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Coupling between the nickel–carbon and carbon–oxygen stretch motion in NiCO

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Linear-combination-of-Gaussian-type-orbital $X\alpha$ calculations on NiCO are described. The electronic structure and equilibrium bond distances $R_{\text{Ni}-\text{CO}}=3.11a_0$ and $R_{\text{NiC}-\text{O}}=2.18a_0$ are consistent with recent configuration-interaction calculations employing core pseudopotentials. The computed Ni–CO and NiC–O harmonic vibrational frequencies are 656 and 1933 cm^{-1}. The CO stretch vibration is within 100 cm^{-1} of experiment and the ratio of intensities for those two modes, 640, is consistent with the fact that the Ni–C stretch has not been seen in matrix isolation experiments. The relevance of NiCO as a model for CO adsorbed on solid nickel is discussed and found to be marginal.

I. INTRODUCTION

As a model for CO adsorbed on transition-metal surfaces, numerous calculations of CO on transition metal clusters have been performed. The earliest "first principles" calculations used the multiple-scattering (MS)-$X\alpha$ method and focused on electronic energy levels[1–3] for an assumed geometry, as geometry optimization is unreliable in this method.[4] Nevertheless, this work[1] predicted the degeneracy of the CO 1π-like ($1\tilde{\pi}$) and 5σ-like ($5\tilde{\sigma}$) levels when adsorbed on nickel which was verified in experimental[5] and theoretical[6] studies of angle-resolved photoemission. More recently, MS-$X\alpha$ calculations have been performed on all the mononickel carbonyls Ni(CO)$_n$ ($n=1,4$), with all of them found to be diamagnetic (singlet states), a result which is consistent with available experimental data.[6] Also, shake up upon core-level photoemission from transition-metal carbonyls has been considered within the MS-$X\alpha$ formalism.[7,8]

The discrete-vibrational (DV)-$X\alpha$ method,[10] which avoids the muffin-tin approximation of MS-$X\alpha$ by effective three-dimensional integration, has been modified to give accurate geometries for small molecules.[11] This improved method has not, to our knowledge, been applied to transitional-metal compounds. However, the electronic structure of a number of transition-metal carbonyls have been studied at fixed geometries using the original DV-$X\alpha$ method.[12] The self-consistent-charge (SCC) approximation to DV-$X\alpha$ uses Mulliken population analysis to determine self-consistently overlapping spherical atomic potentials.[13] This method is quite economical, but its ability to predict accurately geometries has not been thoroughly tested, although SCC-$X\alpha$ and DV-$X\alpha$ calculations have been compared for Ni$_5$CO as a function of Ni$_5$–CO distance.[14] A number of geometry optimization studies for CO bonded to transition-metal clusters using SCC-$X\alpha$ have appeared in the literature.[15–17] Using another variant of the DV-$X\alpha$ method which avoids the direct use of the total energy,[18] the Ni(CO)$_3$–L (ligand) distance has been optimized for a variety of ligands (L) in Ni(CO)$_3L$ assuming tetrahedral geometry.[19]

A number of *ab initio* calculations of NiCO have been performed. These include generalized valence bond (GVB) using a pseudopotential for the argon core of the nickel atom,[20] in which the Ni–CO distance (CO distance fixed at $2.17a_0$) was optimized for the $^3\Sigma^+$, $^3\Pi$, and $^3\Delta$ states. The $^3\Delta$ state was found to lie lowest in energy with equilibrium Ni–CO distance $R_{\text{Ni}-\text{CO}}=3.59a_0$ and dissociation energy $D_{\text{Ni}-\text{CO}}=1.15$ eV. However, singlet states were not considered in that study.[21] NiCO and linear Ni$_2$CO were studied using the all-electron Hartree-Fock (HF) method, for the first molecule the optimal Ni–CO distance (holding the CO distance fixed at $2.13a_0$) was $3.17a_0$ for the $^3\Delta$ state (HF ground state).[22] More recently, this approach has been used in a thorough test of the Schönhammer-Gunnarsson[23] model of core-level satellite structure in NiCO.[24] The possibility that NiCO was bent has been considered in another HF treatment.[25] Using fixed distances of Ni$-$C$=3.477a_0$ and C$-$O$=2.173a_0$, the experimental values for $Ni(CO)_4$,[26] total energies of linear and bent ($\angle$Ni$-$C$-$O$=146°$) configurations were compared for electronic structures which become $^3\Delta$ and $^1\Sigma$ in the linear case. A slight tendency for the $^3\Delta$ state to be bent and the $^1\Sigma$ state to be linear was found. A recent reexamination of LEED data[27] indicates a linear NiCO bond, consistent with the σ bond formation involving the 5σ orbital of CO as molecular orbital theory predicts.

Recently, a linear-combination-of-Gaussian-type-orbital (LCGTO) $X\alpha$ method has been developed[28] which is an extension of the method of Sambe and Felton.[29] In these methods both the charge density (used in computing the electron-electron Coulomb repulsion energy) and the cube root of the charge density (used in computing the exchange energy) are fit to LCGTOs. The use of (incomplete) fitting basis sets the size of which are on the order of the size of the orbital basis (N) results in an N^3 self-consistent-field (SCF) method which is more economical computationally than the N^4 Hartree-Fock (HF) method in which exchange and electron-electron Coulomb repulsion are treated exactly.

While our LCGTO-$X\alpha$ method is economical and thus can be applied to larger systems, it has been shown to give a reliable, within the Born-Oppenheimer and $X\alpha$ approximations, treatment of the effects of changing nuclear configurations. Thus, in this work we focus on the vibrational frequencies and dynamical dipole moments of the Ni$-$CO versus NiC$-$O stretch vibrational modes. This is an interesting problem in that both vibrations have been seen for CO adsorbed on single crystal Ni(100) (Ref. 30) but only the NiC$-$O stretch has been observed in matrix isolation experiments on isolated NiCO.[31] This difference stimulated the present work.

II. METHOD

In our method, in order to take into account *a priori* that we will fit the charge density $\rho=\sum_i n_i u_i^* u_i$ where n_i and u_i are the occupation number and eigenfunction of the ith orbital, we modify slightly Slater's $X\alpha$ Hamiltonian:

$$E=T(\rho)+[\rho\,|\,\rho_N]+[\rho\,|\,\tilde{\rho}]-\tfrac{1}{2}[\tilde{\rho}\,|\,\tilde{\rho}] + \tfrac{9}{4}\alpha\,(3/4\pi)^{1/3}\int(\rho_\uparrow^{4/3}+\rho_\downarrow^{4/3})d\vec{r}\,, \tag{1}$$

where the kinetic energy

$$T(\rho)=-\tfrac{1}{2}\sum_i n_i u_i^*(\vec{r})\nabla^2 u_i(\vec{r})\,,$$

where ρ_N is the nuclear charge density, $\rho_\uparrow$ and $\rho_\downarrow$ are the spin-up and spin-down components of the charge density, square brackets denote Coulomb repulsion integrals, and tildes denote fitted quantities. (α is set to 0.7 in this work.) The conventional one-electron $X\alpha$ equations are derived from Eq. (1) by requiring the energy to be stationary with respect to variations of the u_i.[32] In order to treat the exchange terms, the fifth and sixth terms in Eq. (1) we fit $\rho_\uparrow^{1/3}$ and $\rho_\downarrow^{1/3}$ to LCGTOs on a numerical grid whose size is the product of 12 angular points and every tenth point of the Herman-Skillman radial grid about each atom.[28] However, this effective numerical integration is used only in the fitting process not in the construction of the one-electron matrix elements or the computation of the energy.[11]

The equations for fitting the charge density follow variationally from Eq. (1) and thus the energy is stationary with respect to the error made in fitting the density. In our LCGTO approach they are

$$\sum_l S_{kl}a_1=\sum_{\sigma ijk} n_\sigma c_i^\sigma c_j^\sigma V_{ijk}\,, \tag{2}$$

where $\vec{a}$ is the vector of the expansion coefficients of the fitting basis and $\vec{c}^{\,\sigma}$ is the vector of the coefficients of the σth orbital in the orbital basis. S_{kl} and V_{ijk} are the appropriate two- and three-center Coulomb repulsion matrix elements. Equation (1) when written in matrix form

$$\vec{a}=S^{-1}\vec{V} \tag{3}$$

is identical to the conventional least-squares-fit problem[5] apart from the use of the metric $1/r_{12}$. We impose the constraint

$$\int\tilde{\rho}\,d\vec{r}=n_e\,,$$

where n_e is the number of electrons, by means of Lagrange multipliers. This constraint is not essential for reliable use of the method.[33] This method has been used in additional work[34–36] including studies of NiH and Ni_2.[37]

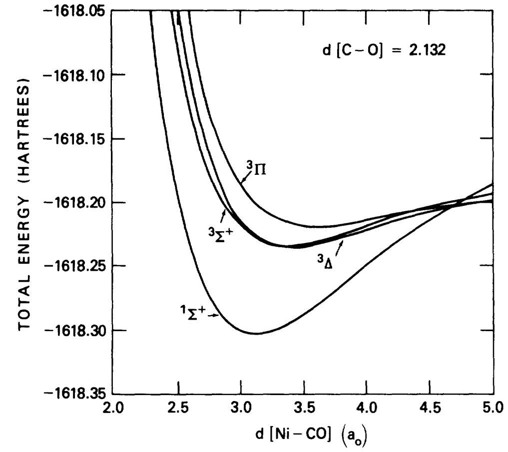

FIG. 1. The lowest-lying singlet and triplet Ni—CO potential-energy curves. These curves are for the carbon—oxygen distance d[C—O] fixed at its value in free CO.

Our orbital basis set consisted of Wachter's[38] ($14s/9p/5d$) basis augmented by additional p and d functions of exponent 0.1 bohr^{-2} for nickel, and van Duijneveldt's[39] ($9s/5p$) basis augmented with d functions of orbital exponent 1.0 bohr^{-2} for carbon and oxygen. Our basis for the fit to the charge density $\tilde{\rho}$ was, in part, derived from the orbital basis. We doubled all of the s orbital exponents for the s charge-density fitting (CDF) basis and doubled some of the p orbital exponents (in decreasing order, those basic functions were 1, 3, 5, 7, 9, 10 on nickel and 1, 3, 5 on carbon and oxygen) to yield one each $d_\perp$ and $d_{\|}$ (where $\perp$ and $\|$ refer to the linear NiCO axis) exponents for the CDF basis. The $p_{\|}$ CDF basis for nickel was $1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}$, and $\frac{1}{6}$ bohr^{-2} which have maxima along the internuclear axis at ±0.5, ±1.0, ±1.5, ±2.0, ±2.5, and ±3.0 bohr. For carbon and oxygen we chose the exponents 0.71, 0.35, and 0.24 bohr^{-2} for the $p_{\|}$ components of our CDF basis. In order to fit the cube root of the density $\tilde{\rho}^{1/3}$ used in computing the Slater exchange energies, we take the s and d CDF basis functions divided by three and include unchanged the $p_{\|}$ exponents.

Thus, we have a precise one-to-one correspondence between our CDF and exchange-fitting (XF) bases. While $\rho^{1/3}$ is much smoother than ρ let alone the Coulomb potential generated by ρ, it might appear that the XF basis is relatively too large. However, the error in our computed total energy is quadratic in the error made fitting ρ but linear in the error made in fitting $\rho^{1/3}$, which means that greater care should be taken to fit $\rho^{1/3}$ adequately. Both fitting bases are slightly smaller than the orbital bases. But in previous studies[28] of convergence with respect to basis set size on smaller molecules it was found that for similar ratios of basis sizes, the error made due to orbital basis set incompleteness dominates.

III. DISCUSSION

Our ($9s/5p$) s and p basis for CO is smaller than that ($11s/6p$) used in a previous study of CO. (However, the polarization basis is the same size.) Thus, we performed a calculation for CO using this smaller basis at $R_{\mathrm{CO}}=2.132a_0$, the experimental gas-phase equilibrium distance. Relative to the previous work the binding energy of CO is reduced by 0.3 eV. However, we found a virial ratio of $-V/T=1.999\,96$ indicating this distance is within $\pm0.001a_0$ of the equilibrium for this basis. To this accuracy, the equilibrium separation is unchanged from the earlier calculation using a larger basis and in the following we assume the shape of the CO potential-energy curve is unchanged from the previous work.

Consistent with the most recent CI calculation[40] (similar to the GVB calculations of Ref. 20 but also considering singlet states), we find the ground state of NiCO to be $^1\Sigma$. In this state the nickel atom is predominantly in a $3d^{10}$ configuration. The Ni—CO potential energy curves for this state together with and the next lowest-lying (triplet) states are graphed in Fig. 1 for the CO distance fixed at its distance in free CO. These triplet states involve a hole of the appropriate symmetry in the otherwise filled d shell of nickel. As found in Ref. 40, an approximately closed nickel $3d$ subshell allows a stronger and shorter Ni—CO bond.

In order to study the interaction between the two stretch motions for the $^1\Sigma$ ground state of NiCO we performed calculations at 27 different Ni—C and C—O bond distances in the linear configuration with each bond distance within $0.2a_0$ of its equilibrium value. Using a quadratic fit to these total energies we find the dissociation energies, geometry, and force constants given in Table I, $R_{\mathrm{Ni-CO}}=3.11a_0$ is in close agreement with the nickel-carbon distance of about $3.2a_0$ which we get from the $^1\Sigma^+$ ground-state curve of Ref. 40. This is considerably shorter than the $3.59a_0$ found for the $^3\Delta$ state in Ref. 20, and our Ni—CO binding energy of 3.1 eV is greater than the 1.1 eV found for this triplet state. This is consistent with the description of the bonding found in the more recent investigation.[40] Relative to $\mathrm{Ni(CO)_4}$ the

TABLE I. Dissociation energies, equilibrium distances, and force constants. [The results of this work are compared with experiments for CO, NiCO, and $Ni(CO)_4$.]

	CO		NiCO		$Ni(CO)_4$
	$X\alpha$	Expt.	$X\alpha$	Expt.	Expt.
D_{C-O} (eV)	12.0	11.23			
D_{Ni-CO} (eV)			3.1		
$R_{C-O}(a_0)$	2.13	2.13	2.18		2.17
$R_{Ni-C}(a_0)$			3.11		3.48
$f_{NiC,NiC}$ (mdyn/Å)			5.17	3.24[a]	2.08 (Ref. 41)
$f_{NiC,CO}$ (mdyn/Å)			0.78	0.52[a]	0.52 (Ref. 41)
$f_{CO,CO}$ (mdyn/Å)			14.18	15.57[a]	17.85 (Ref. 41)

[a] From Ref. 31, as only the CO stretch was seen, $F_{NiC,CO}$ from Ref. 41, was used to deduce $f_{NiC,NiC}$.

Ni—C bond is stronger leading to a shorter R_{Ni-CO} and concomitant weakening and lengthening of the C—O bond due to a π back donation from the nickel atom. Our force constants are consistent with experimentally derived[31] force constants based on the use of the $f_{NiC,CO}$ cross term from $Ni(CO)_4$.[41] However, our work indicates this cross force constant is larger in NiCO than in $Ni(CO)_4$ due to the shorter R_{Ni-CO}.

In Table II we give the vibrational frequencies and intensities [proportional to $(\partial\mu/\partial q)^2$ where μ is the dipole moment and q is the appropriate normal coordinate] relative to free CO. These intensities were obtained using $\partial\mu/\partial R_{Ni-CO} = e^*_{Ni-CO} = 1.02$ and $e^*_{NiC-O} = -3.82$ in units of electron charge. We note that they are both larger than the corresponding quantity for free CO, $e^*_{C-O} = 0.64$, yet the Ni—CO intensities are quite weak due to the mixing of these modes caused by the diagonalization of the force constant matrix. The second row is appropriate to NiCO. We find the NiC—O harmonic frequency to be 1933 cm^{-1} compared to the experimental 0→1 frequency of 1996 cm^{-1}.[31] This agreement is somewhat worse than it seems, as we have not included the anharmonic correction (27 cm^{-1} for free CO),[42] which would lower our value. However, our result is most likely accurate to within 100 cm^{-1} as is our prediction of the Ni—CO frequency of 656 cm^{-1}. Also, our calculations indicate the ratio of these two intensities is 640 consistent with the experimental[31] nonobservance of the Ni—CO stretch. Finally, the CO stretch intensity is enhanced relative to free CO by a factor of 48. Such large enhancements have been observed and discussed for other transition-metal carbonyl systems.[43,44]

There is much interest in the degree to which absorbed CO on solid transition metals are similar to the appropriate molecular carbonyl. Thus, we have considered masses other than 58.71 amu for the nickel atom. Since the Debye frequency of bulk nickel is much less than the CO stretch frequency, the effects of the coupling of the modes can be approximated by using a larger mass for the nickel atom provided the bonding in NiCO is similar to the bonding in adsorbed CO. Using an infinite mass for the nickel atom does not appreciably change the frequencies and intensities. In particular, the intensity of the Ni—CO stretch is extremely small, but this stretch is seen at 480 cm^{-1} in high-resolution electron-energy-loss (HREELS) experiments.[30] Thus, we conclude the bonding is

TABLE II. Frequencies and intensities (normalized to free CO) for various nickel atom mass using NiCO force constants on $e^*_{Ni-CO} = 1.02$, and $e^*_{NiC-O} = -3.82$ and $e^*_{C-O} = 0.64$.

Mass (amu)	ω_{Ni-CO} (cm^{-1})	I_{Ni-CO}	ω_{NiC-O} (cm^{-1})	I_{NiC-O}
0	∞	0	1865	38.2
58.71	656	0.0749	1933	47.7
∞	541	0.0616	1930	47.4
free CO			2160	1

different in these systems. This is also supported by LEED analysis indicating a Ni–C distance, of $3.4\pm0.2a_0$,[27] much closer to that in $\mathrm{Ni(CO)_4}$ than to our results for NiCO. Furthermore the Ni–CO stretches are seen in $\mathrm{Ni(CO)_4}$ at 371 and 423 cm^{-1},[41] which again are in closer agreement with HREELS than our frequency of 656 cm^{-1}.

Another aspect of the transition-metal systems that has received considerable attention recently is the applicability of the image model. It has been used to predict CO vibrational shifts,[45–47] valence level photoemission shifts,[48] and binding-energy contributions[49] in particular. Recently, Davenport[50] has extended the model appropriately for molecules by considering the polarizibility of the transition metal. We extend his model slightly to include self-consistency in the computation of the electric field at the center-of-mass (COM) of the CO molecule. Viewed as a sum of its parts, the (dynamical) dipole moment of NiCO can be written

$$\mu_T=\mu_{\mathrm{CO}}+\alpha_{\mathrm{Ni}}E_{\mathrm{Ni}}+\alpha_{\mathrm{CO}}E_{\mathrm{CO}}\ ,$$

where α_i and E_i are the (dynamical) polarizibilities and electric fields at the COM of both constituents. In the presence of an applied electric field E the total fields at the two sites are

$$E_{\mathrm{Ni}}=E+\left[a_{\mathrm{CO}}\frac{2}{r_0^3}\right]E_{\mathrm{CO}}=\frac{2}{r_0^3}\mu_{\mathrm{CO}}\ ,$$

$$E_{\mathrm{CO}}=E+\left[\alpha_{\mathrm{Ni}}\frac{2}{r_0^3}\right]E_{\mathrm{Ni}}\ ,$$

where $r_0=2.3$ Å is our computed Ni to CO COM distance. Solving these equations for the total moment yields

$$\mu_T=\left[\left[\alpha_{\mathrm{CO}}+\alpha_{\mathrm{Ni}}+\alpha_{\mathrm{CO}}\alpha_{\mathrm{Ni}}\frac{4}{r_0^3}\right]\Big/D\right]E$$
$$+\left[1+\left[1=\alpha_{\mathrm{CO}}\frac{2}{r_0^3}\right]\alpha_{\mathrm{Ni}}\frac{2}{r_0^3}\Big/D\right]\mu_{\mathrm{CO}}$$
$$=\gamma E+\sigma\mu_{\mathrm{CO}}\ ,$$

where $D=1-\alpha_{\mathrm{CO}}\alpha_{\mathrm{NI}}(4/r_0^6)$. Since α_{CO} is dominated by its electronic contribution, it is the second term, not the first (used in Ref. 50) that determines the structure in the frequency dependence of IR adsorption. Using $\alpha_{\mathrm{CO}}=2.6$ $\mathrm{Å}^3$ for the axial electron polarizability of CO[46] and 10.2 $\mathrm{Å}^3$ for the electronic polarizability of nickel[50] we find $\sigma=9.44$ somewhat larger than our value of 6.91 for the square root of the ratio of the CO stretch vibrations in NiCO versus CO. Furthermore, our value includes coupling between the two modes. Really, σ should be compared with 6.18, the square root of the relative intensity for the mass of the nickel atom taken to be zero which prevents mode coupling. Nevertheless, the polarization model is within 50% of our values.

In a similar vein, the polarization model can be used to estimate the shift in the CO stretch frequency due to formation of NiCO. Using a harmonic-oscillator model for the CO vibration we find the new oscillation frequency. The equation of motion is

$$m\ddot{\mu}+m\omega_0^2\mu+2m\Gamma\mu=e^{*2}E_{\mathrm{CO}}\ ,$$

where m is the reduced mass. Solving this with the self-consistent E_{CO} gives a new frequency resonant frequency,

$$\bar{\omega}_0^2=\omega_0^2-\frac{e^{*2}}{m\alpha_{\mathrm{CO}}}\Big/\left[\frac{r_0^6}{4\alpha_{\mathrm{Ni}}\alpha_{\mathrm{CO}}}-1\right],$$

and the frequency shift is

$$\Delta\omega=-\frac{e^{*2}}{2m\alpha_{\mathrm{CO}}\omega_0}\Big/\left[\frac{r_0^6}{4\alpha_{\mathrm{Ni}}\alpha_{\mathrm{CO}}}-1\right]$$
$$=-52\ \mathrm{cm}^{-1}$$

which is a third of the experimentally observed value. (In passing we note that the polarization model is not inconsistent with the π- electron back-bonding models since these are the most polarizable electrons in NiCO.)

IV. CONCLUSIONS

We have performed LCGTO-$X\alpha$ calculations on NiCO for various linear Ni–CO and NiC–O bond distances. The basis sets used were moderately large, approximately double zeta, and thus are fairly accurate within the $X\alpha$ approximation. The electronic structure and equilibrium bond distances are consistent with recent CI calculations which indicate a much stronger Ni–CO bond than occurs in $\mathrm{Ni(CO)_4}$. We agree to within 100 cm^{-1} with the experimentally observed NiC–O stretch frequency and predict the Ni–CO stretch to occur at 656 cm^{-1}, however, it should be 640 times less intense. In comparison with experimental results for CO adsorbed on single crystal Ni(100), we found our computed vibrational frequencies and intensities less appropriate than the relevant experimental values for $Ni(CO)_4$. We interpret this to mean that an accurate description of the electronic structure of the nickel atom participating directly in the surface bond requires proper accounting of the bonds to its other nearest neighbors. Finally, we compare our computed enhancement of the CO stretch intensity in NiCO with a modified version of the model of Davenport and found qualitative agreement.

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