

Field-Induced Vibrational Frequency Shifts of CO and CN Chemisorbed on Cu(100)P. S. Bagus, C. J. Nelin,^(a) W. Müller,^(a) M. R. Philpott, and H. Seki

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Analysis of *ab initio* cluster wave functions shows 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 intraligand stretch frequencies of chemisorbed CO and CN have been observed when an electric field 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 Lambert¹ has argued that the shift is a physical Stark effect that can be described by perturbation theory. On the other hand, Holloway and Norskov⁴ and Ray and Anderson⁵ argued that the field changes the chemical bond. Korzeniewski *et al.*⁶ concluded that both physical and chemical effects operate.

In this paper, we present the first definitive theoretical evidence that the changes in vibrational frequency, ω , due to an applied field are given by first-order perturbation theory and that chemical changes are small. Further, we show that 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 . 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,^{7,8} 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 small while the change in the metal-CN ω is large. The coupling of these stretching modes leads to the change in the dominantly C-N stretch normal mode. Our conclusions are based on cluster-model studies of CO/Cu(100) and CN/Cu(100). We describe first the clusters, adsorption geometry, electronic wave functions, and internal coordinates used. Next, we consider the metal-ligand bond in the absence of a field. Finally, we show how ω is changed when an electric field is applied.

The cluster used to model Cu(100) has ten 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, there is strong evidence for this adsorption geometry.⁹ For CN, this linear geometry is often found for metal-CN complexes.¹⁰ This cluster and others, larger and smaller, have been used to

study several properties^{8,11-13} 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 a uniform electric field normal to the surface. A pseudopotential is used for the core electrons of the nine environmental Cu atoms. Bagus and co-workers^{12,14} discuss the computational approach. For Cu₁₀CO, the ligand geometry is varied about the positions $R(\text{Cu-C})=3.70$ and $R(\text{C-O})=2.15$ bohrs; these are close to the equilibrium distance from low-energy electron diffraction.⁹ For Cu₁₀CN, the equilibrium $R(\text{Cu-C})$ and $R(\text{C-N})$ 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 $R(\text{C-N})$. 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 does not yield exact absolute values of ω , the 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 wave function to characterize the transfer of charge between the metal and ligand units. This projection, $\Phi_i^L\Phi_i^{L\dagger}$, is summarized in Table I.

The charge-transfer and dative-covalent bonding between a metal and CO is normally¹⁵ divided into donation from CO to the metal and back donation from the metal to CO. The projection of the CO 1σ to 5σ and 1π orbitals measures the extent to which these orbitals are occupied in the cluster. For Cu₁₀CO, this projection gives nearly fourteen electrons in these CO orbitals (see Table I) showing that the CO donation is small. The magnitude of the metal $2\pi^*$ back donation is determined from the difference, $\Delta P_{2\pi}$, between the projection of the CO $-2\pi^*$ orbital from the Cu₁₀CO cluster and from the bare Cu₁₀ cluster. This difference takes into account the overlap of the ligand $2\pi^*$ orbital with the metal orbitals. The increase of $2\pi^*$ character given by $\Delta P_{2\pi}$ is a measure of the back donation which occurs in the bonding

TABLE I. Projections of the ligand orbitals on Cu_{10}CO [$R(\text{Cu-C})=3.70$ and $R(\text{C-O})=2.15$ bohrs] and Cu_{10}CN [$R(\text{Cu-C})=3.90$ and $R(\text{C-N})=2.20$ bohrs]. For the occupied orbitals, the σ and π projections, P_σ and P_π , are given separately.

Ligand orbitals	Cu_{10}CO		Projections					
	P_σ	P_π	$[\text{Cu}_{10}\text{CN}]^0$		$[\text{Cu}_{10}\text{CN}]^+$		$[\text{Cu}_{10}\text{CN}]^-$	
			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^- ; $2\pi^*$	...	0.28 ^a	...	0.01 ^a	...	0.00 ^a	...	0.01 ^a

^aThese are values of $\Delta P_{2\pi}$, the difference of the 2π projection from $\text{Cu}_{10}L$ and bare Cu_{10} ; see text.

process. The value of $\Delta P_{2\pi}=0.28$ electron indicates a substantial dative covalent Cu-CO π bond in agreement with other determinations.^{8,12}

The projections for the $[\text{Cu}_{10}\text{CN}]^-$, $[\text{Cu}_{10}\text{CN}]^0$, and $[\text{Cu}_{10}\text{CN}]^+$ 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 fourteen electrons occupy these orbitals. A further test of the CN^- character is made by projecting the free CN^- orbitals; this leads (Table I) to a projection even closer to fourteen. For the projection of $\text{CN}^- 2\pi^*$, $\Delta P_{2\pi}$ is negligible showing that there is no π back donation to CN^- . We consider only the $\text{Cu}_{10}\text{CN}^-$ stretching frequencies in the following.

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

For a cluster in a uniform electric field, $\mathbf{F}$, the SCF first-order perturbation theory energy, $E_P(F)$, is obtained by subtraction of $\boldsymbol{\mu} \cdot \mathbf{F}$ from the field-free SCF energy where $\boldsymbol{\mu}$ is the field-free dipole moment. The SCF variational energy, $E_{\text{SCF}}(F)$, is obtained by addition of $(\sum \mathbf{r}_i - \sum Q_N \mathbf{R}_N) \cdot \mathbf{F}$ to the field-free Hamiltonian; i denotes electrons, N nuclei, and Q_N is the nuclear charge. These $E_P(F)$ and $E_{\text{SCF}}(F)$ are for given nuclear positions. The fields considered are $F = \pm 0.01$ a.u.

$= \pm 5.2 \times 10^7$ V/cm. The field used by Lambert¹ 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.¹⁶ 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 r_e computed from the $E_P(F)$ and $E_{\text{SCF}}(F)$ 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%. If we regard $\mathbf{F}$ to be a variable, the average tuning rate, $d\omega/dF = 1.3 \times 10^{-6}$ $\text{cm}^{-1}/(\text{V/cm})$, is close to the $(1.1 \pm 0.4) \times 10^{-6}$ measured¹ 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 rate³ to that of 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.

Lambert¹ 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 po-

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

Stretch	F	Full variational $r_e(\Delta r_e)$	$\omega(\Delta\omega)$	Perturbation theory	
				$r_e(\Delta r_e)$	$\omega(\Delta\omega)$
C-O	0	2.12	2273	...	...
	+0.01	2.11(-0.013)	2339(+66)	2.11(-0.013)	2343(+70)
	-0.01	2.13(+0.014)	2195(-78)	2.13(+0.015)	2199(-74)
C-N	0	2.19	2294	...	...
	+0.01	2.19(0.00)	2298(+5)	2.19(0.00)	2304(+11)
	-0.01	2.19(0.00)	2277(-16)	2.19(0.00)	2283(-11)
Cu-CN	0	3.96	245	...	...
	+0.01	3.77(-0.18)	318(+73)	3.78(-0.18)	318(+72)
	-0.01	4.31(+0.35)	135(-110)	4.35(+0.39)	120(-125)

TABLE III. Taylor-series expansion coefficients in a.u.: a_i for the molecular potential and M_i for the dipole-moment curves. The changes for r_e , Δr_e in bohrs, and for frequency, $\Delta\omega_1$, $\Delta\omega_2$, and $\Delta\omega$ in reciprocal centimeters, are also given; see Eqs. (2)–(4).

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

tential curve is

$$V(r, F) = a_0 - M_0 F - M_1 F(r - r_e)^1 + (a_2 - M_2 F)(r - r_e)^2 + \dots, \quad (1)$$

where the expansion coefficients for the potential, a_i , and the dipole moment, M_i , are for the zero-field wave functions. The first derivative of the dipole moment, M_1 , leads to a change in r_e when $F \neq 0$:

$$\Delta r_e(F) = M_1 F / 2(a_2 - M_2 F). \quad (2)$$

The change in ω , $\Delta\omega$, due to F results from a change in the curvature of Eq. (1), $\partial^2 V(r, F) / \partial^2 r$, at $r_e(F)$. It has an indirect contribution, $\Delta\omega_1$, from the change in r_e , Eq. (2), and a direct contribution, $\Delta\omega_2$, from the curvature of the dipole moment, M_2 :

$$\Delta\omega_1 = (3\omega/2a_2)(a_3\Delta r_e), \quad (3)$$

$$\Delta\omega_2 = -\frac{1}{2}\omega(M_2 F/a_2), \quad (4)$$

where ω is the $F=0$ frequency and a_3 represents the anharmonicity of the molecular potential curve. The total change is $\Delta\omega = \Delta\omega_1 + \Delta\omega_2$. The Taylor series coefficients and Δr_e and $\Delta\omega$ are given in Table III.

For the ligand stretches, the exact perturbation-theory results, Table II, are closely reproduced by the Taylor-series expansion. 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. The small M_1 for Cu₁₀CN can be understood because CN⁻ is isoelectronic to homopolar N₂. The center of charge of CN⁻ is near the geometric center of CN and also near the center of mass of CN. For the ligand stretch internal coordinate, the CN center of mass is fixed. Hence, there is no substantial motion of the center of charge and M_1 is small.

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 $M_1 = -2$ since when CN⁻ is translated by Δ , its image also moves Δ . The Taylor-series expansion gives large $|\Delta r_e| = 0.2$ bohr for $|F| = 0.01$ a.u.; see Table III. These Δr_e are smaller

than the exact perturbation-theory results, Table II, because Eq. (2) is not appropriate for large changes in r_e . However, it is clear that the large $|M_1|$ is the main reason for the large values of $\Delta\omega$ in Table II.

The normal coordinates are a mixture of the internal C-N and Cu-CN modes. We have used standard expressions¹⁷ for the coupling of two springlike force constants to determine the mixing approximately. This treatment neglects the interaction force constants but will enable us to estimate the magnitude of the mixing. 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 F . When this effect is added to the $\Delta\omega$ in Table II, we obtain $\Delta\omega(F=+0.01) = 15$ and $\Delta\omega(F=-0.01) = -24$ cm⁻¹, significantly larger values than those for the C-N internal coordinate. Thus, the reason for the shift of the high-frequency normal mode is the shift in the metal-CN stretch which is coupled with the ligand stretch. However, our present treatment for the coupling cannot give quantitative values for the shift.

For Cu₁₀CO, we have calculated M_1 for the Cu-CO stretch and find $|M_1| < 0.05$. For the low-frequency, metal-CO, normal mode for CO/Ni(100), the value $|M_1| \approx 0.2$ has been measured.¹⁸ These small values show that the metal-ligand internal coordinate ω will hardly change in an electric field. The shifts due to the coupling of the internal coordinates will be nearly constant irrespective of imposed electric field.

In conclusion, 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

TABLE IV. Differences, $\Delta\omega$, between the approximate normal modes and the internal coordinates for Cu₁₀CN⁻.

F (a.u.)	$\Delta\omega$ (cm ⁻¹)	
	Lower mode	Higher mode
0	-1.7	+15.6
+0.01	-3.6	+26.1
-0.01	-0.3	+4.7

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. 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. The dipole-moment derivative of the CN stretch internal coordinate is small and, hence, the change in ω is small. However, the dipole derivative for the metal-CN stretch is large and this is relayed to the CN stretch by 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 Raman spectroscopy in which the low-energy modes are readily accessible.^{3b} We expect these origins of the field-induced ω shifts to be true for other metal surfaces, in particular the noble metals, since the ligand bonding is likely to have similar features.¹⁴

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