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Origin of satellite structure in the valence x-ray photoelectron spectrum of CO: A theoretical study

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The satellite structure in the valence shell x-ray photoelectron spectrum (XPS) of CO is studied. The configuration interaction method is used to construct correlated many-electron wave functions for the different final states of CO^+. It is found that (1) the conventional shake-up model cannot explain the satellite structure; (2) a considerable amount of intensity is lost from the main, "single-hole," ${}^2\Sigma^+$ states ($3\sigma^{-1}$, $4\sigma^{-1}$, and $5\sigma^{-1}$) due to electron correlation; and (3) the $3\sigma^{-1}$ peak satellites are at lower, rather than higher, binding energy than the main peak. Franck-Condon broadening is estimated and shown to be a major cause of the large width of the observed structures on the high-binding-energy side of the $4\sigma^{-1}$ peak. Our conclusions are supported by the results of other electron spectroscopies in addition to XPS.

I. INTRODUCTION

Various electron spectroscopies have been used to study the nature of the valence exited states of the ions of simple gas phase molecules. For these spectroscopies, the valence region exited states are defined as those within roughly 50 eV of the ground state of the ion. For the CO molecule, the subject of this paper, photoemission spectra using several photon energies have been reported. These include (i) ultraviolet photoemission (UPS) using He II (40.86 eV) radiation[1,2]; (ii) x-ray photoemission (XPS) using Al $K\alpha$ (1487 eV) radiation[3]; and (iii) $YM\zeta$ (132 eV) radiation.[4] Inelastic electron scattering measurements which involve the coincidence counting of the scattered and ejected electron, $(e,2e)$, have also been reported.[5,6] In the work of Hamnet *et al.*,[5] inelastic forward-scattered electrons are observed and variable photon energy photoemission is simulated. In the work of Dey *et al.*,[6] the cross section as a function of momentum transfer to the ejected electron is measured. This measurement is unique in that it permits identification of the symmetries of the molecular orbitals (MO's) involved in the ionization process.

The MO configuration of the $X\,{}^1\Sigma^+$ ground state of CO is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$. The 3σ, 4σ, 5σ, and 1π orbitals are the molecular valence levels consisting of appropriate combinations of atomic C and O $2s$ and $2p$ characters.[7] For both photoemission and $(e,2e)$, the transition from the $X\,{}^1\Sigma^+$ state to the various states of the CO^+ ion and an ejected electron is determined by a one-electron operator. In a one-electron theory of the ionization process only four states of the CO^+ ion (each one corresponding to the removal of a valence shell electron) could be observed. These states, and their spectroscopic notations, are

$$\begin{aligned}
&\text{(a)}\quad X\,{}^2\Sigma^+(5\sigma^{-1})\quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^4\,,\\
&\text{(b)}\quad A\,{}^2\Pi(1\pi^{-1})\quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3\,,\\
&\text{(c)}\quad B\,{}^2\Sigma^+(4\sigma^{-1})\quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4\,,\\
&\text{(d)}\qquad\qquad (3\sigma^{-1})\quad 1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 5\sigma^2 1\pi^4\,.
\end{aligned}\tag{1}$$

All of the experimental results referenced above[1-6] report additional structure and are much more complex than Eq. (1) would suggest. It is the purpose of this paper to provide a theoretical analysis of the origin and nature of this structure.

Clearly, structure beyond that given in Eq. (1) must be due to many-electron effects. Two different mechanisms may be responsible for the additional structure. The first is commonly called shake-up and involves the response of the passive (unionized) electrons to the sudden change of potential upon ionization.[8,9] In this process the ionized electron is suddenly removed from a molecular orbital, leaving all other electrons undisturbed. The wave function for this state may be denoted by $\Psi^{(-\alpha)}(1,\ldots,N-1)$, where the electron is removed from the αth-MO. This wave function may be expanded into eigenstates $\Phi_k(1,\ldots,N-1)$ of the $N-1$ electron Hamiltonian.

$$\begin{aligned}
\Psi^{(-\alpha)} &= \sum_k C_k \Phi_k\,,\\
C_k &= \langle \Psi^{(-\alpha)} | \Phi_k \rangle\,.
\end{aligned}\tag{2}$$

The relative probability that an ejected electron corresponding to the state Φ_k will be observed is, in this approximation, simply C_k^2. The MO's of the $N-1$ electron wave functions Φ_k respond to the presence of the hole in the αth MO, ϕ_α, by "relaxing" and changing their distribution from that in the initial state Ψ. It is this relaxation that leads to nonzero values for C_k when Φ_k involves other than one-electron ionization from

ϕ_α.

In general, the shake-up process is viewed as photoionization plus excitation of a second electron from an occupied to an unoccupied orbital. In CO, such a statellite might correspond to the state $1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^2 5\sigma 6\sigma 1\pi^4$, where the electron from the 3σ shell is ionized and one of the 5σ electrons is excited to the 6σ shell. From this picture the photoelectrons corresponding to the shake-up satellites will have lower kinetic energy, higher apparent binding energy, than the main line.

It is normally assumed that the states in Eq. (2) can be well represented by one-configuration Hartree-Fock (HF) wave functions. This assumption is important in order to distinguish orbital relaxation from other many-electron effects. We know from the results of atomic calculations that the shake-up model of Eq. (2) gives correct total probabilities for multielectron transitions if the ionization takes place in the inner shell of the atom.[10] However, when the ionization occurs from an outer shell of the atom, the probabilities are underestimated with HF wave functions.[10]

The second mechanism involves electron correlation and arises from the fact that, because of the electron-electron repulsion, the many-electron wave function cannot be represented as a single Slater determinant. Many mathematical approaches, Green's function,[11,12] many-body perturbation theory,[13] and configuration interaction[14-17] (CI) have been applied to this problem. When there are nearly degenerate configurations (the differences of diagonal matrix elements $H_{ii} - H_{jj}$ is comparable in magnitude to the interaction matrix element H_{ij}), the CI model provides an extremely convenient physical picture for the origin of these satellites. This is exactly the case where one would expect to find satellites with large intensities. In this paper we shall, in fact, consider CI wave functions for the final ionic states of CO. Our results show that the dominant mechanism for the origin of the observed complex structure is due to electron correlation.

An additional effect, important in the interpretation of the CO spectra, is the vibrational broadening of the electronic transitions. The observed transitions are between states with both electronic and nuclear quantum numbers. When the minimum in the potential curve of an ionic state is significantly shifted from that of the ground state, Franck-Condon factors will allow transitions to final states with many vibrational excitations. We shall show that this Franck-Condon effect is particularly significant for the $3\sigma^{-1}$ state and its satellites leading to large estimated broadenings.

In a report of the $(e, 2e)$ spectra,[6] a preliminary description of our results has been given. In this paper we present a more detailed account of both the computational model and the results obtained. Further, we concern ourselves in particular with the analysis of the high-resulution XPS spectra[3] of CO. Because of the difficulties involved in estimating photoionization cross sections,[18,19] we are not able to provide even a semiquantitative analysis of the UPS spectra. Some comments on the *YMζ* results will be made.

Section II contains the description of our model for the many-electron wave functions. In Sec. III we will discuss the approximations involved in the estimation of relative photoionization cross sections. The technical details of our calculation are given in Sec. IV. The results will be reported and discussed in Secs. V and VI. Section VII contains our concluding remarks.

II. MODEL FOR THE WAVE FUNCTION

From the complexity of the different experimental results of valence ionized states in CO,[1-6] it is clear that a one-electron model is insufficient to describe the ionization process. Many-body effects should therefore be included in the wave functions for both the initial and final states. A quantitatively correct treatment of the excited states observed in the photoemission and $(e, 2e)$ experiments is difficult. We have chosen instead to perform a model calculation which would elucidate the many-body mechanisms which lead to the surprisingly high-intensity satellite structure. As we shall show in later sections, this model gives, in fact, a reasonably good description of the observed structure. Its major defect appears to be in the determination of the energies of the photoelectrons. Both the satellites and the main peaks are shifted towards higher apparent binding energies with respect to the $5\sigma^{-1}$ peak.

For simplification of the analysis, we have chosen to neglect correlation effects in the initial state and use the Hartree-Fock wave function for this state. An advantage of this approach is that it enables us to make approximations in the calculation of the intensities observed in the XPS Al$K\alpha$ and $(e, 2e)$ experiments. The discussion of the details of the intensity calculations in the XPS spectra will be given in the next section. CI calculations of the initial state show that the most important correlation effect involves excitations to the 2π orbital.[20] The natural orbital occupation number of this orbital is 0.1, indicating, in fact, that we would not expect any significant new structure to arise from correlation in the initial state. The results of the $(e, 2e)$ momentum transfer experiments[6] provide further justification for the neglect of correlation in the initial state.

For the $^2\Sigma^+$ and $^2\Pi$ final states, we used the CI model to obtain correlated many-electron wave functions. We are interested in the interactions between the singly ionized configurations of Eq. (1) and configurations which are nearly degenerate and have a large interaction with them. From our CI we want to obtain several excited states of the same symmetry. This limits the kinds of excitations we can consider (choice of configurations) and the number of virtual orbitals (choice of orbital basis) we can use. A key requirement in our choices is that we obtain descriptions of equal quality for the different final states of interest.

Our choice for the terms in the CI expansion was to include all configuration state functions (CSF's)[21] which can be constructed in the valence space of the CO$^+$ ion. This means all CSF's of $^2\Sigma^+$ or $^2\Pi$ symmetry with nine electrons distributed in the 3σ, 4σ, 5σ, 6σ, 1π, and 2π molecular orbitals. The innermost 1σ and 2σ (O 1s and C 1s) MO's were doubly occupied in all configurations. This model gives us 320 $^2\Sigma^+$ and 486 $^2\Pi$ configurations. The model allows for the near degeneracy CI effects and also includes the most important shake-up configurations. It does not, however, allow for a full relaxation of the atomic orbitals in the different ionic states. In this model the only way that the electrons can respond to the potential change due to ionization is to occupy orbitals which always have to be expressible as rotations in the valence space of either $X\,^1\Sigma^+$ state of CO or $X\,^2\Sigma^+$ state of CO$^+$ depending on the choice for the MO basis.

There is another type of excitation, namely Rydberg excitations, which we have not included in our model CI. Some of the Rydberg states would be nearly degenerate in energy with the singly ionized states of Eq. (1). However, the interaction between the Rydberg states and the states in Eq. (1) is likely to be small. The reason for this is that the electrons in the diffuse Rydberg orbitals occupy a very different region in space than the valence electrons. Therefore the interaction matrix element

$$\int\int [\phi_i^*(1)\phi_j^*(2)1/r_{12}\phi_k(1)\phi_l(2)]\,d\tau_1\,d\tau_2\,,$$

where one or two of ϕ_k and ϕ_l are Rydberg orbitals, has a small value. The inclusion of the Rydberg excitations would certainly have an effect on the magnitude of the ionization energies and intensities we calculate. However, the CI model which only considers excitations in the valence space includes the physically most important excitations to describe the ionized states in the valence region and it is still computationally conveniently small. Therefore, we expect the results from this model to be good enough for a qualitative analysis of the results from XPS and $(e,2e)$ measurements.

The configuration interaction calculation was done in a fixed molecular orbital basis. This means that we assume that every state which interests us can be adequately described with a wave function which is expanded in one and the same set of molecular orbitals. This is equivalent to optimizing the coefficients in the CI expansion but not the molecular orbitals in terms of which the expansion is made. Given the limited nature of our CI model, the results of the calculation may depend strongly upon the choice of the MO basis. For this reason, we made tests using different sets of orbitals which were chosen because we felt that there was a reasonable physical basis for their use. The CI calculations were performed using four different sets of MO's. In the first set, denoted O1, the occupied orbitals $1\sigma - 5\sigma$, and 1π are the occupied Hartree-Fock orbitals from the $X\,^1\Sigma^+$ state of CO and 6σ and 2π are the lowest unoccupied orbitals of their symmetries. The same occupied space is also used in the second set, O2, but the unoccupied orbitals are obtained as follows. The 6σ orbital is the highest occupied σ orbital from a Hartree-Fock calculation for the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 5\sigma^1 6\sigma^1 \pi^4 (^4\Sigma^+)$ state of the CO$^+$ ion; the 2π is the highest occupied π orbital from the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi (^4\Delta)$ state. The third and the fourth sets, O3 and O4, consist of the occupied Hartree-Fock orbitals of the $X\,^2\Sigma^+$ state of the CO$^+$ ion. The 6σ and 2π orbitals are as in sets O1 and O2, respectively. For MO sets O2 to O4, the 6σ and 2π orbitals were Schmidt-orthogonalized to the 1σ-5σ and 1π orbitals to form orthonormal MO sets.

III. IONIZATION CROSS SECTIONS AND INTENSITY

In the analysis of the XPS and $(e,2e)$ spectra it would certainly be convenient to have estimates for the intensity distribution. The intensity of a peak in an XPS spectrum is best described as a cross section, i.e., the probability of a photoionization from a given molecular orbital by a photon of a given energy. An accurate calculation of molecular photoionization cross sections is difficult, the main difficulty being the choice for the wave function of the ionized electron.[18,19] Since we do not include an explicit representation of this continuum electron in our ionic wave functions, we are not able to perform a direct calculation. Instead we have to estimate the cross section for each ionic state from a simplified model which is very close to that developed by Gelius[22] for the relative intensities of XPS spectra from molecules. According to this model the cross section for photoionization from a given MO can be estimated from the cross sections and populations of the constituent atomic orbitals.

The major object is to estimate the relative values of integrals I_i,

$$I_i = \left| \int \phi_i(\vec{r})\vec{t}\epsilon\lambda(\vec{r})\, dv \right|^2 ; \tag{3}$$

where ϕ_i is an occupied HF orbital for the ground state of CO, $\epsilon\lambda$ is the wave function of the continuum electron, with kinetic energy ϵ, appropriate to an ionic state of CO^+, and $\vec{t}$ is the transition operator for photoemission (usually taken as the dipole term $\vec{r}$). We take $\epsilon\lambda$ to represent a suitable sum over the allowed angular momenta ($\lambda = \sigma, \pi, \delta, \ldots$) of the continuum wave function. The kinetic energies of the valence shell photoelectrons are large ($\approx$1400 eV for Al$K\alpha$), whereas the energy range of interest in the valence XPS spectra is only about 50 eV. Therefore, it is reasonable to assume[23] that the integral in Eq. (3) is independent of the electron energy ϵ in the 50 eV range which interests us. This leaves ϕ_i as the only variable in I_i. If the MO ϕ_i is represented as a linear combination of atomic orbitals, i.e., $\phi_i = \sum a_{i\nu}\chi_\nu$, the integral in Eq. (3) can be approximated as

$$I_i = \sum_\nu \sigma_\nu a_{i\nu} a^*_{i\nu} . \tag{4}$$

In the case of CO, ν runs over the O(2s), O(2p), C(2s), and C(2p) atomic orbitals, and i is one of the 3σ, 4σ, or 5σ valence MO's. Values for the atomic photoionization cross sections σ_ν have been taken from the theoretical results of Scofield[24] for 1.5 keV photons. The cross sections for the 2p orbitals are only 10% of that for the 2s and are neglected. The values of $a_{i\nu}a^*_{i\nu}$ are determined for our ground-state HF MO's by a Mulliken gross population analysis.[25] Relative values of I_i, in arbitrary units, as calculated from Eq. (4) are given in Table I. The population analysis values of $a_{i\nu}a^*_{i\nu}$ and Scofield's[24] values of σ_ν are also given in the table. Rabalais *et al.*[26] have computed values of the transition integral of Eq. (3) using orthogonalized plane waves for the continuum orbitals $\epsilon\lambda$. Their values for Mg$K\alpha$ x-rays (1254 eV) are given in Table I for comparison with our results.

TABLE I. Relative molecular orbital photoionization intensities for Al$K\alpha$ x rays, I(AP), and gross atomic populations AP, for the σ valence orbitals of CO. The orthogonalized-plane-wave results of Ref. 26, I(OPW), are included for comparison.

	AP(O_{2s})	AP(C_{2s})	I(AP)	I(OPW)[a]
3σ	0.47	0.29	4.3	5.2
4σ	0.34	0.19	3.0	1.6
5σ	0.4	0.40	1.3	1.0
σ_ν[b]	1872	635		

[a] Relative values at 1254-eV (Mg$K\alpha$) photon energy from Ref. 26.

[b] Atomic O_{2s} and C_{2s} cross sections in 10^{-24} cm^2 at 1500-eV photon energy from Ref. 24.

The intensity of a transition to a given N-electron final state F is proportional to the integral I_F between two many-electron wave functions:

$$I_F = \left| \int \Psi_I(1, \ldots, N) \sum_i \vec{t}_i \Psi_F(1, \ldots, N)\, dv \right|^2 . \tag{5}$$

Here Ψ_I is the N-electron wave function for the ground state of CO and Ψ_F is a final-state wave function with $N-1$ electrons in a discrete square integrable function Ψ'_F and one in a continuum orbital $\epsilon\lambda$:

$$\Psi_F = \mathcal{A}\{\Psi'_F(1, 2, \ldots, N-1)\epsilon\lambda(N)\} . \tag{6}$$

We recall that the CI expansion of Ψ'_F is written

$$\Psi'_F = \sum C_{Fi}\Phi_i , \tag{7}$$

where the Φ_i are the CSF's discussed in Sec. II. If Ψ_I and Ψ_F are expressed as sums of Slater determinants, the expression for I_F in terms of one-electron integrals has been given by Löwdin.[27] However, this general expression is quite complex.

In order to simplify this expression, we have used the approximations discussed in the previous section. Namely, (a) Ψ_I is a single Slater determinant; and (b) the CI expansion for Ψ'_F uses the same set of (orthogonal) MO's used to construct Ψ_I (plus of course 6σ and 2π). We require further that (c) the orbital overlap integral $\langle \phi_i | \epsilon\lambda \rangle = 0$ for $i = 1\sigma$ to 5σ and 1π. For any reasonably chosen function $\epsilon\lambda$, with $\epsilon \approx 1400$ eV, this overlap must be very small. With these assumptions I_F becomes

$$I_F \propto \left| \sum_i C_{Fi} \int \phi_i(1) t(1) \epsilon\lambda(1)\, dv_1 \right|^2 . \tag{8}$$

For final states of $^2\Pi$ symmetry, i is a single term for the $1\pi^{-1}$ state of Eq. (1b) and, for states of $^2\Sigma^+$ symmetry, i is summed over the 5σ, 4σ, and 3σ states of Eq. (1). From Eqs. (3) and (4) we can form only an estimate of the squares of the one-electron transition integrals in Eq. (8). We have no information concerning their phase. We have made the crude assumption to completely neglect cross terms in the case of $^2\Sigma^+$ final states and write

$$I_F \propto \sum_i |C_{Fi}|^2 I_i ; \tag{9}$$

where I_i is given by Eq. (4) and tabulated in Table

I. This approximation is not as severe as it might seem. As we shall show in the results, for almost every final state with significant intensity, one coefficient C_{Fi} is much larger than the other two.

As is clear from this section our computation of the intensities is far from accurate. However, the results of Gelius[22] for molecules containing light atoms give us reason to believe that the qualitative conclusions of our calculations are, in fact, valid.

Note the similarity between the intensity formulas from shake-up, Eq. (2), and from Eq. (9). In both of them, the probability of a multielectron transition is proportional to an expansion coefficient. The expansion coefficient C_k in Eq. (2) is an overlap integral between two wave functions, both of which are usually single Slater determinants. The deviation of this coefficient from zero for a shake-up state is a measure of the orbital relaxation. On the other hand, the coefficients C_{Fi} in Eq. (9) are affected both by relaxation and electron correlation. The amount of relaxation and correlation depends, of course, on the CI model as discussed in the previous section. Satellites may gain intensity through either mechanism. For inner-shell ionization, relaxation is the dominant effect,[10,23] and Eq. (2) gives transition probabilities in good agreement with experiment. For valence region ionization, relaxation is smaller but electron correlation becomes more important. How meaningful it is to try to separate the contributions of shake-up and correlation to the intensity of the satellites will be discussed further in later sections.

The analysis[6] of the $(e, 2e)$ momentum transfer makes use of assumptions (a) to (c) for the wave functions, but it does include an explicit description of the continuum electron, $\epsilon\lambda$.

IV. DETAILS OF CALCULATIONS

The LCAO molecular orbitals for CO and CO^+ were expanded in a basis set consisting of 19σ and 11π Slater-type functions on each atom.[28] The exponents of the basis functions are given in Table II. The CO distance of 2.15 a.u. was used for both CO and CO^+. This distance is reasonably close to the experimental equilibrium separation[31] for the $X\,^1\Sigma^+$ state of CO (2.132 a.u.) and to the calculated Hartree-Fock equilibrium[32] (2.081 a.u.). The computations were performed using the ALCHEMY program system written by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine. The SCF calculation for the $X\,^1\Sigma^+$ ground state of CO gave the total energy $-112.788\,837$ a.u.; the SCF energy for the $X\,^2\Sigma^+$ state of CO^+ was calculated to be $-112.294\,934$ a.u.

TABLE II. Quantum numbers l and n and exponents ζ for the Slater basis sets for C and O. For $l \geq 1$, both σ and π basis functions were generated.

l	n	ζ(carbon)[a]	ζ(oxygen)[a]
0	1	9.055	12.418
	1	5.025	6.995
	3	6.081	8.681
	2	2.141	2.922
	2	1.354	1.818
	2	3.1	3.9
	2	1.2	1.6
1	2	6.827	8.450
	2	2.779	3.744
	2	1.625	2.121
	2	1.054	1.318
	3	3.5	4.7
	3	1.0	1.3
2	3	3.8	4.0
	3	2.4	3.0
	3	1.4	2.0
3	4	4.0	4.0
	4	2.0	2.0

[a] The basis sets are those optimized for the free atoms, see Ref. 29, supplemented by additional basis functions chosen for molecular calculations, see Ref. 30.

In Table III, we have listed some results from the internal valence CI calculations of the $^2\Sigma^+$ states with the four different sets of orbitals, O1 to O4 (see Sec. II). These should be useful for assessing the stability and accuracy of our wave functions. In this table, we give total and relative energies for the three $^2\Sigma^+$ states which are most nearly the single-hole configurations of Eq. (1). The absolute total energies of these states differ by as much as 0.14 a.u. (4 eV). We are, however, more interested in the relative energies (with respect to the $X\,^2\Sigma^+$ state) in the CO XPS spectrum. These are reproduced to about 1.2 eV for the $B\,^2\Sigma^+$ state and to about 4 eV (out of ≈25 eV) for the highest $(3\sigma^{-1})$ state. Thus the variation of the relative energies is less than 20% which, for the purposes of our model calculation, is satisfactory. We have also examined the coefficients of the CI wave functions and the natural orbital[27,33] occupation numbers which were obtained using these four orbital sets. There are no qualitative changes in the nature of the CO^+ states among the four sets of calculations. The conclusions which we make in Secs. V and VI are supported by the results of all four CI calculations.

Unless otherwise stated, the results presented in the following sections were obtained using the

TABLE III. Test results from the valence CI calculation with orbital sets O1 to O4.

Set	$E(X\,^2\Sigma^+)$ (a.u.)	$E(B\,^2\Sigma^+)$ (a.u.)	$E(^2\Sigma^+\,3\sigma^{-1})$ (a.u.)	$E(X^2\Sigma^+)-E(B\,^2\Sigma^+)$ (eV)	$E(X\,^2\Sigma^+)-E(^2\Sigma^+\,3\sigma^{-1})$ (eV)
O1	−112.252 479	−112.036 702	−111.325 395	5.87	25.23
O2	−112.357 416	−112.125 358	−111.304 505	6.31	28.65
O3	−112.364 777	−112.104 461	−111.294 269	7.08	29.13
O4	−112.392 967	−112.145 757	−111.327 581	6.73	28.99

orbital set O2 which combines the occupied CO ground-state orbitals with 6σ and 2π orbitals from excited states of CO$^+$. The CO occupied orbitals are likely to give descriptions for each of the CO$^+$ states which are of about the same quality. However, the occupied orbitals from the $X\,^2\Sigma^+$ state of CO$^+$ are likely to favor this state, in comparison with other ionic states, since orbital relaxation effects are properly treated only for the $X\,^2\Sigma^+$ state. The 6σ and 2π orbitals in set O2 are solutions of Fock equations for low-lying excited states of CO$^+$ and should be a more reasonable choice than the ground-state CO virtual orbitals. These virtual orbitals are determined for a field of 14 electrons[33] and, very roughly, are appropriate for CO$^-$.

V. RESULTS

Before going to a detailed analysis of the satellite structure in the XPS spectrum of CO, we will discuss briefly the $5\sigma^{-1}$, $4\sigma^{-1}$, and $3\sigma^{-1}\,^2\Sigma^+$ and the $1\pi^{-1}\,^2\Pi$ states of CO$^+$. These states correspond to the main features in the XPS spectrum. The simple orbital interpretation of the states in Eq. (1) is lost in the CI calculation. It is possible, however, to construct natural orbitals (NO's) from the CI density matrix. The occupation numbers of these NO's contain information about how the many-electron state in question could most compactly be described in terms of one-electron orbitals.[27,33] For a Hartree-Fock wave function, the NO occupation numbers will be the integer shell occupations for the occupied MO's and zero for the unoccupied MO's.

In Table IV, we give the calculated energies of the $4\sigma^{-1}$, $3\sigma^{-1}$, $^2\Sigma^+$, and $1\pi^{-1}\,^2\Pi$ states relative to the $5\sigma^{-1}$ state. The square of the CI coefficient, C_{Fi}, for the appropriate state of Eq. (1) and the NO occupation numbers are also given. The NO's are identified by the molecular orbital notation 3σ, 4σ, etc. However, the NO's are, in fact, linear combinations of the molecular orbitals: $\phi_i(\mathrm{NO}) = \sum_k A_{ik}\,\phi_k(\mathrm{MO})$. The NO identified, for example, as 3σ is that NO for which the coefficient $|A_{i3\sigma}|$ has its largest value; i.e., the NO which is most nearly like the 3σ MO. For all the states in Table IV, this identification is always clear; in the worst case, the "5σ" NO for the $3\sigma^{-1}$ state, the coefficient is still as large as 0.88.

Looking at the NO occupations, we can see that the $5\sigma^{-1}$ state is still well described with the Hartree-Fock configuration of Eq. (1a). The same information can be extracted from the CI coefficients. The coefficient for the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4$ configuration is 0.93 ($C^2 = 0.86$) which shows that the state is dominantly determined by this configuration only. Almost the same is true for the $B^2\Sigma^+$ state, although it can be seen that the single configuration picture is somewhat less adequate.

TABLE IV. Some properties of the dominantly single-hole CI states. The relative energies (eV), intensities (arbitrary units), and natural orbital occupation numbers are shown. The one-electron intensity which neglects orbital relaxation is denoted by I_{F0} and the CI intensity by I. The square of the coefficient of the leading term in the CI expansion, C_{Fi}^2, is also given.

						Intensity loss	NO occupation numbers					
	E_{rel}(calc)	E_{rel}(exp)[a]	C_{Fi}^2	I_{F0}	I	$1-I/I_{F0}$	3σ	4σ	5σ	6σ	1π	2π
$5\sigma^{-1}$	0.0	0.0	0.859	1.3	1.12	14%	2.00	1.98	1.01	0.00	3.85	0.15
$4\sigma^{-1}$	6.3	5.6	0.817	3.0	2.47	18%	2.00	1.09	1.85	0.00	3.87	0.19
$3\sigma^{-1}$	28.7	24.3	0.515	4.3	2.22	48%	1.40	1.78	1.62	0.14	3.41	0.64
$1\pi^{-1}$	4.4	2.9	0.915	⋯	⋯	8.5%	⋯	⋯	⋯	⋯	⋯	⋯

[a] See Ref. 3.

TABLE V. Relative energies (eV) and intensities (arbitrary units) for the $^2\Sigma^+$ CI states. All states up to $E_{\rm rel} = 41$ eV with an intensity greater than 1% of CI root 2 are shown. The total intensities, $I_{\rm tot}$, and orbital contributions to the total, $I_{{\rm part},i}$, are given separately. The coefficients of the single-hole configurations, $C_{F,i}$, are also given.

CI root	$E_{\rm rel}$	$C_{F,5\sigma}$	$C_{F,4\sigma}$	$C_{F,3\sigma}$	$I_{{\rm part},i}$			$I_{\rm tot}$	Dominant configuration
					5σ	4σ	3σ		
1	0	−0.927	0.033	−0.018	1.12	0.00	0.00	1.12	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4$
2	6.31	0.099	0.904	0.017	0.01	2.45	0.00	2.47	$3\sigma^2 4\sigma^1 5\sigma^2 1\pi^4$
3	10.64	−0.169	0.239	0.080	0.04	0.17	0.03	0.24	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi$
4	17.26	0.135	−0.102	−0.067	0.02	0.03	0.02	0.07	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi$
5	19.48	−0.072	−0.019	0.058	0.01	0.00	0.01	0.02	$3\sigma^2 4\sigma^2 6\sigma^1 1\pi^4$
6	20.32	0.076	−0.146	0.187	0.01	0.06	0.15	0.22	$3\sigma^2 4\sigma^1 5\sigma^2 1\pi^3 2\pi^1$
7	20.52	−0.072	0.023	0.203	0.01	0.00	0.18	0.19	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$
8	22.18	−0.027	−0.081	0.117	0.00	0.02	0.06	0.08	$3\sigma^2 4\sigma^1 5\sigma^1 6\sigma^1 1\pi^4$
9	23.18	−0.042	0.107	−0.068	0.00	0.03	0.02	0.06	$3\sigma^2 4\sigma^1 5\sigma^1 6\sigma^1 1\pi^4$
10	24.41	0.057	0.142	−0.107	0.00	0.06	0.05	0.11	$3\sigma^2 4\sigma^1 1\pi^4 2\pi^2$
11	24.68	−0.048	−0.021	−0.173	0.00	0.00	0.13	0.13	$3\sigma^2 4\sigma^1 1\pi^4 2\pi^2$
12	24.91	0.028	0.020	−0.283	0.00	0.00	0.34	0.35	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$
13	25.49	−0.061	0.018	0.197	0.00	0.00	0.17	0.17	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$
15	27.55	0.027	−0.002	−0.350	0.00	0.00	0.53	0.53	$3\sigma^2 4\sigma^2 6\sigma^1 1\pi^3 2\pi^1$
16	28.65	0.035	0.003	0.718	0.00	0.00	2.22	2.22	$3\sigma^1 4\sigma^2 5\sigma^2 1\pi^4$
18	32.95	0.105	−0.046	0.042	0.01	0.01	0.01	0.03	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$
19	33.47	0.137	−0.002	0.027	0.02	0.00	0.00	0.03	$3\sigma^2 5\sigma^1 1\pi^4 2\pi^2$

In this state 0.9 electrons are missing from the 4σ NO and 0.1 from the 5σ. The results for the $^2\Sigma^+$ state which is dominantly $3\sigma^{-1}$ are strikingly different. From the NO occupation numbers, we can see that the single configuration picture is completely lost. The hole is now distributed over all occupied σ valence NO's; i.e., there are 0.60, 0.28, and 0.38 electrons missing from the 3σ, 4σ, and 5σ orbitals, respectively. Also, the 6σ and 2π orbitals, which are unoccupied in the Hartree-Fock configuration, now have 0.14 and 0.64 electrons, respectively. We note also that the coefficient of the dominant configuration [Eq. (1c)] is only 0.72.

The most important thing, however, is to notice that this breakdown of the one-electron picture [the deviation of the coefficients C_{Fi} in Eq. (9) from 1 and 0], leads to a decreased intensity of the XPS peaks corresponding to the final states of Eq. (1). In Table IV, the relative intensity in the one-electron picture is denoted I_{F0} [cf., Eqs. (3) and (4) and Table I] and the CI many-electron relative intensity computed from Eq. (9) is denoted I. The loss of intensity, i.e., the difference between the one-electron picture and our CI model, is 48% for the $3\sigma^{-1}$ state. For the two lowest $^2\Sigma^+$ states, the corresponding losses are 14% and 18%. We will show that this loss of intensity from the states corresponding primarily to single ionization leads to substantial intensity in other states which often cannot be described in terms of one configuration only.

The Hartree-Fock configuration, Eq. (1d), for the lowest $^2\Pi$ state has a coefficient of 0.96 in the CI wave function. This is equivalent to an intensity loss of 8.5% to other $^2\Pi$ states. The 1π orbital is a linear combination of O(2p) and C(2p) orbitals only. The ratio of atomic cross sections $\sigma(2p)/\sigma(2s)$ for both oxygen and carbon is ≈ 0.1 for 1.5-keV photons.[24] Therefore it is very improbable that any structure due to states of $^2\Pi$ symmetry could be resolved in an XPS experiment. Consequently, we will not consider the $^2\Pi$ states any further.

The details of the calculated intensity distribution among the $^2\Sigma^+$ states are given in Tables V and VI. We consider all states with $E_{\rm rel}$ up to 41 eV above the $X\,^2\Sigma^+$ ground state of CO. (This corresponds to an absolute ionization potential of ~ 55 eV.) In this energy range, covered by the first 30 roots of the CI calculation, we list those states whose XPS relative intensity, calculated using Eq. (9), is greater than 1% of the state with the highest intensity ($4\sigma^{-1}$). In Table V, we give relative energies, values of C_{Fi}, XPS intensities, denoted $I_{\rm tot}$, and the contributions to $I_{\rm tot}$ from each single-hole state, $I_{{\rm part},i} = C_{Fi}^2 I_i$. The states are numbered according to which CI root they are found to be. Finally, we give, for each state, the configuration which has the largest coefficient in the CI expansion. In Table VI, we provide further information about the nature of the states. The magnitude of the coefficient of the dominant configuration and the NO occupation numbers are given. [A configuration can often have more than one angular momentum coupling. The $5\sigma^1 1\pi^3 2\pi^1$ configuration, for example, gives rise to two $^2\Sigma^+$ states (CSF's); $5\sigma^1(1\pi^3 2\pi^1;\ ^3\Sigma^+)$ and $5\sigma^1(1\pi^3 2\pi^1;\ ^1\Sigma^+)$. For such cases, we give in Table VI the coefficient summed over all CSF's arising from the configuration; specifically, the square root of the sum of the C^2_{Pk}.]

The notation for the NO's is the same as for Table IV. In most cases, the dominant configuration does not describe the state at all well since its coefficient is much less than 1 and may be as small as 0.53. The essential multiconfiguration nature of these states can also be seen from the NO occupation numbers. Here, there are large deviations from the integral values characteristic of a single dominant configuration.[33]

The two lowest states are, of course, $X\,^2\Sigma^+$ and $B\,^2\Sigma^+$. The first state which is not primarily the result of a one-electron ionization is calculated to have an energy of 10.64 eV relative to the lowest ($X\,^2\Sigma^+$) state. Spectroscopic notation for this state is $C^2\Sigma^+$. Its intensity is relatively high; 20% of the intensity of the $X\,^2\Sigma^+$ state or 10% of that of the $B\,^2\Sigma^+$ state. It is interesting to examine the mechanism responsible for the observed XPS intensity of this state. From Table V, we note that the single-hole state contributing most, 70%, of the intensity is $4\sigma^{-1}$ ($B\,^2\Sigma^+$). However, the dominant configuration is $3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^1$ which has a coefficient of 0.92. The NO occupation numbers, Table VI, further support this characterization. This is a classical shake-up configuration for the $X\,^2\Sigma^+$ state; ionization from 5σ and exciation $1\pi \rightarrow 2\pi$. Yet, such an assignment would require that the $C\,^2\Sigma^+$ state would get its intensity primarily from the X rather than the B state which is not the case. In order to find out the possible shake-up contribution to the intensity we calculated the total Hartree-Fock shake-up intensity [Eq. (2)] of the $X\,^2\Sigma^+$ state. It was found to be 6.3% of the $X\,^2\Sigma^+$ intensity. Even in the extremely unlikely case that all this intensity went to the $C\,^2\Sigma^+$ state, shake-up could still account for only 25% of the calculated intensity. Thus correlation effects play a key role in determining the intensity of this state.

The next group of states of interest is at $\simeq 20.5$ eV relative to $X\,^2\Sigma^+$. Here the intensity comes mainly from the $3\sigma^{-1}$ single-hole states, though the dominant configurations have the 3σ orbital doubly occupied. The same is true for the states at energies 24.0–28.0 eV. This would introduce an interesting contradiction if the XPS peaks corresponding to these states would be called shake-up. Namely, the state from which they gain their intensity, $3\sigma^{-1}$, lies at higher apparent binding energy.

There is further a group of satellites with a low calculated intensity at the low kinetic energy side of the $3\sigma^{-1}$ state.

It is shown in Table V, that there is one dominant single-hole contribution, $I_{\text{part},i}$, to the total intensity for almost all states. The exceptions, roots 4, 9, 10, and 18, all have rather low intensity; the most intense, root 10, is less than 5% of the

TABLE VI. Characteristics of the CI wave functions for the $^2\Sigma^+$ states. The dominant configuration, the magnitude of the coefficient of this configuration, $|C_{\text{dom}}|$, and the NO occupation numbers are given.

CI Root	Dominant configuration	$\lvert C_{\text{dom}}\rvert$	NO occupation numbers 3σ	4σ	5σ	6σ	1π	2π
1	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4$	0.927	2.00	1.98	1.01	0.00	3.85	0.15
2	$3\sigma^2 4\sigma^1 5\sigma^2 1\pi^4$	0.904	2.00	1.09	1.85	0.00	3.87	0.19
3	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^1$	0.920	2.00	1.93	1.06	0.00	3.05	0.95
4	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^1$	0.642	2.00	1.88	1.06	0.06	2.66	1.35
5	$3\sigma^2 4\sigma^2 6\sigma^1 1\pi^4$	0.766	1.99	1.83	0.34	0.82	3.57	0.44
6	$3\sigma^2 4\sigma^1 5\sigma^2 1\pi^3 2\pi^1$	0.608	1.96	1.46	1.40	0.15	3.04	0.99
7	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$	0.648	1.95	1.62	1.32	0.08	2.66	1.37
8	$3\sigma^2 4\sigma^1 5\sigma^1 6\sigma^1 1\pi^4$	0.733	1.98	1.15	1.23	0.61	3.42	0.62
9	$3\sigma^2 4\sigma^1 5\sigma^1 6\sigma^1 1\pi^4$	0.734	1.99	1.60	0.53	0.86	3.64	0.39
10	$3\sigma^2 4\sigma^1 1\pi^4 2\pi^2$	0.761	1.98	1.12	0.52	0.19	3.71	1.48
11	$3\sigma^2 4\sigma^1 1\pi^4 2\pi^2$	0.532	1.95	1.35	0.91	0.14	3.13	1.52
12	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$	0.742	1.90	1.70	1.20	0.08	2.59	1.53
13	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^2$	0.873	1.94	1.97	1.00	0.06	2.34	1.70
15	$3\sigma^2 4\sigma^2 6\sigma^1 1\pi^3 2\pi^1$	0.857	1.86	1.93	0.37	0.82	3.03	0.98
16	$3\sigma^1 4\sigma^2 5\sigma^2 1\pi^4$	0.718	1.40	1.78	1.62	0.14	3.41	0.64
18	$3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi^2$	0.569	1.97	1.16	0.98	0.13	3.28	1.49
19	$3\sigma^2 5\sigma^1 1\pi^4 2\pi^2$	0.583	1.96	1.00	0.92	0.11	3.29	1.73

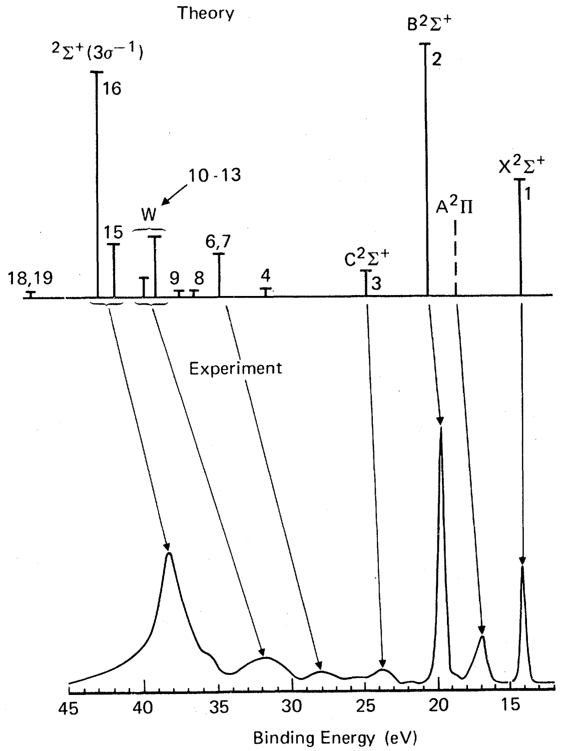

FIG. 1. Comparison between our theoretical results and the high-resolution XPS spectrum of Gelius *et al.*, Ref. 3. The position of the first calculated peak has been adjusted to coincide with experiment. The height of the solid bars indicates calculated intensities. The CI root numbers are shown for each calculated peak.

highest $(4\sigma^{-1})$ peak. Clearly, this reduces the importance of the neglect of the cross terms in formula for the intensity, Eq. (9).

Up to the 30th CI root, which has $E_{\rm rel} = 40.74$ eV, we have obtained a very large fraction of the total valence shell intensity. The sums over C^2_{Fi} for these 30 roots are $0.99(5\sigma^{-1})$, $0.95(4\sigma^{-1})$, and $0.92(3\sigma^{-1})$. The largest amount of intensity not accounted for is 8% of that due to $3\sigma^{-1}$ ionization. Within our model, this intensity would be distributed over states with $E_{\rm rel} \gtrsim 41$ eV ($\gtrsim 55$ eV absolute binding energy). The $(e, 2e)$ results of Dey *et al.*[6] provide evidence that this intensity is indeed observed at higher binding energies.

VI. DISCUSSION

A comparison between our results and the high-resolution XPS (Al$K\alpha$) spectrum of Gelius *et al.*[3] is shown in Fig. 1. In this figure, we have indicated the computed positions and relative intensities of the $^2\Sigma^+$ states, taken from Table V, by solid vertical lines of appropriate height. Peaks within 0.5 eV are combined into a single line and the low-intensity peak due to CI root 5 is omitted. The number associated with each peak or group of peaks is the CI root number and is given in order to facilitate reference to Table V. The calculated position of the $A\,^2\Pi(1\pi^{-1})$ peak, taken from Table IV, is shown by a dashed line to indicate that its relative intensity has not been estimated. The position of the first calculated peak, $X\,^2\Sigma^+$, has been adjusted to coincide with the first observed peak. Each calculated peak with significant intensity is associated with a peak in the experimental spectrum.

Our calculation agrees reasonably well with the experimental results in terms of the number, energy, and intensity of the peaks. The major discrepancy is in the position of the structure above 25-eV binding energy ($E_{\rm rel} = 11$ eV); here our calculated relative energies are ~5–7 eV higher than the observed values. We believe that this discrepancy is due, at least in part, to the neglect of orbital relaxation effects. Rabalais *et al.*[26] have obtained experimental relative intensities for the principal, one-electron, peaks from the XPS spectrum of Ref. 34. Our calculated intensities are, at best, in only fair agreement with "experiment." This is true both when we use our estimates for the transition integrals of Eq. (3) or the calculated orthogonalized-plane-wave values,[26] cf. Table I. However, no particular conclusion can be drawn from this comparison. The XPS experiments[3,34] measure a differential rather than a total cross section. The angular dependence of the cross section,[18,19] which is a function of photon energy and final ionic state, is not known in this case. In effect, different experimental and theoretical quantities are being compared. Further, more accurate theoretical values for the transition integrals[18,19] would also be desirable for a meaningful comparison.

It is not possible to get enough information from the XPS spectrum[3] to unambiguously support the detailed results of our calculation. In particular, we cannot obtain information regarding our predictions about the orbital (single-hole configuration) origin of the intensity of the satellite structure. Fortunately, however, this information is available from the results of other types of experiments.

Hamnet *et al.*[5] have measured "photoionization" branching ratios to various states of CO$^+$ using the electron-electron coincidence technique. They have studied the satellite structures at ~23 eV and ~32 eV and have labeled these as $C\,^2\Sigma^+$ and W, respectively. (We have included these labels in Fig. 1.) Of particular interest to us is the asymptotic high-energy limit of the $B\,^2\Sigma^+/C\,^2\Sigma^+$ intensity ratio which they measure to be ~0.12. This value agrees well with our result of 0.10 (see Table V) and supports our assignment of the origin of the intensity of the $C\,^2\Sigma^+$ state as being due primarily to the $4\sigma^{-1}(B\,^2\Sigma^+)$ single-hole configuration. We recall that the $C\,^2\Sigma^+$ state is well described by the configuration $3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^1$ which, for this state, has a coefficient of 0.92. According to one-electron shake-up theory, it would be assigned as an $X\,^2\Sigma^+$ satellite; 5σ ionization plus $1\pi \rightarrow 2\pi$ excitation. However, correlation effects determine that it is, in fact, a satellite of $B\,^2\Sigma^+(4\sigma^{-1})$.

Hamnet *et al.*[5] also find that the $B\,^2\Sigma^+/C\,^2\Sigma^+$ intensity ratio has already reached its limiting value at 50-eV "photon" energy. This means that the $C\,^2\Sigma^+$ peak should also be seen with an intensity ~10% of the $B\,^2\Sigma^+$ peak in $YM\xi(h\nu = 132$ eV) photoemission. However, this peak is not observed at all in the $YM\xi$ spectrum of Banna and Shirley.[4] This may be due to poor counting statistics in their measurements.

In the noncoplanar $(e, 2e)$ experiments of Dey *et al.*,[6] the orbital origin of the intensity of the different ionized states can be studied. Their experiment provides direct confirmation of our assignment of the structure at ~28 eV and ~32 eV as having mainly $3\sigma^{-1}$ character.

Recently, the name "shake-down" has been applied[5] to these $3\sigma^{-1}$ satellites, CI roots 6, 7 and 10–13, which derive their intensity from a main peak at higher binding energy. It should be emphasized that these states cannot be described by configurations which involve ionization of one electron plus simultaneous excitation of another, cf. Tables V and VI. They do not obtain their intensity from a mechanism involving a sudden change of potential as is the case for the conventional one-electron picture of shake-up.[8,9,23] These satellites of the $3\sigma^{-1}$ state are mixtures of several one-electron configurations and have their origin in many-electron correlation effects for CO$^+$. They are, therefore, best described as "correlation" peaks.

Okuda and Johnathan[35] and Potts and Williams[1] have given much more limited CI analyses of the satellite structure in the photoemission spectra of CO. Okuda and Jonathan[35] performed INDO calculations and considered the interaction of eight $^2\Sigma^+$ configurations. Potts and Williams used an empirical approach based on relating known excitation energies in the neutral molecule to unknown values in the ion. The configurations considered in both Refs. 1 and 35 were limited to ionization plus, at most, single excitation. Our results and assignments are significantly different from those in both these references. In particular, they do not identify the strucutre at 28 and 32 eV as being low-energy satellites of the $3\sigma^{-1}$ peak at 38 eV. Further, we find that the role of configurations involving ionization plus double excitations is quite important as shown in Tables V and VI.

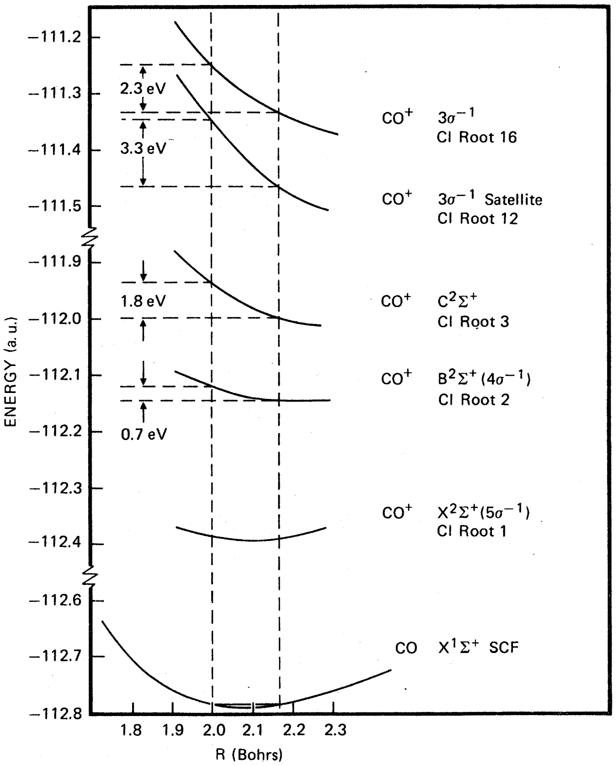

FIG. 2. Potential curves for CO and five states of CO$^+$. The dotted vertical lines show the Franck-Condon envelope of the first vibrational level of CO. The estimated broadening of each CO$^+$ state is given.

In order to obtain an estimate of Franck-Condon broadening effects, potential curves for CO and CO$^+$ are required. We have computed CI wave functions, using orbital set O4 (see Sec. II), at four internuclear separations about the equilibrium of CO; $R = 1.95$, 2.05, 2.15, and 2.25 bohrs. Hartree-Fock wave functions for the ground state of CO were computed at 14 distances between $R = 1.7$ and 2.5 bohrs. In Fig. 2, we present the curves for CO and for five $^2\Sigma^+$ CI states of CO$^+$. The three states which are dominantly the single-hole configurations of Eq. (1) are given. In addition, two states representative of the correlation satellite peaks are shown. These are the $C\,^2\Sigma^+$ state, root 3 of the CI calculation, and the $3\sigma^{-1}$ satellite root 12. The calculated zero-point vibrational level of $X\,^1\Sigma^+$ CO at 1210 cm^{-1} (the experimental value[31] is 1107 cm^{-1}) and the Franck-Condon envelope of this level are also shown. The figure indicates that there will be negligible broadening of the $X^2\Sigma^+(5\sigma^{-1})$ peak, ≈ 0.7 eV broadening of $B^2\Sigma^+(4\sigma^{-1})$ and ≈ 2.3 eV broadening of $3\sigma^{-1}$. The $3\sigma^{-1}$ broadening is quite reasonable since 3σ is a strongly bonding MO. Hence, if the $3\sigma^{-1}$ state is bound at all, the equilibrium separation will be much larger than for CO and the potential curve will be very repulsive near the $X^1\Sigma^+$ CO minimum. Both satellite curves shown are also repulsive and will lead to rather broad peaks. These results are consistent with the peak widths observed in the XPS spectra[3] as shown in Fig. 1. Thus Franck-Condon factors appear to contribute importantly to the broadness of the observed structure above 25-eV binding energy. Our results are also consistent with the cross sections for C^+ and O^+ ion production[5,36] which indicate dissociation of the $3\sigma^{-1}$ state and its low-binding-energy satellites.

VII. CONCLUSIONS

In our study of the valence ionized states of CO we have found that many-electron correlation effects are mainly responsible for the satellite structure in the XPS spectrum of CO. Results of other types of electron spectroscopies support our interpretation of the origin of the satellites. The importance of final-state correlation effects is in strong contrast to the conventional shake-up model[8,9] according to which the satellites obtain intensity because of final-state orbital relaxation. This model leads to a physical picture of the satellites as having their origin in ionization plus simultaneous excitation of a second electron. We have shown that it does not account for the satellites which arise for valence shell ionization of a molecule.

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