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# Explanation of the satellite structure observed in the photoemission spectra of coordinated CO

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We provide a general discussion of the photoemission spectra of transition-metal–carbonyl compounds and CO adsorbed on a transition-metal surface. The screening of the photoexcited hole and the resultant satellite structure due to the excited states of the ion are discussed. The importance of multiplet splittings in the spectra is illustrated, and it is shown that electron correlation must be included to achieve a correct description of the multiplet splitting. This analysis leads to a general interpretation of the core-level spectral region of molecular carbonyls and CO adsorbates.

## I. INTRODUCTION

One of the major applications of photoelectron spectroscopy is the study of adsorption systems. The desired information is the nature of the bonding between the substrate and the species being adsorbed. Three types of experimental information are reported for adsorption systems using angle integrated detection:

(a) The shift in the one-electron binding energies of the ligand upon adsorption.[1–17]

(b) Energy positions and intensities of satellite lines (shake-up) accompanying a "main" line (see, e.g., Refs. 4 and 9–15).

(c) Changes in the Auger spectra of the ligand upon adsorption.[4,16,17]

We will discuss only the first two in this paper. Our objective is to clarify the language and concepts involved in discussing the photoionization process, especially from a core hole. We will show how the shift in binding energy (a) is intimately related to the production of satellite lines (b) in a spectrum. This interrelationship results in sum rules on the intensity and energies of the peaks in a core-level spectrum. Experimental data will be compared to theoretical calculations to illustrate the physical phenomena, to evaluate theoretical procedures, and, most importantly, to eliminate any misunderstanding resulting from semantics.

Free carbon monoxide and coordinated CO will be used as the prototype system, because more work has been done on this system than on any other adsorption system. We must state at the onset our personal bias. Any calculation scheme which is to be used to investigate the core-level spectrum of an absorbed molecule must be tested first on the isolated molecule and then on any known molecular complexes. Therefore, we will concentrate on explaining the core-level spectra of CO and transition-metal carbonyls and then show that the physical processes are the same for absorbed CO. Figure 1 illustrates the effects that we will discuss in the C 1*s* and O 1*s* spectra of CO and coordinated CO. The bottom two spectra are for gas-phase CO. There is one dominant peak in both spectra which is usually referred to as the "main line" resulting from removal of one electron from the appropriate core level. If one looks carefully at the spectra there are a multitude of low-intensity satellite peaks to the higher-binding-energy ($E_{\rm BE}$) side of the "main line" (see next section for definition of $E_{\rm BE}$). These satellite peaks are commonly referred to as shake-up peaks. When CO is bound to a transition metal to form a carbonyl like $\rm W(CO)_6$, two changes are obvious in the core-level spectra: (1) the "main line" shifts to lower binding energy ~ 5 eV, and (2) the satellite peaks are more intense. We will show that a shift in the main line will usually be accompanied by increased satellite intensity. The third set of spectra (from bottom) shown in Fig. 1 are for CO absorbed on W(110).[16] They are included to illustrate how similar they are to the carbonyl spectra. The final set of spectra[11] for CO absorbed on Cu is the cause of much of the controversy and confusion in this subject. Here "main line" becomes ambiguous, since two peaks have nearly the same intensity. The general questions to be answered are the following: (1) What are the states of the complex which are associated with each peak in the spectra? (2) Why does the intensity distribution change so dramatically when CO is coordinated in a transition-metal complex?

In Sec. II we discuss in detail the physical process of ionization of a core level in free CO and coordinated CO. In Sec. III we will specifically discuss various theoretical techniques applied to CO and carbonyls, and finally we will discuss briefly in Sec. IV satellite structure in valence spectra.

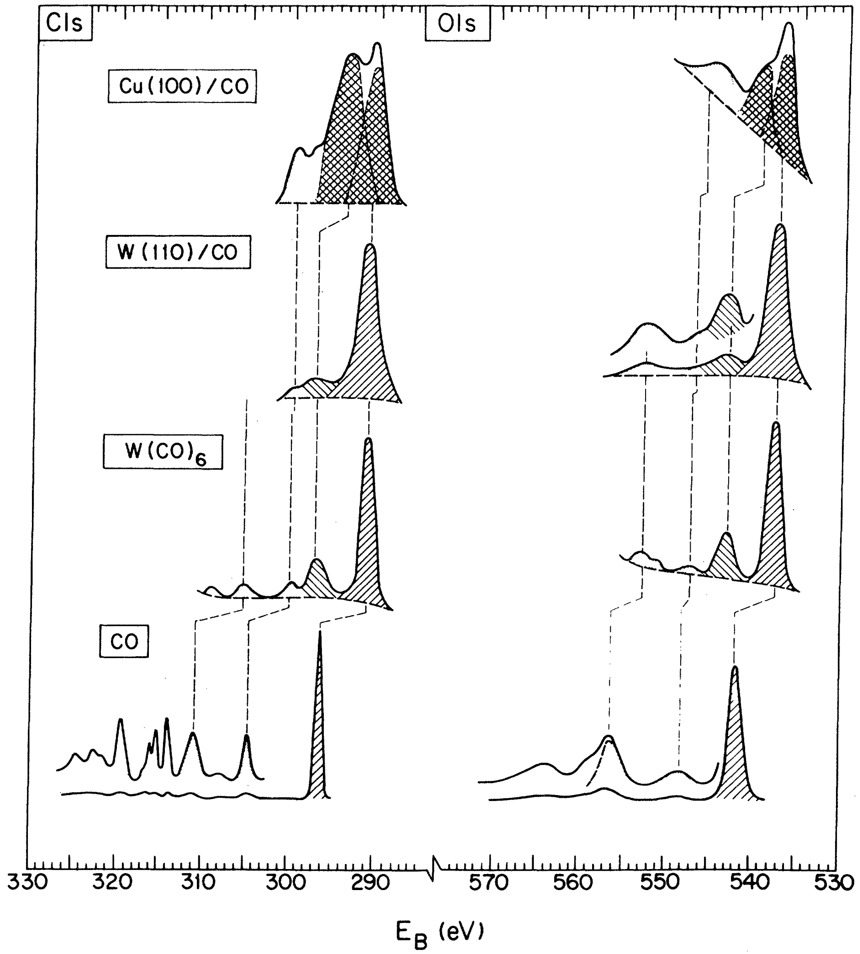

FIG. 1. X-ray photoemission spectra of free and coordinated CO. C 1*s*: CO (gas) [Ref. 10(a)], W(CO)$_6$ (gas) [Ref. 4(a)], W(110)/CO (Ref. 16), Cu(100)/CO [Ref. 11(b)]. O 1*s*: CO (gas) (Ref. 18), W(CO)$_6$ (gas) [Ref. 4(b)], W(110)/CO (Ref. 16), Cu(100)/CO [Ref. 11(b)]. The main lines of the adsorbate ionizations have been aligned with the carbonyl main lines.

## II. CORE-LEVEL PHOTOIONIZATION

### A. Carbon monoxide

Photoionization is the process of absorption of a photon resulting in ionization. The kinetic energy of the ejected electron is given by the energy difference of the system before and after ionization,

$$E_{Ke}(i) = E_0^N + \hbar\omega - E_i^{N-1}, \qquad (1)$$

where $E_0^N$ is the total energy of the neutral $N$-electron system in its ground state, $E_i^{N-1}$ is the total energy of the ion in the $i$th state, and $\hbar\omega$ is the photon energy. If we shift the photon energy to the left-hand side of the equation, we obtain an energy which just depends upon the energy states of the ion. This is called the binding energy of the state $i$:

$$E_{\mathrm{BE}}(i) = \hbar\omega - E_{Ke}(i) = E_i^{N-1} - E_0^N. \qquad (2)$$

To understand the satellite structure shown in Fig. 1 let us turn to a simple molecular orbital scheme. Figure 2 shows a schematic orbital diagram with one core level (bottom) and three fully occupied valence orbitals. The diagram (000) is the ground state of the neutral; (004) is the ground state of the ion. The 4 denotes our counting scheme, i.e., the deepest orbital is 1. Thus the

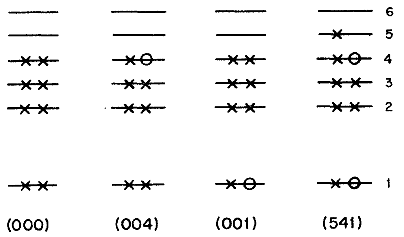

FIG. 2. Schematic orbital diagram for various states of the neutral system and the ions.

diagram (001) is for ionization of the deep core level. For CO this requires a minimum of 296 eV for a C 1$s$ and 543 eV for the O 1$s$. The final diagram is the important one for satellite structure. It is labeled (541) because not only is there a hole in the core level but a valence electron has been excited. The excited electron is in the 5th state and the hole in the 4th. There are numerous such states, which are excited states of the ion. In principle, they are just other states $i$ of the ion with total energy $E_i^{N-1}$, but it is convenient to introduce two additional labels $E_{ijk}^{N-1}$. $k$ denotes the deep core level, for example, O 1$s$ in CO, and $i$ denotes the state of the excited electron and $j$ the hole state. When $(i,j)=0$ we have the configuration shown in (001) state in Fig. 2, i.e., the valence occupancy is the same as in the neutral. In principle, it is easy to find the energies of all of the peaks shown in the spectra of Fig. 1. Just calculate $E_{ijk}^{N-1}-E_0^N$ for a specific $k$ (O 1$s$ or C 1$s$) and all pairs of $(i,j)$ possible. It has been assumed until recently that the state $E_{00j}^{N-1}$ is the "main line" in the spectra and the intensity is larger than any of the other states $(i,j)\neq 0$. We will show that the latter assumption is not always true for coordinated systems, especially when the interaction is weak.

The intensity of any peak $l$ in the spectrum can be determined from the matrix element

$$M_{if} \cong \langle \Psi_f(l)|\vec{A}\cdot\hat{P}|\Psi_0\rangle \ ,$$

where $\Psi_f$ is the final state of the ion and $\Psi_0^N$ is the ground state of the system. $\vec{A}$ is the polarization vector of the light and $\hat{P}$ the momentum operator. The index $l$ denotes the states of the ion represented by $E_l^{N-1}$ in Eqs. (1) and (2). Again, we simplify this by considering a one-electron picture so that we label the final state by three indices $(i,j,k)$ with the same meaning as discussed in Fig. 2. Then the intensity of each peak in the core-level spectra of Fig. 1 is given by

$$I_{ijk} \propto |\langle \Psi_f(i,j,k)|\vec{A}\cdot\hat{P}|\Psi_0^N\rangle|^2 , \tag{3a}$$

with the requirement that

$$E_{\rm BE}(i,j,k)=E_{ijk}^{N-1}-E_0^N . \tag{3b}$$

Now we make the basic assumption that will be used throughout this paper, i.e., the sudden approximation.[19,20] The physical picture is the following. The ionization process is so rapid that the valence electrons do not have time to readjust to the new potential, i.e., they are frozen. They find themselves in a state which is not an eigenstate of the $N-1$ electron Hamiltonian but which is a mixture of ionic states.[20] Putting this in a more formal way, we write the ground state as

$$\Psi_0^N=\phi_k\Psi_k^R(N-1), \tag{4a}$$

where $\phi_k$ is the inner-shell orbital and $\Psi_k^R$ is the properly antisymmetrized determinant of the remaining $N-1$ electrons. Likewise, we have the ionic wave function

$$\Psi_f(i,j,k)=U_K\Psi_{ijk}^{\rm ion}(N-1), \tag{4b}$$

where $U_K$ is the wave function of the excited electron and $\Psi_{ijk}^{\rm ion}(N-1)$ represents the eigenstates of the ion with a hole in the $k$th core level and a valence electron excited from state $j$ to $i$. This gives the following equation for the intensity:

$$I_{ij}=|\langle U_K|\vec{A}\cdot\hat{P}|\phi_f\rangle\langle\Psi_{ijk}^{\rm ion}|\Psi_k^R\rangle|^2 . \tag{5}$$

The first factor in Eq. (5) gives the photoemission intensity. The intensity is distributed over the main peak $(i,j)=0$ and its satellites $(i,j)\neq 0$ for a specific core level $k$. The relative intensity of each peak is given by

$$P_{ijk}=|\langle\Psi_{ijk}^{\rm ion}|\Psi_k^R\rangle|^2 . \tag{6}$$

Since $\Psi_{ijk}^{\rm ion}$ forms a complete orthonormal set we have the following sum rule on the intensities:

$$\sum_{(i,j)} P_{i,j,k}=1 , \tag{7}$$

where the sum is over all excited states $(i,j)$ including the continuum $(\infty,j)$. Equations (5) and (7) can be used to prove another sum rule on the intensity weighted average energy,[19,20]

$$\sum_{(i,j)}^{\infty} P_{ijk}E_{\rm BE}(i,j,k)=E_{\rm BE}^F(k), \tag{8}$$

where $E_{\rm BE}^F(k)=E_F^{N-1}(k)-E_0^N$. The subscript or superscript $F$ describes the frozen orbital ionic state represented by Eq. (4a). This value $E_{\rm BE}^F(k)$ has special meaning in a Hartree-Fock calculation because it is the negative of the orbital energy and is therefore the Koopmans binding energy.[21] $E_{\rm BE}^F(k)$ is totally a property of the ground state and is only measurable via the sum expressed in Eq. (8). Shifts in $E_{\rm BE}^F(k)$ as an atom is placed in different bonding configurations are caused by true chemical shifts.

We are now in a position to understand both the energies and intensities of the peaks in the core-level spectrum, using Eqs. (3b), (6), (7), and (8). Assume that the system being studied does not relax when the hole in the $k$th level is formed. Then the states of the ion $\Psi_{ijk}^{\rm ion}(N-1)$ are identical to the neutral function $\Psi_k^R(N-1)$. This means that

$$P_{ijk}=|\langle\Psi_{ijk}^{\rm ion}|\Psi_k^R\rangle|^2=\delta^2_{(i,j),(0,0)} .$$

There is only one peak in a core-level spectrum, and its energy is given by Koopmans's value in the Hartree-Fock scheme (orbital energy) or by $E_{\rm BE}^F(k)$

in a non-Hartree-Fock scheme. If the valence electrons relax when the core hole is formed then

$$\langle\Psi_{00k}|\Psi_k^R\rangle \neq 1 .$$

By definition, the energy of the ionic state $E_{00k}^{N-1}$ is lower than the frozen noninteracting energy $E_F^{N-1}(k)$. Equations (7) and (8) tell us that there now must be satellite peaks with intensity equal to

$$1 - |\langle\Psi_{00k}^{\text{ion}}|\Psi_k^R\rangle|^2$$

and an energy distribution such that Eq. (8) is satisfied. It is convenient to define the energy shift of the "main line" with respect to the frozen orbital energy as the relaxation energy $E_{\Delta\,\text{rel}}$ :

$$E_{\Delta\,\text{rel}}(j) = E_F^{n-1}(k) - E_{00k}^{N-1} = E_{\text{BE}}^F(k) - E_{\text{BE}}(00k) . \quad (9)$$

Table I shows calculated values for $E_{\text{BE}}^F(k)$ and $E_{\text{BE}}(00k)$ for the C 1*s* and O 1*s* levels of CO. The first set of calculations is for the frozen-ion configuration, using several theoretical techniques (see Sec. III). The numbers differ by about 3% depending upon the approximations used. The second set of numbers is for calculations of $E_{\text{BE}}(00k)$ using total energy differences for a self-consistent solution for the neutral and ion. These values are much closer to the experimental binding energies. The last set of numbers is the relaxation energy from each calculation. All three theoretical procedures produce the same relaxation energies and they are large numbers.

The calculated values for the frozen-ion binding energy given in Table I predicts that the weighted energy sum of all of the satellite peaks given in the CO spectra of Fig. 1 should produce an energy ~20 eV higher in binding than the O 1*s* main line. We have measured the intensity of the satellite lines out to ~30 eV and the shift in energy is only 4.5 eV.[18] The additional strength must be distributed in the continuum, or correlation effects become very important. It has been shown, however, that the correlation contribution to the relaxation energy is only of the order of a few percent for a core ionization.[27]

Figure 3 illustrates the effect of the reorganization of the valence levels. This difference charge-density plot from Baerends[28] is a plot of the change in the valence-electron charge density upon creating a C 1*s* hole. This contour is approximately $|\Psi_{00k}^{\text{ion}}|^2 - |\Psi_k^R|^2$.[29] If the electrons did not respond to the C 1*s* hole, the difference would be zero, and there would be one peak in the C 1*s* spectrum at Koopman's value. Thus the charge rushes in to screen the C 1*s* hole, lowering the energy of the ionic state $\Psi_{00k}^{\text{ion}}$ compared to the artificially frozen orbital ionic state $\Psi_k^R(N-1)$. Several papers[26,30,31] have analyzed the changes in each orbital of the CO when an oxygen or carbon 1*s* hole is present compared to the neutral CO. They find the major change upon creation of the hole occurred in the 1$\pi$ orbital. It is obvious from Eq. (6) that those orbitals which

TABLE I. CO core-level binding energies.

| Calculational scheme | C 1*s* (eV) | O 1*s* (eV) | Reference |
|---|---|---|---|
| $E_{\text{BE}}^F$ frozen-ion approximation (Koopman's value) | | | |
| Hartree-Fock | 309.61 | 562.76 | 22 |
| | 309.4 | 562.4 | 23 |
| | 310.23 | 557.31 | 24 |
| $X\alpha$ scattered-wave | 321.23 | 574.33 | a |
| | 315.0 | 570.38 | b |
| $E_{\text{BE}}$ relaxed-ion approximation | | | |
| Hartree-Fock ($E_{\Delta\text{SCF}}$) | 298.28 | 542.55 | 22 |
| | 297.6 | 541.9 | 23 |
| $X\alpha$ ($E_{\Delta\text{SCF}}$) | 308.9 | 552.16 | a |
| $X\alpha$ (transition state) | 302.7 | 549.6 | b,c |
| | 304.5 | 550.6 | |
| Experimental | 296.2 | 542.6 | |
| Relaxation energy $E_{\Delta\text{rel}}$ | | | |
| Hartree-Fock | 11.38 | 20.21 | 22 |
| | 11.8 | 20.5 | 23 |
| $X\alpha$ ($E_{\Delta\text{SCF}}$) | 12.4 | 22.2 | a |
| $X\alpha$ | 12.5 | 20.9 | b |

[a] Total energy difference calculations for CO using touching sphere muffin tins (Ref. 25).

[b] Overlapping sphere (0.77 and 0.66 Å radii) calculations described in Ref. 26.

[c] Transition state calculation for touching spheres (Ref. 25).

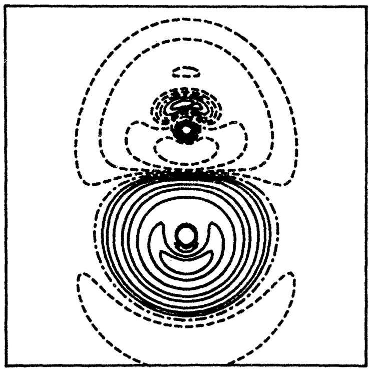

FIG. 3. Electron density difference plot after Baerends (Ref. 28) between the free CO ion and a C 1s hole and the neutral CO ground state. The core-electron densities are not included. Full lines represent electron density gain, while broken lines represent density loss. The C atom is down.

change the most will be the ones involved in the valence excitations.[26,30] Therefore we would expect the major satellite peaks to be $1\pi \rightarrow n\pi$. The $1\pi$ orbital is the only occupied $\pi$ orbital in CO.

We must now discuss multiplet structure. Figure 2 showed a neutral system which was a closed-shell configuration, i.e., a singlet state. But the excited state of the ion shown in configuration (5, 4, 1) has three unpaired spins, which may couple to give two doublet and one quartet states (see Appendix). Only transitions to the doublet state are possible [Eq. (6)]. Thus, it is clear that each excited state like (5, 4, 1) will give rise to two well-defined final states. The energy splitting of this multiplet structure must be calculated for the ion, because it can be quite different than values calculated for the neutral.

Guest *et al.*[31] report on a calculation including correlation for the C 1s core hole of CO. They calculate the $1\pi \rightarrow 2\pi$ excitation to be the lowest energy excitation in the ion. The multiplet splitting between the two possible doublet states resulting from this excitation in the ion is calculated to be 7.2 eV (see Fig. 1, C 1s ionization in CO). The two final doublet states are related to the singlet $^1\Sigma^+$ and the triplet $^3\Sigma^+$ states of the $1\pi \rightarrow 2\pi$ excitation in the neutral molecule. In the neutral molecule case McKoy *et al.*[32] calculate a triplet energy of 7.1 eV and deduced a singlet energy of 14.6 eV giving rise to a multiplet spitting of 7.1 eV. The creation of a core hole basically leads to a similar stabilization of the $1\pi$ and $2\pi$ orbitals and, therefore, similar excitation energies for these transitions in the ion. It is clear that because of the unequal weight of the wave functions on the carbon and on the oxygen atoms, there will be differences in the excitation energies and intensities of the satellite peaks accompanying the O 1s and C 1s ionization. Figure 1 shows that this assignment is basically correct; Sec. III will justify this assignment in more detail. The assignment of the satellite peaks at higher binding energy is nebulous. Guest *et al.*[31] favor a double excited $1\pi \rightarrow 2\pi$ or, alternatively, $\sigma \rightarrow \sigma^R$ Rydberg transition.

### B. Coordinated carbon monoxide

We will discuss only nondissociative bonding of CO to transition metals. In this case the molecule bonds carbon end to the metal, and the two molecular orbitals primarily involved in the bonding are the highest occupied CO $\sigma$ state ($5\sigma$) and the first unoccupied $\pi$ state ($2\pi$). The conventional view of this bond is $\sigma$ donation to the metal from CO $5\sigma$ orbital and back donation from the metal $d\pi$ to the CO $2\pi$.

Figure 4 shows a schematic picture of the orbitals of CO on the left and the orbitals of a metal CO complex on the right. The orbitals of the complex are denoted by their primary character, i.e., $\tilde{M}$ means primarily metal. For example, the amount of $2\pi$ mixed into the occupied $\tilde{M}$ $d\pi$ state is only $0.1e$.[6,24]

The fact that the valence orbitals, both occupied and unoccupied, change when bonding occurs means that we should expect changes in the core-level satellite structure in coordinated CO compared to isolated CO. We will show subsequently that all theoretical calculations for carbonyls predict a very small change in the core-level binding energy as a result of initial-state shifts. This means $E^F_{\text{BE}}(k)$ should be the same for coordinated and free CO. But Fig. 1 shows that the "main line" shifts by many volts and new and/or more intense satellite peaks appear in the spectra.

This situation is a clear test of the sum rules presented in Eqs. (7) and (8). The main lines in carbonyl spectrum must lose intensity to the satellite lines in such a way that the intensity weighted average is the same that as for CO. This sum rule has been tested on $Fe(CO)_5$ and CO and it works extremely well.[18] The main line in the O 1s spectrum of $Fe(CO)_5$ is shifted to lower binding energy by 3.3 eV and loses 29% in intensity compared to the CO main line. The increase in the satellite intensity in $Fe(CO)_5$ accounts for almost all of the loss in intensity from the main line, and the intensity weighted mean for CO is 546.6 eV compared to 546.1 eV for $Fe(CO)_5$. We take these data as proof that Eqs. (7) and (8), derived from the sudden approximation, are correct and we proceed to interpret the spectra within the context of this model.

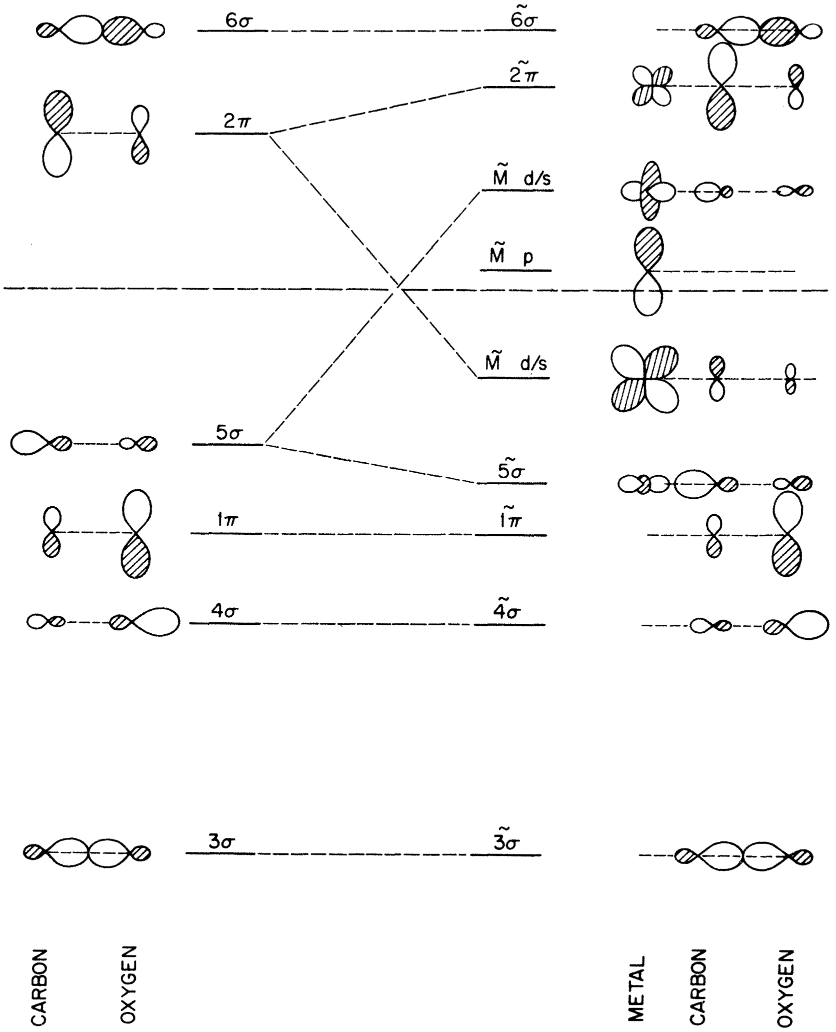

FIG. 4. Schematic one-electron orbital diagram for a CO-metal interaction. The magnitude of the atomic orbitals indicates the corresponding coefficient in the linear-combination-of-atomic-orbitals wave function. The orbital nomenclature for free CO is used for the coordinated system. $\tilde{M}$ means orbitals with dominating metal character.

The changes in the core-level spectra of coordinated CO compared to free CO must be caused by the different ionic states in the two systems. The "main line" shifts to lower binding energy in the carbonyl because the ionic state has lower energy compared to the neutral system. This results from the fact that the core hole can be screened more effectively in the complex than in isolated CO. It is the origin of, or the description of, the screening process that has produced the controversy in this subject. The basic process is quite simple. Since the metal levels are the highest occupied levels in the complex (Fig. 4), there will be charge transfer from the metal to the CO when a core hole is present on the CO molecule. Lang and Williams were the first to propose that this screening for an atom adsorbed on a surface occurred by charge transfer from the metal to the first unoccupied orbital of the atom with a core hole.[33] In the case of a molecule like CO this picture predicts that the CO 2π orbital is occupied to screen the hole. This has been interpreted to mean that an excited-state configuration-like orbital scheme (541) of Fig. 2 is the lowest energy state of the ion.[4,11(a),33–37]

For CO bound to a transition metal the interpretation of the core-level spectra using the Lang and Williams[33] model is that the lowest binding-energy peak is a screened state, where the screening results from a charge transfer from the metal *d* orbitals to the previously unoccupied CO 2π orbital. The 2π orbital is pulled down by the presence of the core hole. The first big shakeup in the spectrum (~5 eV for carbonyls and ~2 eV for CO on Cu) is the unscreened state corresponding to the (001) orbital configuration of Fig. 2. We are faced with semantic questions: (1) What do we now mean by "main line," since we had assumed the ionic state (001) of Fig. 2 to be the main line, and (2) what is a charge-transfer state? In addition to these semantic questions, there is a real issue surrounding this interpretation. Is the two-hole–one-particle state represented by (541) in Fig. 2 lower in energy than the one-hole state (001)? We will show that for coordinated CO it is not.

The process of screening can best be illustrated by a charge contour plot similar to Fig. 3. Figure 5(a) is from a calculation by Baerends for $Cr(CO)_6$.[28] This is the charge-density difference due to the screening of the C 1*s* hole in the CO molecule to the right of the figure. If you compare Fig. 5(a) for $Cr(CO)_6$ with Fig. 3 for isolated CO you see that the region around the C 1*s* hole is very similar. It should be, since the relaxation energy is predominantly intramolecular. For the C 1*s* hole, Table I showed that the relaxation energy was ~12 eV for isolated CO. It is only ~15 eV for $Cr(CO)_6$ (see Table II). A better view of the extramolecular screening effects are shown in Fig. 5(b).[28] From this figure in comparison with Fig. 5(a) one can visualize the difference between the intra- and extramolecular screening. The calculated charge-density difference in the $Cr(CO)_6$ molecule with a localized C 1*s* hole and a neutral Cr atom, five neutral CO's and one C 1*s* core-hole CO ion is shown. You can see that the extramolecular screening looks like a $\pi$ orbital, in fact, like the CO $2\pi$ orbital. It is also apparent that the $\sigma$ valence states in the coordinated CO are not screening as effectively as they did in the isolated CO. Messmer *et al.*[26] argue from a $Cu_5CO$ calculation that this $\sigma$ effect is caused by the bonding of the $5\sigma$ CO orbital in coordinated CO.

If Lang and Williams had calculated the charge density around an ionized CO molecule adsorbed on the surface of jellium, the charge-density difference would have looked qualitatively like that shown in Fig. 5. This type of charge-density difference plot lead Lang and Williams[33] to label this the "excited atom" model for screening. The logical extension of this picture is to assume that the lowest energy configuration of the ionic system is an excited state, i.e., an electron-hole state of the form (541) in Fig. 2.[4,34–37] We will show that at least for CO adsorption this is not the case. We can see that the origin of the screening is easy to understand by studying the interaction of the CO $2\pi$ orbital with the metal *d* orbitals for the neutral and core-hole configurations. Figure 6 illustrates on the left what we have already seen

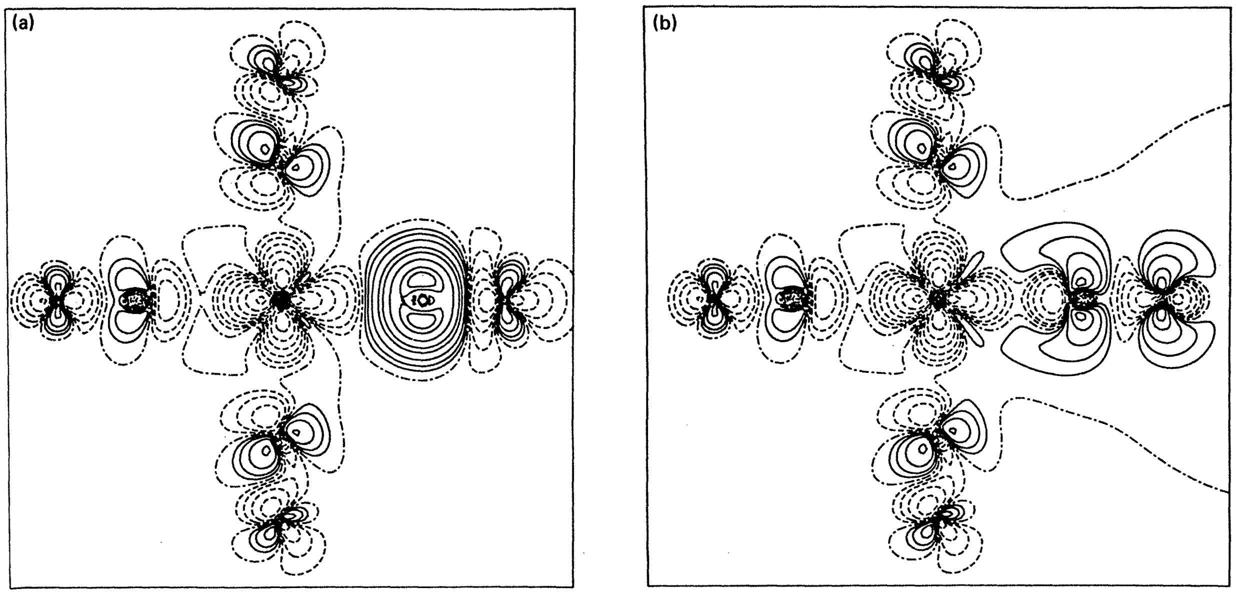

FIG. 5. Electron density difference plots after Baerends (Ref. 28) for $Cr(CO)_6$ ions (through the plane of four CO molecules and the metal). The core electrons are not included. From the valence-electron densities of the ions with a C 1*s* core hole are subtracted the valence density of (a) neutral Cr atom and six neutral CO's and (b) neutral Cr atom, five neutral CO's and a C 1*s* core hole CO ion. Plot (b), therefore, demonstrates the difference in screening when a CO is coordinated to a metal atom, compared to the free ion. Full lines represent electron density gain, while broken lines represent density loss.

TABLE II. Carbonyl binding energies.

| Set | Calculational scheme of system | C 1*s* (eV) | O 1*s* (eV) | Reference |
|---|---|---|---|---|
| I | $E^F_{\mathrm{BE}}$ frozen-ion approximation | | | |
| | Hartree-Fock $Cr(CO)_6$ | 309.1 | 555.2 | 24 |
| | $X\alpha$ $Cr(CO)_6$ | 318.86(317.11) | 573.04(570.77) | a |
| | Hartree-Fock $Ni(CO)_4$ | 310.33 | 557.31 | 24 |
| | Hartree-Fock CO | 309.9 | 557.51 | 24 |
| II | $E_{\mathrm{BE}}$ relaxed-ion approximation | | | |
| | Hartree-Fock $Ni(CO)_4$ | 285.3 | 528.0 | 38 |
| | $X\alpha$ transition state $Cr(CO)_6$ | 302.56(303.9) | 549.83(549.42) | a |
| III | Experimental $Cr(CO)_6$ | 293.1 | 539.4 | |
| IV | $\Delta E^F_{\mathrm{BE}}$ | | | |
| | Hartree-Fock $Cr(CO)_6$ | 1.1 | 2.1 | b |
| | Hartree-Fock $Ni(CO)_6$ | 0.4 | −0.2 | b |
| | $X\alpha$ discrete variational method (DVM) $Cr(CO)_6$ | 0.7 | −0.4 | 8(a) |
| | $X\alpha$ DVM $Fe(CO)_5$ | 0.5 | −0.4 | 8(a) |
| | $X\alpha$ DVM $Ni(CO)_4$ | 0.2 | −0.7 | 8(a) |
| V | $E_{\Delta\mathrm{rel}}$(carbonyl) − $E_{\Delta\mathrm{rel}}$(CO) | | | |
| | $X\alpha$ DVM $Cr(CO)_6$ | 3.3 | 3.7 | 8(a) |
| | | 2.8 | 3.1 | 8(a) |

[a] R. Messmer, private communication; the transition state for a CO molecule contained within the same sphere geometry as the $Cr(CO)_6$ is given in parentheses for each level (Ref. 26).

[b] From Ref. 24. The large numbers in IV reflect numerical problems in the calculation.

in Fig. 4 for the neutral metal-CO system. The occupied metal *d* levels interact with the unoccupied CO 2$\pi$ level to form an occupied bonding and unoccupied antibonding pair of orbitals. The bonding orbital is predominantly metal *d* in character. For example, a typical carbonyl will have only ~0.1 of 2$\pi$ character in this orbital. The antibonding orbital is predominantly 2$\pi$ in character. The energy separation between these two orbitals is ~5 eV in the carbonyls. The picture changes considerably when we consider the interaction of a CO molecular ion with a C 1*s* core hole with a metal. The presence of the core hole pulls the 2$\pi$ level down below the metal levels as shown by the drawing to the right in Fig. 6. Again, a bonding and an antibonding molecular orbital are formed from the interaction of the metal *d* states with the CO 2$\pi$ state. But now the bonding orbital has much more 2$\pi$ character than it did in the neutral case. This is the screened state. It is a single-hole statelike configuration (001) in Fig. 2. Compared to the neutral state there is charge transfer from the metal to CO in this state. The first excited state (two-hole–one-particle) results from an excitation of an electron from the bonding to the antibonding orbital. This ionic state is the first satellite line in the coordinated CO spectrum.

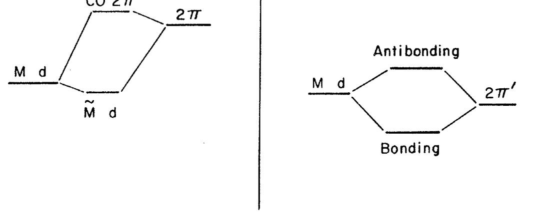

FIG. 6. Schematic representation of the metal-2$\pi$ CO interaction in the neutral and in the ion with a core hole.

Calculations for $Cr(CO)_6$ by Baerends[28] and $Ni(CO)_4$ by Loubriel[30] and by Mitchenson and Hillier[39] show that the lowest energy ionic state with a hole in a single CO molecule is the single-hole state shown in Fig. 6. Messmer *et al.*[26] have come to the same conclusion in a calculation of $Cu_5CO$ aimed at understanding the core-level spectra of CO adsorbed on Cu. Similar results were produced using a many-body formalism for the Ni-CO system,[40] and a Hartree-Fock calculation of the Auger spectra of NiCO.[41] The overwhelming evidence from numerical calculations coupled with the very simple arguments presented in Fig. 6 proves that in the case of coordinated CO the lowest energy core-hole state is the single-hole state. The new intense satellite line in the coordinated CO spectra compared to the isolated CO spectra is due to an ionic state which is a two-hole-one-electron state, involving a transition from the $2\pi$-$d$ bonding to $2\pi$-$d$ antibonding orbital. This ionic state also has some degree of charge transfer from the metal to the CO, so both states can be called charge transfer or screening states.

What remains is to discuss qualitatively the origin of the large change in the intensity ratio for the two ionic states seen in the spectra for CO coordinated to various metals. For example, in the CO on Cu spectrum the two peaks have nearly identical intensity, whereas in the $W(CO)_6$ spectrum the satellite is only 40% of the "main line." The easiest way to visualize what happens is to do the following "*Gedanken* experiment." Start with a configuration like $Cr(CO)_6$ and then separate the CO to be ionized from the molecule, i.e., change the interaction of the CO with the metal. We use Eq. (6) to predict what will happen. That is, we remove an electron from a core level leaving behind the frozen configuration $\Psi^R_k(N-1)$. Then we project this wave function onto the states of the ion $\Psi^{\text{ion}}_{ijk}$. To simplify the argument, let us assume that the major changes between the ion and frozen neutral occur only in the $2\pi$-$d$ states of Fig. 6. When the CO is close to the metal so that it interacts strongly, the $2\pi$-$d$ bonding orbital of the neutral will have some significant contributions of CO $2\pi$ character and the bonding state of the ion will have both CO $2\pi$ and metal $d$ character so the overlap between $\Psi^R_k$ and $\Psi^{\text{ion}}_{00j}$ will be large. However, there will be appreciable weight in the $2\pi$-$d$ antibonding ionic state. As the CO molecule is removed from the metal, the $2\pi$-$d$ bonding states of the neutral and ion become much more dissimilar. The neutral state becomes more and more $d$-like and the ionic state becomes more $2\pi$-like. The intensity of the peak in the spectrum corresponding to the bonding $2\pi$-$d$ ionic state decreases. The antibonding ionic state becomes more $d$-like as the interaction decreases, so the satellite-line intensity increases. At infinite separation the bonding ionic state corresponds to removing an electron from the metal and putting it on the CO, and the antibonding is just an isolated CO ion and a neutral metal, so all of the weight in the spectra is in the antibonding (satellite) peak.

There is another way to represent the nature of each ionic state appearing in the core-level spectra. Each ionic state $\Psi^{\text{ion}}_{ijk}$ can be expanded in terms of the frozen $N-1$ electron states of the neutral (including excited states):

$$\Psi^{\text{ion}}_{ijk} = \sum C_{m,n} \Psi^R_{mnk}(N-1),$$

where the $(m,n,k)$ represents excited states of the frozen state with an electron removed from the $k$th hole. In this representation the intensity of any state $\Psi^{\text{ion}}_{ijk}$ in the core-level spectra is given by $|C_{0,0}|^2$ [see Eq. (6)] because the functions $\Psi^R_{mnk}$ are orthogonal. This says that the intensity is given by the Koopmans character of each ionic state. In this case we have a clear meaning of main line. It is the peak with the dominant intensity because that ionic state looks more like the frozen $N-1$ neutral state $\Psi^R_k(N-1)$. In Fig. 7 we show a schematic picture of the core-level spectra of a coordinated CO molecule as a function of separation of the CO from the metal. We really intend this plot to represent the change in the spectra as the metal-CO interaction decreases.

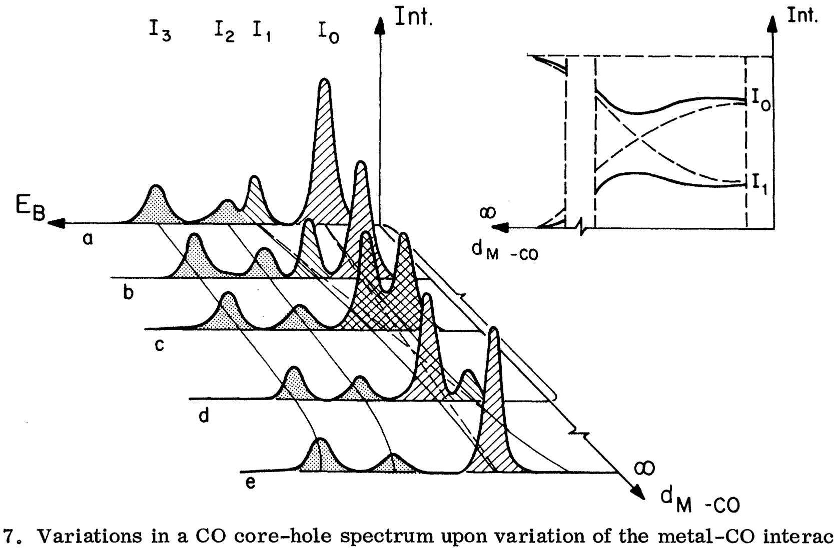

FIG. 7. Variations in a CO core-hole spectrum upon variation of the metal-CO interaction.

Curve *a* is a typical spectrum for a carbonyl or room-temperature stable CO adsorption system. The big peak $I_0$ is by our definition the "main line," since it has most of the Koopmans character. Peaks $I_2$ and $I_3$ are the two doublet $1\pi \to 2\pi$ excitations which are intramolecular CO shake-up lines (see Fig. 1). Peak $I_1$ is the ionic state corresponding to an excitation from the $2\pi$-$d$ bonding to the $2\pi$-$d$ antibonding (Fig. 6). Therefore let us analyze all four ionic states in terms of four neutral states. $\Psi^R_{0k}$ is the frozen orbital single core hole state. $\Psi^R_{1k}$ is the two-hole single-particle state corresponding to a $d$-to-$2\pi$ excitation in the neutral with a core hole. (The 1 denotes two indices $i, j$.) $\Psi^R_{2k}$ and $\Psi^R_{3k}$ are the $1\pi \to 2\pi$ molecular doublet states. We assume that the localized $1\pi \to 2\pi$ transitions will retain their character with metal-CO interaction, so peaks $I_2$ and $I_3$ maintain their relative intensity ratios and energies with respect to the main line. The fact that peak $I_0$ is large compared to $I_1$ in curve *a* means that this ionic state is mostly of Koopmans's character, i.e., $\Psi^R_{0k}$. And since we are only considering three other neutral states, $I_1$ is predominantly $\Psi^R_{1k}$, which is the charge-transfer state. At large separation or weak interaction the charge-transfer state is at lower binding energy (curve *d*) and the main line is at higher binding energy. When the CO molecule is at infinity, the charge-transfer state, metal *d* to CO $2\pi$, is lower in energy but has no Koopmans's character. If the ionic states were represented by single determinants, then the energy of Koopmans's state $\Psi^R_{0k}$ and the charge-transfer state $\Psi^R_{1k}$ would cross over in energy as the metal-CO distance or interaction was changed. This energy crossover is shown by the dashed lines in the figure. The intensity variation is shown in the right-hand corner. The real representation of the ionic states will be a multideterminant one, the states will not cross over, and the energy and intensity will follow the solid lines in Fig. 7.

There is no clear definition of charge-transfer state, screened state or, for that matter, main line. In a multideterminant representation we can call a given state the "main line" if its intensity is much larger than the other lines. There is some degree of charge transfer in all of the peaks in the core spectra of coordinated CO, so the definition of the screened state is very model dependent. For example, if we analyze spectrum *a* using only the four neutral states described above, we are forced to conclude that peak $I_1$ is the charge-transfer state. However, if we look at Fig. 5, which is state $I_0$ in $Cr(CO)_6$, we immediately see that there is large charge transfer in this state also. It is not a case of one analysis being right and the other wrong, but instead a problem of oversimplified descriptions of the states involved.

Table II shows the calculated values for the core-level binding energies in several carbonyls. The frozen-ion binding energies for $Cr(CO)_6$ and $Ni(CO)_4$ show very little shift compared to free CO. The numbers of set IV show that

$$\Delta E^F_{\mathrm{BE}}(i) = E^F_{\mathrm{BE}}(i)^{\mathrm{CO}} - E_{\mathrm{BE}}(i)^{\mathrm{carbonyl}} \tag{10}$$

is small compared to the shift in the main line ~3 eV. This number reflects true chemical shifts in the initial state. The last set of numbers (V) is the additional relaxation shift in the carbonyl compared to isolated CO. This additional relaxation due to the screening of the core hole by the metal electrons is small compared to the intramolecular screening in the CO molecule. It really is not even molecular screening, since the calculated relaxation energies for C and O atoms with a 1*s* hole are 13.7 and 19.3 eV,[42] respectively. This should be compared to 11.4 eV (14.7) for the C 1*s* ionization and 20.2 eV (23.9 eV) for the O 1*s* ionization, respectively, for CO [$Cr(CO)_6$]. Some caution has to be taken in this comparison, since the relaxation energy depends on the multiplicity of the atomic state.

## III. THEORETICAL APPROACHES

We will describe in this section the important considerations for calculating the energies and intensities of the peaks in a core-level spectrum. The conclusions can be summarized as follows.

(1) The binding energy of the main line can be calculated fairly accurately with a self-consistent single-particle scheme if the energy difference between the ion and neutral is calculated [Eq. (2)]. The only restriction on this statement is that for complexes containing several CO molecules the symmetry in the calculation must be reduced to localize the hole on one molecule.

(2) The initial-state shift between CO and coordinated CO is calculated to be small. Therefore the several-eV shift in binding energy when CO is coordinated is due to screening of the ionic state and must be accompanied by new or more intense shake-up peaks so that the sum rules are obeyed [Eqs. (6) and (8)].

(3) A many-body-type calculation is needed to accurately describe the multiplet splitting in the satellite structure resulting from two-hole–one-particle states.

(4) A quantitative calculation of the satellite intensities must include the continuum states.

There are two approaches used to calculate the energies and intensities of the peaks in a core-level spectrum. Obviously the most direct procedure is to calculate the energy differences between the ionic states and the neutral ground state [Eq. (2)] and the projections given in Eq. (6). Owing to the perversity of theorists this procedure has been labeled the "indirect method." The second procedure which is surely indirect is called the "direct method."[42] The so called direct method starts with the neutral states using perturbation theory to arrive at the ionic states. Both methods, in principle, should produce the same results, but the direct method will invoke many-body effects to explain experimental data that the indirect methods will claim are explainable in a single-particle picture. The reason is that the direct method starts with neutral wave functions and it takes several of these wave functions to describe an ionic state. Therefore in a Hartree-Fock-type calculation you end up doing a configurational interaction calculation,[43] that is, you must use a multideterminant wave function to represent the ionic state.

### A. Ionization energies

In Fig. 8 we have tried to illustrate the various levels of approximation of a numerical calculation of the ionization energies. The left-hand column is the energy of the closed-shell neutral $N$-particle system, the right-hand side is the open-shell $N-1$ ionic system, and the center column is the energy difference [Eq. (2)]. The first row shows the exact energies for the neutral $E_0^N$ and the ion $E_{(i)}^{N-1}$. By definition, the binding energy $E_{\mathrm{BE}}(i)$ is the difference between these two energies. The second row shows the result of using the Hartree-Fock (HF) approximation. The calculated neutral energy $E_{\mathrm{HF}}^N$ is not as low as the real energy $E_0^N$,

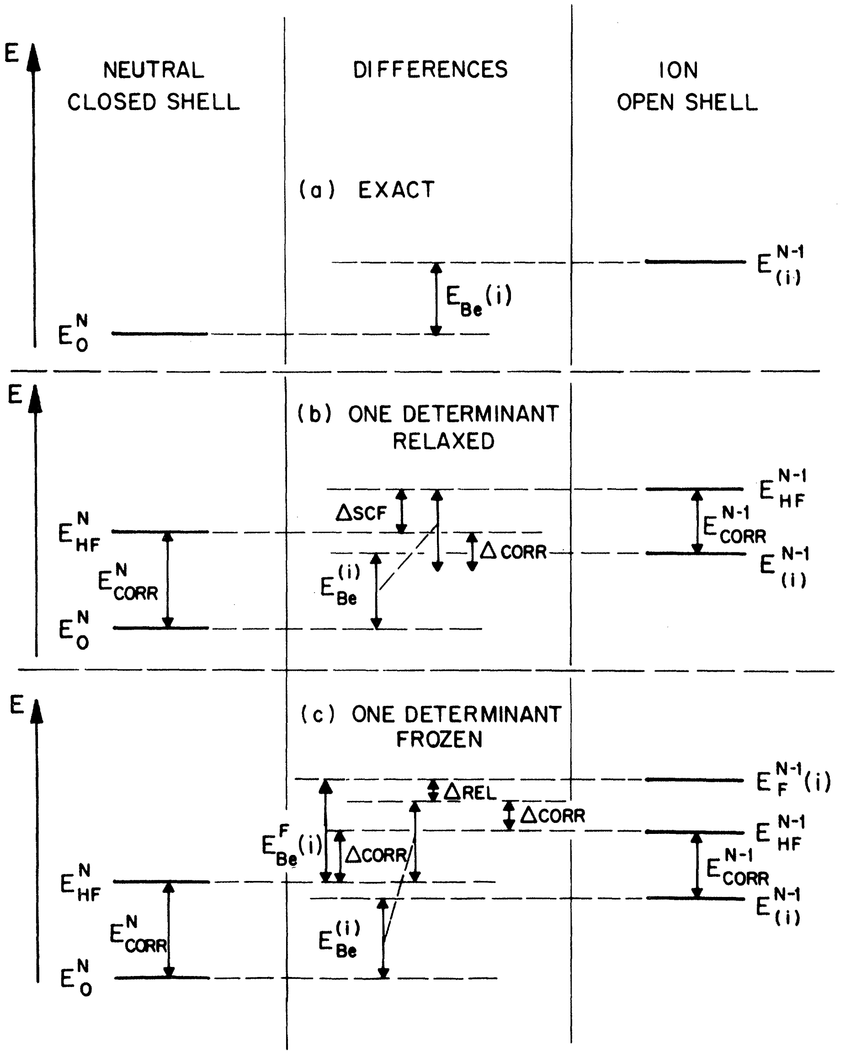

FIG. 8. Energy diagram to illustrate different approximations for the calculation of ionization energies. Explanation, see text.

there the difference is by definition the correlation energy ($E^N_{\rm corr}$). The same argument holds for the $i$th ionic state, where $E^{N-1}_{\rm corr}$ is the difference between the Hartree-Fock energy $E^{N-1}_{\rm HF}(i)$ and the real ionic energy $E^{N-1}_{(i)}$. The binding energy in this Hartree-Fock scheme is called the $E_{\Delta \rm SCF}$ (self-consistent field) energy and is defined as

$$E_{\Delta \rm SCF} = E^{N-1}_{\rm HF}(i) - E^{N}_{\rm HF} .$$

The error in the $E_{\Delta \rm SCF}$ value compared to the real binding energy is the difference in neutral and ionic correlations energies,

$$E_{\rm BE}(i) = E_{\Delta \rm SCF} + [E^N_{\rm corr}(i) - E^N_{\rm corr}] , \qquad (11a)$$

$$E_{\rm BE}(i) = E_{\Delta \rm SCF} - E_{\Delta \rm corr} . \qquad (11b)$$

The center column of Fig. 8 shows in (b) the relative energies for the binding energy ($E_{\Delta \rm SCF}$) calculated by Hartree-Fock compared to the actual binding energy. $E_{\Delta \rm corr}$ can have either sign so that $E_{\Delta \rm SCF}$ could be larger or smaller than the actual binding energy.

The local-density schemes like $X\alpha$ calculate an energy difference between the neutral and ion so the picture should be very similar to that shown in row (b) of Fig. 8. The difference is that the local-density approximation includes to some degree correlation effect. Therefore the difference between an HF $\Delta$SCF calculation and a $X\alpha$ transition-state calculation should reflect the effect of the local-density approximation for exchange and correlation. This assumes that both calculations are done without other approximations.

The final row is included to make contact with the so-called direct methods.[43] The starting point in these schemes is the Koopmans ionization potential, which is calculated as the energy difference between the frozen orbital ionic state $E^{N-1}_F(i)$ and the calculated neutral energy. This procedure is only used within the Hartree-Fock approximation because the energy difference is the HF orbital energy. Obviously $E^{N-1}_F(i) > E^{N-1}_{\rm HF} > E^{N-1}_{(i)}$, so $E^F_{\rm BE}(i) > E_{\Delta \rm SCF}$. The difference between this frozen orbital, Koopmans's ionization potential, and the real binding energy is referred to by the practitioners of the direct method as the relaxation energy, where $E_{\Delta \rm rel}$ is defined as

$$E_{\Delta \rm rel} = E^F_{\rm BE}(i) - E_{\rm BE}(i) .$$

$E_{\Delta \rm rel}$ is a positive number. Since almost all direct calculations are based upon an HF calculation, $E_{\Delta \rm rel}$ can be decomposed into two terms

$$E_{\Delta \rm rel} = E_{\Delta \rm reorg} + E_{\Delta \rm corr} , \qquad (12a)$$

where the reorganization energy

$$E_{\Delta \rm reorg} = E^F_{\rm BE}(i) - E_{\Delta \rm SCF} \qquad (12b)$$

and $E_{\Delta \rm corr}$ was described by Eq. (11). $E_{\Delta \rm reorg}$ is the energy you gain by doing a self-consistent HF calculation for the ionic state. $E_{\Delta \rm corr}$ is the energy you can never calculate using an HF scheme. We will show by comparison with experimental data that $E_{\Delta \rm corr}$ is small compared to $E_{\rm BE}(i)$ or $E_{\Delta \rm reorg}$ for CO or coordinated CO.

The energies shown in Fig. 8 seem to connect the direct and indirect schemes by defining the term $E_{\Delta \rm rel}$, which is calculated by perturbation theory. For example, $E_{\Delta \rm corr}$ could be determined by comparing a direct and indirect calculation starting from an HF orbital energy calculation. An HF $\Delta$SCF (indirect) calculation [row (b) of Fig. 8] would give the value of $E_{\Delta \rm reorg}$ using Eq. (12b). A direct calculation including many-body effects should produce $E_{\Delta \rm rel}$ of Eq. (12a) (Refs. 6 and 43) and consequently $E_{\Delta \rm corr}$. In practice this procedure is not well defined. The definition $E_{\Delta \rm corr}$ shown in Fig. 8(b) and given by Eq. (11) is not unique. The reason is that there is no rigorous definition of the one-electron Hartree-Fock solution for an open-shell system.[44] Depending upon how you choose the wave functions, the correlation energy can vary considerably. This leads to variations in $E_{\Delta \rm corr}$. In other words, by choosing a certain procedure to calculate the open-shell HF energy, the amount of implicity included in correlation energy is not defined.

The problem alluded to in the previous paragraph can be easily illustrated by considering the ionization from the O $1s$ level of $\rm Cr(CO)_6$. A straightforward HF molecular-orbital calculation of the ionic state will place $\frac{1}{6}$th of a hole on each oxygen atom so that the proper $O_h$ symmetry is maintained. Bagus and Schaeffer[45] showed for $\rm O_2^+$ that the energy $E^{N-1}_{\rm HF}$ was significantly lowered when the symmetry was reduced to localize the hole. Baerends and Ros[7(a)] reduced the symmetry in a $\rm Cr(CO)_6$ calculation from $O_h$ to $C_{4v}$ resulting in an energy $E^{N-1}(i)$ several volts lower, even for near valence levels. Figure 5 showed the charge-density difference for C $1s$ ionization when the symmetry is reduced. A problem of definition is clearly present. If on one hand you compare a $\Delta$SCF calculation with $O_h$ symmetry to a many-body calculation you will find a large $\Delta$corr energy, resulting primarily from the hole localization in the ion. On the other hand, if you compare a $\Delta$SCF calculation of $\rm Cr(CO)_6$ with $C_{4v}$ symmetry to a many-body calculation you will find a small $E_{\Delta \rm corr}$ because the hole has been artificially localized in the HF calculation.

If you want to achieve agreement with experimental data with a $\Delta$SCF-type calculation you must localize the hole state, especially for core ionization. Obviously the ionic wave function should have the correct symmetry[46] so that in the case of $Cr(CO)_6$ a linear combination of six symmetry-unrestricted determinants describing holes on each oxygen atom should be used for the total wave function.[7(a)] The total energy of the ion should be lower with this linear combination of symmetry-unrestricted determinants than it was for a single restricted determinant. It is easy to see what is happening. The symmetry-unrestricted single determinant and the properly symmetrized combination of symmetry-unrestricted determinants are the first steps to doing a configuration interaction calculation. The specific configurations have been chosen because we know that the hole should be localized. Therefore the definition of $E_{\Delta\,\mathrm{corr}}$ depends upon how much correlation we build into our ionic wave function.

Lozes *et al.*[47] pointed out recently that the energy stabilization of the broken symmetry solution using one determinant with respect to a symmetry-restricted solution occurs at a critical distance between two atoms. These authors calculated an even stronger energy stabilization by using a many-determinant symmetry-restricted wave function. This is another example demonstrating that a special one-determinant treatment does include part of the many-particle problem, but you do not know how much correlation has been included. Therefore, the partition into $E_{\Delta\,\mathrm{reorg}}$ and $E_{\Delta\,\mathrm{corr}}$ in Eq. (12a) is somewhat artificial. It is still a useful concept for analyzing the numerical data on free and coordinated CO shown in Tables I and II. These energies only concern the main ionization peak.

The Hartree-Fock eigenvalues for CO in Table I, as well as the frozen-orbital binding energy calculated within the $X\alpha$ scheme, lead to ionization energies of the correct order of magnitude compared to experiment. The HF $\Delta$SCF calculation brings the calculated binding energies for the main ionization line within 0.05 and 2 eV of the O 1*s* and C 1*s* binding energies, respectively. This indicates that $E_{\Delta\,\mathrm{corr}}$ plays only a minor role. This conclusion is supported by the analysis of Pickup and Goscinski[27] in the framework of the direct calculational scheme. They showed using an order-by-order analysis of the relaxation energy that for a core ionization the dominant contribution was $E_{\Delta\,\mathrm{reorg}}$. Table I shows that the $X\alpha$ SW (scattered-wave) results are on an absolute scale off by 8–13 eV. The relaxation energies, however, agree within 1–2 eV with those calculated from HF $\Delta$SCF. The error in $X\alpha$ is probably due to both the muffin-tin potential (touching and overlapping spheres) and the choice of $\alpha$ which is used in these calculations.[25,26] The absolute magnitude of the relaxation energies for the core ionizations in the CO molecule are nearly the same as those calculated for the free atoms, namely, 13.7 eV for C 1*s* and 19.3 eV for O 1*s*.[42]

Table II shows the orbital energies for two carbonyls compared with a calculation on CO within the same basis set. The difference in orbital energies $\Delta E^F_{\mathrm{BE}}(i)$, as pointed out before, is rather small. The quoted $\Delta$SCF energies are not in as good an agreement with experiment as those on free CO. This is not due to a large correlation effect, but to variational instabilities in the Hartree-Fock calculation.[38] The values therefore cannot be compared with those of free CO. The only set of data where the $\Delta E^F_{\mathrm{BE}}(i)$ can be compared with those for the relaxed ion is that reported by Baerends and Ros.[8(a)] These results show that the difference in binding energy for carbonyls with respect to CO is not an initial- but a final-state effect, due to relaxation. Since the classical chemical-shift interpretation is related to properties of the neutral ground state it is not meaningful to use binding-energy differences directly from the spectrum as indicating a chemical shift.[7(a)] It is logical to use Eq. (10) as the definition of chemical shift. Quite similar results are found in model calculations on surface systems using clusters of a few metal atoms. For a $Ni_5CO$ cluster Ellis *et al.*[8(c)] calculated a relaxation energy difference with respect to CO of 3.7 eV (O 1*s*) and 5.0 eV (C 1*s*), respectively, using a discrete variational $X\alpha$ method. These shifts are in fairly good agreement with experimental shifts measured by Norton *et al.*[11(c)] for CO on Ni.

So far we have seen that the $\Delta$SCF calculations done in any calculational scheme discussed here provide us with the information on the main line with an acceptable accuracy, if the core hole is localized. From this we concluded that $E_{\Delta\,\mathrm{corr}}$ does not play an important role in the determination of the binding energy of the main line. There are cases, however, for which this is not true, namely:

(a) valence electron ionizations in general, and
(b) the shake-up satellites in core ionizations.

(a) will be discussed in Sec. IV and we concentrate here on the shake-up satellites (b).

The fact that configuration interaction (CI) is of importance can be seen by considering a $1\pi$-to-$2\pi$ excitation in neutral free CO. The $1\pi$ is filled with four electrons. A single excitation into the $2\pi$ orbital creates three symmetry states, namely, the two unpaired spins lead to three singlet and three triplet states. Without CI the splitting between these states vanishes, showing that the neglect of CI produces qualitatively incorrect results, i.e., the wrong number of states. McKoy *et al.*[32] and Rauk and Barriel[48] have shown that these states are split by configuration interaction over an energy range of about 7 eV. The $^3\Sigma^+$ is the lowest and $^1\Sigma^+$ the state of highest excitation energy. Correlation effects are large in the neutral system, so they will surely be of similar magnitude in the ion. The creation of a C 1*s* core hole leads to a primary hole state of $\Sigma^+$ symmetry. This state only couples to the two $\Sigma^+$ states originating from the $1\pi \rightarrow 2\pi$ excitation. By the creation of a core hole the $1\pi$ and the $2\pi$ orbitals are stabilized by approximately the same amount, leading to a similar excitation energy in the ion compared to the neutral. The experimental results in Fig. 1 show that the energy splitting observed in the ion is similar to the extended molecule and does not change dramatically upon coordination. This example shows that configuration interaction dominates the excitation energies. Large-scale CI calculations on the basis of the Hartree-Fock orbital give a successful description of the satellites.[31] "Directly" calculated shake-up energies are generally in good agreement with experiment.[49, 50] It is, of course, in principle, possible to get the same information from an $X\alpha$ scheme, but so far an effective scheme to include configuration interaction has not been developed. The main problem is to find an efficient way to carry out the integral evaluation. A development in this direction will certainly have a major impact on the theoretical assignment of shake-up spectra.

### B. Intensities

The discussion on shake-up intensities presented here is based on the sudden approximation. In other words, the problem is reduced to the calculation of the projection

$$P_{ijk} \propto |\langle \Psi_{ijk}^{\text{ion}} | \Psi_k^R \rangle|^2 .$$

While $\Psi_{ijk}^{\text{ion}}$ is a true, completely correlated state of the ion, $\Psi_k^R$ is a hypothetical state of the neutral system where an electron has been annihilated, i.e., the correlation of at least one electron is left out. The continuum for both states must be included in order to calculate the intensities correctly. In terms of the normalized total intensity [Eq. (8)], the shake-up transitions into the continuum carry about 15% of the total intensity.[18] If $|\Psi_{ijk}^{\text{ion}}\rangle$ and $|\Psi_k^R\rangle$ have been calculated without taking the continuum into account, which is usually the case for Hartree-Fock calculations, the intensities are not accurate. The error on the relative intensities should, however, not be too large. All calculations reported so far give relative intensities with respect to the main line. A shake-up intensity is large if the ion-state wave function contains a large contribution of the hypothetical $(N-1)$ state $|\Psi_k^R\rangle$ (i.e., the Koopmans state). In general, the projection has to be carried out with the inclusion of the spin of the two open-shell states. Usually this problem is reduced to the projection of the spatial parts of the wave functions. It is interesting, however, to ask whether we expect an intensity difference for two states originating from the same spatial part with only different spin parts. Let us assume for this purpose that the spatial part of the state can be described in a configuration-interaction picture by the superposition of two determinants, namely, the ground state of the ion calculated in a Hartree-Fock procedure $|\phi_{\text{HF}}^{N-1}\rangle$ and one singly excited determinant.

$$|\Psi_{ijk}^{\text{ion}}\rangle = d_0 |\phi_{\text{HF}}^{N-1}\rangle + d_{ij} a_i^\dagger a_j |\phi_{\text{HF}}^{N-1}\rangle .$$

The ground state involves only one unpaired spin, while the excited states involve three spins. The two final doublet states resulting from the three unpaired spins lead to different intensities, namely (the transition to the quartet state is spin forbidden):

$$P_{ijk}^1 \propto |d_0 \langle \phi_{\text{HF}}^{N-1} | \Psi_k^R \rangle + \sqrt{2}\, d_{ij} \langle a_j^\dagger a_i \phi_{\text{HF}}^{N-1} | \Psi_k^R \rangle|^2 \tag{13a}$$

and

$$P_{ijk}^2 \propto |d_0 \langle \phi_{\text{HF}}^{N-1} | \Psi_k^R \rangle|^2 . \tag{13b}$$

A closer inspection shows that (13a) belongs to the singlet-coupled doublet state, while (13b) is connected with the triplet-coupled doublet state. Since $d_0$ is usually small in a configuration expansion, the triplet-coupled shake-up peak has smaller intensity than the singlet-coupled one. Referring to Fig. 1, the shake-up peaks assigned to the two final states of the $1\pi \rightarrow 2\pi$ excitation in free CO show this behavior. For C 1*s* and O 1*s* ionization the peak at lower excitation energy has smaller intensity than the one at larger excitation energy. The different intensity ratios for these peaks for C 1*s* and O 1*s* ionization are due to the different weight of the orbital wave functions on the carbon and oxygen atoms. Since these excitations remain basically localized on the CO molecule, even if the molecule is coordinated to a metal atom and the spin is the determining factor, the intensity ratios should remain similar. This result is consistent with the assignment given in Fig. 1.

Most calculations agree on this assignment.[31, 39] In particular, the intensity calculated for the charge-transfer satellites is larger than for the local $1\pi \rightarrow 2\pi$ excited states. Loubriel,[30] however, reports on $X\alpha$ calculations for satellite intensities in $Ni(CO)_4$. He calculates very intense local $1\pi \rightarrow 2\pi$ excitations and nearly vanishing intensity for the charge-transfer satellites. Since the $X\alpha$ calculation did not include configuration interaction, the intensity of the two final $1\pi \rightarrow 2\pi$ doublet states are superposed. Inclusion of these effects must lead to a substantial reduction of the intensity of each single peak. The relative intensities of the local excitations to the charge-transfer excitations would still come out too large compared to other calculations. It is not clear yet what the reason is for this discrepancy, but one might suspect that the muffin-tin potentials used in this calculation lead to this result.

So far, we have been rather unspecific as far as the comparison of a finite (molecular) and an infinite (adsorbate) CO-coordinated system is concerned. The evolution of the band structure might have important consequences on the shape of the core-electron spectrum. One might expect, for example, that the shake-up associated with the electron transfer between the metal and the molecule is spread out over the energy region of initial metal states, which is essentially determined by the bandwidth of the substrate. This would lead to a broad low-intensity satellite band quite different than that seen in the carbonyl spectra. Experimentally, the similarity of spectral features in $W(CO)_6$ and W(CO)/CO and other systems does not substantiate this hypothesis. These results show that, as far as the spectroscopic properties of CO-coordinated systems are concerned, the adsorbate may be describable in a localized picture including only the adsorbed molecule and a few metal atoms. This implies that a metal cluster can be used to simulate the substrate in theoretical studies. These finite cluster systems have been investigated by Messmer *et al.*[26] and Baerends *et al.*[8]

From the previous discussion we know that the excitations between the bonding and antibonding metal-$2\pi$ combinations formed in the ion upon creation of a core hole determines the strong satellite. The Ellis *et al.*[8(c)] calculation on an $Ni_5CO$ cluster shows that there are basically only a few metal levels that couple to the $2\pi$ orbital. This indicates that we retain a rather discrete description even as the number of metal atoms increases. Messmer *et al.*[26] show similar results for a $Cu_5CO$ cluster calculation. On the other hand, there are calculations by Gunnarsson and Schonhammer[35] on the same system (Cu/CO) using a model Hamiltonian description. The theoretical technique used in this study cannot be easily compared with the above-mentioned methods since those quantities, which are explicitly calculated by the cluster methods are treated as adjustable parameters in the Gunnarsson and Schonhammer calculation.[35] The latter authors come to a conclusion at variance with Messmer *et al.*[26] that the observed shape of the core-hole spectrum is determined by the band structure of the substrate. Especially, the peak at about 7-eV excitation energy is interpreted as being due to tunneling of an *s* or *p* electron close to the bottom of the band into a $2\pi$ orbital. Messmer *et al.*, however, find that the peak is due to the excitation of a $1\pi$ CO electron to the metal-$2\pi$ bonding combination, which is only partially occupied in the case of a cluster. It has, therefore, the character of being a mixture of a local $1\pi \rightarrow 2\pi$ excitation and a charge-transfer excitation. This latter interpretation of the spectra is in conceptual agreement with the general picture of satellite structure in CO-coordinated systems presented in this study. We, therefore, conclude that although band-structure effects are certainly present in CO-adsorbates, the spectral features are dominated by the local properties of the impurity states induced through the presence of the adsorbed molecule.

## IV. VALENCE PHOTOIONIZATION

In comparison to the core ionizations the energetic situation becomes more complicated for the valence ionizations, since there are several hole states in the same energy region. Figure 9 shows a similar scheme as in Fig. 2. (000) represents the $N$-electron ground state; (004) represents the ground state of the ion. (544) is a two-hole–one-electron state already discussed in connection with Fig. 2. (003) schematically shows the first excited hole state relative to (004). Now consider the same electron being excited that led to (544). This leads to a state characterized by either (543) or (534) because it is a two-hole–one-electron state with respect to the (004) as well as to (003). In other words, it will no longer be possible, in general, to assign a shake up to one hole state. To each hole state belongs a whole series of par-

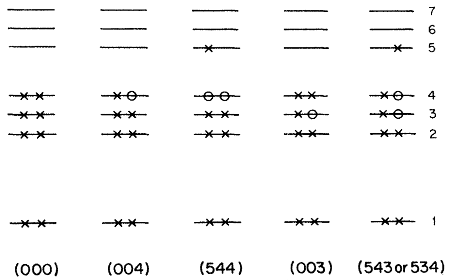

FIG. 9. Schematic orbital diagrams to illustrate the occurrence of shake-up satellites in valence photoionization.

ticle-hole excited configurations, part of which belongs to other hole states as well. In other words, there is a much larger number of excited ion states which may be coupled by configuration interaction. This leads to satellite structure in the valence region, shown in Fig. 10, for the highest occupied orbitals in free CO and carbonyls. It is no longer possible by inspection to easily identify a main line and the accompanying shake-up peaks. Using Hartree-Fock calculations or $X\alpha$ calculations it is possible, however, to identify the main ionizations. It turns out that even for the valence ionizations, hole localization seems to be important in order to accurately describe the ionization energies, especially those which are spatially localized in the molecule.[7(a)] The results published so far, however, must be regarded as preliminary. As mentioned above, the reason why calculations of energies of valence ionization are not as clear as for core ionization is that configuration interaction plays a much more important role.[51,52] Pickup and Goscinski demonstrated that for valence ionizations a much stronger correlation influence is expected, in contrast to the core ionizations where correlation only plays a minor role.[27]

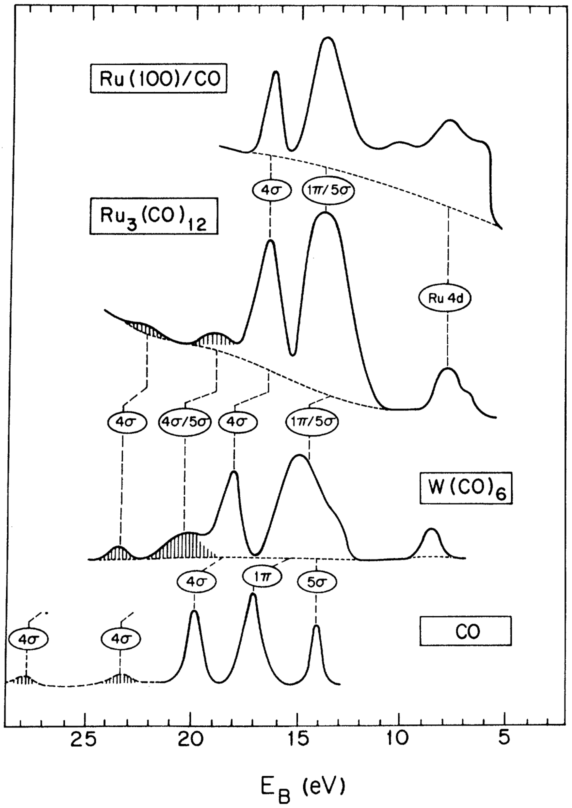

FIG. 10. Ultraviolet photoemission spectra (He II) of free and coordinated CO. CO (gas) (Ref. 5), W(CO)$_6$ (condensed, the ionization potential of peak at lowest energy is aligned with the He I gas-phase spectrum [Ref. 4(b)]), Ru$_3$(CO)$_{12}$ (condensed) [Ref. 4(a)], and Ru(100)/CO (Ref. 17).

Recently, a first attempt has been made to apply a direct calculational scheme to the study of satellites in the valence ionization region of CO coordinated to a metal atom.[40] These investigations provide a simple interpretation of the valence orbital region. The lowest lying excited states in any system usually originate from transitions between the highest occupied and lowest unoccupied orbitals. In the case of free CO, the three lowest ionization energies, due to the 5σ, 1π, and 4σ orbitals are smaller than this energy. Therefore, these ionizations are not expected to show extensive shake-up structure. The 3σ ionization, on the other hand, is larger than the smallest ionization energy and is situated therefore in the region of excited ion states. This explains why the 3σ emission is very broad and exhibits shake-up structure at the lower binding energy side of the main line. Coordination to a single metal atom will decrease the energy of the low-lying excited states. The low-lying states are charge-transfer excitations and metal excitations. This produces a situation where the 5σ, 1π, and 4σ ionizations also fall in a region of excited states, like the 3σ ionization in the case of free CO. It is likely to observe pronounced shake-up structure in this energy region. The magnitude of these effects depends, of course, on the coupling between the excited configuration and the primary ionization. As an example, we show in Fig. 11(a) the case of Ni(CO)$_4$ according to Koopmans's theorem in the frozen-orbital approximation and in Fig. 11(b) after coupling to the excited ion states. The shake-up peaks are due to coupling to charge transfer and local ligand excitations. As an example, let us look at the charge-transfer excitations coupled to the 4σ and 5σ ionization. A given excitation in the ion of proper symmetry from a metal to a ligand level can couple to both a 4σ and a 5σ hole. Since the energy difference between 5σ and 4σ hole states is smaller upon coordination than in the free molecule the charge-transfer excitations can couple rather effectively. Therefore, the shake-up peaks, which are mainly attributable to either a 4σ or 5σ hole state, always carry a strong weight of the complementary component. The situation, as far as the intensity is concerned, is similar to the core ionizations. The charge-transfer excitations lead to rather intense lines, while the local excitations induce low intense satellites. It is clear that by the coupling to the excited states the frozen-orbital energies are changed, which is equivalent to the relaxation

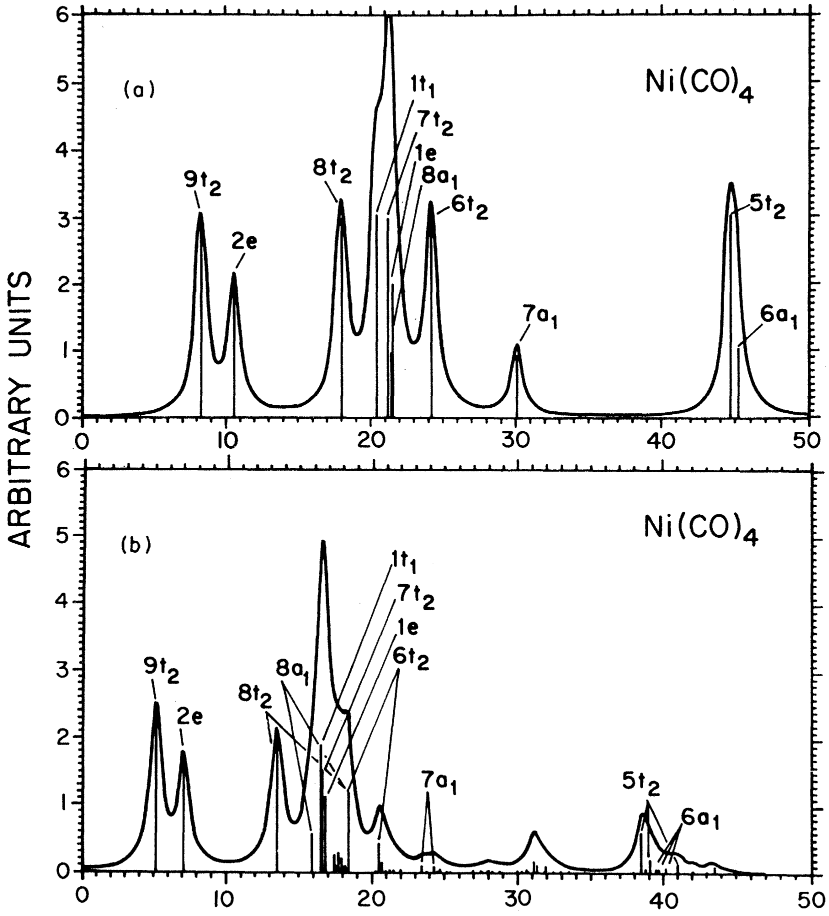

FIG. 11. Lorentzian convoluted eigenvalue spectrum of Ni$(CO)_4$ for the valence region. The intensities are taken proportional to the degeneracy of the orbital. (a) One-electron description (Ref. 6); (b) after inclusion of many-body effects [Ref. 40(b)].

in our discussion of the core holes. Unfortunately, the experimental information is limited. In the case of Cr$(CO)_6$ this is not the case. Therefore, we show, as a second example in Fig. 12, a comparison between the experimental valence spectrum excited with Mg$K\alpha$ radiation[4] and a Lorentzian convoluted calculated spectrum using a direct method. The experimental differential cross sections[53] have been introduced in the calculation to correct for the energy dependence of the one-particle cross section in Eq. (5). The Cr $2p$ states were not included in the calculation. The observed satellite structure results mainly from the $4\sigma$ and $5\sigma$ ionizations. Very-low-intensity satellite structure accompanying the $5\sigma$ and $1\pi$ ionizations are calculated in the region of the high-intensity $4\sigma$ peak. On the basis of these calculations we assign the satellites indicated in Fig. 12 for the carbonyls to the $4\sigma$ and $5\sigma$ ionizations.

Now let us qualitatively consider an adsorbate. One of the most obvious differences between a carbonyl compound and an adsorbate is the increase in the number of metal atoms relative to the number of CO molecules. This implies that the number of excited ion states increases over the energy region of the evolving band structure. The density of excited ion states is broadened. This leads to a distribution of intensities over a broad manifold of excited states. Depending on the system, we expect to observe spectra ranging from the limiting case of single sharp lines to the case of a smear of satellite lines. Recent experiments on the valence spectra of CO and $N_2$ on different substrates seem to indicate this kind of behavior.[54]

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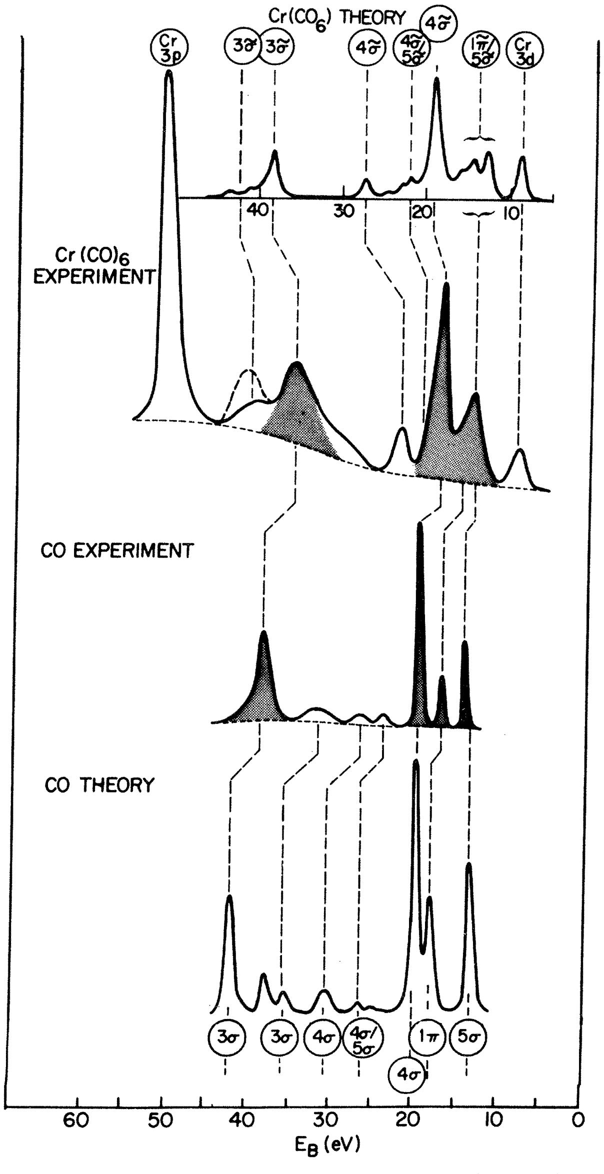

FIG. 12. Comparison of experimentally [Refs. 4 and 10(d)] measured and calculated (Refs. 37 and 65) ionization spectra in the valence region. In the Cr(CO)$_6$ spectrum the part of the peak at 43 eV, which is due to the excitation of the Cr $3p$ electrons by the satellite in the unmonochromatized Mg $K\alpha$ radiation has been taken out (broken line).

## APPENDIX

If the ionization occurs from a closed-shell system in a totally symmetric singlet ground state, the final states have doublet multiplicity by spin selection rules in the dipole approximation. (Consider Fig. 2.) The primary core-hole state (01) can be represented by $|(01)\alpha, (01)\beta\rangle$ including spin. Figure 13 shows one component schematically. If in addition to the core hole an electron is excited in the valence shell, three unpaired spins are created. From three spins $2^3 = 8$ spin determinants may be formed:

$$\begin{aligned}&|\alpha\alpha\alpha\rangle,\\ &|\alpha\alpha\beta\rangle,\ \ |\alpha\beta\alpha\rangle,\ \ |\beta\alpha\alpha\rangle,\\ &|\beta\beta\alpha\rangle,\ \ |\beta\alpha\beta\rangle,\ \ |\alpha\beta\beta\rangle,\\ &|\beta\beta\beta\rangle.\end{aligned} \tag{A1}$$

These determinants are eigenfunctions to one component of the spin operator $(S_z)$. Figure 13 shows a representation for two spin determinants (A1). The spins involved in the excitation are coupled like a singlet and a triplet excitation and can therefore be related to the excitations in the neutral system. These functions are, however, not eigenfunctions of $S$. Linear combinations have to be formed. Under the restriction of orthonormality a possible representation takes the following form. For $S_z = \frac{3}{2}$, quartet:

$$\begin{aligned}&|\alpha\alpha\alpha\rangle,\\ &\frac{1}{\sqrt{3}}\left(|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle\right),\\ &\frac{1}{\sqrt{3}}\left(|\beta\beta\alpha\rangle + |\beta\alpha\beta\rangle + |\beta\beta\alpha\rangle\right),\\ &|\beta\beta\beta\rangle,\end{aligned}$$

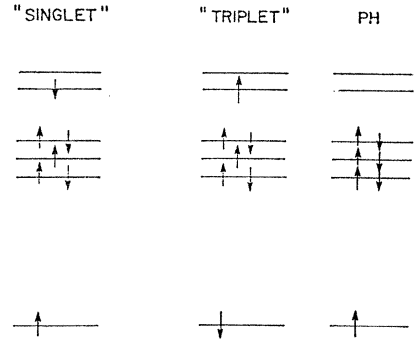

FIG. 13. Schematic representation of spin-configuration leading to singlet and triplet-coupled doublet states.

For $S_z = \frac{1}{2}$, doublet I:

$$\frac{1}{\sqrt{2}}\left(|\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle\right), \qquad \frac{1}{\sqrt{2}}\left(|\beta\alpha\beta\rangle - |\beta\beta\alpha\rangle\right). \tag{A2}$$

For $S_z = \frac{1}{2}$, doublet II:

$$\frac{1}{\sqrt{6}}\left(2|\beta\alpha\alpha\rangle - |\alpha\beta\alpha\rangle - |\alpha\alpha\beta\rangle\right), \qquad \frac{1}{\sqrt{6}}\left(2|\alpha\beta\beta\rangle - |\beta\alpha\beta\rangle - |\beta\beta\alpha\rangle\right).$$

This representation has the advantage of showing the correspondence to the spin states in the neutral molecule (Fig. 13). The three spins are not equivalent in the sense that one of them is associated with a core electron and the other two with valence electrons. Doublet I corresponds to the singlet scheme in Fig. 13; doublet II corresponds to the triplet scheme. The latter statement can be easily verified by evaluating the weight of the determinants in the linear combination. The determinant belonging to the triplet scheme accounts for 50% of the spin density, while the other determinants contribute only 25% each.

If we now evaluate the projection according to Eq. (13) using the configuration ansatz equation (14) we get Eq. (15), namely,

$$P_{ij}^1 \propto \left|d_0\langle\phi_{\mathrm{HF}}^{N-1}|\Psi_j^R\rangle + \sqrt{2}\,d_{ij}\,\langle a_j^\dagger a_i\,\phi_{\mathrm{HF}}^{N-1}|\Psi_j^R\rangle\right|^2, \qquad P_{ij}^2 \propto \left|d_0\langle\phi_{\mathrm{HF}}^{N-1}|\Psi_j^R\rangle\right|^2. \tag{A3}$$

Usually the projection of the ground state on the excited states is small in a configuration expansion, i.e., $d_0 \ll 1$. If we, furthermore, assume that $\langle\phi_{\mathrm{HF}}^{N-1}|\Psi_i^R\rangle \simeq 1$, we obtain

$$P_{ij}^1 \propto 2\,d_{ij}^2\left|\langle a_j^\dagger a_i\phi_{\mathrm{HF}}^{N-1}|\Psi_j^R\rangle\right|^2 \qquad P_{ij}^2 \propto d_0^2. \tag{A4}$$

This result indicates that the intensity of the triplet-deduced satellite is smaller than the singlet-deduced satellite. If we, furthermore, set

$$\langle a_j^\dagger a_i\phi_{\mathrm{HF}}^{N-1}|\Psi_j^R\rangle \simeq \langle X_j|\xi_i\rangle,$$

where $X_j$ is the $j$th unoccupied orbital in the ion and $\xi_i$ is the $i$th occupied orbital in the neutral system, we obtain

$$P_{ij}^1 \propto 2d_{ij}^2\left|\langle X_j|\xi_i\rangle\right|^2, \qquad P_{ij}^2 \propto d_0^2,$$

which is the result of Darko *et al.*[31]

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