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Binding and energy-level shifts of carbon monoxide adsorbed on nickel: Model studies

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Hartree-Fock calculations on linear NiCO and Ni_2CO clusters have been used to model the local binding of CO upon adsorption on Ni. The Ni-CO bond is determined by a mixing of the CO(5σ) and Ni($3d$) orbitals; the Ni($4s$) electrons are not directly involved in the bond as can be seen from orbital contour plots. A knowledge of the absolute and relative shifts of molecular ionization potentials from their free-molecule values is important for the interpretation of the photoelectron spectra of chemisorbed species. For our model clusters, we have made a detailed analysis of the origins of the shifts for CO on Ni. The different contributions to the energy-level shifts of the CO-like orbitals show a grouping into core, nonbonding valence, and bonding valence levels. Chemical shifts due to the changed environment of the adsorbed molecule are seen to be important for the initial-state shifts of the nonbonding orbitals. A bonding shift appears to be important only for the CO 5σ level. The relaxation shifts are different among the different groups of levels. Analysis of the calculated and observed shifts gives support to the assignment that the order of the 5σ and 1π levels for CO adsorbed on Ni is the same as for free CO; 5σ less strongly bound than 1π. The O($1s$) and C($1s$) core-level shifts indicate that the CO bond is stretched only slightly upon adsorption. The multiplet splitting of the final ionic states is considered and found to be small.

I. INTRODUCTION

A large amount of experimental as well as theoretical studies have been reported for the interpretation of uv photoemission spectra (UPS) of adsorbed molecules on metal surfaces. These studies can provide a great deal of valuable information about the nature of the chemisorptive bond. In the case of CO adsorbed on Ni surfaces, it has been found that there are two additional peaks in the UPS spectra which are due to the presence of the adsorbate. They were first assigned to ionization out of the CO 5σ and the CO 1π orbital, respectively (the 4σ orbital ionization was claimed not to be seen in the spectrum).[1-4] Without giving a detailed history of the various reassignments, we note that it is now generally accepted that the higher binding-energy peak in the spectrum is due to ionization out of the adsorbate 4σ orbital and the lower binding-energy peak is a composite one due to ionization out of the adsorbate 5σ as well as the 1π orbital. This assignment has been suggested by several theoretical studies[5-9] and confirmed by photoemission experiments using synchrotron radiation.[10] In addition, Gustafsson *et al.*[10] claim that, within the composite peak, the 5σ contribution lies at lower binding energies than the 1π contribution; that is, the order of the free CO molecule is maintained upon adsorption. However, recent angular-resolved UPS studies[11] have led to the assignment of an inverted order of the CO 5σ and 1π ionization potentials in the adsorbate relative to the free molecule.

In the existing theoretical studies on the problem—mostly based on cluster type calculations—three kinds of CO-Ni interaction schemes have been proposed for the chemisorptive bond formed on the surface. Blyholder[6] claims from complete neglect of differential overlap (CNDO) calculations on a $Ni_{10}CO$ cluster that the Ni-CO bond is exclusively determined by a CO(5σ)-Ni($4sp$) interaction. He finds that the low-energy peak is indeed due to both 5σ and 1π ionization. However, in view of the approximations made in these calculations the results should be treated with care. On the other hand, Doyen and Ertl[12] assume, in a calculation using an Anderson model Hamiltonian with rather restricted assumptions about the orbital interaction, a CO(5σ)-Ni($3d$) coupling to be responsible for the bond being formed on the surface and neglect the CO(5σ)-Ni($4sp$) interaction. Finally Batra and Bagus[7] find in a multiple-scattering $X\alpha$ (MS$X\alpha$) calculation on Ni_5CO that both the CO(5σ)-Ni($3d$) and the CO(5σ)-Ni($4sp$) mixing contribute to the CO-Ni bond. In all these calculations, it has been assumed that the molecular axis of the adsorbed CO is perpendicular to the surface (with carbon pointing to the nickel). This assumption has recently been confirmed by angular resolved UPS measurements[13] combined with a theoretical study of the angular dependence of the uv photoionization cross sections of gaseous CO.[14]

The comparison of the photoemission spectra of adsorbed molecules with those of the respective free molecule plays an important role in the interpretation of the spectra. In the CO-Ni adsorption system it has been found that the CO 4σ and 1π levels of the free molecule are shifted more or less rigidly towards lower binding energies when the molecule interacts with the surface. The CO 5σ

level is shifted downwards (to higher binding energy) relative to 4σ and 1π. The large relative shift of 5σ has been interpreted as due to the binding feature of this orbital.[10] In general, the level shifts of free molecules due to the interaction with surfaces have been discussed in terms of two contributions. First, the relaxation shift contribution ΔE_R, given by the difference between the relaxation energy of the respective level in the adsorbed and the free molecule. This final-state shift is normally positive resulting in a lower ionization potential for the adsorbate level. The origins of the relaxation energy are: charge flow towards the positive hole, polarizability of the surrounding medium, etc. These are all expected to be larger for the adsorbed than for the free molecule. The second contribution, the bonding shift ΔE_B, originates because certain molecular orbitals may form chemical bonds with the substrate. The initial-state shift normally increases the ionization potential. In the case of hydrocarbons adsorbed in Ni,[15] an interpretation of the spectra and a deduction of reasonable values for the chemisorption energy was possible by assuming that ΔE_R is constant[16] for all valence levels and ΔE_B is nonzero only for the bonding π levels. The applicability of these assumptions to a variety of systems has been critically reviewed.[17] There is another initial-state contribution to the level shifts, the chemical shift, which is caused by the change in the chemical environment of the adsorbate. It has been known for some time that the potential due to this change can cause significant shifts in the core levels of atoms in free molecules.[18] This is, in fact, the basis of the application of XPS (x-ray photoelectron spectroscopy) to chemical analysis. The importance of the chemical shift in condensed matter has been pointed out in an XPS study on rare-gas atoms implanted in metals,[19] and its effect on adsorbed molecules has been considered in two recent theoretical studies.[9,20]

In the present paper, we report *ab initio* Hartree-Fock calculations on linear NiCO and Ni_2CO clusters as model systems for the interaction of CO with nickel. In both systems, we find that in the ground state the Ni-CO bond is formed essentially by an interaction of the CO(5σ) orbital with Ni($3d$) orbitals as is illustrated later by orbital contour plots. From calculations of the frozen orbital as well as the fully relaxed final CO hole states in both clusters, we are able, for our model systems, to separate the above-mentioned initial- and final-state contributions to the level shifts. We have studied their behavior for the different CO orbitals in detail. We find that the size of the chemical shift of the CO core and nonbonding valence orbitals is comparable to the bonding shift of the 5σ orbital. In addition, final- as well as initial-state shifts vary significantly among the different levels. The second Ni atom in Ni_2CO has no effect on the initial-state shifts but increases the relaxation shifts of all CO levels slightly. Although systems such as NiCO or Ni_2CO are much too small to be able to describe the actual adsorption system quantitatively, we can obtain rigorous and detailed results within the model system. We believe that the qualitative conclusions from the models are applicable to the real adsorption system.

In a preliminary report[9] of our calculations on NiCO, we showed that the CO-like levels could be classed into three groups according to the behavior of the various energy-level shifts. In this paper, we give a detailed analysis of the shifts including the effects of varying bond distances and the results of the Ni_2CO cluster calculations. We show that the energy-level shifts yield information about the ordering of the 5σ and 1π levels and about the (small) amount of CO bond stretching upon adsorption on Ni. We also consider the size of final-state multiplet splittings which arise from the interaction of the singly occupied CO-like level with the unpaired Ni electrons.

In Sec. II, we discuss the computational details of our calculations. The nature of the bonding of CO to Ni is considered in Sec. III A for the NiCO cluster and in Sec. III B for the Ni_2CO cluster. The ionization potentials (IP's) of the CO-like levels of the clusters are presented in Sec. III C and are applied to an analysis of adsorbate energy level shifts. The multiplet splitting of the IP's is also discussed. The order of the $\tilde{5}\sigma$ and $\tilde{1}\pi$ IP's is considered in Sec. III D and consequences of variation of the CO bond length in Sec. III E. Finally, the conclusions are summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

The interatomic distances for the linear NiCO cluster are taken from x-ray measurements on a $Ni(CO)_4$ molecular crystal,[21] $d_{Ni-C} = 3.477$ bohrs and $d_{C-O} = 2.173$ bohrs, respectively. In order to study the dependence of the cluster on its geometry, calculations have been performed where d_{Ni-C} has been varied by ±0.5 bohrs about the $Ni(CO)_4$ value. The $Ni(CO)_4$ C-O distance has also been used for the calculations on free CO. The effect on the electronic structure of free CO due to a change of d_{C-O} from this value to its experimental equilibrium value ($d_{C-O} = 2.132$ bohrs) is quite small. The differences of the total energies at these two separations is only 0.004 hartree compared to a total energy of -112.7 hartree. The effect of other variations of the CO bond distance will be estimated only from the results of ground-state calculations on the free CO molecule. For calculations on the linear Ni_2CO (Ni-Ni-C-O) cluster, the values from $Ni(CO)_4$ were used and the Ni-Ni distance was chosen to be the nearest-neighbor distance in Ni metal, $d_{Ni-Ni} = 4.70$ bohrs. This value was also used for the Ni_2 complex.

Self-consistent field (SCF) analytic basis set Hartree-Fock calculations for various electronic states of the clusters were carried out following the Roothaan approach as implemented in the program system MOLALCH.[22] The contracted Gaussian basis sets for C and O were taken from Van Duijneveldt's calculations[23] on the respective free atoms. Here 9*s* and 5*p* functions were contracted to (4, 3) and a *d* function (exponent $\alpha = 1.0$)[24] has been added. The basis set for Ni was taken from Wachter's calculations[25] on the atom to which two *p* functions (exponents $\alpha = 0.228$ and $\alpha = 0.08$) were added to allow for *p* hybridization of the Ni 4*s* orbital. The Ni basis consisted of 14*s*, 11*p*, and 5*d* functions contracted to (8, 6, 3). The SCF calculations were performed using the Cartesian representation of the spherical harmonics which in the case of a *d* orbital is overcomplete because it gives six different angular functions (x^2, y^2, z^2, xy, xz, yz) compared to five necessary. It is easy to see that this overcompleteness leads to the addition of extra *s* basis functions ($x^2+y^2+z^2$) beyond the number of explicit *s* functions used. On the whole the basis sets used in the present calculations are of better than "double-ξ" quality[26] and it is very unlikely that the results obtained will change significantly if larger basis sets are used.

The symmetry point group of the present clusters is $C_{\infty v}$ ($D_{\infty h}$ for Ni_2). For the closed-shell free CO molecule, the degenerate π_x and π_y orbitals were required to satisfy the symmetry and equivalence restrictions.[27,28] In all other open-shell cases, except Ni_2, the symmetry restriction was satisfied but the two components of the π and δ representations were not equivalent. The effect of this is extremely small. For example, for the $^2\Pi$ state of free CO^+ (1π hole state), the energy of $1\pi_x^1 1\pi_y^2$ (where $1\pi_x$ is different from $1\pi_y$) is only 0.04 eV lower than for the case of $1\pi^3$ where the equivalence restriction is imposed. For this reason and for computational convenience, we did not perform further calculations using the equivalence restriction. For Ni_2, an additional interesting feature of the orbitals was observed. We did not impose symmetry with respect to inversion about the center of the internuclear axis (separation in *g* and *u* states). We find that the open shell 3*d* orbitals ($3d_\delta$) were localized about one or the other center. The remaining 3*d* and the 4*s* orbitals were found to have *g* or *u* symmetry. In effect, this configuration cannot be expressed as a single determinant using $D_{\infty h}$ symmetry orbitals.

III. RESULTS AND DISCUSSION

A. Electronic structure of the NiCO cluster

We describe in this section the results of our calculations on the initial unionized states of the NiCO, Ni_2, and Ni_2CO clusters. Our principal object is to give a qualitative description of the nature of the bonding of CO to a Ni surface as given by these model systems.

From the calculations on various electronic configurations of the NiCO cluster [using the $Ni(CO)_4$ interatomic distances], it was found that the lowest energy configuration is $^3\Delta$ with open-shell structure $12\sigma^1$(Ni 4*s*)$1\delta^3$(Ni 3*d*). This state is very slightly bound ($D = 0.03$ eV), with respect to $CO(^1\Sigma^+)$ and $Ni(^3D; 3d^9 4s^1)$ at infinite separation.[29] If the Ni-C distance is varied keeping the C-O distance fixed, the total energy minimum turns out to be at $d_{Ni-C} = 3.917$ a.u. which is somewhat larger than the $Ni(CO)_4$ value. The corresponding binding energy is 0.2 eV. The discrepancy between this value and the experimental adsorption energy of CO on a Ni surface of ~1.3 eV clearly shows that a linear NiCO cluster is much too small to yield the interaction energy of CO with a Ni surface.[30] However, clusters of this kind can be used for the qualitative understanding of the electronic behavior of an atom or molecule on a surface. In the following, we will refer, unless stated otherwise, to results on the NiCO cluster using $Ni(CO)_4$ distances. Variations of the Ni-C distance will be discussed later in connection with the geometry dependence of the relative positions of the levels of various ionic states.

In the $^3\Delta$ ground state of the NiCO cluster, the CO-like orbitals retain very much of their molecular character. Thus, these cluster levels are given their CO notation with a tilde added: $\tilde{5}\sigma$, $\tilde{1}\pi$, etc. In Fig. 1, the contour plots of the CO valence orbitals are compared with those of the respective orbitals of NiCO. The plots are given in a plane containing the internuclear axis. The NiCO $\tilde{1}\sigma$ to $\tilde{3}\sigma$ orbitals are (within the accuracy of the drawing) identical to the respective CO orbitals. Therefore they have been left out of Fig. 1; only the molecular CO 3σ orbital is shown in Fig. 1(a). The $\tilde{4}\sigma$ orbital [Fig. 1(b)] has a very small charge contribution at the Ni center and the Mulliken overlap population shows a slightly antibonding character (overlap $p_{Ni-C} = -0.02$) towards the Ni atom. The $\tilde{1}\pi$ orbital [Fig. 1(d)] also has only a very small charge contribution on Ni and the overlap

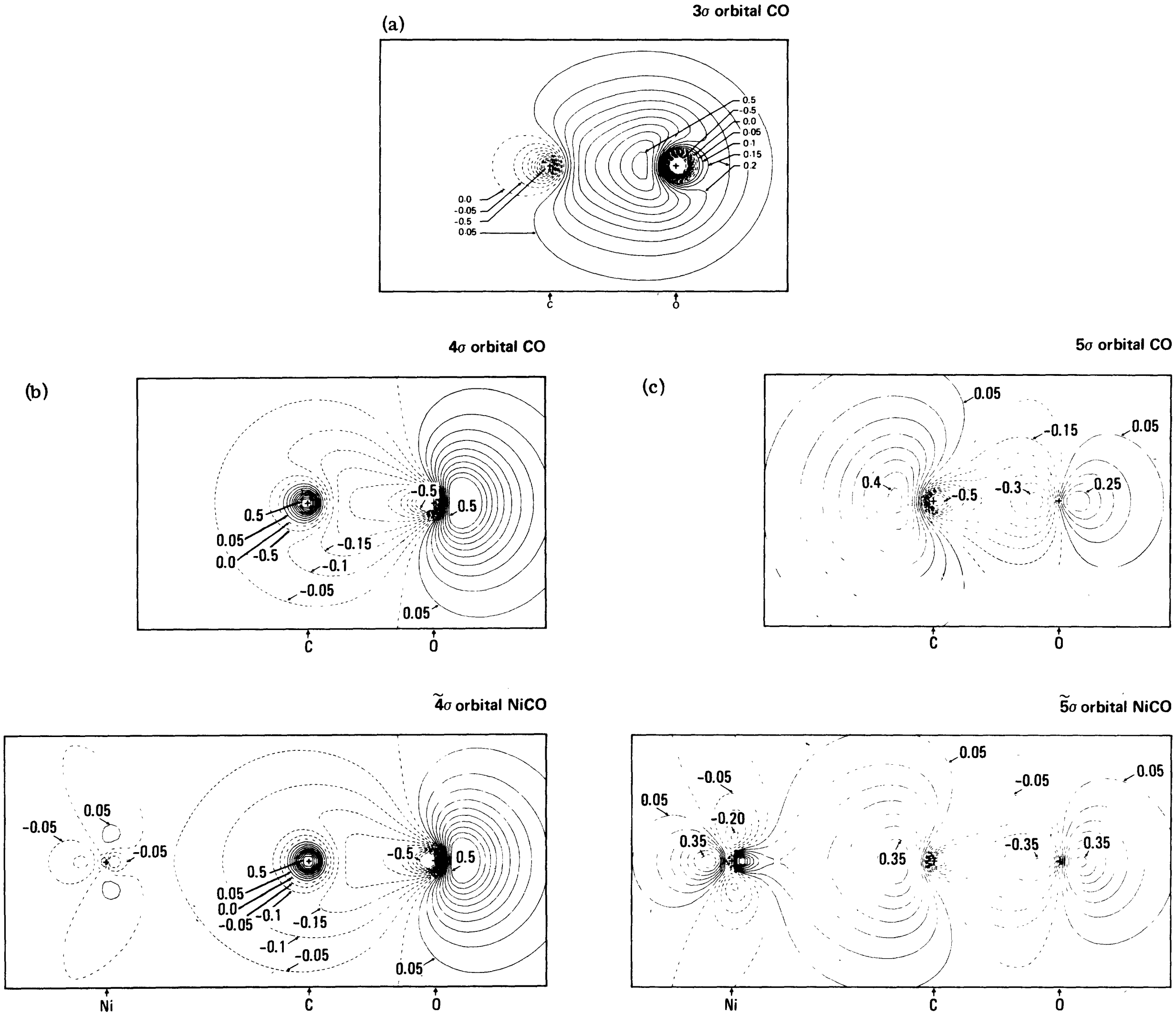

FIG. 1. (a) Contour plot of the CO 3σ orbital. Solid lines refer to positive and dashed lines to negative values; the dashed-dotted lines give zero contours of the wave function. The values of the contours are given in a.u. The contour interval is 0.05 a.u.; this value is also used in Figs. 1(b)–1(e). (b) Contour plots of the CO 4σ and the NiCO $\tilde{4}\sigma$ orbitals. (c) Contour plots of the CO 5σ and the NiCO $\tilde{5}\sigma$ orbitals. (d) Contour plots of the CO 1π and the NiCO $\tilde{1}\pi$ orbitals. (e) Contours plots of the NiCo 11σ (Ni3*d*) and 12σ (Ni 4*s*) orbitals. For the 12σ orbital, a large amount of charge to the left of the Ni atom, $\langle z\rangle_{12\sigma}=-1.59$ bohrs for Ni at $z=0$, is not shown.

analysis gives $p_{\mathrm{Ni\text{-}C}}=0.004$ which indicates that this orbital has no bonding tendency toward the Ni. In contrast, the population analysis for the $\tilde{5}\sigma$ orbital [Fig. 1(c)] reveals a 13% Ni admixture (almost entirely Ni 3*d*) which can also be seen in the plot. Furthermore, the overlap analysis gives $p_{\mathrm{Ni\text{-}C}}=0.07$, the largest value for all the orbitals. Therefore this orbital characterizes the bond between the Ni atom and the CO molecule. The NiCO 11σ orbital [Fig. 1(e)] which arises from the Ni $3d_{z^2}$ orbital has a very small charge contribution on the C and O centers. It remains essentially a $d_{z^2}(d\sigma)$ orbital with a 16% mixture of Ni 4*s* character. The NiCO 4π orbital which arises from Ni($3d_{xz}$) and Ni($3d_{yz}$) orbitals (its contour plot is not given) shows 6% charge contributions from C and O. This means that, in this cluster, there is some Ni(3*d*)-CO(2π*) "backbonding" taking place. The singly occupied NiCO 12σ orbital [Fig. 1(*e*)] which arises from the Ni 4*s* orbital becomes a 4*s*-4*p* hybrid with 66% Ni 4*s*, 26% Ni 4*p*, 4% Ni 3*d*, and 3% C (both 2*s* and 2*p*) character. The 26% Ni 4*p* admixture is such as to direct this orbital away from CO and, in effect, removes charge from the

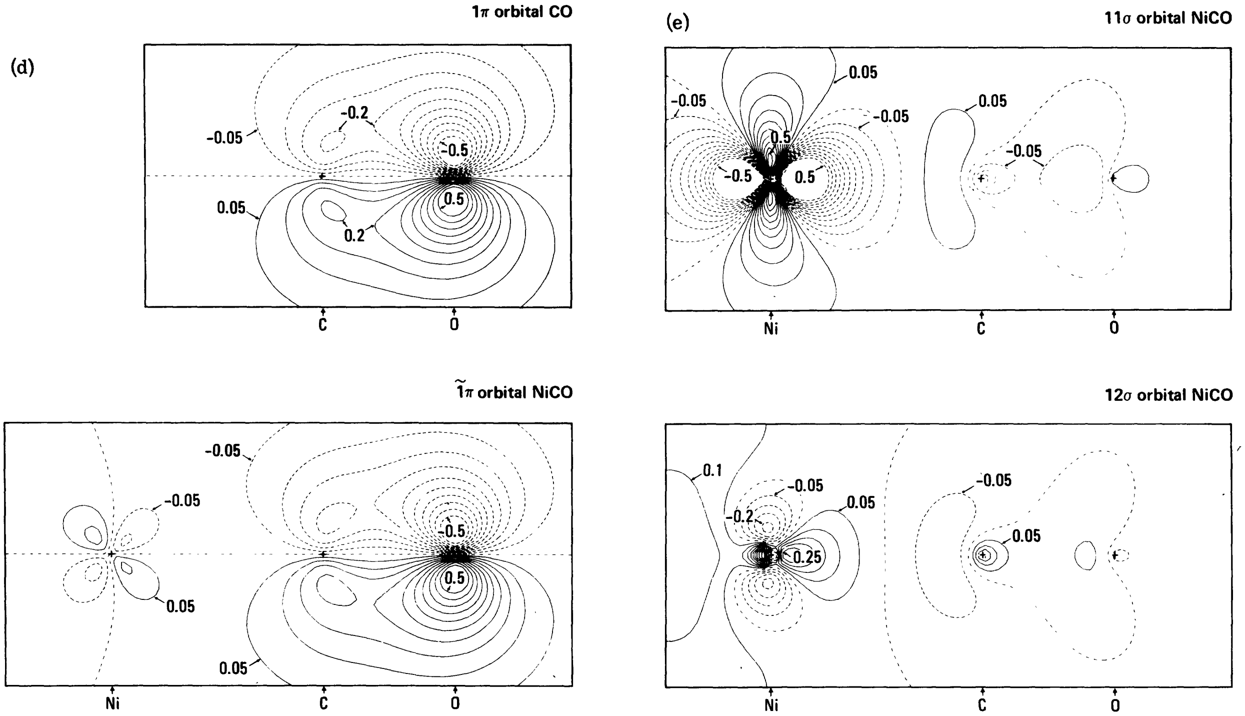

FIG. 1. *(Continued)*

region between Ni and C. The center of the gravity of the charge distribution $\langle z\rangle_{12\sigma}$, is 1.59 bohrs from the Ni center on the side opposite to C. (The plot of this orbital overemphasizes the small d contribution which has a strongly varying shape in the region shown.)

Altogether the bond between Ni and CO in the NiCO cluster is determined by the interaction between the Ni $3d$ orbitals with the 5σ orbital of the CO molecule. From the gross atomic population analysis, the configuration of the Ni atom in the cluster is described as $3d^{8.67}4s^{0.98}4p^{0.36}$, yielding an essentially neutral CO molecule. The latter result agrees with the usual experimental interpretation of work function changes in the CO-Ni adsorbate system.[31]

TABLE I. Calculated orbital energies, in hartree, of the CO like orbitals in the NiCO cluster and in $Ni(CO)_4$. The values for free CO are given for comparison. Orbital assignments in parenthesis refer to the $Ni(CO)_4$ molecule.

Orbital	ϵ (NiCO)	ϵ [$Ni(CO)_4$] [a]	ϵ (CO)
$\tilde{1}\sigma(2t_2, 3a_1)$	−20.7093	−20.657	−20.669
$\tilde{2}\sigma(3t_2, 4a_1)$	−11.4218	−11.419	−11.370
$\tilde{3}\sigma(5t_2, 6a_1)$	−1.5473	−1.530	−1.510
$\tilde{4}\sigma(6t_2, 7a_1)$	−0.8456	−0.793, −0.809	−0.801
$\tilde{5}\sigma(8t_2, 8a_1)$	−0.6849	−0.644, −0.693	−0.557
$\tilde{1}\pi(1e, 7t_2, 1t_1)$	−0.6716	−0.665, −0.662, −0.653	−0.692

[a] The values for $Ni(CO)_4$ are taken from Ref. 32.

It is interesting to note that the orbital energies of NiCO are quite similar to those found for nickel carbonyl,[32] $Ni(CO)_4$. In Table I, we give the values for the CO-like levels in NiCO, the $Ni(CO)_4$ molecule, and the free CO molecule. It is clear from the data that NiCO and $Ni(CO)_4$ are much closer to each other than to free CO; this is most obvious for the valence levels, 4σ, 5σ, and 1π. The differences between NiCO and $Ni(CO)_4$ arise from two effects. First, the bonding in the two systems will be somewhat different. Second, our basis set for NiCO is considerably larger than the one used for $Ni(CO)_4$.[32] This latter fact probably explains why the NiCO orbital energies are generally lower than those for $Ni(CO)_4$. The analogy between the behavior of CO levels in carbonyls and chemisorbed on Ni has been used to propose an assignment of the UPS spectra of the chemisorbed system.[33] Our results are consistent with the use of this analogy and provide support for it.

B. Electronic structure of the Ni_2 and Ni_2CO clusters

We have also performed calculations for a linear Ni_2CO cluster. This was done in order to determine the effect on various properties of interest of allowing the CO molecule to interact with more then one Ni atom. In particular, we are interested in the effect of this second atom on the IP's of the CO-like orbitals to be discussed below in Sec. III C.

To get a better understanding of the Ni-CO interaction in linear Ni_2CO, it is useful to study the Ni_2 diatomic cluster first. It turns out that the energetically lowest state of Ni_2 at its metal nearest-neighbor distance is a triplet with open-shell structure $\delta^1_{xy}(\text{Ni } 3dA)\ \delta^1_{x^2-y^2}(\text{Ni } 3dB)$ (the z axis coincides with the internuclear axis). The notation $3dA$ and $3dB$ is used to indicate that the δ_{xy} orbital is localized on one of the two equivalent Ni atoms and $\delta_{x^2-y^2}$ is localized on the other. However, the total charge on each atom is the same and is $3d^{8.9}4s^{1.0}4p^{0.1}$ as given by a Mulliken population analysis. The $4s$ electrons are in a doubly occupied $4s\sigma_g$ orbital. The general picture of the structure is one in which the $3d$ electrons are localized about each Ni atom and the $4s$ electrons form a delocalized covalent bond. The same results have been obtained in a more extensive study of Ni_2 by Melius *et al.*[34] The SCF binding energy of this state is 1.15 eV. (We note that we have used real rather than complex functions for the open-shell d orbitals. Hence, the SCF wave function does not possess spatial symmetry but is, in fact, a combination of ${}^3\Gamma$ and ${}^3\Sigma^-$ symmetries. The energy difference between these states is given by a combination of two center Coulomb and exchange integrals involving the $d\delta$ orbitals.[35] These integrals are very small. Melius *et al.*[34] have shown that all the states which arise from the $\delta^1_{xy}\delta^1_{x^2-y^2}$ configuration are within 0.0006 eV of each other.)

The ground-state configuration in Ni_2CO is found to be a triplet with the same open-shell structure as Ni_2. It is energetically stable ($D = 0.23$ eV) with respect to the ground states of the separate systems $CO({}^1\Sigma^+)$ and Ni_2(triplet). As for NiCO, the CO-like orbitals in the cluster retain their molecular character. In fact, they are almost identical to the corresponding orbitals in NiCO; the contour plots of these orbitals in Ni_2CO are almost indistinguishable from those given in Fig. 1 for NiCO. In sum, the presence of a second Ni atom in the linear arrangement does not influence the character of the CO-like orbitals and the Ni-CO bond is formed principally by the CO 5σ orbital admixing some $3d\sigma$ character of the nearest Ni atom.

The 18σ orbital which arises from atomic Ni $4s$ orbitals and formed the σ_g orbital in Ni_2 that determined the Ni-Ni bond becomes strongly asymmetric in Ni_2CO since some charge is shifted towards the Ni atom further away from CO. In addition, compared to Ni_2, this orbital has larger $4p$ character at the Ni center nearest to CO. In effect, this moves charge from the Ni-CO bonding region to the Ni-Ni bonding region. This behavior is equivalent to that of the 12σ orbital in NiCO discussed above. In the case of Ni_2CO this charge reorganization leads to an increase of the Ni-Ni bond which can be seen from the fact that the Ni-Ni bond energy in Ni_2

$$E_B(\text{Ni},\text{Ni}_2) = |E_{\text{tot}}(\text{Ni}_2) - 2E_{\text{tot}}(\text{Ni})| = 1.15 \text{ eV}$$

is smaller than the Ni-Ni bond energy in Ni_2CO

$$E_B(\text{Ni},\text{Ni}_2\text{CO}) = |E_{\text{tot}}(\text{Ni}_2\text{CO}) - E_{\text{tot}}(\text{Ni}) - E_{\text{tot}}(\text{NiCO})| = 1.37 \text{ eV}.$$

The gross atomic population analysis gives a population $3d^{8.64}4s^{0.84}4p^{0.35}$ for the Ni atom nearest to CO and $3d^{8.87}4s^{1.23}4p^{0.04}$ for the Ni atom further away from the CO. This leads, as in the NiCO cluster, to an essentially neutral CO molecule.

C. Ionization potentials of the CO-like levels: adsorbate energy level shifts

As we have discussed earlier, the shifts of the adsorbate photoemission peaks with respect to those of the free molecule are used to interpret the adsorbate spectra.[1-10] In order to understand, in a quantitative way, the origins of these shifts for the various CO-like levels, we have performed calculations of the IP's of these levels in NiCO and Ni_2CO. These are compared with the calculated values for free CO.

Since the initial states of both NiCO and Ni_2CO are open shells with triplet spin, there are multiplet split final ionized states with quartet and doublet spin.[36] (This is roughly equivalent to removing either a majority, spin up, or a minority, spin down, electron from the CO-like level) We shall concern ourselves almost entirely with the quartet, high spin, final states. However, the size and significance of the multiplet splittings will be discussed briefly later in this section. When a $\bar{1}\pi$ electron is removed, final states with different spatial symmetry are also obtained. This leads to a further multiplet splitting. We consider only the averages of these states described by open-shell configurations constructed from real orbitals:

$$\psi(\text{NiCO}) = 1\delta_{xy}(\text{Ni } 3d)12\sigma(\text{Ni } 4s)\bar{1}\pi_x\,, \qquad (1)$$

$$\psi(\text{Ni}_2\text{CO}) = \delta_{xy}(\text{Ni } 3dA)\delta_{x^2-y^2}(\text{Ni } 3dB)\bar{1}\pi_x\,. \qquad (2)$$

[Clearly, some other open-shell configurations constructed from different orbitals, $\bar{1}\pi_y$ instead of $\bar{1}\pi_x$, for example, are exactly degenerate with the configurations of Eqs. (1) and (2).] The energies of the different spatial states are separated by combinations of two center integrals involving 1π and

TABLE II. Calculated ionization potentials, in eV, of the CO-like orbitals of linear NiCO and Ni_2CO. The notation I(Koopmans) refers to the frozen orbital IP to a high spin final state (see text); I(Relaxed) is obtained by taking differences of the Hartree-Fock total energies of the initial and final (high-spin) states.

	NiCO		Ni_2CO	
Orbital	I(Koopmans)	I(Relaxed)	I(Koopmans)	I(Relaxed)
$\tilde{1}\sigma$ (O 1s)	563.532	541.988	563.508	541.573
$\tilde{2}\sigma$ (C 1s)	310.782	297.685	310.806	297.276
$\tilde{3}\sigma$	42.091	38.496	42.080	38.150
$\tilde{4}\sigma$	22.973	20.986	22.985	20.742
$\tilde{5}\sigma$	18.423	16.400	18.572	16.372
$\tilde{1}\pi$	18.259	16.007	18.245	15.676

the Ni open-shell orbitals which are expected to be very small. No final-state splittings arise for CO which has a $^1\Sigma^+$ closed-shell ground state.

The IP's are computed in two ways. In the first, we obtain the ionized final-state wave functions and energies using the initial-state orbitals. We refer to this as I (Koopmans) even though, for open-shell systems,[37] this is not exactly equivalent to using $I = -\epsilon$. In this frozen orbital approach, the orbitals are not allowed to relax to respond to the removal of the ionized electron. In the second way, we compute SCF wave functions for the ionized states. I (relaxed) is the difference of the initial- and final-state SCF energies. For the analysis of the adsorbate shifts, it is appropriate to define the following shifts, ΔE:

$$\Delta E_{\text{tot}} = I(\text{Relaxed; CO}) - I(\text{Relaxed; cluster}), \tag{3}$$

$$\Delta E_I = I(\text{Koopmans; CO}) - I(\text{Koopmans; cluster}), \tag{4}$$

$$\Delta E_R = \Delta E_{\text{tot}} - \Delta E_I . \tag{5}$$

Clearly, only the total shift ΔE_{tot} may be observed in an experiment. The initial-state contribution ΔE_I is due to two mechanisms. First, a level may be shifted because it becomes involved in a bond to the Ni (bonding shift). Second, a level may be shifted by the changed environment in the cluster (environmental or chemical shift). The second is the only mechanism to affect nonbonding levels. The relaxation shift ΔE_R arises because of the different final-state behavior between the free and "adsorbed" CO molecule. This decomposition of shifts is commonly used in the analysis of chemical shifts in core-level photoemission spectra.[36] It has also been used, most often qualitatively, for the analysis of adsorbate shifts.[15,17,20] Our theoretical approach permits us to obtain quantitative estimates of the magnitudes and behavior of the individual terms for different adsorbate levels.

The IP's for the CO-like levels in NiCO and Ni_2CO are given in Table II. The final states of NiCO and Ni_2CO, for both I (Koopmans) and I (Relaxed) are the high-spin quartet states as discussed above. The CO IP's are given in Table III. They are calculated for $d(\text{CO}) = 2.173$ bohrs, the CO distance in $Ni(CO)_4$, and are compared to values obtained from x-ray[38] and uv[39] photoemission experiments. The I (Relaxed) for CO agree fairly well with the experimental values. If the experimental CO internuclear separation is used, the computed relaxed IP's change slightly towards a better agreement with the experimental values.[40] From the significant differences between the IP's calculated with and without orbital relaxation in both CO and NiCO, it is clear that relaxation effects cannot be neglected in calculations of this kind as has been done quite often in the past.

The vertical IP's reported in Tables II and III are the appropriate quantities to compare with the maxima of the observed peaks or (in the case of free CO) bands. Geometry changes in the relaxed final state lead, through Franck-Condon overlap, to vibrational broadening of these peaks. The calculated values of the adsorbate shifts as defined in Eqs. (3)–(5) are given in Table IV. Before we discuss these ΔE, we shall consider briefly the effects of multiplet splitting in the final states.

TABLE III. Computed and experimental ionization potentials, in eV, of the free CO molecule.

Orbital	I(Koopmans)	I(Relaxed)	I(exp)
1σ (O 1s)	562.424	541.947	542.3[a]
2σ (C 1s)	309.390	297.550	296.2[a]
3σ	41.076	38.311	38.9[a]
4σ	21.799	19.867	19.7[b]
5σ	15.149	13.525	14.0[b]
1π	17.123	14.960	16.9[b]

[a] See Ref. 38.

[b] See Ref. 39.

TABLE IV. Calculated level shifts, in eV, of the CO orbitals due to the interaction with nickel. ΔE_I and ΔE_R are, respectively, initial- and final-state contributions to the total shift ΔE_{tot}.

	ΔE_{tot}		ΔE_I		ΔE_R	
State	NiCO	Ni_2CO	NiCO	Ni_2CO	NiCO	Ni_2CO
$\tilde{1}\sigma$ (O 1*s*)	−0.04	0.37	−1.11	−1.08	1.07	1.45
$\tilde{2}\sigma$ (C 1*s*)	−0.13	0.27	−1.39	−1.42	1.26	1.69
$\tilde{3}\sigma$	−0.19	0.16	−1.01	−1.00	0.82	1.16
$\tilde{4}\sigma$	−1.12	−0.87	−1.17	−1.19	0.05	0.32
$\tilde{5}\sigma$	−2.88	−2.85	−3.27	−3.42	0.39	0.57
$\tilde{1}\pi$	−1.05	−0.68	−1.14	−1.12	0.09	0.44

The final states of NiCO and Ni_2CO have three open shells. It is possible to form three distinct final states with this open-shell structure: one quartet and two doublets. A convenient measure of the multiplet splitting among these final states is the energy difference between the quartet state and the center of gravity of the three photoemission peaks. With some reasonable assumptions about intensities,[37,41] this energy difference, $\Delta\bar{E}_{MS}$, is given by[42,43]

$$\Delta\bar{E}_{MS} = \tfrac{1}{3}\{K[\varphi_1(\text{Ni}),\tilde{\varphi}(\text{CO})] + K[\varphi_2(\text{Ni}),\tilde{\varphi}(\text{CO})]\}\,, \tag{6}$$

where the *K* are exchange integrals between the Ni-like open-shell orbitals and the open-shell (ionized) CO-like orbital $\tilde{\varphi}$(CO). For NiCO, the Ni-like orbitals are $\varphi_1(\text{Ni}) = 12\sigma(\text{Ni } 4s)$ and $\varphi_2(\text{Ni}) = 1\delta_{xy}(\text{Ni } 3d)$; for Ni_2CO, $\varphi_1(\text{Ni}) = \delta_{xy}(\text{Ni } 3dA)$ and $\varphi_2(\text{Ni}) = \delta_{x^2-y^2}(\text{Ni } 3dB)$. For each $\tilde{\varphi}$(CO) ionization, the value of $\Delta\bar{E}_{MS}$ is given in Table V. These values are calculated from Eq. (6) using the initial-state (frozen) orbital values for the exchange integrals. From the table, we see that the $\Delta\bar{E}_{MS}$ for NiCO are always larger than those for Ni_2CO. Further, for either NiCO or Ni_2CO, the largest value of $\Delta\bar{E}_{MS}$ is for $\tilde{5}\sigma$ ionization. In fact, for Ni_2CO, $\Delta\bar{E}_{MS}$ is essentially zero except for this case. This behavior of the multiplet splittings is not at all surprising. Of the integrals involved in Eq. (6), it is clear that $K[12\sigma(\text{Ni } 4s), \tilde{\varphi}(\text{CO})]$ will be the largest. The NiCO 12σ(Ni 4*s*) orbital is the most diffuse of all the Ni-like open-shell orbitals and has a reasonable density in the regions where the CO-like orbitals are large, cf. Fig. 1. It is also clear from Fig. 1 that the exchange integrals involving $\tilde{5}\sigma$ will be larger than those involving any other $\tilde{\varphi}$(CO).

It is not reasonable to expect that diffuse Ni 4*s*-like orbitals will have unpaired spin density for atoms in the bulk or at the surface of Ni metal. The relatively large values of $\Delta\bar{E}_{MS}$ for NiCO are most likely to be artifacts of that cluster. Hence, they do not correspond to multiplet splittings which would be observed in photoemission for CO adsorbed on Ni.

The results of several spectroscopies which directly measure the *d*-level behavior in Ni metal appear to require an analysis based on localized *d* electrons.[44-46] Both our Ni_2 and Ni_2CO clusters have this localized *d* character. Hence, the $\Delta\bar{E}_{MS}$ for Ni_2CO may provide a reasonable basis for an estimate of the multiplet splitting to be expected for CO adsorbed on Ni. As seen from Table V, $\Delta\bar{E}_{MS}$ is negligible except for the $\tilde{5}\sigma$ level where it is only 0.06 eV. Clearly, multiplet splitting effects can be expected to be very small and do not contribute significantly to the observed[10,47] ~2 eV widths for the valence region, $\tilde{4}\sigma$, $\tilde{1}\pi$, and $\tilde{5}\sigma$, resonances.

The multiplet splittings do have some effect on the calculated values of the adsorbate shifts for the $\tilde{5}\sigma$ level. The large $\Delta\bar{E}_{MS}$ for $\tilde{5}\sigma$ in NiCO means that the quartet final state lies below the center of gravity more than is reasonably expected. Thus, $\Delta E_I(\tilde{5}\sigma)$ for NiCO will be too negative (too large in absolute value). In fact, $\Delta E_I(\tilde{5}\sigma)$ for NiCO is 0.15 eV lower than the value for Ni_2CO. This is just the difference between the values of $\Delta\bar{E}_{MS}(\tilde{5}\sigma)$ given in Table I. In order to determine the effect of multiplet splitting on ΔE_{tot} and ΔE_R for $\tilde{5}\sigma$ ionization, we have performed final-state SCF calculations for the center of the gravity of the multiplet for NiCO and Ni_2CO. The final state $\Delta\bar{E}_{MS}(\tilde{5}\sigma)$ are the same as the initial-state values given in Table V. Hence $\Delta E_R(\tilde{5}\sigma)$ is unaffected by the multiplicity of the final state and both $\Delta E_{\text{tot}}(\tilde{5}\sigma)$ and $\Delta E_I(\tilde{5}\sigma)$ for NiCO are artifically too small (negative) by ~0.15 eV. For the other CO-like levels, the multiplet splitting is too small to merit any further consideration.[48]

We consider now a detailed analysis of the adsorbate shifts given in Table IV. The initial-state shifts ΔE_I are essentially the same for NiCO and Ni_2CO except for $\Delta E_I(\tilde{5}\sigma)$ which, as discussed

TABLE V. Final-state multiplet splitting for ionization from the CO-like orbitals of NiCO. The splitting is characterized by $\Delta\bar{E}_{MS}$ which is defined in the text. Initial state (frozen) orbitals are used to evaluate the $\Delta\bar{E}_{MS}$ Values are given in eV.

Orbital	$\Delta\bar{E}_{MS}$(NiCO)	$\Delta\bar{E}_{MS}$(Ni_2CO)
$\tilde{1}\sigma$ (O 1*s*)	0.003	0.000
$\tilde{2}\sigma$ (C 1*s*)	0.024	0.000
$\tilde{3}\sigma$	0.014	0.000
$\tilde{4}\sigma$	0.040	0.006
$\tilde{5}\sigma$	0.214	0.065
$\tilde{1}\pi$	0.017	0.006

above, is effected by the relatively large final-state multiplet splitting in NiCO. This means that the bonding of CO to Ni is the same in both clusters and, as noted earlier, that the CO-like orbitals are almost identical in both clusters. It also means that the second (more distant) Ni atom is sufficiently screened that it does not cause a significant chemical shift of the CO levels in Ni_2CO. The ΔE_I have negative values of ~-1 eV for all but the bonding $\tilde{5}\sigma$ orbital. This orbital is the most strongly bonding one with respect to Ni and therefore it is plausible that its bonding shift is larger compared to the other states. For the CO core orbitals $\tilde{1}\sigma$, $\tilde{2}\sigma$, and also the $\tilde{3}\sigma$ orbital (which determines the CO bond), ΔE_I is exclusively a chemical shift. This shift is smaller for the $\tilde{1}\sigma$ orbital (corresponding to O 1*s*) than for the $\tilde{2}\sigma$ orbital (corresponding to C 1*s*). The oxygen center is further away from Ni than the carbon center and, therefore, the $\tilde{1}\sigma$ orbital experiences a weaker influence from the Ni atom than the $\tilde{2}\sigma$ orbital. For the valence orbitals $\tilde{4}\sigma$ and $\tilde{1}\pi$, there is no rigorous way to make a quantitative separation between the bonding and the chemical contribution to ΔE_I. However, the charge distributions of $\tilde{4}\sigma$ and $\tilde{1}\pi$ shown in Figs. 1(b) and 1(d) and the orbital characters discussed in Secs. III A and III B strongly suggest that the dominant contribution to ΔE_I is a chemical shift. The fact that $\Delta E_I(\tilde{4}\sigma)$ and $\Delta E_I(\tilde{1}\pi)$ are very nearly the same as the ΔE_I for the core and $\tilde{3}\sigma$ levels also supports this idea.

The physical origin of the final-state relaxation shifts ΔE_R arises from the response of the Ni electrons to the removal of a (dominantly) CO electron from the cluster. These shifts, for both NiCO and Ni_2CO, show different behavior for different sets of CO-like orbitals. The values of $\Delta E_R(\tilde{1}\sigma)$ and $\Delta E_R(\tilde{2}\sigma)$ corresponding to *K*-shell core ionization are the largest; ~1 eV in NiCO and ~1.5 eV in Ni_2CO. These large values can be understood from the nature of the core orbitals. The removal of a $\tilde{1}\sigma$ ($\tilde{2}\sigma$) electron occupying a very contracted orbital may be regarded as increasing the effective charge of the oxygen (carbon) nucleus by one.[49] Thus, the ionization out of a core orbital leads to a reorganization of charge over the entire cluster, including the Ni electrons, and yields large values of ΔE_R. The relatively large ΔE_R value for the $\tilde{3}\sigma$ orbital can be understood in a similar way. Since $\tilde{3}\sigma$ determines the strong CO bond, the ionization out of this orbital leads to a major reorganization of electrons within the CO system which in turn results in a spatial redistribution of Ni electrons. In this sense $\tilde{3}\sigma$ may be considered a core level. The nonbonding valence levels, $\tilde{4}\sigma$ and $\tilde{1}\pi$, have the smallest ΔE_R, ~0.1 eV for NiCO and ~0.4 eV for Ni_2CO. These rather diffuse orbitals are distributed mainly about the O atom, cf. Figs. 1(b) and 1(d). Thus, the Ni electrons, screened by C, contribute less to ΔE_R. Since the $\tilde{5}\sigma$ orbital is bonding with respect to Ni, the Ni electrons will participate to a larger extent in the electronic relaxation when this orbital is ionized. This explains the larger value of ΔE_R, 0.4 eV for NiCO and 0.6 eV for Ni_2CO, relative to the other (nonbonding) valence orbitals. Because of the physical origin of ΔE_R, this quantity should increase in going from NiCO to Ni_2CO since the number of Ni electrons increases. The main effect of the addition of another Ni atom to the NiCO cluster is a roughly constant shift of ΔE_R for all levels by ~0.3–0.4 eV towards larger values (cf. Table IV).

On the whole, the behavior of ΔE_I and ΔE_R in NiCO and Ni_2CO indicates a grouping of the CO-like orbitals into three categories. First, the core orbitals $\tilde{1}\sigma$, $\tilde{2}\sigma$, and the CO bonding orbital $\tilde{3}\sigma$ which have a ΔE_I value of ~1 eV (due to chemical shifts) and large ΔE_R values. Second, the nonbonding valence orbitals $\tilde{4}\sigma$, $\tilde{1}\pi$ which again have ΔE_I ~1 eV but also the smallest ΔE_R values. And, third, the bonding valence orbital $\tilde{5}\sigma$ which has a very large ΔE_I value of ~3 eV (due to the bonding shift) and a somewhat larger ΔE_R than $\tilde{4}\sigma$ and $\tilde{1}\pi$. This grouping into three sets of orbitals, core (including $\tilde{3}\sigma$), nonbonding valence, and bonding valence, is also reflected in the behavior of ΔE_{tot}. This is particularly important since this is the only shift which is an observable quantity in a photoemission experiment.

In order to determine the effect of the geometry variation on these conclusions about level shifts, we have, for NiCO, performed SCF calculations for a few different values of $d_{Ni\text{-}C}$. (The $d_{C\text{-}O}$ has been kept fixed). We find that, within a reasonable range of $d_{Ni\text{-}C}$ about its $Ni(CO)_4$ value, both $I_{Koopmans}$ and $I_{Relaxed}$ vary parallel to each other. That is $I_{Koopmans} - I_{Relaxed}$ is roughly constant within this range. That is, the relaxation shift,

$$\Delta E_R = \Delta E_{tot} - \Delta E_I = (I^{NiCO}_{Koopmans} - I^{NiCO}_{Relaxed}) + (I^{CO}_{Relaxed} - I^{CO}_{Koopmans}),$$

is roughly independent of $d_{Ni\text{-}C}$. Thus, the conclusions about the behavior of ΔE_R for the different CO-like orbitals in NiCO are, within reasonable limits, independent of the cluster geometry. Furthermore, the variation of ΔE_I and ΔE_{tot} is such that the qualitative conclusions made about the behavior of these level shifts still remain valid, even though the numerical values of the shifts change somewhat. We believe that it is likely that in Ni_2CO the level shifts are similarly independent of the cluster geometry.

It is possible that the actual bonding of CO on a

TABLE VI. Experimental values of the IP's and total energy-level shifts, ΔE_{tot}, for CO adsorbed on Ni. The IP's are referenced to vacuum level by adding a work function to the observed values. The shifts are calculated using the free CO IP's given in Table III. Our calculated ΔE_{tot} for Ni_2CO is included for comparison. All values are in eV.

	Experiment Gustafsson *et al.* (Ref. 10)		Experiment Brundle and Carley (Ref. 47)		This work Ni_2CO cluster
Orbital	I^{a}	ΔE_{tot}	I^{b}	ΔE_{tot}	ΔE_{tot}
$\tilde{1}\sigma$ (O 1s)	...	...	536.9	5.4	0.37
$\tilde{2}\sigma$ (C 1s)	...	...	291.1	5.1	0.27
$\tilde{3}\sigma$	...	...	...	...	0.16
$\tilde{4}\sigma$	16.6	3.1	16.6	3.1	−0.87
$\tilde{1}\pi$	13.6	3.3	13.6	3.3	−0.68
$\tilde{5}\sigma$	12.3	1.7	11.8	2.2	−2.85

[a] Work function of 5.8 eV was used as reported in Ref. 10.
[b] Work function of 5.5 eV was used as suggested in Ref. 47.

Ni surface is somewhat different from that found here. A different surface geometry, a bridge or fourfold adsorption site, for example, could lead to a modification of the bonding contributions of ΔE_I. [Note, however, the close similarity of our results with those for the quite different geometry $Ni(CO)_4$ shown in Table I.] We do believe, however, that the essential mechanisms which cause the level shifts seen in photoemission of CO adsorbed on Ni surfaces are already contained in our model clusters. Calculations on larger Ni_nCO clusters where n is increased until the cluster properties become independent of the size would provide a somewhat deeper understanding of the local binding situation between CO and Ni and of the level shift behavior. (Unfortunately, such Ni_nCO calculations using *ab initio* Hartree-Fock methods without further approximations or limitations in the atomic basis sets are rather difficult to perform.) It is certainly clear that the relaxation contribution ΔE_R is still strongly underestimated in Ni_2CO. The number of Ni atoms in the neighborhood of an adsorbed CO molecule—for any possible adsorption site—is much larger than two. From the discussion above one could speculate that adding further Ni atoms to Ni_2CO merely results in an increase of the relaxation shift ΔE_R. The initial-state contributions ΔE_I would remain approximately the same as long as the additional Ni atoms did not directly modify the Ni-CO bond. This would lead to a correction of the Ni_2CO (or NiCO) values for ΔE_{tot} towards larger values for all CO-like orbitals.

In this spirit, we compare, in Table VI, our computed ΔE_{tot} for Ni_2CO with experimental values obtained by Gustafsson *et al.*[10] (valence levels only) and by Brundle and Carley[47] (valence and core levels). The gas phase CO IP's used are those given in Table III. The experimental IP's for CO adsorbed on Ni are referenced to vacuum by adding a work function of 5.8 eV to the results of Ref. 10 and of 5.5 eV to those of Ref. 47. These are the work function values suggested in Refs. 10 and 47, respectively. The experimentally determined ΔE_{tot} differ from our values in that they are ~4–5 eV larger for all levels which have been observed. This is consistent with our belief that our calculations strongly underestimate ΔE_R. The experimental results support our grouping of the CO-like levels into three sets. The $\tilde{3}\sigma$ level, which has not been observed so far, would provide a very useful test of our predictions of this grouping.

D. Order of the $\tilde{5}\sigma$ and $\tilde{1}\pi$ ionization potentials

As noted in the introduction, there has been discussion about whether the order of the $\tilde{5}\sigma$ and $\tilde{1}\pi$ ionization potentials of CO [in the gas phase $I(1\pi) > I(5\sigma)$] is reversed when this molecule is adsorbed on Ni. Gustafsson *et al.*[10] assign the adsorbed IP's in the same order as observed in the free CO molecule and Brundle and Carley[47] have also used this order. Williams *et al.*[11] make the reverse assignment, $I(\tilde{5}\sigma) > I(\tilde{1}\pi)$, based on an analysis of angle resolved uv photoemission experiments. From Table II, we note that for Ni_2CO, I (Relaxed; $\tilde{5}\sigma$) is 0.7 eV larger than I (Relaxed; $\tilde{1}\pi$). This would, at first glance, appear to support the assignment of Williams *et al.*[11] However, it is important to recall that the SCF calculations do not treat the $\tilde{1}\pi$ and $\tilde{5}\sigma$ ionized states with the same accuracy. In other words, there are different correlation errors[26] in the SCF energies of these two states. This is clearly seen in the free-CO results; cf. Table III. The calculated I (Relaxed, 1π) is 1.4 eV larger than I (Relaxed, 5σ) but from the experi-

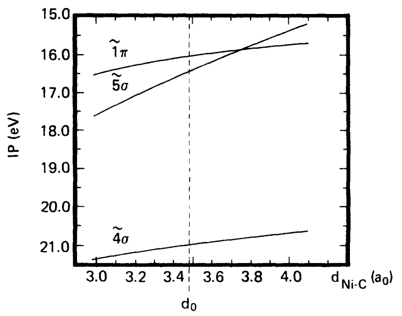

FIG. 2. Relaxed ionization potentials (IP) of the CO valence orbitals $\tilde{4}\sigma$, $\tilde{5}\sigma$, and $\tilde{1}\pi$ in NiCO as a function of the Ni-C distance. The experimental Ni-C distance in Ni(CO)_4 is indicated by d_0. The C-O distance is fixed at 2.173 bohrs.

mental results[39] we find that $I(1\pi)$ is actually 2.9 eV larger than $I(5\sigma)$. Thus, the relative error of the SCF $I(1\pi)$ with respect to $I(5\sigma)$ is 1.5 eV. Since the electronic structure of CO in Ni_2CO is very much like that of free CO, it is reasonable to estimate that the relative error of the SCF cluster $I(\tilde{1}\pi)$ is also ~1.5 eV. If this correction is applied to the calculated cluster IP's, then $I(\tilde{1}\pi) > I(\tilde{5}\sigma)$ in agreement with the gas phase ordering.[10,47]

The relative position of the CO-like IP's is affected by the cluster geometry. The dependence of the IP's on the Ni-C distance was first discussed by Waber *et al.*[5] Based on the results of discrete variational method, local density ($X\alpha$) molecular-orbital (MO) calculations which modeled the approach of CO to Ni(100), they found that the $\tilde{5}\sigma$ and $\tilde{1}\pi$ levels crossed for CO at ~3 bohrs above the surface. In Fig. 2, we plot our values for the $\tilde{4}\sigma$, $\tilde{1}\pi$, and $\tilde{5}\sigma$ I (Relaxed) of the NiCO cluster as a function of $d_{\text{Ni-C}}$. The curve shows that $I(5\sigma)$ is decreasing more rapidly, with decreasing $d_{\text{Ni-C}}$, than is $I(1\pi)$. Taking account of the crude 1.5 eV correlation correction discussed above, we also estimate that the $\tilde{1}\pi$ and $\tilde{5}\sigma$ IP curves should cross at $d_{\text{Ni-C}}$ ~3 bohrs. Even for this rather short Ni-C distance, we are still rather far from the assignment of Williams *et al.*,[11] where $I(5\sigma)$ is placed 1.6 eV larger than $I(1\pi)$.

An analysis of the energy-level shifts provides even more compelling arguments against the reordering of these levels from their free molecule order. If the assignment of $\tilde{1}\pi$ and $\tilde{5}\sigma$ to the experimental peaks in Table VI is reversed, very different values of $\Delta E_{\text{tot}}(\tilde{1}\pi)$ and $\Delta E_{\text{tot}}(\tilde{5}\sigma)$ are obtained. For the reverse assignment, $\Delta E_{\text{tot}}(\tilde{5}\sigma) \sim 0.4$ eV (Refs. 10 and 47) and $\Delta E_{\text{tot}}(\tilde{1}\pi) \sim 4.5$ eV,[10] or ~5.0 eV.[47] (Similar ΔE_{tot} are obtained if we use the slightly different peak positions of Williams *et al.*[11]) We consider first the $\tilde{5}\sigma$ shift and then turn to $\tilde{1}\pi$. If we assume that our calculated $\Delta E_I(\tilde{5}\sigma) \sim -3.5$ eV (Table IV) is roughly correct, then $\Delta E_R(\tilde{5}\sigma)$ would have to be ~1.5 eV smaller than $\Delta E_R(\tilde{4}\sigma)$ to be consistent with $\Delta E_{\text{tot}}(\tilde{5}\sigma) \sim 0.4$ eV. This seems rather unlikely especially since our calculations indicate a somewhat larger ΔE_R for bonding than for nonbonding orbitals. If we assume that our result that the valence orbitals ΔE_R are roughly equal is correct, then ΔE_I would have to be ~-5 eV or ~1.5 eV smaller (more negative) than our calculated value. This is possible but the larger bonding shift would suggest,[15] although it does not require, that the adsorption energy of CO on Ni would be larger than ~1.3 eV.[30] It is even harder to make $\Delta E_{\text{tot}}(\tilde{1}\pi) \sim 5$ eV consistent with our results. As we have shown in Figs. 1(b) and 1(d), the $\tilde{1}\pi$ and $\tilde{4}\sigma$ orbitals are both dominantly centered about the O atom. Thus they should be expected to have similar ΔE_I and ΔE_R and hence ΔE_{tot}. Indeed, this is exactly the case for our calculated shifts. However, reversing the assignment of $\tilde{1}\pi$ and $\tilde{5}\sigma$ requires that $\Delta E_{\text{tot}}(\tilde{1}\pi)$ be 1.5–2.0 eV larger than $\Delta E_{\text{tot}}(\tilde{4}\sigma)$. Further, if the adsorption were at a bridge or fourfold site (rather than head-on as in our model), we would reasonably expect there to be more π bonding. This π bonding would mean that $\Delta E_I(\tilde{1}\pi)$ would be more negative than $\Delta E_I(\tilde{4}\sigma)$. Our results also suggest that ΔE_I is somewhat more negative for bonding than for nonbonding valence orbitals. Thus we would expect $\Delta E_{\text{tot}}(\tilde{1}\pi) < \Delta E_{\text{tot}}(\tilde{4}\sigma)$ if there were significant π bonding. However, this is exactly opposite to the order of shifts required by the assignment[11] $I(\tilde{5}\sigma) > I(\tilde{1}\pi)$. In sum, while our calculated shifts are quite consistent with the ordering $I(\tilde{5}\sigma) < I(\tilde{1}\pi)$, they do not support the reverse assignment.

E. CO bond length

Much of the analysis above depends on the assumption that the CO bond distance for CO adsorbed on Ni is not too different from its value in free CO. Or, equivalently, that any changes in bond distance upon adsorption do not have a significant effect on the IP's of the CO-like orbitals. This assumption is required particularly for the assignment of the orbitals into three groups (core, nonbonding valence, and bonding valence) according to their energy-level-shift behavior and for the assignment of the order $I(\tilde{1}\pi) > I(\tilde{5}\sigma)$.

Cotton and Wing[50] have shown that the CO bond distance in various bonding situations (characterized by the "bond order") is not changed significantly until the bonding is very different from that in free CO. (More specifically, it does not increase significantly until the bond order is reduced

TABLE VII. Variation of the Koopmans-theorem ionization potentials $-\epsilon$ with changes in bond length for the free CO molecule. The difference of the ionization potentials, denoted ΔI, are given with respect to the values for $d_{\mathrm{C-O}} = 2.15$ bohrs. The values of $I(\mathrm{Koopmans}) = -\epsilon$ are given for this distance. All values are taken from the results of Ref. 52. Energies are in eV and distances in bohrs.

$d_{\mathrm{C-O}}$	$\Delta I(1\sigma)$	$\Delta I(2\sigma)$	$\Delta I(3\sigma)$	$\Delta I(4\sigma)$	$\Delta I(5\sigma)$	$\Delta I(1\pi)$
2.00	−0.112	−0.990	+1.524	+0.194	−0.279	+0.993
2.05	−0.063	−0.659	+1.009	+0.129	−0.179	+0.648
2.10	−0.030	−0.327	+0.500	+0.063	−0.085	+0.317
2.15	0	0	0	0	0	0
2.20	+0.019	+0.322	−0.490	−0.061	+0.075	−0.303
2.25	+0.028	+0.641	−0.969	−0.117	+0.140	−0.595
2.30	+0.034	+0.947	−1.433	−0.167	+0.192	−0.873
$-\epsilon(R=2.15)$	562.330	309.251	41.230	21.873	15.132	17.311

to ~1.5 from the 3 characteristic of free CO.) For practically all metal carbonyls,[50] $d_{\mathrm{C-O}}$ is between that of free CO, 2.13 bohrs, and 2.20 bohrs, or 0.07 bohrs larger. The value used in our clusters, 2.16 bohrs, is halfway between these two limits. By analogy with the carbonyls, we expect the CO bond distance to change (increase) only slightly upon adsorption. This expectation is supported by our calculation which shows (see Fig. 1) that the CO orbitals are not greatly changed in the clusters. It is further supported by the fact that the chemisorption bond energy for CO on Ni is fairly small[30] indicating that the CO bond will not be greatly perturbed upon adsorption.

An estimate of the effect of changes in $d_{\mathrm{C-O}}$ on the IP's may be made by examining the changes of the CO orbital energies, ϵ's, for free CO. These are, of course, just the Koopmans -theorem IP's. It is reasonable to expect that this geometry effect for free CO will be very similar to that for adsorbed (perturbed) CO. Demuth and Eastman[51] used, in a similar way, the results of free-molecule SCF calculations to determine possible geometry changes from the photoemission spectra of adsorbed hydrocarbons. The free CO ϵ's, taken from extended Slater type basis set[26] near Hartree-Fock limit SCF calculations,[52] are shown in Table VII for several values of $d_{\mathrm{C-O}}$ between 2.0 and 2.3 bohrs. Since we wish to focus on changes rather than absolute values, the ϵ's in Table VII are given as differences with respect to the values for $d_{\mathrm{C-O}} = 2.15$ bohrs. It is clear that any variation of $d_{\mathrm{C-O}}$ within, or even somewhat outside, the reasonable range 2.13 to 2.20 bohrs will not affect the conclusions drawn above. The effect of a change in $d_{\mathrm{C-O}}$ will be largest for the 3σ level (which has not been observed in adsorption). This is quite understandable since the 3σ is the most strongly bonding orbital. Here, assuming that $d_{\mathrm{C-O}}$ for adsorbed CO is larger than for free CO, the effect will be to decrease $\mathrm{IP}(\bar{3}\sigma)$ and to increase $\Delta E_{\mathrm{tot}}(\bar{3}\sigma)$. (For free CO, Franck-Condon and correlation effects lead to a very broad 3σ photoemission peak.[53] A broad $\bar{3}\sigma$ peak for adsorbed CO is also to be expected.)

The calculated and observed values of the K-shell ($\bar{1}\sigma$ and $\bar{2}\sigma$) energy-level shifts also provide additional and independent support that $d_{\mathrm{C-O}}$ does not increase significantly when CO is adsorbed in Ni. Our computed result, for both NiCO and $\mathrm{Ni_2CO}$ (cf. Table IV), is the $\Delta E_{\mathrm{tot}}(1\sigma)$ and $\Delta E_{\mathrm{tot}}(\bar{2}\sigma)$ are nearly equal, $\Delta E_{\mathrm{tot}}(\bar{1}\sigma)$ being 0.1 eV larger than $\Delta E_{\mathrm{tot}}(\bar{2}\sigma)$. As we have noted, the cluster calculations do not take account of any possible variation of $d_{\mathrm{C-O}}$. From Table VII, we note that $\epsilon_{2\sigma}$ increases by ~0.65 eV for each 0.1 bohr increase in $d_{\mathrm{C-O}}$; the increase of $\epsilon_{1\sigma}$ is an order of magnitude smaller. Thus, if $d_{\mathrm{C-O}}$ increased significantly upon adsorption $\Delta E_{\mathrm{tot}}(\bar{1}\sigma)$ would be significantly larger than $\Delta E_{\mathrm{tot}}(\bar{2}\sigma)$. However, the observed value[47] of $\Delta E_{\mathrm{tot}}(\bar{1}\sigma)$ is only ~0.3 eV larger than $\Delta E_{\mathrm{tot}}(\bar{2}\sigma)$. This near equality is consistent with a small increase, ≲0.05 bohrs, in $d_{\mathrm{C-O}}$.

IV. CONCLUSIONS

The present Hartree-Fock SCF calculations on NiCO and $\mathrm{Ni_2CO}$ show that the bond being formed between CO and nickel arises dominantly from an interaction of the CO 5σ orbital with $3d$ orbitals of the nickel and that the Ni $4s$ electrons do not participate directly in the bond. In the real situation of CO adsorbed on a Ni surface one could expect changes in the Ni-CO binding, particularly if CO does not adsorb directly above a surface Ni atom (bridge, threefold or fourfold coordination site). However, the close similarity of our NiCO results with those[32] for $\mathrm{Ni(CO)_4}$ suggest that the changes may be small. On the whole, we believe that the local binding situation in the real CO-Ni adsorption system is qualitatively described in our linear NiCO or Ni_2CO models.

This binding situation is reflected in the energy-level shifts of the CO orbitals when the molecule interacts with Ni. It is suggested that these shifts consist of three contributions: (i) an environmental (chemical) shift, (ii) a bonding shift, and (iii) a relaxation shift. On this basis it is possible, from the NiCO and Ni_2CO data in Table IV, to assign the adsorbate CO-derived levels to three groups with the levels in each group behaving in a similar way. The first group contains the core level $\tilde{1}\sigma$ (O 1s), $\tilde{2}\sigma$ (C 1s) and the CO bonding level $\tilde{3}\sigma$. These levels, which are nonbonding with respect to Ni show, a relatively large initial-state shift ΔE_I which is exclusively a chemical shift. In addition, they show a large relaxation shift ΔE_R. The valence levels $\tilde{4}\sigma$ and $\tilde{1}\pi$ which are also essentially nonbonding with respect to the Ni form the second group. Here ΔE_I is comparable to those found for the first group but ΔE_R is much smaller, Finally, the third group consists of the $\tilde{5}\sigma$ level which behaves differently from all others for both ΔE_I and ΔE_R.

A comparison of the energy-level shifts obtained for NiCO and Ni_2CO shows that the major effect of the second Ni atom is to increase ΔE_R by a roughly constant amount for all the CO-like orbitals. The values of ΔE_I are essentially the same for both clusters. Thus ΔE_{tot} increases by ~0.4 eV for all CO levels in going from NiCO to Ni_2CO (For the $\tilde{5}\sigma$ level, the behavior of ΔE_I and ΔE_{tot} is masked by the different multiplet splitting in the two clusters.) This increase brings the calculated shifts closer to the experimental results[10,47] for CO adsorbed on Ni. However, we believe that the calculations strongly underestimate ΔE_R because of the small number of Ni atoms in the clusters.

Two general conclusions concerning the interpretation of the uv photoemission spectra of chemisorbed molecules[10,15,17,47,54] can be drawn from our analysis of the contributions to the energy-level shifts. First, the relaxation shift ΔE_R need not to be constant for all valence levels.[17,47,54] Second, chemical shifts can contribute significantly to E_I and therefore yield nonvanishing values for the nonbonding valence levels.[20] Both points have been made before; however, the present results give a direct theoretical justification that these effects must be taken into account in the analysis of photoemission spectra.

The detailed analysis of the energy-level shifts also leads to specific conclusions for the Ni-CO system. Our results are consistent with and strongly support the assignment[10,47] that $I(\tilde{1}\pi)$ is greater than $I(\tilde{5}\sigma)$. They cannot be easily reconciled with the reverse assignment proposed by Williams *et al.*[11] The near equality of the $\tilde{1}\sigma$(O 1s) and $\tilde{2}\sigma$(C 1s) shifts provides independent evidence that the CO bond distance for adsorbed CO is not much larger than that for the free molecule.

The multiplet splitting arising from the interaction of the singly-occupied (ionized) CO-like orbital with the unpaired Ni electrons has also been considered. The relatively large values for NiCO occur because there is an unpaired Ni 4s electron and are, almost certainly, an artifact of this cluster. The Ni_2CO values form a reasonable basis for estimating the splitting for adsorbed CO since only Ni 3d electrons are unpaired in this cluster. The Ni_2CO multiplet splittings are negligible for all CO-like levels except $\tilde{5}\sigma$ where it is quite small, of order 0.1 eV. Clearly, this effect does not account for the large observed[10,47] widths of the valence level resonances.

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