CALCULATION OF TRANSITION METAL COMPOUNDS USING AN EXTENSION OF THE CNDO FORMALISM

VII. Simple interpretation of many-body effects in the core-photoionization of adsorbates by the study of CO/Ni and N_2/Ni model systems

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Satellite structure which accompanies core ionization in free and coordinated molecules like CO and N_2 is studied by means of the Green function formalism starting from CNDO-type wavefunctions. Coordination is approximated by the simple model systems NiCO and NiN_2. The latter is discussed in linear and triangular arrangement. In spite of their limitations these models are well suited to explain some of the most important experimental facts observed in comparison between free and coordinated ligands, especially the appearance of a fairly intense satellite in the vicinity of the main peak in the coordinated systems. It turns out that the actual habitus of the satellite structure is not only determined by the relative energy of the different valence excitations but also by the different interaction between Koopmans state and valence excited configuration. This result is discussed in comparison to other theoretical interpretations. The problem of delocalized versus localized core hole states in systems like N_2 or triangular NiN_2 is also dealt with.

1. Introduction

In Part VI of this series [1] we have studied the influence of many-body effects in the valence shell photoionization of small molecules (CO, N_2 etc.) which are bound to a metal atom by a coordinative bond. In this paper we want to extend these investigations to the core region of such systems. Experimentally the appearance of pronounced satellite structure in the C 1s, N 1s and O 1s spectra of a large variety of CO and N_2 adsorbates [2] and of transition metal carbonyls is a well established fact. The observed satellite structure differs not only from the one found for the free ligands but also among different adsorbates. This led some authors to speculate about connections between the occurrence of satellite structure and the bond strength of the metal–adsorbate bond [2e].

A first theoretical explanation of these experimental findings was given by Schönhammer and Gunnarson [3] who based their argumentation on an idea, outlined earlier by Lang and Williams [4]. The latter authors developed an interpretation for core ionizations from adsorbates quite different from the simple image

charge model. Due to the electrostatic potential of the core hole, which is created in the adsorbate by photoemission, unoccupied levels of the neutral system are pulled down below the Fermi level, so that the charge is screened by filling up these levels. Following these ideas, Schönhammer and Gunnarson [3] performed model calculations which showed that the satellite structure in core spectra may indeed be explained by this type of relaxation mechanism. They further pointed out that there should exist a strong dependence of the habitus of the spectrum in the core region on the coupling between the core hole and the empty level of the adsorbate. Depending on this coupling, situations may be found in which the first band (with respect to increasing energy) in the core spectrum is related to a final state where considerable negative charge is transferred from the metal to the adsorbate (screened state).

If this kind of argumentation is compared to the one developed in our preceding study of outer and inner valence shell ionizations [1], striking similarities are found: As outlined in Part VI, the appearance of satellite structure may be understood in terms of intensity borrowing from Koopmans hole states via intermixing one-particle—two-hole configurations. Due to electron interaction terms, specific for the orbital in which the primary hole is created, it is possible that the energy of a 1p2h configuration is lower than the energy of the interacting Koopmans state. Since the most important of these configurations result from charge transfer excitations from occupied metal to unoccupied ligand orbitals, these considerations are equivalent to those proposed by Lang and Williams [4]. In the framework of the many-particle formalism used in ref. [1], the Lang—Williams mechanism is, however, only a special case. Depending on the relative energy of the intermixing configurations and on the magnitude of their respective interactions, it is also possible that other relaxation mechanisms dominate the core spectra.

To study in how far the treatment and especially the simple interpretation scheme which we have applied successfully to the inner valence shell region of photoemission spectra of transition metal containing systems [1,5] is also applicable to the core region of these spectra, we have investigated the same model system as in Part VI, namely a linear NiCO cluster and a linear as well as a triangular arrangement of NiN_2. For the latter system an interesting question arises concerning the localization of the N 1s core hole: What are the consequences with respect to a many-particle description of the resulting ion states? From physical intuition the criterion for the applicability of either description is obvious. If the hopping time for the core hole delocalization is large relative to the time scale of the screening process, we are confronted with a localized hole and vice versa. The work of Bagus and Schaefer [6] and Schwarz [7] brought about that a ΔSCF calculation, which starts from a localized core hole, thus implicating a break of symmetry, yields usually better results on relaxation shifts than a calculation based on a delocalized description. With respect to this, Lozes et al. [8] have claimed that besides of the shift comparison the existence of a localized or delocalized core hole should be experimentally distinguishable via the spectral habitus of the satellite

region. We come back to this suggestion at the end of the present investigation where we try to estimate the occurring differences on the basis of equivalent core considerations.

Since we base our investigations mainly on a valence electron method, it is first necessary to explain how we treat the core electrons in such a framework and what the implications for the many-body calculations will be (section 2). In sections 3 and 4 we then present our results and in section 5 we discuss the connections between our model systems and real adsorbates. In section 6 we finally discuss some experimental implications.

2. Theory

The basic data necessary for our many-particle calculations on transition metal containing systems are obtained from the extended CNDO formalism, introduced in Part I of this serties [9]. As only valence electrons are treated explicitly in this method, it does not contain information on core ionization potentials in a straight forward manner. CNDO results have been applied, however, to the indirect calculation of relative chemical shifts of core ionizations of first and second row elements, using either valence potential correlations of the Gelius-type or more sophisticated equivalent core approximations [10]. The success of these applications underlines the reliability of the underlying assumption that at least in carbon, nitrogen, and oxygen the core orbital can be well regarded as unpolarizable. This implies, that to a good approximation, the interaction between core and valence electrons can be described by Coulomb interactions only.

The simplest way to include core orbitals into many-particle calculations which are based on CNDO-type wavefunctions is to enlarge the coefficient and electron interaction matrices needed for the evaluation of the molecular integrals

$$V_{ijkl} = \langle \phi_i(1)\, \phi_j(2)\, |r_{12}^{-1}|\, \phi_k(1)\, \phi_l(2) \rangle \,. \tag{1}$$

For the coefficient matrix C this is easy since we know from ab initio calculations that the core orbitals can be regarded as nearly purely atomic as long as we do not have cores which are equivalent by symmetry. In Nesbet's calculation on CO [11], for example, the core orbitals originate to 99% from the atomic 1s functions and no coupling between carbon and oxygen 1s orbitals is found. Thus, neglecting the very small mixing between core and valence orbitals, we take the coefficients of the interesting core orbitals simply as 1 in the case of non-equivalent cores. In the case of equivalent cores, like in N_2, the coefficients are fully determined by symmetry. Thus the coefficient matrix has the following structure:

$$\begin{array}{|c|c|} \hline C_{val} & 0 \\ \hline 0 & C_{core} \\ \hline \end{array} \,. \tag{2}$$

C_{val} is the coefficient matrix obtained from the CNDO calculation. The rank of C_{core} is determined by the number of interesting core levels.

The corresponding electron interaction matrix γ has the following form

$$\begin{array}{|c|c|} \hline \gamma_{val} & \gamma_{int} \\ \hline \gamma_{int} & \gamma_{core} \\ \hline \end{array} , \tag{3}$$

where γ_{val} is again the matrix found in the underlying CNDO calculation. The one-center core—core and core—valence integrals appearing in γ_{core} and γ_{int} are calculated from Slater orbitals for which the exponents are derived from the Slater rules [12]. This leads to

$$\gamma_{1s1s} = \tfrac{5}{8}\, \zeta_{1s} \,, \qquad \gamma_{2s2s} = \tfrac{279}{768}\, \zeta_{2s} \,, \qquad \gamma_{1s2s} \approx \tfrac{1}{2}\, \zeta_{2s} \,. \tag{4}$$

The two-center integrals are then evaluated by means of the well known Ohno formula [13]. The numerical values obtained in this way are in quite good agreement with those found in ab initio calculations [14]. In spite of this fact our treatment will probably lead to an overestimation of the core—valence interaction due to the application of the ZDO approximation. This approximation which is used in the derivation of eq. (6) as well as in the evaluation of the V_{ijkl} certainly leads to a partial neglect of screening effects. In this connection we refer to the well-known reduction of γ integrals in the Pariser—Parr—Pople method [15]. It is, however, not our aim to reproduce the experimental data as close as possible. Instead we want to provide a theoretical analysis of the general trends in core ionizations from free and coordinated systems like CO or N_2. Such an analysis should be possible also with unscaled γ integrals.

The coefficients for the valence orbitals are calculated as described in Part I of this series [9] where all the necessary formula are given. The parameters used are the same as introduced in Part II [16] and consequently applied in all succeeding papers.

To calculate many particle effects in the core region we start, as in our preceding papers [1,5], from the diagonal form of the Dyson equation

$$\omega - \epsilon_c - \Sigma_{cc}(\omega) = 0 \,, \tag{5}$$

where c now denotes a specific core orbital. The orbital energy of the core orbital (ϵ_c), which does not appear in the CNDO calculation, also if it is extended in the above mentioned way, can be taken from an ab initio calculation. As we will see later on, the absolute value of ϵ_c, is, however, of little interest.

The diagonal element Σ_{cc} of the self-energy part Σ is calculated by application of the diagonal two-particle—hole Tam—Dancoff approximation (d2ph-TDA) [17] as in Part VI of this series [1]. In case of describing the core orbital by a single atomic orbital with coefficient 1 the expression for Σ_{cc} is strongly simplified by consequent application of the ZDO approximation: From all molecular integrals V_{cjab} appearing in the general diagonal term Σ_{kk_0} (eq. (4) in Part VI) only those

with $a = c$ are different from zero. The contributions to Σ_{kk_0} which result from the affinity poles of Σ (the last three terms of eq. (VI.4)) vanish, since the occupation number n_a is zero for these terms and therefore $c = a$ is impossible. In addition to this formal consequences of the ZDO approximation the neglect of these terms is also plausible with respect to the large energy separation between core orbital energies and electron affinities.

For the core—valence interaction in the remaining three terms of Σ_{cc} we have to consider the following integrals:

V_{cjba} ,   with $\bar{n}_j = 1$ and $n_a = n_b = 1$.

These matrix elements are different from zero only if a denotes a valence orbital and if at the same time $b = c$.

Taking this into account the diagonal element Σ_{cc} takes the form

$$
\Sigma_{cc}(\omega) = \sum_{\substack{\bar{n}_j=1,\,n_a=1 \\ a:\,\text{valence}}} \frac{\frac{1}{2}\,V_{cjca}^2}{\omega - \epsilon_c + \epsilon_j - \epsilon_a + (V_{caca} - V_{cjcj} - V_{ajaj} + \frac{1}{2}V_{aajj})}
$$
$$
+ \sum_{\substack{\bar{n}_j=1,\,n_a=1 \\ a:\,\text{valence}}} \frac{\frac{3}{2}\,V_{cjca}^2}{\omega - \epsilon_c + \epsilon_j - \epsilon_a + (V_{caca} - V_{cjcj} - V_{ajaj} + \frac{3}{2}V_{aajj})}
\tag{6}
$$

If the V_{ijkl} in the denominator are neglected, eq. (6) becomes equivalent to the second order result of the usual order by order expansion [18].

In the case of an A—A molecule like N_2 a somewhat more complicated expression is obtained since there remains an additional summation over the symmetry equivalent core orbitals [19]. Due to the very small overlap between core orbitals located at different atoms the numerical results are, however, nearly the same if we use localized core orbitals instead of delocalized ones [19]. At this point it should be clearly recognized that the use of localized core orbitals for A—A molecules has nothing to do with the possible appearance of a localized core hole in the final state. For a finite system any perturbation treatment which starts from a symmetric initial state can only lead to symmetric final states as long as we do not introduce unsymmetric external forces.

To derive at least an estimate for the effects which have to be expected in case the symmetry is really broken in the ionized state, we use a type of equivalent core approximation [10] to describe the localized core hole. NO^+, e.g., can be regarded as a "localized model" for N_2. Due to the change in symmetry the results should be different, especially if we consider the spectral habitus in the satellite region. How large these differences are and whether it is possible to discern localized and delocalized core holes by comparison of calculated and experimental core spectra will be discussed at the end of sections 3 and 4, respectively.

The results of our calculations are presented in a similar manner as in Part VI [1]: We first discuss the uncoordinated (section 3) and then the coordinated systems (section 4).
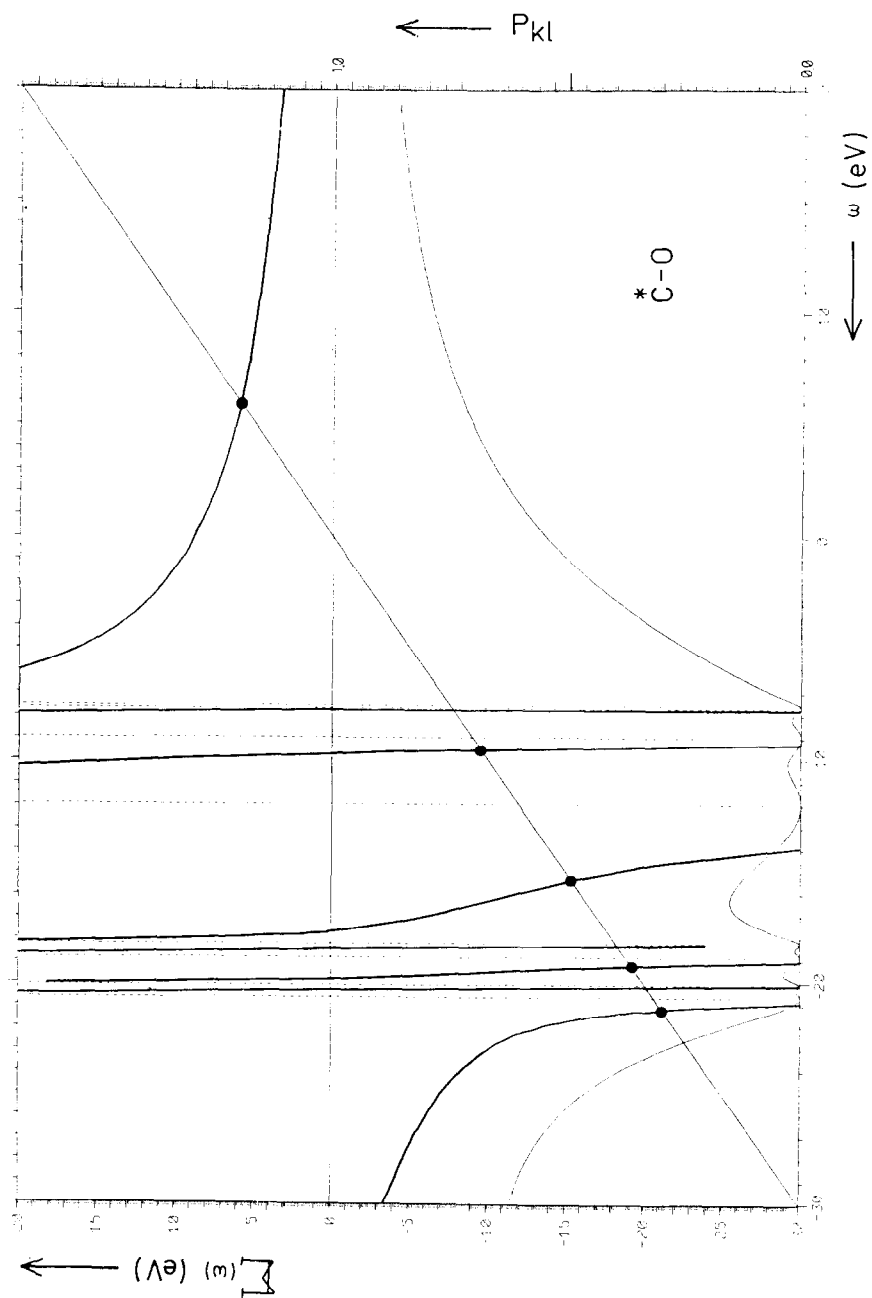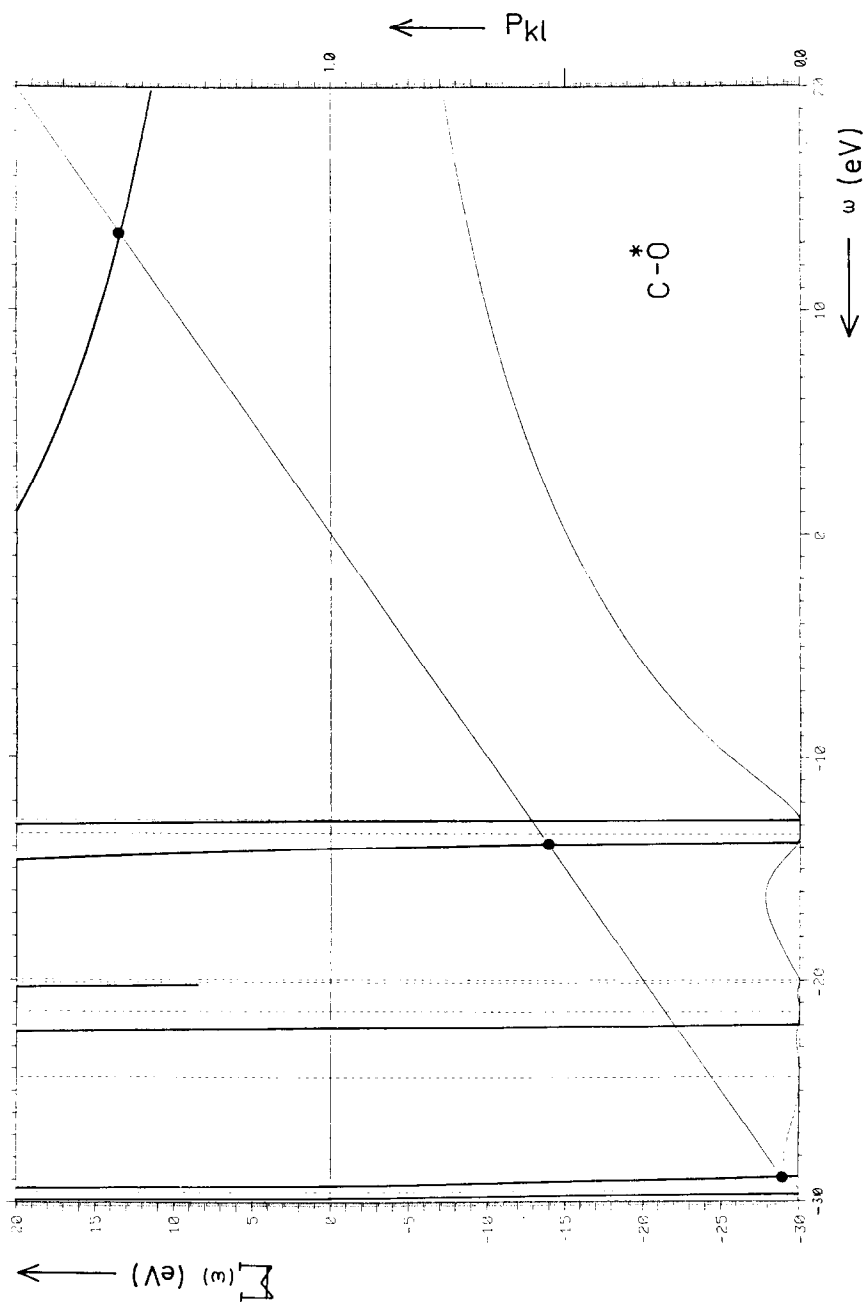
Fig. 1. Graphical solution of the Dyson equation for CO. The asterisk indicates the considered core hole.

3. Results on uncoordinated systems

First we look at the free CO molecule, where we separately consider a carbon and an oxygen core hole. Fig. 1 contains the graphical solution of the Dyson equation for both cases. The energy of the core orbital is set to zero, since neither the satellite structure nor the relaxation shift depends on the absolute value of ϵ_c. This is easily seen, if we introduce a new "relative" variable $X = \omega - \epsilon_c$ in eq. (6). Table 1 collects the important numerical data together with the interacting configurations responsible for the most pronounced satellites. To simplify matters, we only give the configuration energies which are obtained if the exchange interaction is neglected. In the actual calculations, this interaction is, however, taken into account.

For the carbon core hole the situation is best described by a main peak, corresponding to the relaxed (5 eV) Koopmans state which, at the high binding energy side is followed by weak structures starting at about 20 eV apart from the main peak (see fig. 2a). With respect to monopol selection rules the configurations which give rise to the most intense satellite structure correspond to $\sigma\sigma^*$ and $\pi\pi^*$ valence excitations originating from the outer valence orbitals of CO.

The results obtained for the oxygen core hole is also shown in fig. 1. In relation to the unrelaxed Koopmans state the energetic position of the poles of Σ is nearly the same as in the case of the carbon hole state. The main satellites also originate from the same valence excitations. We find, however, a considerable larger relaxation shift for the Koopmans state with the hole in O 1s than for the one with the hole in C 1s. This leads to an increased separation between main peak and satellite region of about 25 eV (fig. 1b).

The experimental core ionization spectra for C 1s and O 1s [20,21] are reproduced in fig. 2. Both spectra exhibit a strong main peak and only very low intense satellite structure. While the satellite structure is well resolved in the available C 1s spectrum [20], the only up to now published O 1s spectrum [21] is of much lower quality so that the individual satellites are not resolved. For both core ionizations

Table 1
Characteristic data for CO (see text)

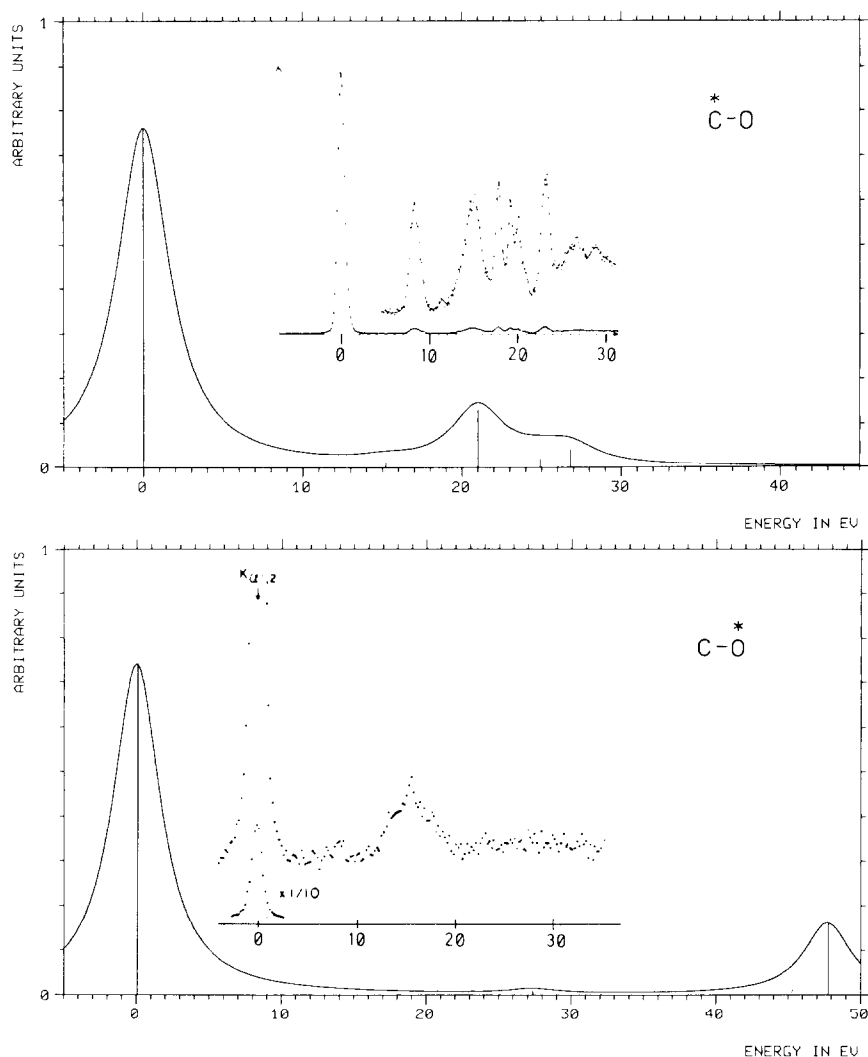| Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
C 1s	$2\pi\,1\pi^{-1}\,1s_C^{-1}$	7.5	6.3
	$6\sigma\,5\sigma^{-1}\,1s_C^{-1}$	17.9	2.7
	$6\sigma\,4\sigma^{-1}\,1s_C^{-1}$	19.8	2.8
O 1s	$6\sigma\,5\sigma^{-1}\,1s_O^{-1}$	12.5	5.8
	$2\pi\,1\pi^{-1}\,1s_O^{-1}$	19.9	18.6
	$6\sigma\,4\sigma^{-1}\,1s_O^{-1}$	29.3	5.6

Fig. 2. Many-particle corrected and experimental [19,20] photoemission spectra of CO. The theoretical spectra are obtained as a super position of ionization peaks resulting from the labelled intersection points of fig. 1, convoluted with a Lorenzian curve of 2 eV half width.

the intensity of the main peak is much larger than the intensity of the satellites. This corresponds well to our theoretical results. For the C 1s ionization spectrum there exists an assignment of the satellite structure which is based on X_α-SW calcualations on N_2 [20,21]. In agreement with our results this calculation assigns that part of the satellite structure next to the main peak to $\sigma\sigma^*$ and $\pi\pi^*$ valence excita-

tions. Those structures at larger separations from the main peak are assigned to excitations of mainly Rydberg-type. Such excitations cannot be included in a calculation operating with a minimal basis and CNDO is therefore not able to deliver information on these satellites. In addition 3h2p configurations should become more important with increasing separation from the main peak.

Another artefact appearing in CNDO-based calculations on core hole ionizations is also due to the minimal basis used. It gets special importance in the case of small and highly symmetric molecules. From fig. 2 one finds that the pole of the Green function resulting from the lowest lying configuration has a rather large pole strength (compare especially the calculated O 1s spectrum). This pole would not be the last one, if the basis of the SCF calculation would have been larger. Such a basis would lead to an increased slope of Σ in the neighbourhood of the above mentioned pole, thus reducing its pole strength. This should be remembered in the discussion of relative shake-up intensities obtained from this type of calculations.

The most important discrepancy between our results and the experimental spectra is the too large separation between main peak and satellite structure onset. Due to the expected overestimation of the core—valence interaction discussed in the previous section, this is not astonishing. In spite of this overestimation, we have used unscaled γ integrals, since the essential results of our investigations do not depend on such a scaling. To demonstrate that this is true and that a better quantitative agreement with experiment can be achieved with scaled electron interaction integrals, we present the results of such a calculation together with the conclusions (fig. 9).

The second case to be studied is N_2, a prototype of an A—A molecule. We first go through the same type of calculations as on CO and then briefly discuss the possible influence of a localized core hole.

Table 2 summarizes the numerical data. The situation which we meet for N_2 is equivalent to the one found for CO. This is especially true with respect to the energetic position of the intermixing configurations and the fact that they correspond to $\sigma\sigma^*$ and $\pi\pi^*$ valence excitations. Though gerade(g)—ungerade(u) transitions should not show up in A—A molecules with respect to monopol selection rules, one should not be confused by their appearance in the present situation. A $g \rightarrow u$ valence excitation in an ion for which the core hole is of g-symmetry may for

Table 2
Characteristic data for N_2 (see text)

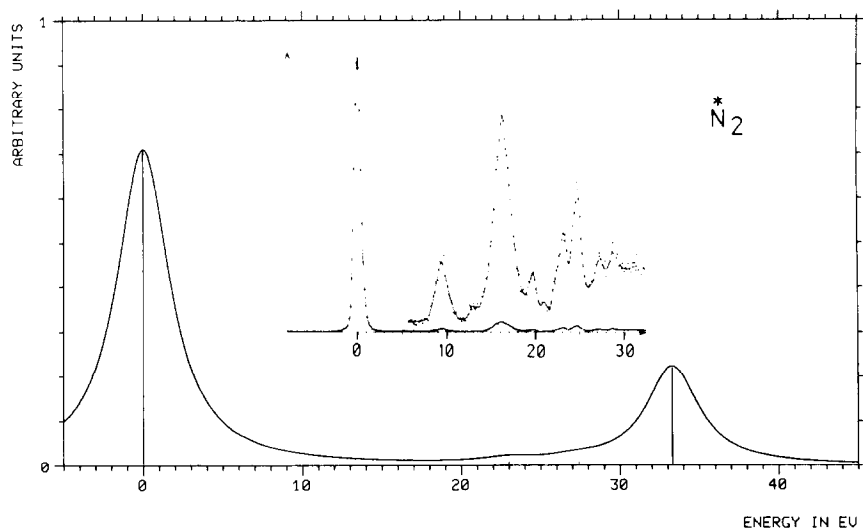| Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
N 1s	$6\sigma 5\sigma^{-1} 1s_N^{-1}$	16.8	5.2
	$2\pi 1\pi^{-1} 1s_N^{-1}$	10.4	13.9

Fig. 3. Many-particle corrected and experimental [19] photoemission spectrum of N_2.

instance couple to a Koopmans state of u-symmetry thereby satisfying the selection rules. In contrast to CO, the configurations originating from the $4\sigma \rightarrow 6\sigma$ excitation do not couple to the Koopmans state in N_2. This is due to the molecular symmetry and the use of equal exponents for s and p orbitals in CNDO/2 [23]. A comparison
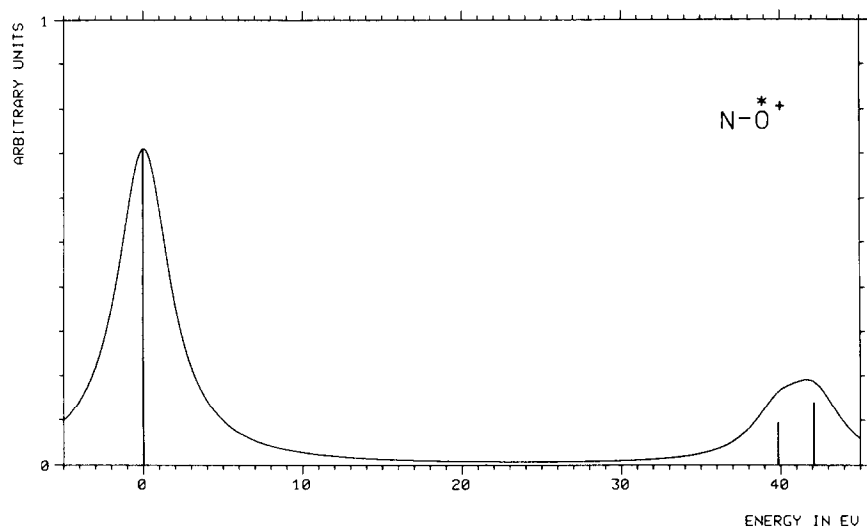

Fig. 4. Many-particle corrected photoemission spectrum for an oxygen core hole in NO^+.

Table 3
Characteristic data for NO^+ (see text)

Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
N^* 1s	$6\sigma 4\sigma^{-1} 1s_{N*}^{-1}$	27.3	2.8
	$6\sigma 5\sigma^{-1} 1s_{N*}^{-1}$	16.5	7.0
	$2\pi 1\pi^{-1} 1s_{N*}^{-1}$	14.3	17.0

to the experimental spectrum of N_2 (fig. 3) [20] brings about the same drawback of the calculated shake-up energies, being too much separated from the main peak.

So far, we have treated both nitrogen centers as indiscernable with respect to electron interaction, when an electron is removed from a core orbital. This situation is typical for a delocalized core hole, where the global symmetry of the molecule is conserved. By creation of a localized core hole the symmetry is broken, since the centers differ with respect to electron interaction. In the equivalent core approximation, mentioned in section 2, the most reasonable model for N_2 with a localized core hole is the isoelectronic system NO^+, where one nitrogen is substituted by an oxygen atom, thereby increasing the core charge by a single unit. We have calculated the NO^+ molecule using the Green function method and came to the results shown in fig. 4 and table 3. Although the general habitus of the spectrum and the interpretation of the admixing configurations are similar to those obtained for a delocalized core hole in N_2, the following differences should be recognized:
(i) The relaxation shift of the Koopmans state increases to a value between oxygen in CO and nitrogen in N_2.
(ii) The shake-up region is influenced by the appearance of new poles of Σ which result from the break of symmetry. This is a general result not depending on the actual parameters.
(iii) The distance between main peak and satellite structure onset is increased.

The statement (i) is in agreement with the findings from ΔSCF calculations that the relaxation shifts are larger for the system with the localized core hole. Usually these calculations are also in better agreement with experiment [6,7]. The most interesting result is, however, that this simple calculation confirms the claim by Lozes and coworkers [8] that localized and delocalized ionizations should be discernable via the investigation of the shake-up structure.

4. Results on coordinated systems

If the theoretical spectra obtained for the model systems NiCO and NiN_2 (figs. 6, 8 and 9b) are compared with the spectra of the free ligands (figs. 2 and 3b) one striking difference becomes immediately obvious: A satellite turns up which lies

Table 4
Characteristic data for NiCO (see text)

Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
C 1s	$S\ 4\sigma^{-1}\ 1s_{\bar{C}}^{1}$	27.1	4.9
	$6\sigma\ 4\sigma^{-1}\ 1s_{\bar{C}}^{1}$	22.0	1.4
	$S\ 5\sigma^{-1}\ 1s_{\bar{C}}^{1}$	21.6	5.4
	$6\sigma\ 5\sigma^{-1}\ 1s_{\bar{C}}^{1}$	18.1	4.4
	$2\pi\ 1\pi^{-1}\ 1s_{\bar{C}}^{1}$	8.9	9.2
	$S\ \sigma_{\bar{M}}^{1}\ 1s_{\bar{C}}^{1}$	−0.2	0.9
	$2\pi\ \pi_{\bar{M}}^{1}\ 1s_{\bar{C}}^{1}$	−4.0	4.7
O 1s	$6\sigma\ 4\sigma^{-1}\ 1s_{\bar{O}}^{1}$	27.4	4.9
	$S\ 5\sigma^{-1}\ 1s_{\bar{O}}^{1}$	25.0	4.7
	$2\pi\ 1\pi^{-1}\ 1s_{\bar{O}}^{1}$	21.1	16.4
	$6\sigma\ 5\sigma^{-1}\ 1s_{\bar{O}}^{1}$	16.9	6.1
	$2\pi\ \pi_{\bar{M}}^{1}\ 1s_{\bar{O}}^{1}$	−2.6	8.4

much closer to the main peak than the satellites found for the free ligands. The satellite structure further apart from the main peak is also somewhat more accentuated than in the case of the free ligands. From the relevant numerical data (tables 4, 5 and 6) we find that the newly appearing satellites result from poles of Σ which correspond to the following two types of configurations:

(i) Charge transfer excited configurations in which, relative to the Koopmans state,

Table 5
Characteristic data for linear NiN$_2$ (see text)

Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
N 1s Ni–N$_a^*$–N$_b$	$6\sigma\ 4\sigma^{-1}\ 1s_{\bar{N}_a}^{-1}$	25.8	1.6
	$S\ 5\sigma^{-1}\ 1s_{\bar{N}_a}^{-1}$	24.5	3.8
	$6\sigma\ \sigma_{\bar{M}}^{1}\ 1s_{\bar{N}_a}^{1}$	16.7	5.9
	$2\pi\ 1\pi^{-1}\ 1s_{\bar{N}_a}^{1}$	11.5	14.1
	$S\ \sigma_{\bar{M}}^{1}\ 1s_{\bar{N}_a}^{1}$	0.06	1.0
	$2\pi\ \pi_{\bar{M}}^{1}\ 1s_{\bar{N}_a}^{1}$	−3.5	1.1
N 1s Ni–N$_a$–N$_b^*$	$6\sigma\ 5\sigma^{-1}\ 1s_{\bar{N}_b}^{1}$	19.1	4.6
	$2\pi\ 1\pi^{-1}\ 1s_{\bar{N}_b}^{1}$	11.0	12.8
	$2\pi\ \pi_{\bar{M}}^{1}\ 1s_{\bar{N}_b}^{1}$	−5.4	4.8

Table 6
Characteristic data for bridged NiN_2 (see text)

Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
N 1s	S $1\pi^{-1} 1s_{\bar{N}}^1$	27.2	4.2
	$6\sigma 5\sigma^{-1} 1s_{\bar{N}}^1$	17.1	5.2
	$2\pi 1\pi^{-1} 1s_{\bar{N}}^1$	13.8	8.8
	$2\pi 1\pi^{-1} 1s_{\bar{N}}^1$	11.0	9.5
	$2\pi\ \ \pi_{\bar{M}}^1 1s_{\bar{N}}^1$	−2.0	5.3
	$2\pi\ \ \pi_{\bar{M}}^1 1s_{\bar{N}}^1$	−3.6	2.1
	$2\pi\ \ \delta_{\bar{M}}^1 1s_{\bar{N}}^1$	−3.2	1.4
	$2\pi\ \ \sigma_{\bar{M}}^1 1s_{\bar{N}}^1$	−3.2	0.5

an electron is transferred from a metal orbital into an unoccupied orbital of the ligand.

(ii) Local metal excited configurations in which the electron is promoted from an occupied into an unoccupied metal orbital.

As in our earlier investigations on inner valence shell ionizations [1] some of the CT configurations (usually $d_M \to 2\pi_L$) are of lower energy than the corresponding Koopmans state. This is due to the fact that the energy necessary for a charge transfer excitation in the valence shell is sometimes overcompensated by a core hole specific correction term (see Part VI of this series [1] for further discussion). Such an overcompensation is equivalent to the idea of Lang and Williams [4] that an unoccupied level of the neutral system is pulled down below the Fermi level in the ion and thereby is partically occupied.

In all three studied examples the configuration of lowest energy is a charge transfer excited one. The first final state, however, evolves from the Koopmans configuration in all three cases. This change in the order of states compared with the order of configurations results from a stronger coupling of the Koopmans configuration with local ligand excited configurations than with charge transfer excited ones (tables 4, 5 and 6). If we use the term "unscreened state" for the one which is most directly related to the Koopmans configuration (to us this seems to be the only reasonable definition of "unscreened state") we find the following order with respect to increasing binding energy: unscreened state < "charge transfer" or "screened" states ≈ "local metal excited" states < "local ligand excited" states.

At this point it is interesting to compare our result to other theoretical investigations. A direct comparison with the model calculations of Schönhammer and Gunnarson [3] is obviously difficult due to the different investigated systems. It might well be that simple systems like NiCO are not sufficient to derive any infor-

mation on many-body effects in photoionization of adsorbates. The appearance of similar structures in the experimental spectra of adsorbed CO and of carbonyls, however, seems to show that the structures specific for coordinated ligands do not necessarily depend on the existence of a semi-infinite metal and its surface. Anyway, some interesting connections can be made between the results of our model calculations and the one obtained by Schönhammer and Gunnarson. This will be
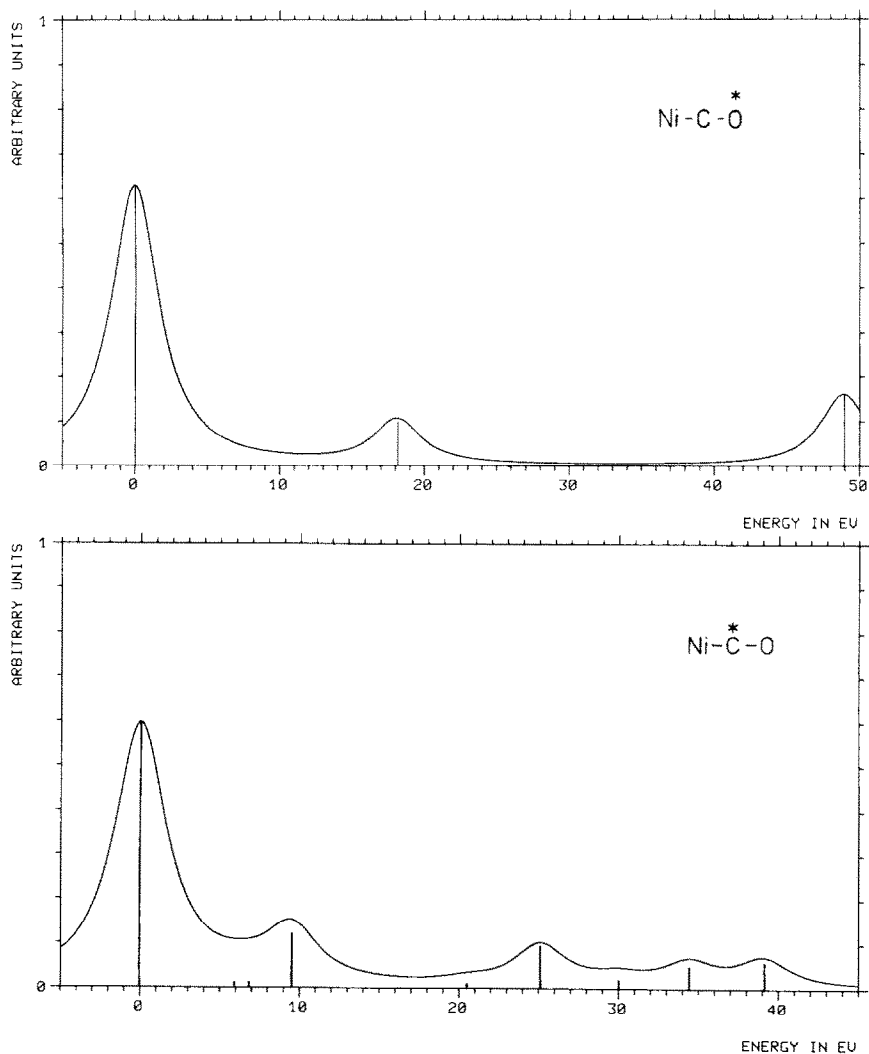

Fig. 5. Many-particle corrected photoemission spectra of NiCO.

done in the next section. Here we want to compare our results only to those derived by Bagus and Hermann (BH) [24] who studied the same model system as we did, namely NiCO.

At a first glance the results of our many-body calculations and those of the ab initio ΔSCF calculations of BH seem to be completely different. BH clearly state (ref. [24], p. 593) that as well in the C 1s as in the O 1s core spectrum the peak at lowest binding energy (P1) is connected with the screened state where a considerable amount of negative charge is transferred to the CO moiety and, correspondingly, the satellite at higher binding energy (P2) with the unscreened state. However, this statement is surprising in the view of the authors own results. To describe the relative intensity of the different bands BH calculated

$$I_{Pi} = \langle \psi_i^{(N-1)} | a_c \psi_0^{(N)} \rangle^2 . \tag{7}$$

This is the squared projection of the Koopmans state $a_c \psi_0^{(N)}$ (where an electron is removed from the core orbital c of the initial state $\psi_0^{(N)}$) on the final state wavefunction $\psi_i^{(N-1)}$. For reasonable metal–CO distances the ratio I_{P2}/I_{P1} is about 0.12 in the case of the C 1s hole and about 0.05 in the case of the O 1s hole, respectively. As both projections together yield 70 to 80% of the Koopmans state [25] this means that the final state reached by the ionization process with the lower energy (termed "screened state" by BH) contains about 60 to 70% of the Koopmans configuration – in full agreement with our result – and the state corresponding to the satellite only about 10%. To us it seems very sophisticated to call a final state which contains more than 50% of the Koopmans configuration "screened state" and another one which contains only a few percent of it the "unscreened one". To our opinion the only reason why BH came to this conclusion is that they find a fairly large charge transfer in the final state related to the first band and very little in the state related to the satellite. Closer inspection of the data given by BH brings about, however, that the final state related to the satellite in the BH calculation mainly evolves from what we would call a "local metal excitation" where a valence electron is excited into a fairly local metal p orbital. As stated above, the corresponding states are found in the vicinity of the "charge transfer states" also in our calculations but they usually lead to satellites of much lower intensity than the charge transfer excitations. We therefore believe that the final state attributed to the satellite by BH is not the one responsible for the main satellite observed in the experimental spectra. It should be mentioned, too, that BH use an initial state in their ΔSCF calculations different from the one used in their previous studies [26]. This newly introduced initial state is 4p instead of 3d backbonding.

From our calculations the following charge distributions are obtained:

initial state	−0.08	+0.20	−0.12
	Ni	C	O
final state connected with main	+0.05	+1.10	−0.15
peak in the C 1s spectrum	Ni	C	O

final state connected with main   +0.53   +0.69   −0.23
satellite in the C 1s spectrum   Ni   C   O

From our results and from the data given by BH we reach the following conclusion:

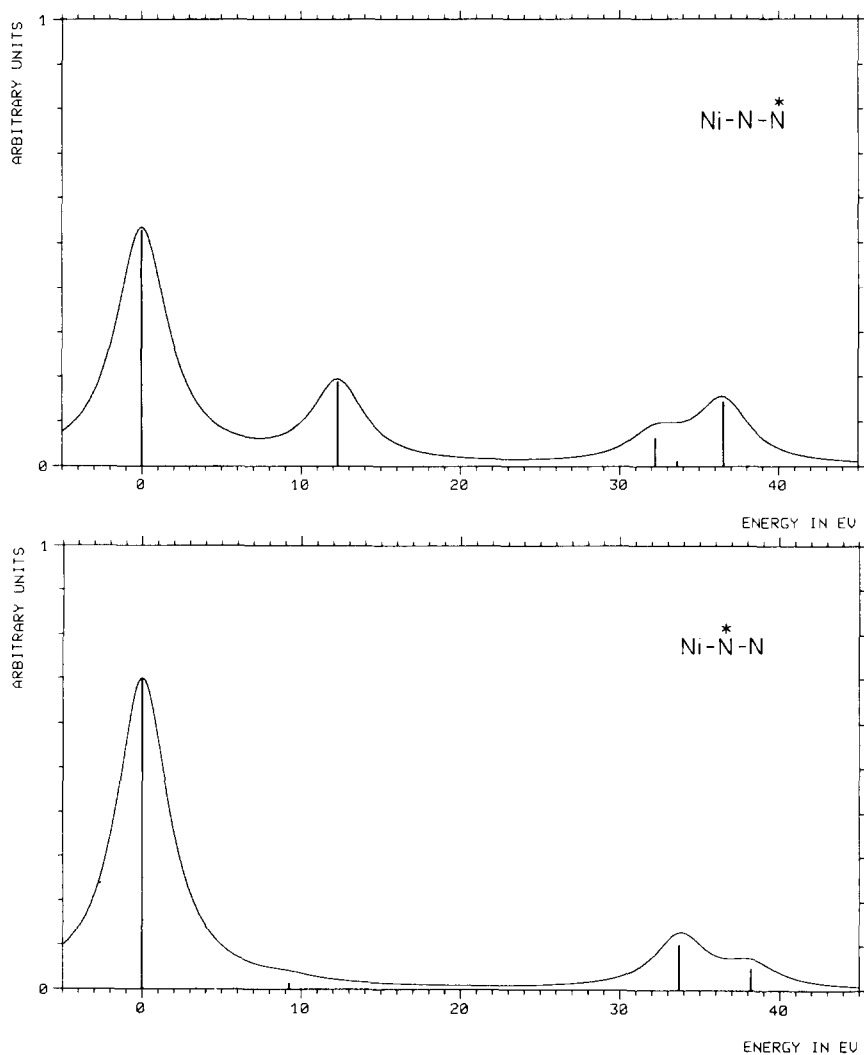(i) The final state which corresponds to the first band in the C 1s and O 1s spectra

Fig. 6. Many-particle corrected photoemission spectra of linear NiN_2.

of NiCO evolves most directly from the Koopmans configuration. Therefore it should be termed "unscreened state".

(ii) The final states connected with those satellites dominating the energy region next to the first band are most directly related to valence excitations with metal to ligand charge transfer character. Therefore these states should be termed "screened states".

We now discuss some further details in our calculated spectra. In NiCO the satellite structure further apart from the main peak is more pronounced than in free CO due to the coupling of the local ligand excited configurations responsible for these satellites with newly appearing charge transfer and local metal excited configurations. Compared to the free ligand the onset of the region of the local ligand excitation satellites is shifted somewhat further from the main peak for both core holes. This is mainly due to the increased relaxation shift of the main peak.

The linear arrangement of NiN_2 is directly comparable to NiCO. By "head-on" coordination of a nitrogen molecule to a Ni atom, two nonequivalent nitrogen atoms are created. Fig. 6 and table 5 summarize the corresponding results. Among the nonequivalent nitrogen atoms the intensity of the charge transfer satellite is greater for the nitrogen farther away from the metal. The relaxation of the Koopmans state is also different for both centers. It is larger for the center which leads to the more intense satellite. The consequences of these findings for the interpretation of experimental spectra of N_2 adsorbates will be discussed in the last section.

For the triangular NiN_2 arrangement we have to consider again the limiting cases of localized and delocalized core holes. Fig. 7 and table 6 contain the information
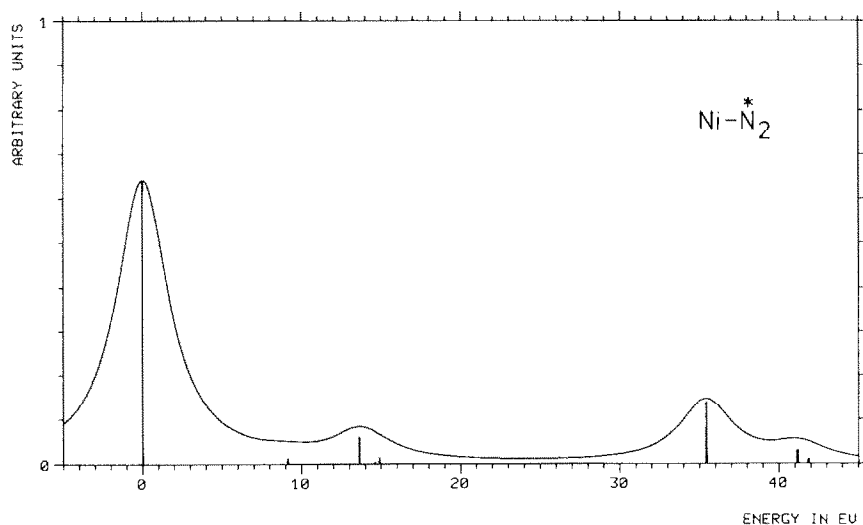

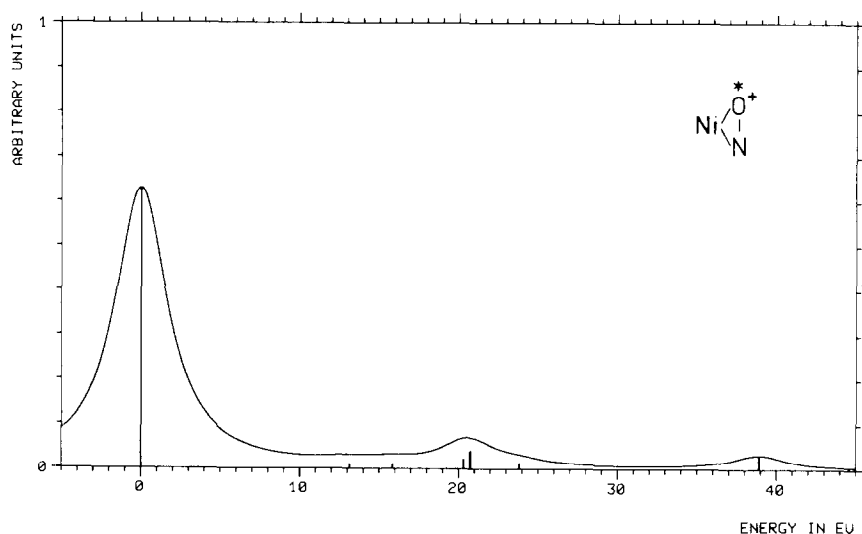Fig. 7. Many-particle corrected photoemission spectrum of bridged NiN_2.

Fig. 8. Many-particle corrected photoemission spectrum of bridged NiNO$^+$.

Table 7
Characteristic data for bridged NiNO$^+$ (see text)

Orbital	Main interacting configuration	Configuration energy (eV)	Interaction matrix element (eV)
N* 1s	$6\sigma\,4\sigma^{-1}\,1s_{N*}^{-1}$	27.4	2.5
	$2\pi\,1\pi^{-1}\,1s_{N*}^{-1}$	25.5	95.
	$2\pi\,5\sigma^{-1}\,1s_{N*}^{-1}$	19.4	1.2
	$6\sigma\,5\sigma^{-1}\,1s_{N*}^{-1}$	17.1	7.2
	$2\pi\,1\pi^{-1}\,1s_{N*}^{-1}$	15.7	11.5
	$S\quad M^{-1}\,1s_{N*}^{-1}$	6.7	2.7
	$6\sigma\,M^{-1}\,1s_{N*}^{-1}$	5.4	0.8
	$6\sigma\,M^{-1}\,1s_{N*}^{-1}$	4.6	0.7
	$S\quad M^{-1}\,1s_{N*}^{-1}$	3.5	2.2
	$6\sigma\,M^{-1}\,1s_{N*}^{-1}$	3.0	0.8
	$2\pi\,M^{-1}\,1s_{N*}^{-1}$	1.0	6.9
	$2\pi\,M^{-1}\,1s_{N*}^{-1}$	−1.9	4.3
	$2\pi\,M^{-1}\,1s_{N*}^{-1}$	−2.6	3.4
	$2\pi\,M^{-1}\,1s_{N*}^{-1}$	−2.7	1.3
	$2\pi\,M^{-1}\,1s_{N*}^{-1}$	−3.0	0.2

on the ionization from a delocalized core hole, while the corresponding data for the localized hole, approximately described by the system $NiNO^+$, are summarized in fig. 8 and table 7. Compared to the other studied systems, nothing dramatically different is found. It is nevertheless interesting to recognize that the delocalized approach predicts a strong satellite at nearly the same energy and of similar intensity as in linear NiN_2 while in the localized description this satellite is less pronounced and shifted towards higher binding energy. The relaxation energy found for the triangular arrangement of NiN_2 is just intermediate between those of the non-equivalent nitrogen atoms in linear NiN_2. In $NiNO^+$ the relaxation energy is considerably larger. This corresponds to what we found for the localized model (NO^+) of free N_2.

5. Comparison with real adsorbates

Before we start to discuss in how far the results obtained for simple model systems can be transferred to real adsorbates we have to deal with the overestimated energy separations found in our CNDO-type calculations.

In the case of the free ligands a comparison of theoretical and experimental results has shown that the distance between main peak and satellite structure onset is too large by a factor of about two. A similar overestimation of energy distances is highly probable in the case of the model systems NiCO and NiN_2, too. If we try to use the theoretical information obtained for these model systems to discuss the core spectra from the adsorbed part of real adsorbates we must be sure that the basic qualitative results derived from our calculations do not depend on the overestimated energy separations. To deal with this problem we have to find out which terms in our calculations are responsible for the overestimation. In our studies on valence ionizations [1] we did not find such a strong deviation from experiment. The calculated energies were only slightly too large. The much too large energy separations observed in the case of core ionizations can therefore not be caused by the valence orbitals. This is in accordance with the fact that the molecular integrals V_{caca}, V_{cjcj} and V_{cjca} which mainly govern the position of the poles of Σ and also the interaction between different configurations (compare eq. (6)) only depend on elements of γ_{int}. As mentioned earlier, an overestimation of these core–valence interactions had to be expected for a ZDO-type method in which the γ integrals are derived from one-center integrals calculated with Slater rule exponents. We therefore reduced all elements of γ_{int} by 30%, a value similar to the one used by Pariser [15] in semiempirical calculations on π systems. An example of such a calculation is shown in fig. 9 for the carbon core hole in NiCO. If this spectrum is compared with the one obtained with unscaled γ integrals (fig. 5) a considerable reduction in the energy separation between main peak and satellite structure is observed. This reduction is in part due to a decrease of the relaxation shift of the main peak, and in part due to a change in the position of the poles of Σ.
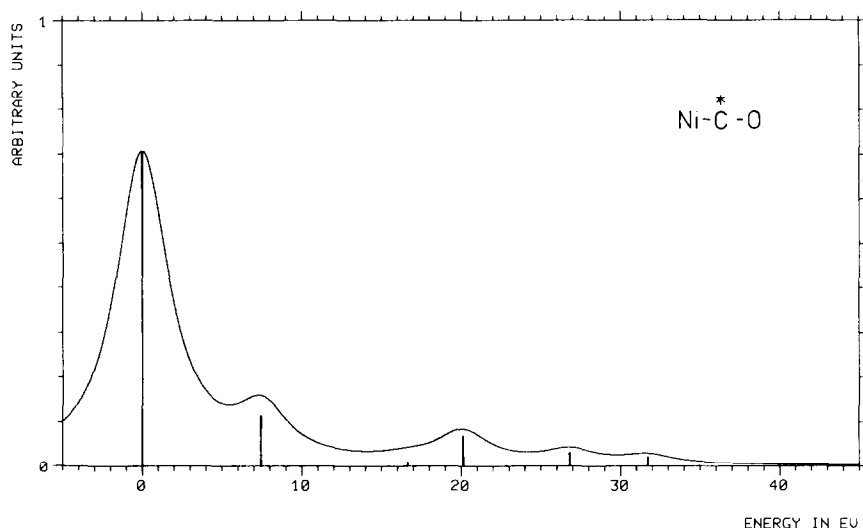
Fig. 9. Many-particle corrected photoemission spectrum for a C 1s hole in NiCO obtained with reduced values of γ_{int} (see text).

The habitus in the spectrum as well as its physical interpretation remain, however, unchanged. This is especially true with respect to the strong satellite next to the main peak which originates from metal to ligand charge transfer excitations. As similar results are found for the other investigated systems, the following conclusions are independent from the use of scaled or unscaled γ integrals:

(i) For the free molecules low intense satellite peaks are found at the high binding energy side of the main peak. The main peak itself is directly related to the detachment of an electron from the considered core orbital. In relation to the energy of the corresponding Koopmans state, the peak is shifted by a few eV to lower binding energies. This relaxation shift increases from carbon to oxygen. A similar increase with increasing atomic number is also found in ΔSCF calculations [27]. The satellites result from an interaction of the Koopmans state with $\sigma\sigma^*$ and $\pi\pi^*$ valence excitations. In relation to the Koopmans state, the energetic position of the corresponding poles of Σ is nearly independent from the nature of the core hole. The increasing separation between main peak and satellite structure onset observed [28] in the order carbon to oxygen is therefore mainly caused by the increasing relaxation shift of the main peak.

(ii) For the coordinated systems a larger number of satellites is found in the calculated core ionization spectra. The newly appearing satellites arise from an interaction of the Koopmans state with charge transfer and local metal valence excitations. Among these two types of excitations the most interesting are the charge transfer ones since the energy of the corresponding configurations is similar or even lower

(compare tables 4–7) than the energy of the interacting Koopmans state. In spite of this fact, the first peak in the calculated spectra (with respect to increasing binding energy) corresponds to the direct electron detachment from the core orbital in all three studied examples (NiCO, NiN_2 linear and NiN_2 triangular). The corresponding pole strength is also considerably high. The satellites, resulting from the charge transfer excitations are predicted to lie in the close neighbourhood of the main peak, thus leading to a completely different spectral habitus than the one obtained for the free ligands. The low intense satellites resulting from the local ligand excitations are shifted somewhat further apart from the main peak if compared to the free ligand. This is mainly due to the enlarged relaxation shift of the main peak in the coordinated systems. Satellites originating from local metal excitations lie mainly in the energy region of the charge transfer satellites, but their intensity is usually low.

(iii) In the cases, in which we have to consider the possibility of delocalized or localized core holes due to the existence of two, or even more, atoms which are equivalent by symmetry, we have used an equivalent core approximation to describe the localized core hole. Due to the break of symmetry incorporated in this treatment the number of poles of Σ is increased, leading to a more extended satellite structure compared to the case of the delocalized core hole. A comparison of experimental spectra and quantitative calculations should therefore allow to differentiate between localized and delocalized core holes. In agreement with ab initio ΔSCF calculations [6], we have also found that the relaxation shift of the main peak is larger in the case of a delocalized core hole. Thus, the separation of main peak and satellite structure onset should be larger if the hole is localized.

If we now try to transfer the results obtained for our model systems to real adsorbates we have to consider the following facts: Local metal excitations in a model compound containing a single metal atom yield only a poor approximation for surface plasmons as used by Schönhammer and Gunnarson (SG) in order to include the possible influence of an image charge. Instead the influence of a core hole at one of the ligand atoms is included in our treatment via the interaction term V_{caca} in eq. (6). We also do not have the possibility to take into account low-energy excitations from the metal which are necessary to describe peak asymmetries. However, all this seems to be of minor importance. The close similarity of the main structures found in core spectra of adsorbates and related organometallic compounds clearly show that these structures must have a common origin — the possible metal to ligand electron transfer in the valence shell. In the SG model the energy of such a charge transfer state is mainly given by (relative to ϵ_c, the Koopmans energy of the core hole)

$$E' = -\epsilon_F + \epsilon_a - U_{ac} ,$$

where ϵ_F is the Fermi level of the metal, ϵ_a the orbital energy of the accepting orbital in the ligand, and U_{ac} the stabilization of this orbital due to a core hole in the ligand. In case E' becomes negative the charge transfer state is more stable than

the corresponding Koopmans state. This is the situation proposed by Lang and Williams [4] in which the accepting level is pulled down below the Fermi level and thereby (partially) occupied.

Neglecting the exchange terms and introducing the lables a for the accepting and d for the donating orbital we obtain from eq. (6):

$$E' = -\epsilon_d + \epsilon_a + V_{cdcd} - V_{caca} - V_{adad} \, .$$

In our treatment the stabilization term corresponding to SG's U_{ac} consists of three contributions: a term (V_{caca}) describing the influence of the core hole on the acceptor level in the ligand, a term (V_{cdcd}) describing the same influence on the donating level in the metal, and a term due to the interaction of the transferred electron with the remaining hole (V_{adad}). For large metal–ligand distances or in case the donor orbital is highly delocalized in the metal the contributions V_{cdcd} and V_{adad} become small.

This leaves

$$E' = -\epsilon_d + (\epsilon_a - V_{caca}) \, .$$

The term in brackets is nothing else but the negative electron affinity of a ligand with a core hole. For the C 1s hole in CO, e.g., it should be well approximated by the electron affinity of NO^+ which is equal to the first IP of NO (9.26 eV [29]). As the work function of most metals is in the order of about 4 eV the charge transfer state should be more stable than the Koopmans state by about 4 to 5 eV. In such a case, however, we have to expect little overlap between donor and acceptor orbital and therefore only weak coupling (compare the nominator in eq. (6)). The result should be a weak satellite at the low binding energy side of the main peak. As this satellite is connected with a charge transfer excitation in the valence shell the corresponding state should be termed "screened state". This result is in agreement with the one obtained by SG for weak adsorbate–substrate coupling.

If we now turn to the strong coupling case, the terms V_{cdcd} and V_{adad} can no longer be ignored. Their relative magnitude is, however, hard to estimate for a real adsorbate, but we have to take into account that also in this case there exist at least some states for which E' is still negative.

If the results for the systems we have studied can be transferred to the real adsorbates – and these systems should be much better models for the strong coupling case than for the weak coupling one – it is highly probable that also in cases where some of the charge transfer excited configurations have lower energy than the Koopmans one the final state of lowest energy evolves mainly from the Koopmans configuration. This is due to the comparatively strong interaction between Koopmans configuration and local ligand excited ones. This interaction is not taken into account in the SG treatment but could be easily included in this model. In the case of strong adsorbate–substrate coupling we therefore except a main peak at the beginning of each core spectrum followed by a low to medium intense satellite at the high binding energy side of the main peak. Again the satellite results from a
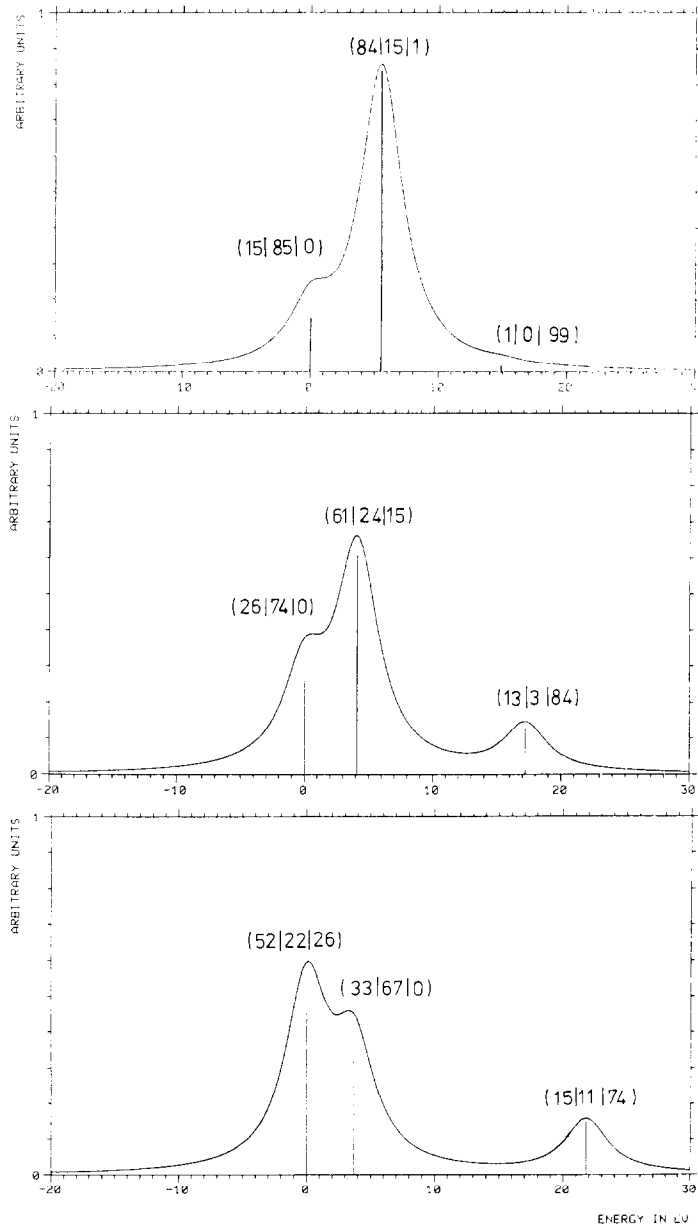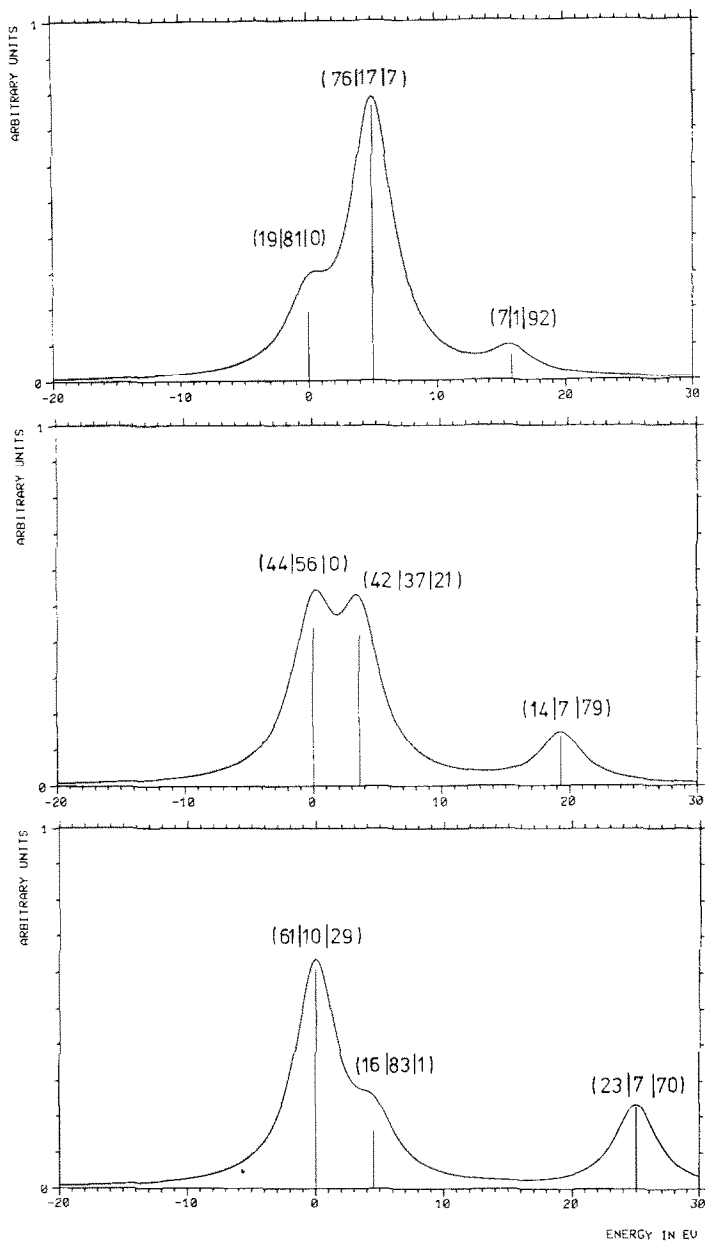
Fig. 10. Theoretical spectra derived from a three level model. For each peak the contribution (in percent) of the three components is indicated in the order: Koopmans configuration, charge transfer excited configuration, local ligand excited configuration. Only the interaction $V_{KS,L \to L}$ between Koopmans configuration and local ligand excited one is varied.

charge transfer excitation in the valence shell. Thus, the satellite connected to the "screened state" has moved from the low binding energy side of the main peak in the case of weak adsorbate—substrate coupling to the high binding energy side in the case of strong coupling. If this is true, then there must exist intermediate cases in which screened and unscreened states are nearly degenerate. This can be studied in more detail if we use a simple three level model. In this model, we only take into account the following configurations: The Koopmans configuration (KC), a single charge transfer configuration (M → L) representing those configurations induced by coordination, and a single local ligand excited one (L → L) representing the satellite structure in the free ligand. With these representative configurations we obtain an illustrative 3×3 interaction problem in which the configuration energies as well as the interaction matrix elements may be varied to study different possible situations. In fig. 10 an example is shown for such a calculation where we have used the following parameters (in eV): $E(KC) = 0; E(M \rightarrow L) = -4; E(L \rightarrow L) = 10$; the interaction between KC and M → L ($V_{KC,M \rightarrow L}$) was set $= -2$ and only $V_{KC,L \rightarrow L}$ varied between -1 and -11. These energies correspond to what we have found in our model systems. The energy of the first peak in the calculated spectra is always set to zero. From the squared mixing coefficients indicated for each peak it becomes obvious that all possible intensity patterns and peak sequences can be obtained by just varying one parameter. Especially the order of main peak and charge transfer satellite is reversed with increasing $V_{KC,L \rightarrow L}$. The crossing point lies at about $V_{KC,L \rightarrow L} = -7$. In this region it becomes difficult to discern between main peak and satellite. Similar patterns as shown in fig. 10 can be obtained if $E(KC)$ is varied instead of $V_{KC,L \rightarrow L}$. It is therefore not possible to decide from an observed sequence of main peak and satellite whether it is caused by a non negligible interaction between Koopmans configuration and local ligand excited ones or by a less pronounced stabilization of the charge transfer configurations. As all these energies depend on the metal, the ligand, and the core hole under consideration it is by no means astonishing that different satellite structure is found experimentally for different core ionizations in the same system.

In general our results for the strong coupling case are again equivalent to those derived by Schönhammer and Gunnarson: The core spectra exhibit a fairly strong peak near threshold and a weaker satellite at the high binding energy side of this peak. The only difference compared to SG is that we attribute the main peak to the Koopmans state (unscreened state) and the satellite to a charge transfer excitation in the valence shell (screened state) also in the case of strong adsorbate—substrate coupling. Besides of this more or less semantic question the basic results derived for small model compounds via many-body perturbation theory coincide completely with those obtained by SG from their adsorption model. Compared to ΔSCF calculations on small model compounds our treatment has the great advantage that we can deal simultaneously with local metal, local ligand, and charge transfer excitations in the valence shell. Thus we are not forced to consider only the satellites next to the main peak. Instead we are able to treat also those satellites which lie further apart from the main peak and result mainly from local ligand excitations.

6. Experimental implications

Experimental ESCA spectra of adsorbates have been reported by several authors [2a–2f]. The satellite structure in these spectra is usually more pronounced than in the corresponding spectra of the free ligands and the satellites lie closer to the main peak. Especially strong satellites are found in the C 1s and N 1s spectra of systems like CO/Cu, N_2/W, and N_2/Ni where the adsorbate is believed to be rather weakly bound to the substrate. This is in good agreement with the theoretical result that the mixing of the Koopmans configuration with charge transfer excited ones is largest for intermediate adsorbate–substrate coupling.

In the case of CO a satellite structure comparable to the one found in the adsorbates is also observed in the C 1s and O 1s spectra of a large variety of molecular compounds [30]. Due to our theoretical results we assume that the satellites observed experimentally at the high binding energy side of the main peak result from metal to ligand charge transfer excitations. This confirms the heuristic assignment given by Plummer et al. [30]. The less intense satellites originating from local metal and local ligand excitations which are predicted to lie further apart from the main peak have been observed for example in the O 1s spectrum of CO adsorbed to W(110) [2a]. To our knowledge no such satellites have been reported for C 1s in the case of CO.

A case of considerable interest is the N_2 adsorption on tungsten, where the N 1s spectrum, depicted in fig. 11 [2f] has been found. Fuggle and Menzel interpreted the splitted emission at lower binding energy as resulting from two different nitrogen atoms which are present, if the nitrogen molecule is adsorbed "head-on" to the surface. Confidence is given to this assignment by a similar splitting which is found in nitrogen complexes, where the N_2 molecule is "head-on" coordinated to the
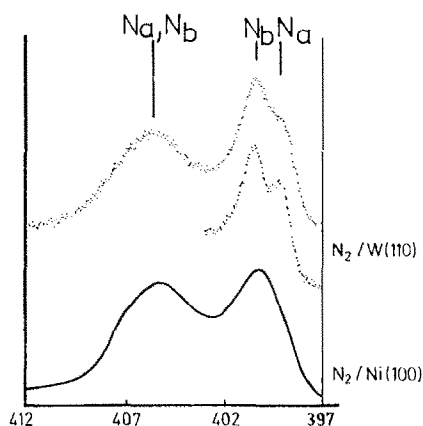

Fig. 11. N 1s region of N_2/W(110) and N_2/Ni(100) taken from ref. [2f].

metal atom [31]. As a first approximation one would expect both N 1s ionizations to be equally probable. By inspection of the experimental spectrum one finds, however, that one line is considerably stronger than the other. This becomes clearly obvious, if we use the N 1s line of N_2O adsorbed on W, reported by the same authors [2f], as a single line for the deconvolution of the N_2/W N 1s spectrum. If we compare this deconvolution with the result of our calculation, we find striking similarities (see figs. 6 and 7). From the charge distribution in NiN_2

$$-0.13 \quad +0.14 \quad -0.01$$
$$Ni \text{———} N_a \text{———} N_b \quad ,$$
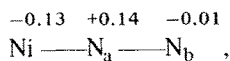
together with the larger relaxation shift of N_b (compare fig. 6), we expect the ionization from N_b 1s to appear at lower binding energy than the one from N_a 1s. Due to the stronger intensity borrowing (fig. 7), N_b should contribute more to the satellite intensity than N_a. This leads to an assignment of the N 1s spectrum of N_2 on W, which is indicated in fig. 11.

Low intense satellites at greater distance from the main peak are not reported for the N_2 adsorbates, too. What is more astonishing is that nothing has been mentioned about satellite structure in "head-on" coordinated N_2 complexes [31]. As in the case of CO the molecular compounds should exhibit similar satellites as the adsorbates do. From a comparative point of view it should be therefore very exciting to prove experimentally whether these satellites really exist or not.

Acknowledgements

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