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CALCULATION OF TRANSITION METAL COMPOUNDS USING AN EXTENSION OF THE CNDO FORMALISM.
V. MANY BODY EFFECTS IN THE INNER VALENCE SHELL PHOTOIONIZATION SPECTRA OF FREE AND COORDINATED CARBON MONOXIDE

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The inner valence shell region in the photoionization spectra of NiCO, $Ni(CO)_4$ and $Cr(CO)_6$ is studied by means of a diagonal two-particle–hole Tamm–Dancoff approximation. Many body effects are found in the energy range of the CO-ligand ionizations. The effects are more pronounced in NiCO and $Ni(CO)_4$ than in $Cr(CO)_6$. Since similar results have to be expected for adsorbate systems, the interpretation of photoemission spectra of such systems on the basis of the simple one particle picture should be handled with care.

1. Introduction

From a great variety of applications it is nowadays well known that the first few ionizations of a molecule can be described quite well in the framework of the one particle picture [1]. Each of the first few states of the ionized system is usually connected with the detachment of a single electron from a well defined molecular orbital. In other words, we can say that a Koopmans state $a_k|\psi_0^{(N)}\rangle$ created by the sudden removal of an electron from the orbital $|\phi_k\rangle$ decays mainly into a single final state $|\psi_j^{(N-1)}\rangle$ as long as k denotes one of the highest occupied orbitals. Correspondingly we usually do not find satellites in the region of the first few ionization bands. This region we will call the "outer valence shell region" (OVSR).

If we go to higher excited ion states Cederbaum and co-workers [2–4] showed for small and medium sized molecules, that the one-to-one correspondence of one particle levels and ionization lines no longer exists. In this region a Koopmans state decays into several final states leading to the appearance of satellite structure. If the decay probability is large and equal for several final states, we reach a situation where it is no longer possible to relate a certain band in the photoionization spectrum to a specific orbital. This energy region is called the inner valence shell region (IVSR).

The different sensitivity of outer and inner valence shell ionizations towards many body effects brings about an interesting question: What happens if a molecule with a relatively high first ionization potential undergoes weak bonding to another species the first ionization potential of which is low? In such a case, the highest occupied orbitals of the considered molecule which definitely belong to the OVSR in the free molecule may become inner valence shell orbitals in the bonded system due to the presence of high lying occupied orbitals of the other species. Therefore we might expect considerable changes in the corresponding part of the photoionization spectrum, even if the orbital wavefunctions are not altered dramatically by this type of bonding. The magnitude of these effects strongly depends on the density of final states in the energy range of the primary Koopmans state and also on the coupling matrix elements between the Koopmans state and the final states. Since both factors depend on the detailed electronic structure, the magnitude of the many electron effects can be rather different even for similar molecules.

From an experimentalist's point of view, situations where outer valence orbitals are "transformed" into

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Table 1
Ionization potentials for NiCO obtained with different theoretical methods and from different numerical approximations. The absolute values of all calculations are shifted in such a way that the first ionization fits the experimental value 7.5 eV above d-band onset found for the Ni/CO adsorbate systems. This type of presentation follows the suggestion of Cederbaum et al. [11]

Orbital	CNDO a)	EHT b)	Ab initio c)	SCF-Xα unrest. d)	SCF-Xα rest. d)	ΔSCF e)	CNDO f)
3σ	31.58		33.3			30.0	31.48
4σ	15.09		11.76	11.9/12.1		12.5	13.14
1π	9.13/8.64	9.0	7.77	7.5/7.7	7.5	7.5	9.63
5σ	7.5	7.5	7.5	9.1/9.3	9.7	7.9	7.5

a) Ref. [9], from application of Koopmans' theorem. (b) Ref. [10], from application of Koopmans' theorem. c) Ref. [11], from application of Koopmans' theorem. d) From ref. [8]. e) From ref. [7]. f) This work, from application of Koopmans' theorem.

inner valence orbitals are approached if a molecule like CO or N_2 is adsorbed on a clean metal surface or bound to an electron rich metal atom in a transition metal complex. In both cases the bonding is very similar which is the reason for the increasing importance of properly selected complexes as model compounds for the study of the chemisorptive bond [5]. The uppermost occupied orbitals of the considered molecule (termed "ligand") are not much altered by this type of bonding but energetically these ligand orbitals are situated about 5 to 8 eV below the highest occupied orbitals of the metal. It is therefore very probable that the ligand orbitals can no longer be considered as outer valence orbitals in the adsorbate as well as in the complex. In the experimental spectra some hints are found which seem to confirm this suggestion:

(i) From measurements making use of techniques like angular and energy dependent photoemission with depolarized and polarized radiation, it seems to be now ascertained that for carbon monoxide adsorption on a transition metal surface the sequence of the ionizations attributed to an electron detachment from the ligand orbitals is altered with respect to free CO [6]. This is especially true for the ionizations which are believed to originate from the orbitals labelled 5σ and 1π in CO. In the free molecule these ionizations are clearly separated with $\mathrm{IP}(5\sigma) < \mathrm{IP}(1\pi)$ ($\mathrm{VIP}(5\sigma) = 14.01$ eV, $\mathrm{VIP}(1\pi) = 16.9$ eV [1]). After coordination to a surface the corresponding ionizations are nearly degenerate with a slight favour for the order $\mathrm{IP}(1\pi) < \mathrm{IP}(5\sigma)$.

For model systems like NiCO this inversion is not found on the level of the one particle approximation but by more advanced calculations like ΔSCF [7] * and Xα-SW [8] (table 1). As the latter methods include parts of the relaxation energy, we are forced to take into account nonuniform relaxation shifts by which the sequence of ionizations can be altered with respect to the one particle result.

(ii) In transition metal carbonyls the average energy of the ligand range of ionizations is shifted towards lower energies as compared to free CO [1,12]. This seems to be true also for CO adsorbates if the energies are referred to the vacuum level. Since bonding to the surface or in the complex results in a stabilizing bond shift, the low energy shift of the ligand range of ionizations must be due to increased relaxation.

(iii) In the ligand range of the ionization spectrum of transition metal carbonyls Plummer and co-workers found satellite structures which they interpretated as shake-up peaks [5c]. If this interpretation is correct, it is the most convincing hint for the existence of non-negligible many body effects.

To study in further detail the decreasing suitability of the one particle description and the increasing importance of many body effects which accompany the possible transformation of an outer valence shell

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* Assuming the same correlation contributions as in free CO the authors of ref. [7] prefer the sequence $5\sigma < 1\pi$ for the final states of NiCO in spite of the fact that their ΔSCF-calculations predict $1\pi < 5\sigma$.

orbital of a free ligand to an inner shell one in a complex or adsorbate, we have investigated the adsorbate model system NiCO and the carbonyls $Ni(CO)_4$ and $Cr(CO)_6$ by means of many body perturbation theory [13]. This method, especially the Green's function approach, has been found to be one of the most suitable ones to describe many body effects in photoionization [3,14]. If applied to wavefunctions obtained from ab initio calculations this method is, however, numerically very expensive in the case of larger transition metal containing compounds. We therefore used wavefunctions obtained from an extended version of the CNDO formalism introduced in part I of this series [15a] which is especially devoted to the treatment of transition metal containing systems. It has been shown earlier [16] that in the case of molecules with light atoms a connection of the Green's function approach with CNDO wavefunctions usually leads to at least the same qualitative conclusions as the more advanced calculations. We therefore expect that the qualitative changes following the bonding of the ligand can be described quite well by this approach.

2. Theory

To study many body effects in photoionization we use the Green's function approach [13,14] in which vertical ionization potentials (VIP's) and electron affinities are obtained as zeros of the inverse Dyson equation

$$\mathbf{G}^{-1}(\omega) = \omega \mathbf{1} - \boldsymbol{\varepsilon} - \boldsymbol{\Sigma}(\omega) . \tag{1}$$

This equation connects the one particle Green's function with the single particle energies ϵ_k (collected in the diagonal matrix $\boldsymbol{\varepsilon}$) and the so-called self-energy part $\boldsymbol{\Sigma}(\omega)$. $\boldsymbol{\Sigma}$ depends on the perturbation

$$H' = H - H_{\mathrm{IPM}} , \tag{2}$$

which is the difference between the exact hamiltonian H of the N-fermion system and the model hamiltonian H_{IPM} used to describe the system in the independent particle approximation. The often used order by order expansion

$$\boldsymbol{\Sigma}(\omega) = \boldsymbol{\Sigma}^{(1)}(\omega) + \boldsymbol{\Sigma}^{(2)}(\omega) + \boldsymbol{\Sigma}^{(3)}(\omega) + \ldots \tag{3}$$

does not reproduce the correct pole structure if one goes beyond second order [17]. For the outer valence shell region which is defined by

$$|\epsilon_k| < |\Sigma^{-1}| , \quad \Sigma^{-1} = 2\epsilon_{\mathrm{HOMO}} - \epsilon_{\mathrm{LUMO}} \tag{4}$$

in this expansion [13,14] this incorrect pole structure does not cause any serious effect since all the poles of Σ resulting from third and higher order contributions are well separated from ϵ_k. For the lower lying levels, however, the orbital energies ϵ_k lie often close to the poles of Σ and thus one has to use an approximation which resembles the correct pole structure of the exact self-energy part. As shown by Cederbaum [17] this structure is analogous to that of the second order contribution

$$\Sigma^{(2)}_{kk_0}(\omega) = \sum_{j,a,b} \frac{V_{kjab}(2V_{k_0jab} - V_{k_0jba})}{\omega + \epsilon_j - \epsilon_a - \epsilon_b} \times (n_j n_a n_b + n_j \bar{n}_a \bar{n}_b) , \tag{5}$$

n_j = occupation number , $\quad \bar{n}_j = 1 - n_j$,

in the order by order expansion.

The most prominent approximations which go beyond second order but retain the correct pole structure are — in the order of decreasing numerical effort and therefore decreasing quality — the "coupled 2ph-RPA" [3], the "uncoupled 2ph-RPA", the "2ph-TDA", and several types of "diagonal 2ph-TDA" [2,3,17,18]. The first two methods are numerically so extensive that no applications have been published up to now. For the latter two, some calculations are available for molecules with light main group elements [2,3,17–19]. These calculations have shown that the different TD approximations lead to very similar results. We therefore use a simple form of the "diagonal two-particle–hole Tamm–Dancoff approximation" (d2ph-TDA) in this work. This incorporates parts of third and even higher orders of the perturbation expansion. For a detailed discussion of these connections we refer to the recent papers of Cederbaum et al. [2,3,17–19].

If the parent N-particle system has a closed shell ground state $|\psi_0^{(N)}\rangle$ the d2ph-TDA leads to the following matrix elements:

$$\Sigma^{\mathrm{d2ph\text{-}TDA}}_{kk_0} = \sum_{j,a,b} \{V_{kjab}(2V_{k_0jab} - V_{k_0jba}) \times (\bar{n}_j n_a n_b + n_j \bar{n}_a \bar{n}_b) / [\omega + \epsilon_j - \epsilon_a - \epsilon_b + (\bar{n}_j n_a n_b - n_j \bar{n}_a \bar{n}_b) \Delta_{jab}]\} , \tag{6}$$

with

$$\Delta_{jab} = V_{abab} - V_{ajaj} - V_{bjbj} \, . \tag{7}$$

With the exception of the term in the denominator containing Δ_{jab}, eq. (6) is identical to eq. (5).

The denominator of eq. (6) introduces two types of poles, the so-called "affinity poles ($n_j\bar{n}_a\bar{n}_b = 1$)" and the "ionization poles ($\bar{n}_j n_a n_b = 1$)". The affinity poles are of little influence for ionizations from inner valence shell orbitals as they lie usually far apart from the corresponding orbital energies. The ionization poles are found at energies

$$\Sigma^{-}_{jab} = \epsilon_a + \epsilon_b - \epsilon_j - \Delta_{jab} \, . \tag{8}$$

Since Δ_{jab} is usually negative the onset of the inner valence shell region is shifted to lower ionization potentials compared to the order by order expansion of Σ [eq. (1)]. For the systems studied in the present paper this however, makes hardly any difference since nearly all the ligand orbitals are inner valence orbitals also if we use eq. (1).

For the outer valence shell region the d2ph-TDA usually yields the same qualitative results as the order by order expansion but from a quantitative point of view the TD-results are less favourable [2,3,17–19]. We therefore give only brief comments on these results.

3. Numerical procedure

As mentioned in the introduction, CNDO/2 wavefunctions have been used successfully in connection with the application of the Green's function approach to the direct calculation of relaxation energies of molecules consisting of light elements [16]. It is therefore, reasonable to use the same approach for transition metal containing systems where the use of ab initio wavefunctions becomes numerically extremely expensive. In the past, however, there had been difficulties with the application of CNDO-type methods to transition metal containing systems. We therefore introduced a modified version of the CNDO-formalism which since then has been successfully applied to the theoretical investigation of different aspects of such systems [15]. For the details of the method we refer to part I of this series [15a]. Here we just want to underline that the main extension, compared to the earlier work of Pople et al. [20] and of Santry and Segal [21] and to the refinements given by Blyholder [22a] and Baetzold [22b, c] is the complete decoupling of the exponents of Slater-type orbitals belonging to different angular quantum numbers l for the metal atoms. The necessary parameters, for the metals appearing in this paper (Cr, Ni) are the same as in part II [15b].

For the non-metal atoms we still use the standard CNDO/2 parameterization (a further extension, where s and p exponents are decoupled also for the second row elements, is in progress). This limits the application of our method to those ligands for which at least the sequence and the relative spacing of the high lying orbitals are reproduced sufficiently well within CNDO/2. Fortunately some of the most interesting ligands as e.g. CO or carboxylates fulfill this requirement. For complexes with such ligands our method yields not only reasonable one particle energies but also reliable electron densities.

One should however be aware of the fact that we cannot necessarily expect absolute values for the vertical ionization potentials from a perturbation treatment based on semi-empirical wavefunctions. Instead we have to discuss the obtained Koopmans' defects themselves and compare these quantities for different ionizations and for different compounds. The observed trends can then be used to interpret many body effects in connection with photoionization. The intensities in our calculated spectra are approximated by the pole strengths obtained from

$$P_{kl} = \left[1 - \frac{\partial}{\partial \omega} (\Sigma + \epsilon)_k \Big|_{\omega = \omega_{kl}} \right]^{-1} \, . \tag{9}$$

The pole strength P_{kl} is related to the squared projection of the Koopmans' state $a_k | \psi_0^{(N)} \rangle$ onto the final states $| \psi_l^{(N-1)} \rangle$. Thus the use of P_{kl} as a measure of the intensity corresponds to the assumption of independent cross sections for all orbitals considered. Since we know that the cross sections may differ considerably for different orbitals and that there is a pronounced energy dependence in some cases the above assumption strongly limits the comparability of theoretical and experimental spectra. In principle it is possible to multiply each P_{kl} by an orbital specific, energy dependent cross section, but too little is known about these cross sections to include them into the present calculations.

4. Results and discussion

Our results are shown in figs. 1–5. The energy scale in the presented spectra is positive as it is in an experimental photoemission spectrum. For the spectra based on single particle results this means that we have plotted $-\epsilon_k$. In the many particle corrected spectra obtained by inclusion of many body effects through the d2ph-TD approximation [eq. (6)], the lines are labelled by the orbital from which they gain their pole strength. Only lines with pole strength greater than 0.01 are shown.

The intensities plotted in the figures are the calculated pole strengths multiplied by the degeneracy of the corresponding level. To get an impression of what the actual spectrum should look like (in spite of the cross section problem) we have convoluted the theoretical line spectra with a lorentzian-type function of 1 eV fwhm. In our opinion, this is an appropriate type of

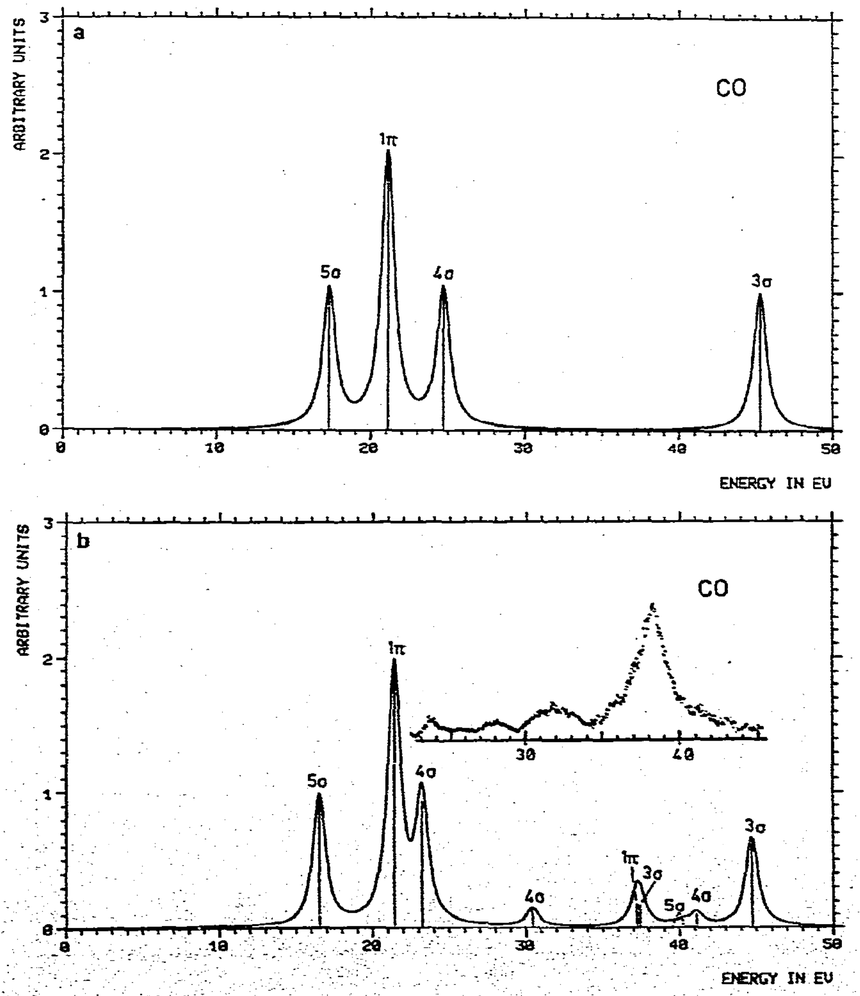

Fig. 1. Theoretical photoemission spectra for CO. (a) Koopmans' approximation; (b) many particle corrected spectrum; inset: experimental spectrum from ref. [24].

presentation, especially for the inner valence shell region, where many body effects often produce a large number of low intensity lines leading to a more or less continuous background. One has to be aware, however, that the strongly varying photoionization cross sections are not considered in such a presentation.

We first discuss the inner valence shell regions (IVSR) of the free CO molecule. The strong many body effects appearing in this region become immediately obvious if we compare the two spectra shown in fig. 1. The upper part contains the single-particle result obtained in CNDO/2 approximation. The lower part shows the result of our d2ph-TD calculation for the IVSR (above 25 eV) together with the result of the usual order by order calculation [16a] for the OVSR (below 25 eV). Several fairly intense satellites appear between 25 and 50 eV which give rise to mainly three additional bands in the many particle corrected spectrum. This is in qualitative agreement, as well with the calculation of Schirmer et al. [23], based on ab initio wavefunctions, as with the experimental observation [24] (compare inset in fig. 1b). The energy of the calculated bands in

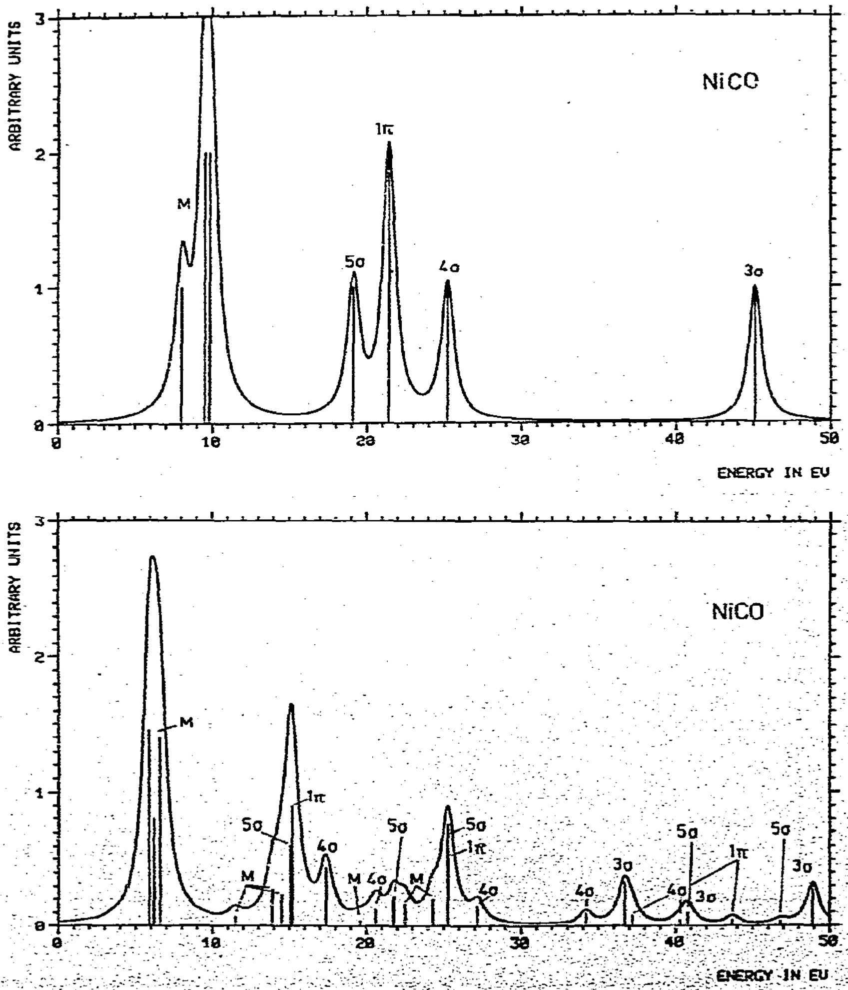

Fig. 2. Theoretical photoemission spectra for NiCO. (a) Koopmans' approximation; (b) many particle corrected spectrum.

our many particle corrected spectrum is, however, about 20% too high. This is about the same value as found for the CNDO-orbital energies if compared to those obtained from ab initio calculations [25]. We therefore conclude that for CO the most important interactions which determine the influence of many body effects are described quite well in the framwork of the standard CNDO-method. We want to mention,

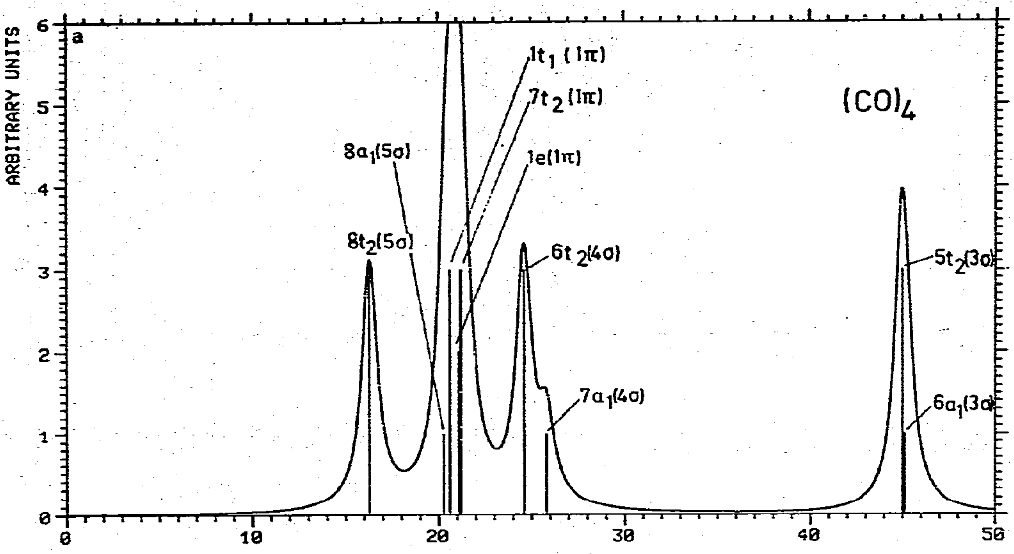

Fig. 3a.

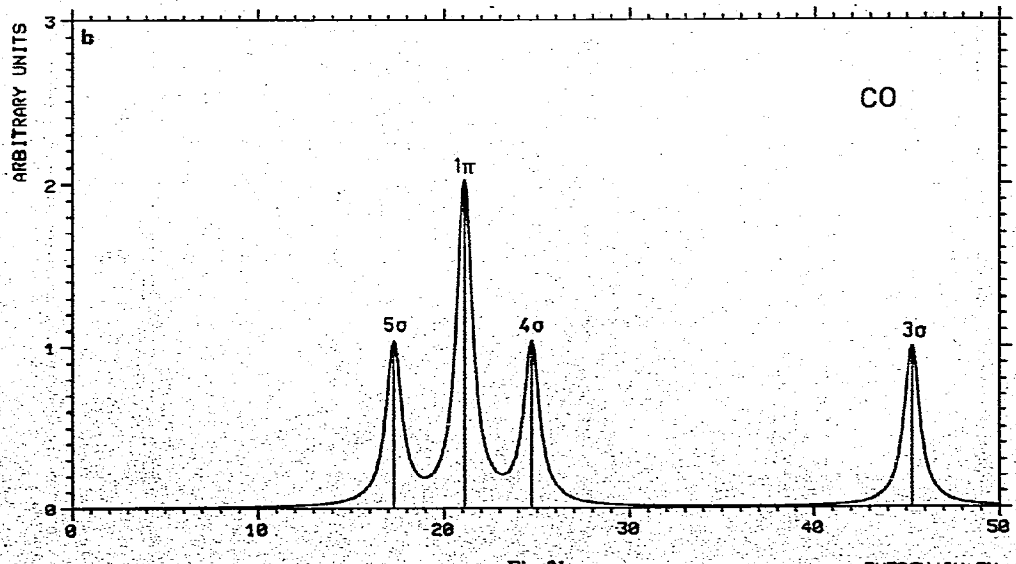

Fig. 3b.

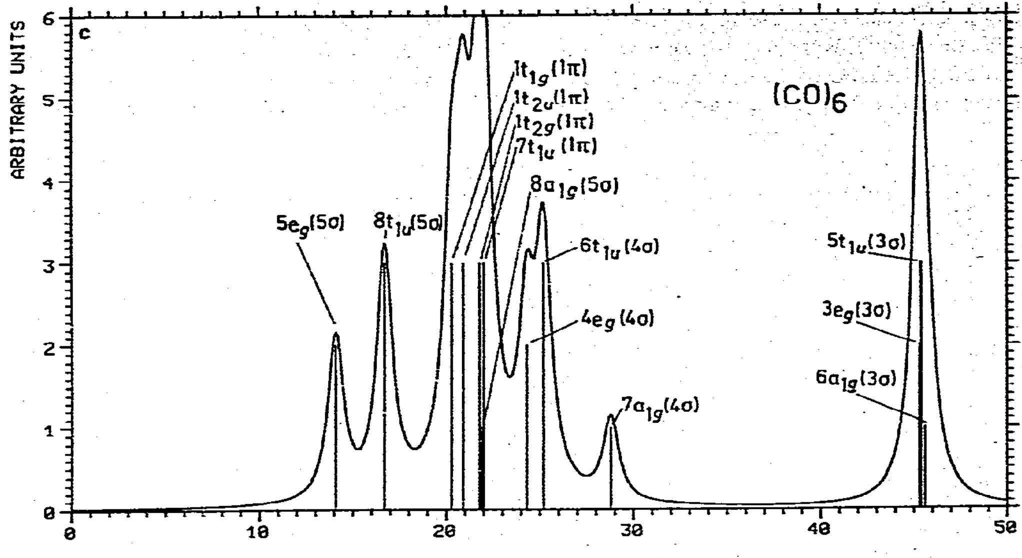

Fig. 3c.

Fig. 3. Single particle result for CO, $(CO)_4$ and $(CO)_6$. The geometry of the clusters is taken from $Ni(CO)_4$ and $Cr(CO)_6$. The orbital labelling is adjusted to the real carbonyls (see text).

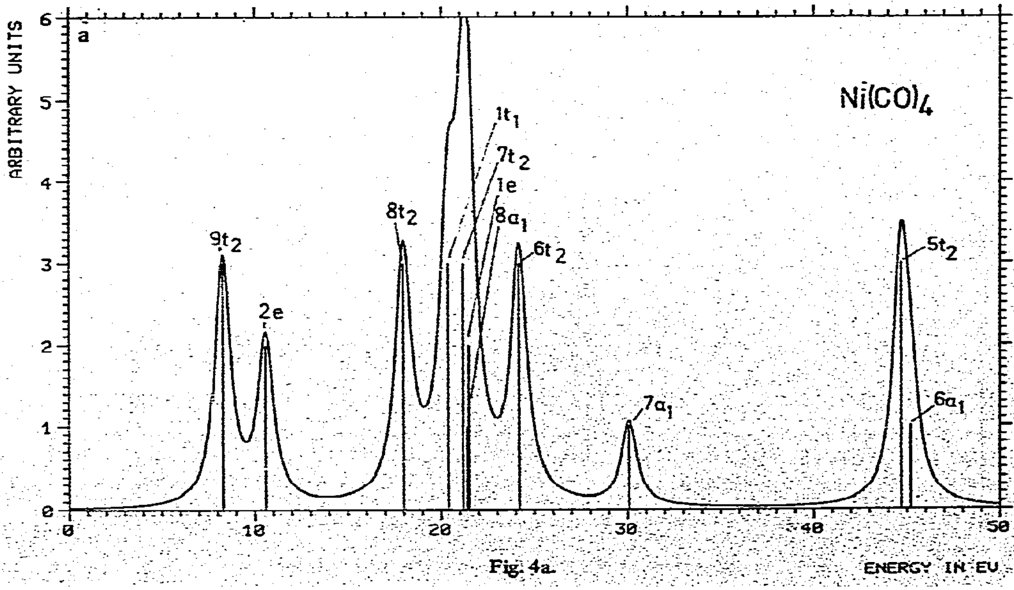

Fig. 4a.

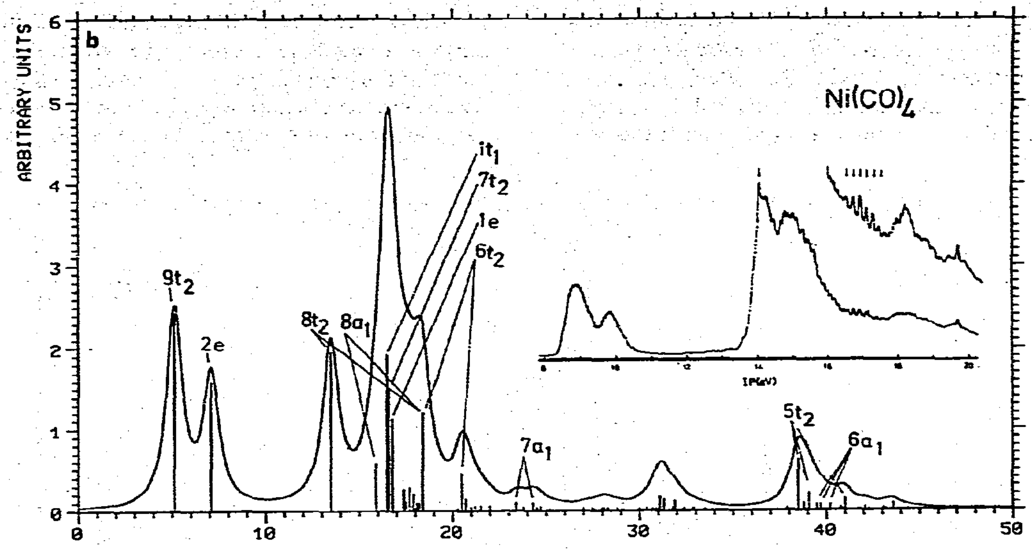

Fig. 4b.

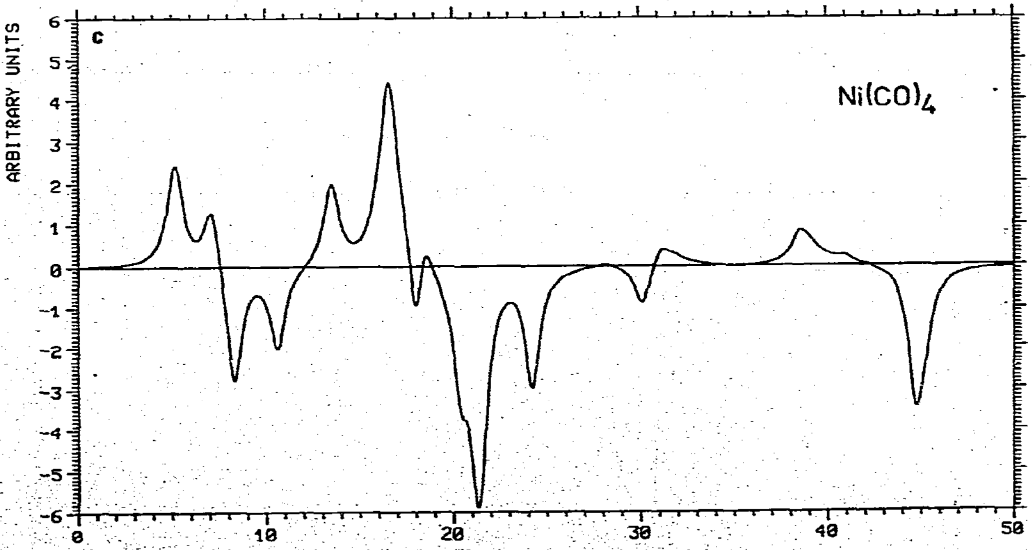

Fig. 4c.

Fig. 4. Theoretical photoemission spectra for Ni(CO)$_4$. (a) Koopmans' approximation; (b) many particle corrected spectrum; (c) difference spectrum between (a) and (b); inset: experimental spectrum from ref. [27a].

however, that this is not true in general.

Let us now turn to the model system NiCO (fig. 2). As expected from qualitative MO considerations we find four valence orbitals closely related to the orbitals 5σ, 1π, 4σ and 3σ of free CO. We therefore label these orbitals in the same way as we do for the free ligand itself. The largest stabilization among the ligand orbitals is found for 5σ, the orbital responsible for the σ-donor bond to the metal atom. Correspondingly, one d-orbital of the metal (d_{z^2}) is destabilized a bit more than the other four. If the one particle picture were applicable to the whole energy range we would have to expect a spectrum (fig. 2a) in which the ligand range – with the exception of a decrease in the distance between 5σ and 1π – is very similar to the spectrum of free CO. The many

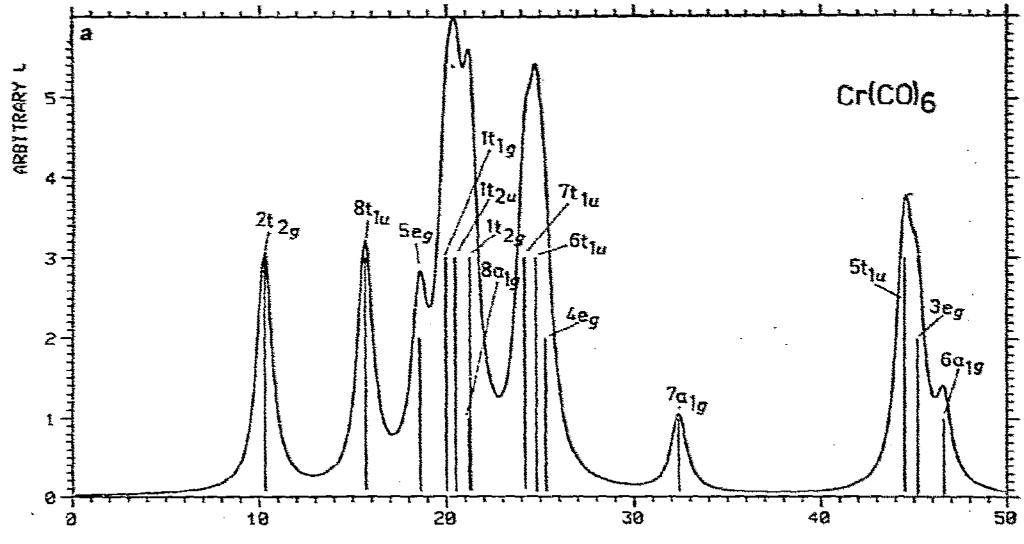

Fig. 5a.

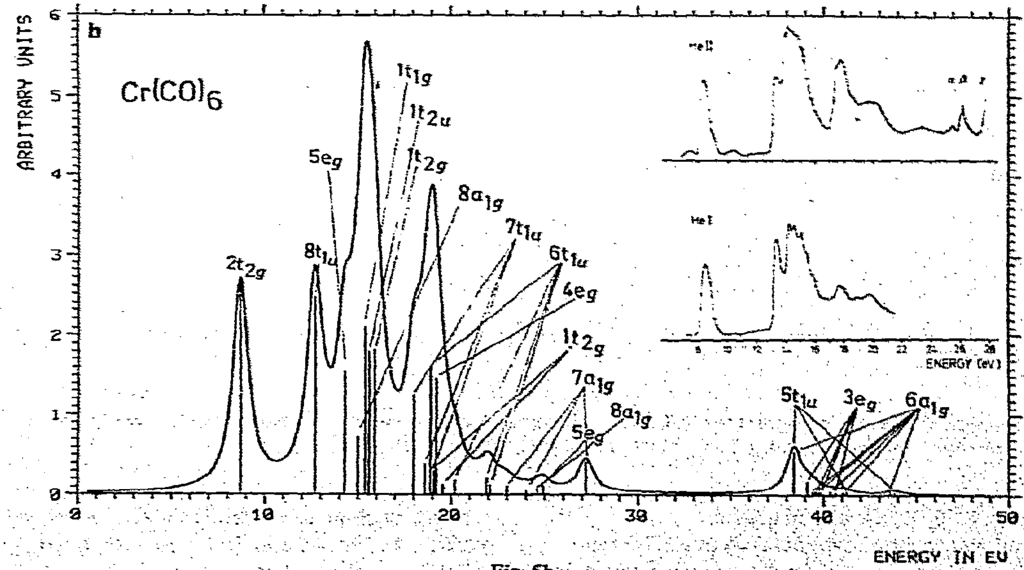

Fig. 5b

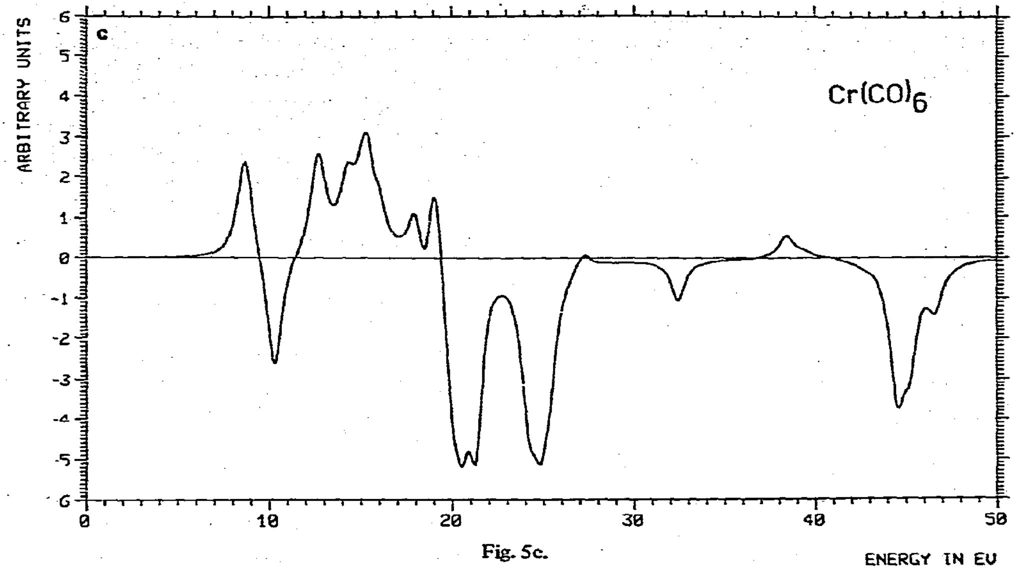

Fig. 5c.

Fig. 5. Theoretical photoemission spectra for $Cr(CO)_6$. (a) Koopmans' approximation; (b) many particle corrected spectrum; (c) difference spectrum between (a) and (b); inset: experimental spectrum from ref. [27b].

particle corrected spectrum (fig. 2b) shows, however, a completely different appearance. Especially in the ligand range this spectrum exhibits hardly any resemblance to the one expected from the one particle picture (fig. 2a). The most drastic effects are observed in the range of the 3σ ionization. In this case we do not find a peak which can be related directly to the one particle detachment. The highest pole strength found among the resulting transitions is 0.33. 3σ is, however, an inner valence shell orbital, too, in free CO and the appearance of strong many body effects is therefore not astonishing. The much more interesting part of the spectrum is the energy range between 10 and 30 eV where we expect the ionizations originating from 5σ, 1π and 4σ. These orbitals, being of outer valence shell type in the free ligand, now belong to the inner valence shell region. [For Σ^{-1} we find −16 eV following eq. (4) and −11 eV following eq. (8).] Correspondingly the many body effects are comparable to those observed for 3σ. The highest pole strengths found for the transitions originating from 5σ, 1π and 4σ are about 0.5, showing that also in this region it is only possible to correlate the final result in an approximate manner to the one particle detachments. In the case of 1π, e.g. the most intense peak is found at 15.2 eV with $P = 0.38$. The situation in this energy range is furthermore complicated by a number of satellites which originate from the metal d states.

If the above mentioned criterion of maximum pole strength is used, the bands most closely related to the Koopmans' states $a_{5\sigma}|\psi_0^N\rangle$ and $a_{1\pi}|\psi_0^N\rangle$ are found at nearly the same energy. If we further take into account that for free CO [25] CNDO/2 yields $\epsilon(1\pi)$ somewhat too low compared to $\epsilon(5\sigma)$ and $\epsilon(4\pi)$, this result is in agreement with ΔSCF- and Xα-calculations on NiCO and with the experimentally observed inversion in the Ni/CO adsorbate system [6,26]. However, as the actual position of a calculated band strongly depends on the density and nature of the poles of Σ in the vicinity of the corresponding Koopmans' state, one should be very careful not to overestimate the results obtained from such a simple model system as NiCO.

The most interesting qualitative result, obtained from our study on NiCO, is the considerable shift of the intense ionizations caused by many body effects. This shift leads to the consequence that the most intense ligand bands appear at lower ionization potentials than in free CO. This is in contradiction to the expected bond shift. For adsorbate systems it is, however, difficult to prove this result. Experimentally it is difficult to directly relate the absolute energy scale of a gas phase spectrum to the scale of a spectrum taken from a surface. Such a comparison is much for easier for the carbonyls $Ni(CO)_4$ and $Cr(CO)_6$ for which gas phase spectra are available [5c,27].

Before we present the results on the carbonyls, we want to make a short comment on the d2ph-TD result for the OVSR included in fig. 2b. The pole strengths are close to one, confirming the outer valence shell character of these ionizations. The shifts relative to the one-particle result are, however, about twice as large as those found from an order by order treatment [28]. This is mainly caused by two facts:

(i) The relative weight of second order contributions is larger in the d2ph-TDA and it is known that these contributions usually overestimate the calculated corrections in the outer valence shell region [2].

(ii) All orbitals resulting from the CNDO-calculation are taken into account in our TD-calculations whereas in the case of the order by order treatment numerical constrains usually limited the set of included orbitals.

An important qualitative result found in the order by order as well as in the d2ph-TD treatment is the reduction of d-band width due to many body effects. It is found for all three investigated species. A similar effect has been proposed recently by Penn [29] for bulk material.

To start the discussion of $Ni(CO)_4$ we first look to a hypothetic cluster of four CO molecules in the same geometric arrangement they have in the real compound. The one-particle spectrum obtained from our CNDO calculation for such a cluster is shown in fig. 3, where it is compared to the one particle spectrum of a single CO-molecule. To facilitate a comparison with $Ni(CO)_4$ the orbitals are labelled as in the real compound, this means three $a_1(s)$ and two $t_2(p)$ are added in the counting. The σ-orbitals of the CO moieties lead to symmetry adapted combinations belonging to the irreducible representations a_1 and t_2. The mixing of the three t_2 combinations originating from 5σ, 1π and 4σ is only moderate. Thus each of the resulting orbitals can be labelled by its symmetry and by its parent orbital in the free ligand. As a whole the one-particle spectrum of the $(CO)_4$ cluster closely resembles the spectrum of CO [15a].

If we now take into account the interaction with the metal atom (Ni) the situation is not changed very much (see fig. 4). As expected, all the ligand orbitals are stabilized to some extent but the overall appearance of the ligand region still exhibits a close relation to the free molecule. As discussed in an earlier paper of this series [15a] this is in full agreement with the results obtained from ab-initio calculations [30]. Again, the levels originating from 1π of free CO appear at somewhat too low energies in the CNDO result but the ordering of the different levels is essentially the same as found from the ab initio data [15a,30]. CNDO as well as ab initio calculations would predict a ligand range in the PE spectrum of $Ni(CO)_4$ similar to the spectrum of CO, but shifted to somewhat higher energies.

Inclusion of many body effects strongly alters this prediction: fig. 4b shows the d2ph-TD result obtained from our CNDO-calculations. The first two bands are again shifted too much if compared to an order by order treatment [28], but the one-particle description for this outer valence region is also valid in the TDA. The two bands are directly related to a detachment of an electron from the orbitals $9t_2$ and 2e, orbitals with predominant metal d-character.

In the inner valence shell region we observe similar drastic effects as in the case of NiCO. For most of the Koopmans' states the interaction with valence excitations is so strong that it becomes difficult to connect the resulting bands with a specific orbital. In fig. 4b only the most intense transitions are labelled according to the Koopmans' state from which they gain their intensity. For the less intense transition the corresponding information is collected in table 2.

The ligand bands which correspond to the ionizations from the orbitals 5σ, 1π and 4σ are located mainly between 13 and 19 eV in the many particle corrected spectrum. This is an average shift of about 5 eV towards lower energies with respect to the single particle result (fig. 4a) which is best seen from the difference spectrum shown in fig. 4c. It is, however, also a shift of about 4 eV in the same direction if compared to the many particle corrected spectrum of free CO (fig. 1b). This shift towards lower ionization potentials is caused by many body effects, as

Table 2

Orbital energies, many particle corrected ionization potentials and associated pole strength as obtained for $Ni(CO)_4$

Orbital	One particle energy	Corrected energy	Pole strength
$6a_1$	−45.2	44.4	0.01
		43.2	0.01
		42.3	0.01
		40.9	0.01
		40.7	0.01
		40.2	0.07
		39.7	0.07
		39.5	0.07
		38.9	0.01
		38.8	0.05
$5t_2$	−44.7	43.6	0.03
		43.1	0.01
		41.0	0.05
		40.8	0.01
		39.1	0.07
		38.8	0.03
		38.5	0.21
$7a_1$	−30.1	33.5	0.02
		32.9	0.03
		32.4	0.03
		31.8	0.04
		30.7	0.02
		29.1	0.01
		27.9	0.01
		27.6	0.01
		26.0	0.01
		24.7	0.04
		24.7	0.01
		24.3	0.1
		23.8	0.04
		23.6	0.01
		23.4	0.1
$6t_2$	−24.2	31.9	0.04
		30.4	0.01
		27.9	0.01
		20.7	0.05
		20.5	0.15
		18.4	0.39
		18.2	0.03
		17.7	0.02
		17.5	0.03
		17.4	0.09
1e	−21.5	42.1	0.02
		31.3	0.07
		30.9	0.01
		28.3	0.01
		21.0	0.02
		18.2	0.01
		18.1	0.05
		16.8	0.57
$8a_1$	−21.4	32.8	0.01
		32.3	0.01
		31.6	0.01
		25.7	0.01
		21.4	0.01
		20.5	0.02
		20.3	0.03
		18.4	0.06
		18.2	0.01
		15.9	0.59
$7t_2$	−21.4	37.9	0.01
		31.1	0.05
		28.8	0.01
		28.3	0.01
		20.9	0.03
		20.7	0.01
		17.9	0.07
		16.6	0.5
$1t_1$	−20.4	42.1	0.01
		31.1	0.06
		30.0	0.01
		28.1	0.01
		17.7	0.1
		17.5	0.04
		16.5	0.64
$8t_2$	−18	28.0	0.01
		18.4	0.04
		18.0	0.01
		13.5	0.65
2e	−10.7	31.0	0.01
		25.2	0.01
		24.5	0.02
		21.5	0.03
		7.1	0.8
$9t_2$	−8.3	27.0	0.01
		22.0	0.02
		21.2	0.02
		5.1	0.81

in the case of the model system NiCO and has nothing to do with destabilization of orbitals.

The experimental spectrum (inset in fig. 4b) [27a] shows an intense band between 13.5 and 16.5 eV and some additional week structures between 17.5 and 20 eV. The first part of the intense band (13.5 to 14.5 eV) is most likely connected with an ionization from the orbital $8t_2$, an orbital which originates from 5σ of free CO. The region between 14.5 and 16.5 eV should – by comparison with the theoretical results – be attributed to a superposition of a number of different transitions, most of which are strongly influenced by many body effects. The weak band observed around 18 eV in the experimental spectrum was assigned to ionizations from $6t_2$ and $7a_1$ (resulting from 4σ of CO) by Hillier et al. [27a,30] in the framework of the one particle picture. From our calculation it is more likely that the 18 eV band corresponds to the structure found at about 20.5 eV in the many particle corrected spectrum. Due to the distribution of the $6t_2$ intensity to several final states this band should not be directly related to the orbital $6t_2$. The intensity of $7a_1$ is also distributed to several final states and it is likely that the corresponding band cannot be discerned from the large number of satellites following the intense bands found around 17 eV in the theoretical spectrum.

Between 25 and 40 eV two further bands are predicted in the theoretical spectrum but up to now there is no detailed experimental investigation available for this energy region.

We now turn to our final example $Cr(CO)_6$. The one-particle spectrum of the pure ligand sphere is shown in fig. 3. As in the case of $Ni(CO)_4$ the numbering of the orbitals of the ligand cluster is adjusted to the final carbonyl by adding three a_{1g} (for 1s, 2s and 3s of Cr) and two t_{1u} (for 2p and 3p of Cr). Again, we find only little mixing of σ and π-contributions in the three t_{1u} orbitals and it is possible to assign all the levels of the $(CO)_6$ cluster by their symmetry and their parent orbitals in the free molecule. Interaction with the metal atom does not change the general appearance of the one particle spectrum very much (fig. 5a). The most pronounced effects are found for the levels $5e_g$, $7t_{1u}$ and $7a_{1g}$ which are considerably stabilized. A comparison with ab initio data [30] shows that this stabilization is overestimated for $7a_{1g}$ and $5e_g$. Taking this into account we would expect mainly three bands in the ligand range if the spectrum would be determined by the one particle result.

Different to NiCO and $Ni(CO)_4$ this prediction is not changed if we include many body effects (fig. 5b). Again the whole ligand range is shifted to lower energies (compare fig. 5c) but the overall structure is conserved. For the first seven transitions the pole strength exceeds 0.6 showing that these transitions can be reasonably well described in the one particle picture in spite of the fact that they originate from inner valence shell orbitals. Correspondingly the number of satellites, the pole strength of which exceeds 0.01 is considerably smaller than in $Ni(CO)_4$. The threefold structure predicted in the many particle corrected spectrum is in agreement with experiment (compare inset in fig. 5b). The intensity enhancement found for the 18 eV band in the HeII-spectrum makes it very probable that this band does not result only from satellites [27b]. Relative to the other transitions, those connected with orbitals originating mainly from π-orbitals of the free ligand are predicted at somewhat too high energies. This is again due to the overestimation of the orbital energy of 1π in CNDO/2.

Above 19 eV extended structure is found in the HeII spectrum [27b] with maxima at about 19.9 and 23.4 eV. The band observed around 20 eV may well be attributed to the satellite peak found at 22 eV in the many particle corrected spectrum.

Contrary to the energy range where we find the ionizations connected with the detachment of an electron from orbitals evolving from 5σ, 1π and 4σ of the free ligand, strong many body effects are again found in the 3σ range. Only a weak intensity band is predicted to appear at 7 eV below the peak expected in one particle approximation. A band is observed at about 35 eV in the X-ray excited spectrum [5c]. This band was already assigned by Hillier et al. [30] to the orbitals $5t_{1u}$, $3e_g$ and $6a_{1g}$ (found around 43 eV in the ab initio calculation) but without any explanation of the 8 eV shift.

Taken as a whole, the induction of satellites in $Cr(CO)_6$ is less pronounced than in the other investigated system. If one thinks of the unoccupied d-orbitals in $Cr(CO)_6$, which give rise to fairly low lying d → d excitations this might be surprising, but our investigation showed, that these excitations do not couple to the one-electron detachments from the ligand orbitals.

5. Conclusions

In transition metal carbonyles and also in CO adsorbates, the orbitals originating from 5σ, 1π and 4σ of CO are no longer outer valence shell orbitals as in the free ligand but belong to the inner valence shell region. This leads to the consequence that the one particle picture which is well applicable to the first three ionizations of CO is not necessarily applicable to the ligand range in the PE spectra of the complexes. Strong many body effects are observed in this energy range due to the energetic neighbourhood of excited configurations. Although the details in the results depend on the energy of these configurations and therefore on the parameterization of a semi-empirical method like CNDO the following generalizations should be independent from the specific numerical results:

(i) The ligand bands are shifted considerably towards lower energies. This shift is usually larger than the shift observed for the outer valence shell ionizations thus reducing the gap between d and ligand-range. The barycenter of the ligand bands is now found at lower energies than that of free CO in agreement with the experimental findings but in contradiction to simple orbital considerations.

(ii) In some cases many body effects become so strong that the one-to-one connection between photoemission bands and single orbitals – always valid in the outer valence shell region in spite of more or less pronounced relaxation shifts – gets lost. Among our examples such situations were especially found in NiCO and $Ni(CO)_4$.

From these two results it becomes obvious that a Koopmans-type of interpretation is not always appropriate to analyse the ligand range of a carbonyl complex or an adsorbate. Also if it is possible to establish a connection between observed bands and certain orbitals by variation of excitation energy or by angular dependence this does not always reveal the expected information on the ordering, spacing and actual position of the parent orbitals. In the model system NiCO, e.g. the actual position of the bands attributed to 5σ and 1π is strongly influenced by many body effects.

The results obtained from our three examples also show that it is difficult to extrapolate the influence of many body effects even in a series of closely related compounds. The many body effects were found to be strong in NiCO and $Ni(CO)_4$ but much less important in $Cr(CO)_6$. A similar result may be found if we go from NiCO to more realistic models of adsorbates containing more than one metal atom. Results on model systems like NiCO must therefore be considered only as a first step beyond the simple application of the single particle picture towards a better understanding of adsorbate systems.

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