intra-ligand stretch frequencies of CO and CN chemisorbed on metal surfac. have been observed when an electric field, F, is applied.[1-3] Experiments have been carried out for CO/Ni(110) in UHV,[1] for CO on Pt electrodes in an electrochemical cell,[2] and for CN on several metals in electrochemical environments.[3] Two distinct explanations for the field induced vibrational shifts have been proposed. Lambert[1] has argued that the shift is a Stark effect with little enough changes in the metal-ligand chemical bonding that it can be described by perturbation theory. On the other hand, Holloway and Norskov[4] have argued that the field changes the nature of the chemical bond and the frequency shift results from changes in the CO $2\pi^*$ occupation. In this letter, we present cluster model studies of CO/Cu(100) and CN/Cu(100). For the changes in vibrational frequency, ω, due to F, we find that the Stark perturbation theory treatment describes the shift of the ω rather well and that chemical changes are small. Further, the most important effect of the field is to change the equilibrium bond length, r_e, which couples with the anharmonicity of the potential energy curve to cause a change in ω. However, since the metal-ligand bonding is quite different for CO and CN, the way in which the field affects ω is also different. For CO, the covalent bonding, dominantly metal to CO $2\pi^*$ back-donation,[5,6] leads to a direct change in the ligand ω. For CN where the bonding is mainly ionic, the direct change in the ligand ω is rather small while the change in the metal-CN ω is large. The coupling of these stretching modes leads to the change in the higher frequency, dominantly C-N stretch, normal mode.

We describe first the clusters, adsorption geometry, electronic wave functions, and internal coordinates used. Next, we consider the nature of the metal-ligand bond in the absence of a field. Finally, we show how the ligand ω is changed when an electric field is applied.

The cluster used to model Cu(100) has 10 atoms, five in the first layer, four in the second and one in the third; the bond distances are from bulk Cu. The ligand is added at an on top site with C nearest the surface and the ligand axis normal to it. For CO/Cu(100), as well as other metals, there is strong evidence for this adsorption geometry.[7] For CN/Cu(100), this linear geometry is often found for metal-CN complexes.[8] This cluster and others, larger and smaller, have been used for the study of several properties[6,9,10] of CO/Cu(100). Self-Consistent Field, SCF, cluster wave functions are obtained for several Cu-C and C-O (C-N) bond distances, with and without of a uniform electric field normal to the surface. The SCF wave functions use a pseudo potential for the core electrons of the nine environmental Cu atoms. Refs. 10 and 11 discuss the computational approach in more detail. For $Cu_{10}CO$, the ligand geometry is varied about the positions R(Cu-C)=3.70 and R(C-O)=2.15 bohrs; these are close to the equilibrium distance from low-energy electron diffraction[7] and from calculations for a Cu_5CO cluster.[12] For $Cu_{10}CN$, the equilibrium R(Cu-C) and R(C-N) were determined and the geometry varied about bond distances near equilibrium. For the ligand vibration, an internal coordinate which fixed the ligand center of mass was used. For the metal-CN stretch, the CN was translated with fixed R(C-N). The equilibrium bond lengths, r_e, and the ω were determined from a polynomial fit to the energy curves along these internal coordinates. Even though our computational approach cannot be expected to yield exact absolute values of ω, the relative changes due to the electric field will be well represented.

Our results show that the bonding of CN/Cu(100) is dramatically different from CO/Cu(100). We use the projection of the free ligand orbitals, Φ_i^L, on the cluster wavefunction to characterize the transfer of charge between the metal and ligand units. This projection, $\Phi_i^L \Phi_i^{L\dagger}$, which gives a more realistic view of the charge transfer than a population analysis,[13] is summarized in Table I.

The charge transfer between a metal and CO is normally[14] divided into σ donation from CO to the metal and back-donation from the metal to the unoccupied CO $2\pi^*$. The projection of the CO 1σ to 5σ and 1π orbitals measures the extent to which these orbitals are unoccupied in the cluster. For $Cu_{10}CO$, this projection gives nearly 14 electrons in these CO orbitals, see Table I, showing that the CO donation is small. The projection of the CO^- $2\pi^*$ orbital measures the metal back-donation. Approximately 0.2 $2\pi^*$ electrons are occupied in $Cu_{10}CO$ bringing the total number of electrons on CO to 14.2. While this is not a precise measure of the CO ionicity, it does indicate the build-up of π charge between CO and the Cu surface expected for a covalent bond.

The projections for the $[Cu_{10}CN]^-$, $[Cu_{10}CN]^0$, and $[Cu_{10}CN]^+$ clusters confirm that CN is adsorbed essentially as CN^-. In all three cases, the projection of the occupied orbitals of neutral CN indicates, as for CO, that almost 14 electrons occupy these orbitals. A further test of the CN^- character is made by projecting the free CN^- orbitals from the $Cu_{10}CN$ wave function; this leads, Table I, to a projection even closer to 14. The projection of CN^- $2\pi^*$ from $Cu_{10}CN$ is smaller by one-half than for $Cu_{10}CO$ indicating a smaller π back-donation to CN. We consider only the $Cu_{10}CN^-$ stretching frequencies in the following.

The field free CO bonding involves an almost neutral ligand with a significant dative covalent bond between the metal and the ligand 2π; the CO σ donation is very small. In contrast, the CN bonding on a Cu surface is largely ionic; the covalent bonding, σ donation and π back-donation, is small.

For a cluster in a uniform electric field, $\vec{F}$, the SCF first order perturbation theory energy, $E_p(F)$, is obtained by subtracting $\vec{\mu} \cdot \vec{F}$ from the field free SCF energy where $\vec{\mu}$ is the field free cluster dipole moment. The SCF variational energy, $E_{SCF}(F)$, is obtained

by adding $(\Sigma\vec{r}_i - \Sigma Q_N\vec{R}_N) \cdot \vec{F}$ to the field free Hamiltonian where i denotes electrons and N nuclei; Q_N is the nuclear charge. These $E_p(F)$ and $E_{SCF}(F)$ are for given nuclear positions. The fields considered are $F = \pm 0.01$ a.u. $= \pm 5.2 \times 10^7$ V/cm. For reference, the field used by Lambert[1] in his UHV study of CO/Ni(110) was 6.0×10^4 V/cm. In an electrochemical cell, an externally applied potential of 1 V can create a field gradient of $\sim 10^7$ V/cm at the electrode surface.[15] Thus, a field of F=0.01 a.u. though considerably larger than used by Lambert[1] is comparable to those believed to exist at electrochemical interfaces. Values of ω and the equilibrium bond length, r_e, computed from the $E_p(F)$ and $E_{SCF}(F)$ curves along an internal coordinate are given in Table II.

For the CO stretch, the Stark and SCF frequency shifts, $\Delta\omega$, are the same within 5%. Regarding $\vec{F}$ to be a variable, the average tuning rate, $d\omega/dF = 1.3 \times 10^{-6}$ $cm^{-1}/(V/cm)$, is close to the $1.1 \pm 0.4 \times 10^{-6}$ measured[1] for CO/Ni(110). For the CN stretch, the $\Delta\omega$ for both Stark and full variational ω's are very small. This is interesting since chemisorbed CN has a similar measured tuning rate[3] as CO.[2] However, the tuning rate for the metal-CN stretch is quite large. It is still largely a Stark effect. We show below that the coupling of the C-N and Cu-CN internal modes leads to a larger shift in the high frequency, dominantly C-N, normal mode.

Lambert[1] made Taylor series expansions of the molecular potential and the dipole moment curves to obtain the first order Stark shift. We carry out this expansion somewhat differently to stress the two different effects involving the field. The perturbation theory potential curve is:

$$V(r,F) = a_0 - M_0F - M_1F(r - r_e)^1 + (a_2 - M_2F)(r - r_e)^2 + \ldots \qquad (1)$$

where the expansion is about the zero field r_e and the expansion coefficients for the potential, a_i, and the dipole moment, M_i, are for the F=0 wave function. The first derivative of the dipole moment, M_1, leads to a change in r_e:

$$\Delta r_e(F) = M_1 F/2(a_2 - M_2 F) \ . \tag{2}$$

The change in the curvature, $\partial^2 V(r,F)/\partial^2(r - r_e)$, at $r_e(F)$ has a direct contribution from the curvature of the dipole moment, M_2, and an indirect contribution from the change in r_e. The changes in ω, $\Delta\omega$, due to these changes in the curvature are:

$$\Delta\omega_1 = \frac{3}{2}\frac{\omega_e}{a_2}(a_3 \Delta r_e) \tag{3}$$

$$\Delta\omega_2 = \frac{-1}{2}\omega_e(M_2 F/a_2) \tag{4}$$

where $\Delta\omega_1$ is due to the change in r_e and $\Delta\omega_2$ is due to the curvature of the dipole moment. The field free frequency is given by ω and a_3 represents the anharmonicity of the molecular potential curve. These formulas lead to a total $\Delta\omega = \Delta\omega_1 + \Delta\omega_2$ essentially the same as Lambert's[1]. The Taylor series coefficients and the changes in r_e and ω are given in Table III.

For the ligand stretches, the exact perturbation theory results of Table II are closely reproduced. The value of $\Delta\omega_1$, is much larger than that of $\Delta\omega_2$. The Δr_e and $\Delta\omega_1$ are much larger for the CO stretch than for the CN stretch because the first derivative of the dipole moment curve, M_1, is larger, by a factor of 6, for CO. For free CO, M_1=-1.02. The $Cu_{10}CO$, or CO/Cu(100), M_1 is almost twice as large as the free CO value. We have

determined that the Cu to CO π back-donation makes the largest contribution to this increase.

For free CN^-, the small $M_1 = -0.4$ a.u. arises because it is isoelectronic to homopolar N_2 which has $\vec{\mu} = 0$. (For CN^-, μ is taken for a point fixed with respect to the CN center of mass.) The Cu-CN bond is largely ionic but the orbital projection, Table I, indicates small σ donation and π back-donation contribute to the decrease of $|M_1|$ for the $Cu_{10}CN^-$ where $M_1 = -0.3$ a.u.. A larger cluster better able to represent the image charge could lead to a larger value of $|M_1|$. The upper limit is given by image charge theory to be $M_1 = -0.8$ but this neglects the chemical changes which our cluster results show reduce $|M_1|$.

For the metal-CN stretch, the dipole derivative, is large, $M_1 = -1.3$. In this internal coordinate, we are moving a negative ion, CN^-, with respect to the surface. Image charge theory predicts a value of $M_1 = -2$ since when CN^- is translated by Δ, its image also moves Δ. However, even with the present cluster, the Taylor series expansion gives large $|\Delta r_e| = 0.2$ bohrs for $|F| = 0.01$ a.u. ,see Table III. These Δr_e are smaller than the exact perturbation theory results, Table II, because the expansions in Eqs. (1) - (4) are not appropriate for large changes in r_e and ω. It is clear that the large $|M_1|$ is the main reason for the large values of $\Delta\omega$ in Table II.

The internal C-N and Cu-CN modes are coupled and the normal coordinates are a mixture of them. In order to investigate this coupling, we have used standard expressions[16] for the coupling of two spring-like force constants which enables us to estimate the magnitude of the coupling. The differences between the internal coordinate frequencies and the approximate normal mode frequencies are given in Table IV. There is a clear difference between the shifts in the higher frequency modes for different values

of $\vec{F}$. When this effect is added to the $\Delta\omega$ in Table II, we obtain $\Delta\omega(F = +0.01) = 15$ and $\Delta\omega(F = -0.01) = -24\text{cm}^{-1}$ significantly larger values than those for the C-N internal coordinate. Thus, the shift of the high frequency normal mode is because there is a shift in the metal-CN stretch which is coupled with the ligand stretch. However, our present treatment, cluster size and coupling of the internal modes, cannot give quantitative values for the shift.

For $Cu_{10}CO$, we have calculated the dipole moment derivative, M_1, near the metal-ligand separation, $R(Cu - C) = 3.70$ bohrs, used. We find $|M_1| < 0.05$. For the low frequency, metal-CO, normal mode for CO/Ni(100), the value $M_1 \simeq 0.2$ has been measured.[17] This small value means that the metal ligand internal coordinate stretch frequency will hardly change in an electric field. Accordingly, the shifts due to the coupling of the internal coordinates will be nearly constant irrespective of imposed electric field.

In conclusion, we have shown that the effect of an electric field on the stretching frequencies of CO and CN chemisorbed on Cu(100) is described, to a very good approximation, by perturbation theory. The most important effect of the field is to change the equilibrium bond length. This change coupled with the anharmonicity of the potential is the dominant reason for changes in the ω. Because the metal-ligand bonding is very different for CO and CN, the effect of the field is different is these two cases. For CO, the covalent chemical bond leads to large changes in ω for the C-O stretch internal coordinate. For CN, the bonding is ionic, chemisorbed CN is essentially CN^-. The derivative of the dipole moment for the CN stretch internal coordinate is small and, hence, the change in ω is small. On the other hand, the dipole derivative for the metal-CN stretch is large and this is transferred to the CN stretch through the coupling of these two

coordinates. We predict that there should be a large field induced shift in the low frequency metal-CN stretch while the shift of the metal-CO stretch should be small. This could be tested by Surface Enhanced Raman Spectroscopy in which the low energy modes are readily accessible[3b]. These origins of the field induced ω shifts are for Cu however we expect them to be true for other metal surfaces too, in particular the noble metals, since the ligand bonding is likely to have similar common features.[11]

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TABLE I

Projections of the occupied and $2\pi^*$ ligand orbitals on the $Cu_{10}CO$ and $Cu_{10}CN$ clusters. For the occupied orbitals, the projections from the σ and π orbitals are given separately, P_σ and P_π. For $Cu_{10}CO$, R(Cu-C)=3.70 and R(C-O)=2.15 bohrs; for $Cu_{10}CN$, R(Cu-C)=3.90 and R(C-N)=2.20 bohrs.

Ligand Orbitals	Projections							
	$Cu_{10}CO$		$[Cu_{10}CN]^0$		$[Cu_{10}CN]^+$		$[Cu_{10}CN]^-$	
	P_σ	P_π	P_σ	P_π	P_σ	P_π	P_σ	P_π
L: occupied	9.99	4.00	9.91	3.98	9.91	3.98	9.91	3.98
L⁻:occupied	---	---	9.96	3.99	9.96	3.98	9.97	3.99
L⁻:$2\pi^*$	---	0.23	---	0.14	---	0.13	---	0.14

TABLE II

Equilibrium bond lengths r_e, in bohr, and vibrational stretching frequencies ω, in cm^{-1}. For the CO or CN stretching mode, r_e is the C-O or C-N distance respectively, whereas for the metal ligand stretch r_e is the Cu-C distance. The differences between the F=0 and F=±0.01 a.u. values, Δr_e and $\Delta\omega$, are given in parenthesis.

		Full Variational		Perturbation Theory	
Stretch	F	$r_e(\Delta r_e)$	$\omega(\Delta\omega)$	$r_e(\Delta r_e)$	$\omega(\Delta\omega)$
C-O	0	2.12	2273	-----	-----
	+0.01	2.11(-.013)	2339(+66)	2.11(-.013)	2343(+70)
	-0.01	2.13(+.014)	2195(-78)	2.13(+.015)	2199(-74)
C-N	0	2.19	2294	-----	-----
	+0.01	2.19(.00)	2298(+5)	2.19(.00)	2304(+11)
	-0.01	2.19(.00)	2277(-16)	2.19(.00)	2283(-11)
Cu-CN	0	3.96	245	-----	-----
	+0.01	3.77(-.18)	318(+73)	3.78(-.18)	318(+72)
	-0.01	4.31(+.35)	135(-110)	4.35(+.39)	120(-125)

TABLE III

Taylor series expansion coefficients, in a.u. for the molecular potential, a_i, and dipole moment, M_i, curves along the ligand and metal-ligand coordinates. The perturbation theory changes for r_e, Δr_e in bohrs, and for frequency, $\Delta\omega_1$, $\Delta\omega_2$, and $\Delta\omega = \Delta\omega_1 + \Delta\omega_2$ in cm^{-1} are also given.

Stretch	C-O		C-N		Cu-CN	
a_2	0.670		0.643		0.030	
a_3	-0.825		-0.716		-----	
M_1	-1.856		-0.296		-1.329	
M_2	-0.823		-0.107		-0.193	
F(a.u.)	+0.01	-0.01	+0.01	-0.01	+0.01	-0.01
Δr_e	-0.01	+0.01	-0.00	+0.00	-0.21	+0.24
$\Delta\omega_1$	+58	-59	+ 9	- 9	----	----
$\Delta\omega_2$	+14	-14	+ 2	- 2	----	----
$\Delta\omega$	+71	-73	+11	-11	----	----

TABLE IV

Differences, $\Delta\omega$, between the approximate normal modes and the internal coordinates for $Cu_{10}CN^-$.

F(a.u.)	$\Delta\omega(cm^{-1})$ Lower Mode	Higher Mode
0	-1.7	+15.6
+.01	-3.6	+26.1
-.01	-0.3	+ 4.7

REFERENCES

1. D. K. Lambert, *Solid State Comm.* **51**, 297 (1984); *Phys. Rev. Lett.* **50**, 2106 (1983).
2. K. Kunimatsu, W. G. Golden, H. Seki and M. R. Philpott, *Langmuir* **I**, 245 (1985); B. Beden, A. Bewick, and C. Lamy, *J. Electroanal. Chem.*, **123**, 335 (1981).
3. (a) K. Kunimatsu, H. Seki, W. G. Golden, J. G. Gordon II, and M. R. Philpott, *Surf. Sci.*, **158**, 596 (1985); (b) R. Kötz and E. Yeager, *J. Electroanal. Chem.*, **123**, 335(1981).
4. S. Holloway and J. K. Norskov, *J. Electroanal. Chem.* **161**, 193 (1984).
5. P. S. Bagus, C. J. Nelin and C. W. Bauschlicher, *Phys. Rev.* **B28**, 5423 (1983).
6. P. S. Bagus, K. Hermann and C. W. Bauschlicher, *J. Chem. Phys.* **81**, 1966 (1984).
7. S. Andersson and J. B. Pendry, *Phys. Rev. Lett.* **43**, 363 (1979) and references therein.
8. L. E. Sutton, *Tables of Intra-Atomic Distances*, Special Publication No. 18 (London, Chemical Society, Burlington House, 1965).
9. P. S. Bagus and K. Hermann, *Phys. Rev.* **B33**, 2987 (1986).
10. P. S. Bagus and W. Müller, *Chem. Phys. Lett.* **115**, 540 (1985); W. Müller and P. S. Bagus, *J. Vac. Sci. Technol.* **A3**, 1623 (1985).
11. P. S. Bagus, C. W. Bauschlicher, C. J. Nelin, B. C. Laskowski and M. Seel, *J. Chem. Phys.* **81**, 3594 (1984).
12. P. S. Bagus, C. J. Nelin and C. W. Bauschlicher, *J. Vac. Sci. Technol.* **A2**, 305 (1984).
13. P. S. Bagus, in Plasma Systhesis and Etching of Electronic Materials, edited by R. T. H. Chang and B. Abeles, *MRS Symposia Proceedings Vol. 38* (Materials Research Society, Pittsburgh, 1985), p.179.
14. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed. (Wiley, New York, 1972).

15. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry Vol. 2* (Plenum Press, New York, 1973).

16. E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955), p. 28.

17. S. Chiang, R. G. Tobin, P. L. Richards and P. A. Thiel, *Phys. Rev. Lett.* **52**, 648 (1984).

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