

## X-RAY PHOTOEMISSION STUDY OF SATELLITE STRUCTURE ACCOMPANYING CORE IONIZATION FROM COORDINATED NITROGEN

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We compare the core ionization of free and adsorbed  $N_2$  to  $N_2$  bound head-on (with a linear  $N_2$ -metal bond) to a metal atom in a mononuclear organometallic compound, namely  $h^5$ -dicarbonyl-cyclopentadienyl-dinitrogen-manganese(I). A comprehensive assignment is given for the full spectrum including main lines and satellite lines on the basis of numerical calculations. The conclusions are compared to those earlier derived for carbon-monoxide complexes and adsorbates. The importance of doubly excited configurations for a correct description of satellite excitation energies is described.

### 1. Introduction

In 1978 Fuggle and co-workers [1,2] found intense satellite structure (called shake-up) accompanying the core ionization of  $N_2$  and CO adsorbates. An explanation of these results was provided by Gunnarsson and Schönhammer [3] in terms of a model hamiltonian treatment. These authors showed that the ionization probability known from the free molecule is redistributed upon adsorption of the molecule due to screening of the core hole on the molecule by metal electrons. The shape of the observed spectral function, e.g. energy distribution of ionization probabilities, was thought to be determined by the particular shape of the density of states of the metal substrate. Subsequently it was shown by comparison between molecular coordination compounds and adsorbates [4,5] that a few metal atoms were already sufficient to reproduce a core- and valence-hole spectral function that is virtually identical to the one observed in an adsorbate. These findings indicated that core- and valence-ionization spectra can be interpreted in

terms of the well-known "surface-molecule approach" [6]. These comparisons were primarily carried through for coordinated CO systems with relatively strong bonding. In these cases the spectrum did not depend very remarkably on the metal involved in the bond. It was questioned [7], however, whether this approach is applicable to systems with weak substrate-adsorbate interaction. Very recently cluster calculations using the X $\alpha$  MS procedure [8] showed that the proposed extension of the surface-molecule approach does work for the case of weakly chemisorbed CO on Cu. Unfortunately weakly bonded CO complexes are not available. Other examples with weak molecule-substrate interaction are  $N_2$  adsorbates which have been studied experimentally [2,7–13] and theoretically [14–18] in the core- and valence-electron region on various metal substrates.

With  $N_2$  coordinated systems we are in the position to compare a weakly chemisorbed species in an adsorbate to a weakly bound molecule in a real complex. Therefore it was decided to study the photoemission from  $N_2$  adsorbates and  $N_2$

complexes Compared to CO systems the  $N_2$  systems are less stable by  $\approx 20$  kcal/mol per molecule-metal bond, both in complexes and adsorbates. To be specific, for CO and  $N_2$  adsorption on a Ni (110) surface the bond enthalpies differ by 84.4 kJ/mol [19,20], and the reaction enthalpy for ligand exchange in, e.g.  $Ru(NH_3)_5N_2^{2+}$  is lower by 74.4 kJ/mol [21,22] than in  $Ru(NH_3)_5CO^{2+}$  ‡.

We report here on the first detailed experimental and theoretical comparison between the N1s core spectrum of a nitrogen complex namely  $h^5$ -dicarbonyl-cyclopentadienyl-dinitrogen-manganese (I) with free nitrogen [23] on the one hand, and  $N_2$ -transition-metal adsorbates [8,24] on the other. We have chosen this complex for three reasons: (i) there are no other nitrogen atoms on other ligands present in the complex, (ii) there is only one nitrogen molecule in the complex so that there exists no ambiguity for assignment of the spectrum and (iii) the equivalent CO complex is known [21] The present comparison leads to an assignment of the full range of satellites accompanying N1s core ionization and to the distinction between those excitations known from the free molecule and those characteristic of the bound molecule. Also, our study indicates that a surface-molecule description indeed is applicable to a weak chemisorptive bond as represented by a  $N_2$ -metal adsorbate, as far as the interpretation of the photoemission spectra is concerned

In this paper, we first describe the experimental procedure to generate the spectra Then we proceed with a short description of the theoretical methods used to carry through the calculations of the core-hole spectral function. In section 3, we describe the qualitative ideas on which our interpretation is based. Section 4 contains a detailed discussion of the experimental and theoretical results in the context of known results from the literature. The last part contains a synopsis

‡ The absolute binding energies are 150.9 kJ/mol for ligand exchange in the CO complex [22] and 125.4 kJ/mol in the CO adsorbate [19], 76.5 kJ/mol for ligand exchange in the  $N_2$  complex [21] and 41.0 kJ/mol in the  $N_2$  adsorbate [20]

## 2. Technical details

### 2.1 Experimental procedure

The photoelectron spectra were recorded using a modified Leybold-Heraeus LHS-10 spectrometer in a  $dE/E = \text{constant}$  [25] mode The samples were prepared by sublimating the complex onto a liquid-nitrogen-cooled metal (Fe, Cu, Ag, Au) substrate. The samples were kept at liquid-nitrogen temperature during data acquisition. This was necessary to prevent the complex from evaporation. The energy scans were 50 eV wide and were covered by 256 channels using a dwell time of 2 s/channel. The spectrum shown in fig. 1 was recorded by averaging the data of four scans and subtracting the signal from the metal substrate. We have chosen the highest possible intensity achievable with the instrument at the cost of high resolution. The resolution was kept at 1.7 eV (fwhm). In this way we were able to get a reasonable signal-to-noise ratio at binding energies further below the main line. The spectra presented have been reproduced using several different metallic substrates in order to rule out possible contributions to the spectrum from electrons of the metal substrates The effect of disintegration of the complex on the spectrum was studied by heating a sample before the spectrum was taken and by irradiating the sample for 30 min before data acquisition. Using this procedure we can rule out the possibility of contributions from disintegration products to the spectrum shown in fig. 1.

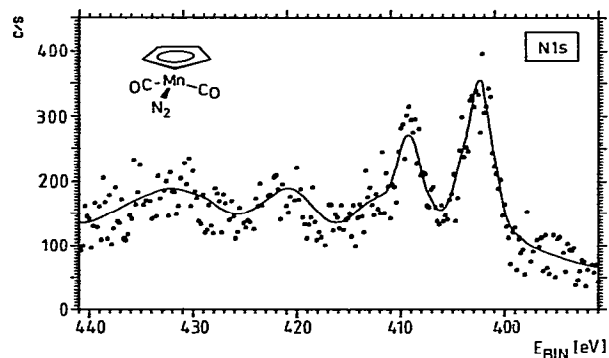


Fig 1 N1s spectrum of  $(C_5H_5)(CO)_2MnN_2$  recorded with MgK $\alpha$  radiation

## 2.2 Computational procedure

Calculations were done using a semi-empirical CNDO LCAO SCF algorithm recently parameterized to mimic ab initio single-particle properties of transition-metal compounds [25,27]. The result obtained by this method is then augmented by a configuration-interaction calculation including doubly excited configurations [28]. In order to describe the core-ionized species we employed the equivalent-core method [29,30]. We substitute the atom with nuclear charge  $Z$  which is to be ionized by the atom with the next higher nuclear charge ( $Z + 1$ ) and calculate the system with unaltered number of valence electrons. This procedure allows us to calculate the motion of the valence electrons in an effectively changed core potential and models the change in potential upon core ionization. The excited core-ionized states were calculated by a configuration-interaction treatment including single and double excitations [28]. In all ionic-state calculations we selected 300 configurations with lowest excitation energy out of 5000 created configurations of proper symmetry. Relative intensities were calculated by projection of the wavefunction of the correlated ion states onto the wavefunctions of the neutral system, according to the sudden approximation [31].

$$I'_{\text{rel}} \propto |\langle \Psi_{\text{relaxed}}^{\text{ion}} | \Psi_{\text{frozen}}^{\text{ion}} \rangle|^2. \quad (1)$$

Within this approximation a sum rule holds stating that the first moment of the spectral function is equal to the Hartree-Fock eigenenergy [32]:

$$E_{\text{HF}} - E_0^{\text{ion}} = \sum_i (E_i^{\text{ion}} - E_0^{\text{ion}}) I'_{\text{rel}}. \quad (2)$$

Since the states involved are linear combinations of determinants created from the set of self-consistently determined orbitals of the neutral  $\phi_i$  and the core-ionized  $\chi_i$  system, we can write the intensity as [33]:

$$I_{\text{rel}} \propto \left| \left\langle \sum_i c_i \|\chi'_i\| \left| \sum_j d_j \|\phi_i^0\| \right. \right\rangle \right|^2. \quad (3a)$$

$$I_{\text{rel}} \propto \left| \sum_i \sum_j c_i d_j \|\chi'_i\| \|\phi_i^0\| \right|^2. \quad (3b)$$

$$I_{\text{rel}} \propto \left| \sum_i \sum_j c_i d_j \|\chi'_i\| \|\phi_i^0\| \right|^2. \quad (3c)$$

which is easily programmable. We include in the intensity calculations only those doublet states that result from spin combinations represented by a singlet excitation in the valence shell. The spectral function calculated in this way can be used to evaluate the sum rule. This in turn allows us to calculate relaxation energies since this quantity is given as the difference between the Hartree-Fock eigenenergy and the true ionization potential.

## 3. Qualitative considerations

For illustrative purposes let us consider the most simple case of a diatomic molecule (AB) interacting with a single metal atom (Me). The orbitals of the neutral system resulting from the metal  $d\pi$  (hereafter called  $d\pi$ ) molecule  $\pi^*$  (hereafter called  $\pi^*$ ) interaction ( $\pi$ -acceptor interaction) and from the molecule  $\sigma$  (hereafter called  $\sigma$ ) metal  $d\sigma/s$  (hereafter called  $d\sigma$ ) interaction ( $\sigma$ -donor interaction) are schematically shown in fig. 2a [5]. A non-interacting molecular  $\pi$  orbital (hereafter called  $\pi$ ) is also indicated. The orbitals appear to be localized predominantly on the two parent fragments. With respect to the uncoordinated free molecule the unoccupied  $\pi^*$  orbital becomes partly populated, while the occupied  $\sigma$  orbital becomes partly depopulated. If we now introduce a core hole on the molecule, e.g. on the center close to the metal, the Coulomb interaction stabilizes the unoccupied  $\pi^*$  and occupied  $\sigma$  and  $\pi$  levels on the molecule with respect to the metal levels. This causes the mixing between molecular and metal levels to change. The main result is an increased mixing between the  $\pi^*$  and the  $d\pi$  orbitals and a decreased mixing between the  $\sigma$  and the  $d\sigma$  orbitals. This is indicated in fig. 2b by changing the weight of the LCAO coefficients on the parent fragments. If we now project the valence orbitals of the core-ionized species onto those of the free molecule we find the  $\pi^*$  orbitals of the AB molecule with larger population than in the neutral system. Population of the  $\sigma$  orbital increases with respect to the neutral coordinated

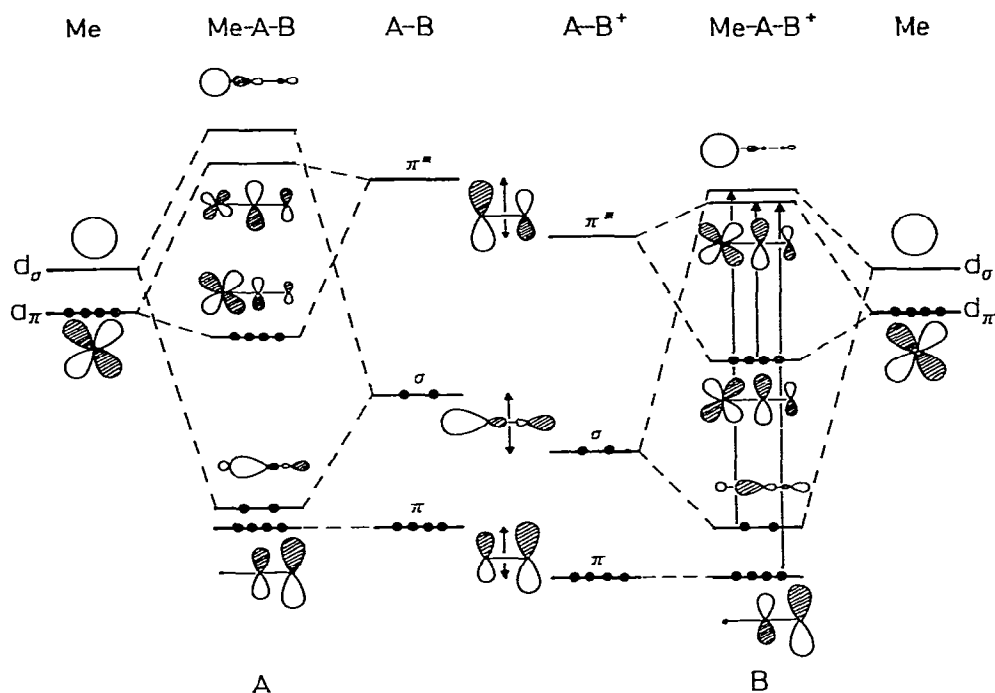


Fig 2 Schematic representation of the interaction of the valence orbitals of a metal atom (Me) with a diatomic molecule (AB) in the neutral (A) and the core-ionized (B) system. Arrows in B indicate possible shake-up excitations

system. This redistribution of electrons in the valence region induced by the ionization process (fig. 2b) leads to an accumulation of electronic charge on the molecular moiety and thus to a screening of the core hole. The details of this screening mechanism determine the observed spectral function, in particular the intensity distribution.

We use as an example to show this the one-electron states depicted in figs. 2a and 2b. In order to calculate the intensity distribution we project the occupied orbitals of fig. 2b onto those of fig. 2a according to eq. (1). Clearly the overlap is not unity since the shape of the orbitals has changed upon ionization. If we now excite an electron into the unoccupied orbitals, e.g.  $\pi^*$ , out of  $\pi$  we create a state that has a finite overlap amplitude with the occupied orbitals of fig. 2a and therefore has a finite ionization amplitude. The absolute magnitude of this overlap amplitude is sensitive to the size and sign of the LCAO coefficients of the wavefunctions. These LCAO coefficients in turn

depend on the interaction between molecule and metal. We have shown [5] that for weaker metal-molecule interaction as compared to carbonyl complexes the overlap amplitude of frozen and equivalent-core-ion ground state, which determines the shake-up intensity, should increase. At the same time the energy separation between satellite and main line should decrease since the splitting between bonding and antibonding contributions gets smaller. The latter statement however, holds only if the nature of the excited state stays the same as the metal-molecule interaction varies. Usually it is assumed that the excited state can be described as a single excitation. However, if the splitting becomes small and the overlap matrix element for a certain singly excited state becomes rather large then the overlap matrix element for a double excitation involving the same orbitals but a larger excitation energy is likely to get large too. The singly and doubly excited states mix, and consequently the intensity may be partly

transferred into the doubly excited state. After this type of configuration mixing has been included, the intensity of the shake-up spectrum may peak at a higher excitation energy than expected without this additional interaction. We conclude therefore, that, even though the metal–molecule bond strength gets smaller, the observed shake-up excitation energy *may* increase. The intensity of the excitation may increase as well.

## 4. Results and discussion

### 4.1. Experimental results

$N_2$  on Ni [8.11] and CO on Cu [34] represent, as mentioned before, cases of rather weak chemisorption as compared to CO adsorption on other transition metals. The model outlined in the previous section predicts rather intense satellite structure for these weakly chemisorbed systems in general, if the metal–molecule interaction determines the intensity of the satellite structure. For  $N_2$  adsorbates these satellites have indeed been observed [8.11]. It has been claimed that in those cases the complete spectral function and particularly the fine structure of the main line is mainly connected with the particular shape of the density of states of the substrate and that the structure in the main line is not due to the inequivalency of the nitrogen atoms [7]. This argument was based on the slight differences observed in the fine structure of the leading peak when adsorption on various substrates was compared [7].

For  $N_2$  complexes there exist only very fragmentary data on N1s satellites [35], while there is a full body of measurements on N1s main lines [35–39], namely to demonstrate the inequivalency of the two nitrogen atoms after coordination to a metal atom. Leigh et al. [35] were the first to report on the split N1s photoemission signal from rhenium– $N_2$  complexes. Their spectra do show satellite structure on the high-binding-energy side of the N1s main line but these authors did not discuss the extra structure. Our spectrum (see fig. 1) shows intense satellite structure on the high-binding-energy side of the N1s main line, with an energy separation of 7–8 eV. Binder and Sellmann

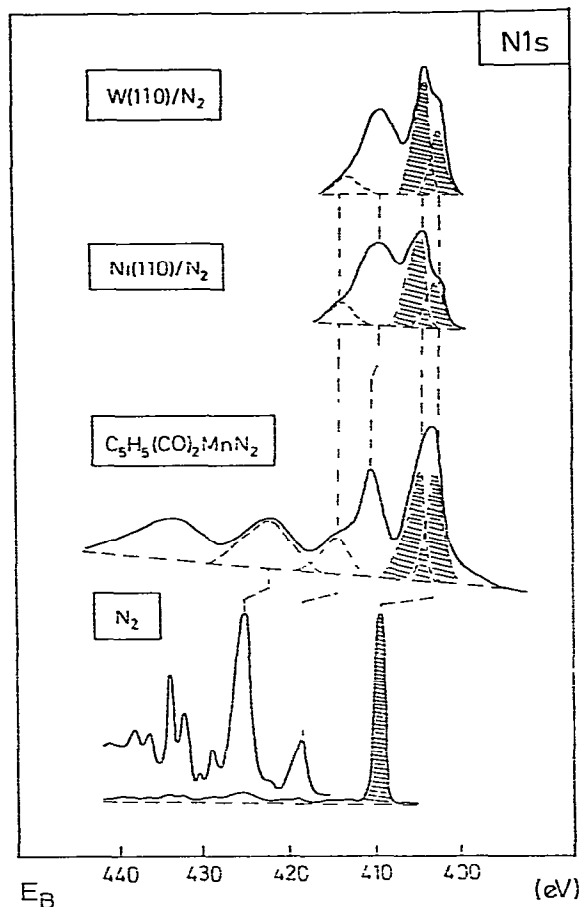


Fig. 3 Comparison of N1s spectra of free  $N_2$  [23],  $(C_5H_5)(CO)_2MnN_2$  and the adsorbate systems Ni(110)/ $N_2$  [9] and W(110)/ $N_2$  [24]. The binding energies of the leading peak in the adsorbate systems have been aligned with those of the complex.

[36] have studied the identical complex but did not investigate the satellite region. They studied the main line with higher resolution and found a split main line with a peak separation of  $\approx 2$  eV. It should be noted that the spectrum of Binder and Sellmann [36] very well fits underneath our main line.

Fig. 3 compares the spectra of the  $N_2$  complex with those of free  $N_2$  [23] and  $N_2$  adsorbates [9,24] taken from the literature. Fig. 3 is intended to use the known assignment of the satellite structure of free  $N_2$  [40] to establish a comprehensive assign-

ment for the coordinated systems.

The two satellites at lowest excitation energy in the free molecule have been assigned to be due to the two doublet states resulting from the  $1\pi_u-1\pi_g^*$  excitation in the presence of the core hole [40]. It is known that the states originating from a  $1\pi_u-1\pi_g^*$  excitation are split by  $\approx 7$  eV as a result of configuration interaction [40]<sup>‡</sup>. The intensity of the shake-up satellites caused by these states is rather small. The intensity of the satellite above 16 eV excitation energy is by a factor of 3 larger than that of the one at  $\approx 10$  eV. This latter satellite borrows its intensity through secondary spin coupling [5]. The satellites as well as the main line shift towards lower binding energy upon coordination (see fig. 3) since in the presence of the hole the excited electrons feel the changed potential caused by extramolecular screening by metal electrons. The various peaks are shifted towards lower binding energies by slightly different amounts due to the fact that the final state ( $\pi^*$ ) of the excitation is not identical to the free molecule. In particular the  $1\pi_u-1\pi_g^*$  satellite at small excitation energy is shifted close to the region of very intense satellites, which inhibits us to locate this peak definitely. In addition to the peaks that are due to excitations on the adsorbed molecule the most intense satellite occurs at  $\approx 7$  eV below the main line. We assign this peak to excitations between those orbitals resulting from the coupling between  $N_2$  and metal levels as discussed in section 3. The electronic excitations giving rise to this satellite peak take place into the same level ( $\pi^*$ ) as in the case of the local intramolecular  $N_2$  satellites, but start from an orbital with large metal character as opposed to the high  $N_2$  character for the starting level of the local  $N_2$  excitation (see fig 2b). This will be discussed further below. The structure at  $\approx 29$  eV excitation energy has not been discussed so far. It is not clear how to assign it. Whether it is due to shake-off structures (observed in this energy range for CO coordinated systems) could be decided on the basis of the Auger N-KLL spectrum of the complex [4]. Studies in this direction are in progress.

<sup>‡</sup> See also ref [41] for the splitting of the  $\pi-\pi^*$  excitation in free  $N_2$

This qualitative discussion, presented so far, shows that a comprehensive, unique interpretation of the satellite structure of compounds and adsorbates can indeed be found on the basis of a surface-molecule concept. The excitations on the adsorbed molecule can be identified in comparison with the free molecule. Intermolecular excitations are found, the intensities of which are in accord with qualitative predictions.

#### 4.2. Theoretical results and comparison to experiment

In order to lend additional theoretical support to our qualitative interpretation we present the results of a configuration-interaction study on the entire complex to describe the two possible N1s core-hole ionizations of the complex as well as the electronic structure of the neutral system. Fig 4 contains the charge distribution calculated for the

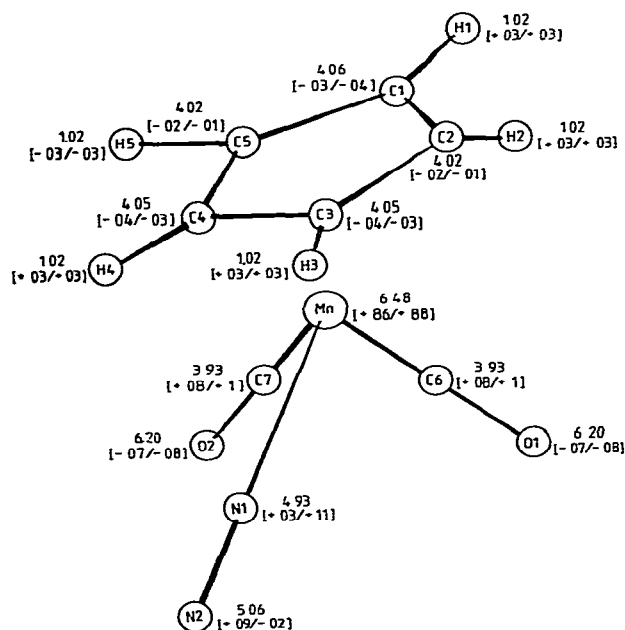


Fig 4. Atomic electron densities for the neutral molecule and charge densities for the ions. The first value in brackets is the charge density upon core ionization of the metal adjacent nitrogen (N1), the second is the charge density upon core ionization of the nitrogen further separated from the metal (N2).

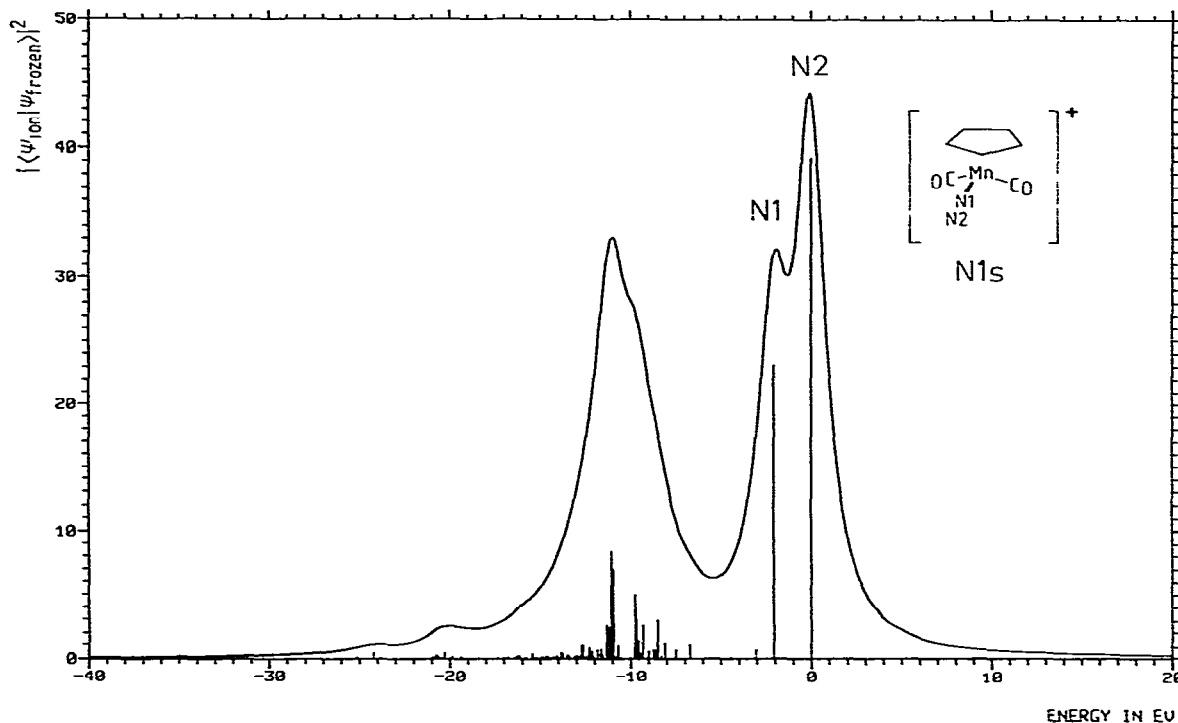


Fig 5 Calculated N1s spectrum of  $(C_2H_5)(CO)_2MnN_2$ . Energies are given relative to the line at lowest binding energy. Spectrum convoluted by a lorentzian of fwhm 1.7 eV

ground state of the neutral system and for the two equivalent-core states. The important result for the further discussion is the charge distribution on the nitrogen moiety for the neutral system. We find the nitrogen atom separated from the metal atom negatively charged, while the metal adjacent nitrogen carries a positive charge. Using this charge distribution we calculate a relative chemical shift for the two nitrogen atoms of 2.46 eV with the metal adjacent nitrogen at higher binding energy. We used the ground-state potential model as discussed by Gelius [42] and employ the optimal parameter for nitrogen [30]. For comparison with experimentally observed chemical shifts differential relaxation energies have to be included. In order to do this according to the procedure outlined in section 3 the complete spectral function of each core hole has to be known. Fig. 5 shows the superimposed spectral functions of the two core holes. Fig. 6 shows the separate contributions. The

sum rule [eq. (2)] yields a relaxation energy by 0.4 eV larger for the metal adjacent nitrogen as compared to the second nitrogen which then decreases the relative chemical shift to 2.06 eV, keeping the sequence of the core ionizations as expected from ground-state charge distribution. The calculated chemical shift of 2.06 eV compares fortuitously well with the experimental value of Binder and Sellmann [36].

The consequences of the ionization process for the electron distribution for both nitrogen atoms are shown in fig. 7. In fig. 7 the density-difference maps in the plane indicated in the inserts of fig. 6 are plotted. The  $z$  axis is a measure for the charge density. The difference is taken between the frozen ion state, described by the valence-electron wavefunction of the neutral system, and the equivalent-core-ion ground state. For both hole states a rather high electron density accumulates on the ionized atom to screen the core hole. The

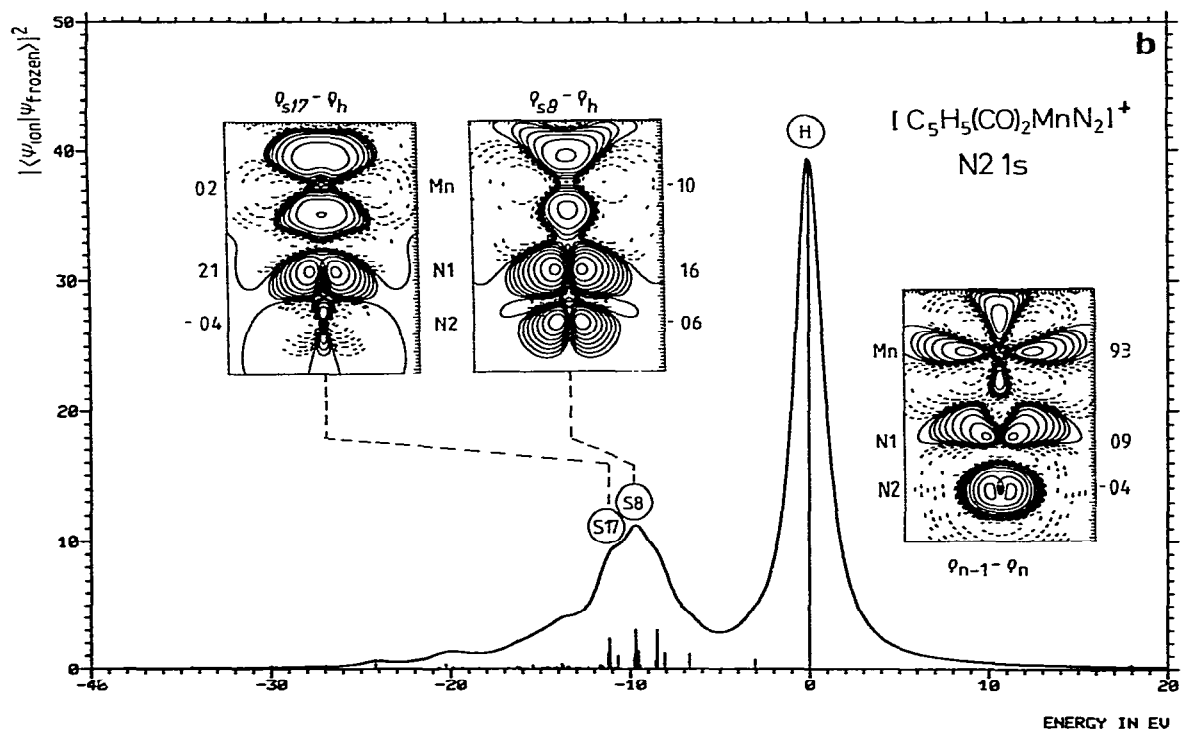
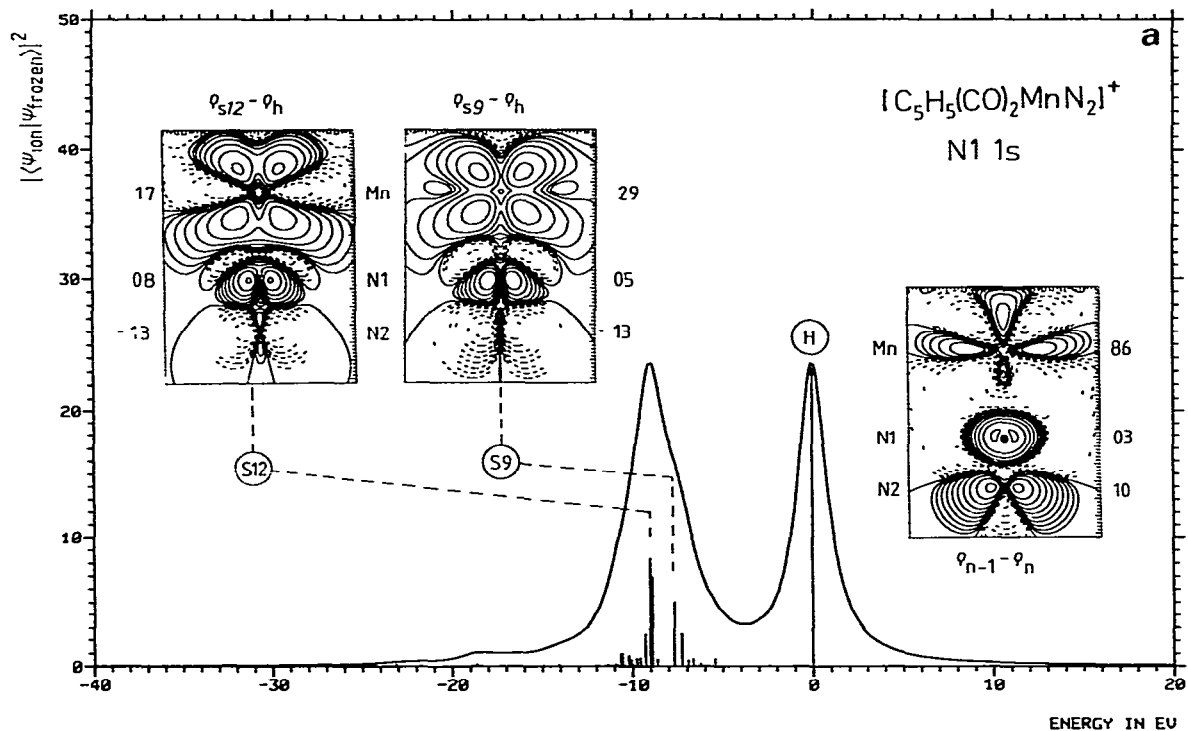


Fig 6. (a) Calculated N1s spectrum of the metal adjacent nitrogen of  $(C_5H_5)(CO)_2MnN_2$ . For electron-density difference maps see text (b) Calculated N1s spectrum of the non-metal adjacent nitrogen of  $(C_5H_5)(CO)_2MnN_2$ . For electron-density difference maps see text (The plotting plane is the same as in fig 7)



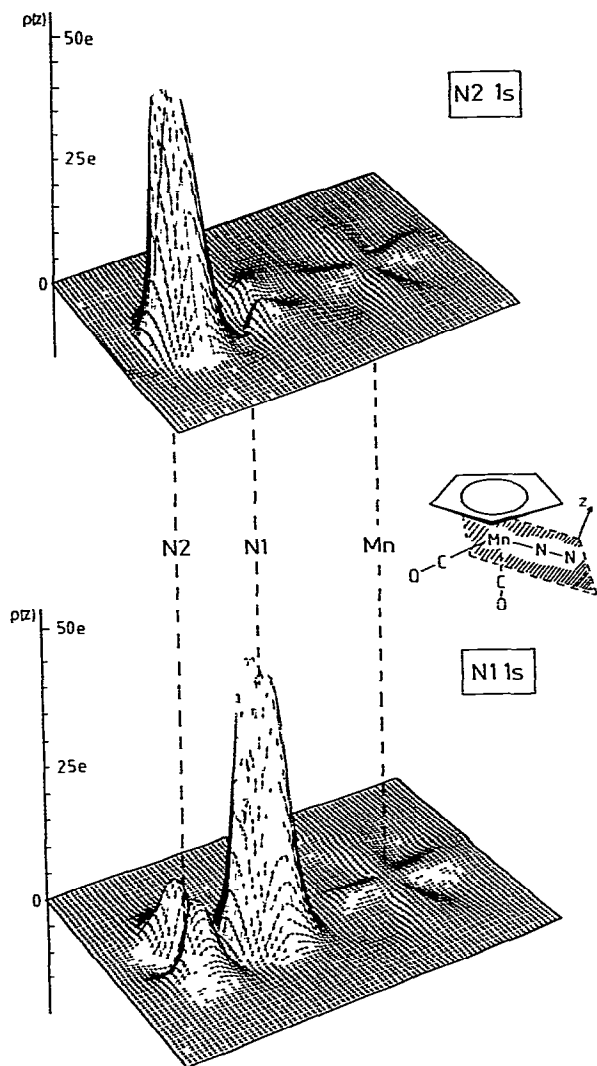


Fig. 7. Three-dimensional plots of the primary hole states marked  $(\rho_{N-1} - \rho_N)$  in fig 6a and fig 6b. The plane chosen in the molecule is indicated.

size of the peak indicates the localization of the screening charge. The absence of “negative” peaks of comparable size is another indication for this localization. It seems reasonable by inspection of fig. 7 that the relaxation energy is similar for the two core holes. The slightly larger relaxation energy of the metal adjacent nitrogen, however, has a rather strong influence on the relative intensities

of the shake-up satellites for the two core holes (see fig. 6). This is a quantitative documentation of the statement made in section 3 that the satellite intensity is very sensitive to the size of the LCAO coefficients of the wavefunctions. This will be discussed in detail further below.

The calculated satellite excitation energies (see fig. 5) as well as the overall relative intensities are in qualitative agreement with the experiment of fig. 1. Out of the 600 excited states used to calculate the spectral function of the two N1s core holes only 142 states get non-zero intensity. At this point it is interesting to investigate the influence of double excitations on satellite intensity and excitation energy. We have therefore attempted an equivalent calculation using only singly excited states. The result is presented for the two hole states in fig. 8. The qualitative result is similar to the one found for the full calculation, in particular as far as the trend in satellite intensities for the two different core holes is concerned. The relative satellite intensity, however, is much smaller in fig. 8 compared to fig. 6. Also, the excitation energy is smaller as compared to an equivalent calculation of coordinated CO [43]. From this we learn that in the case of coordinated  $N_2$ , the doubly excited states play an important role to reproduce the observed rather large excitation energy and the intense satellite structure. This result discussed already qualitatively in section 3 is quite in accord with chemical intuition. It is well known that a Hartree-Fock description fails to correctly describe the dissociation of a system, or the bonding in a weakly interacting system. In order to achieve the correct behaviour, correlation has to be taken into account. For a closed-shell system the lowest-order contributions in a configuration-interaction expansion to describe the correlated wavefunction are doubly excited configurations [44]. This is a reason why doubly excited states do not contribute as significantly in coordinated CO systems, where the metal-molecule bond is stronger [43].

Let us now investigate in detail the nature of the ion states involved in the most intense shake-up transitions. Using the electron density distribution inserted in figs. 6a and 6b we can achieve this goal. We start with the N1s core hole on the metal adjacent nitrogen. On the right-hand side of fig. 6a

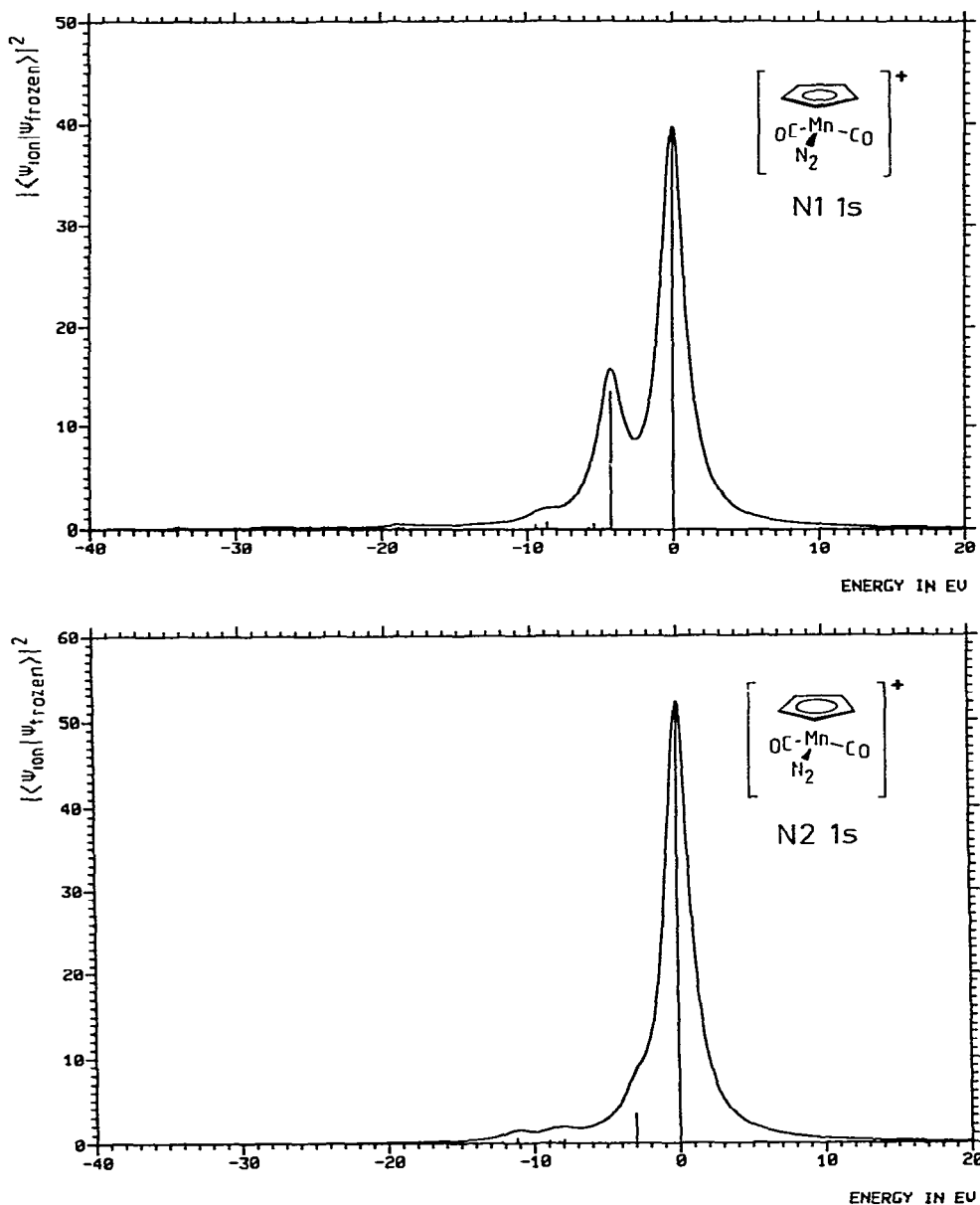


Fig 8 (a) Same as fig 6a using only singly excited ion states (b) Same as fig 6b using only singly excited ion states

the electron-density difference map (see also fig 7 for a definition of the plotting plane) calculated from the frozen ion state, described by the valence-electron wavefunction of the neutral system, and the equivalent-core-ion ground state is plotted.

Solid lines represent electron gain in the ion, while broken lines represent electron loss. The effect of core-hole creation on the valence-electron distribution is obvious: A rather high electron density accumulates on the ionized atom to screen the core

hole. As a consequence the valence-electron density is redistributed all over the system. Within the plane plotted, the entire  $N_2$  moiety gains electrons, even the non-ionized nitrogen atom, while the metal atom loses electrons. The integrated total densities per atom are shown in fig 6 for comparison. The net effect of the N1s ionization in the complex is a loss of  $0.3 e$  relative to the neutral system, where the metal center already carries  $0.52 e$  positive charge. This loss is small compared to the electron-density loss calculated for N1-CO ( $0.9 e$ ) upon creation of a C1s hole. The larger charge transfer in the latter system is partly due to the higher electron density on the metal atom in the neutral N1-CO system. In both cases, namely C1s ionization in N1-CO and N1s ionization in the manganese complex the metal atom carries an absolute charge of  $\approx 0.9 e$  after ionization. This charge is transferred from the metal towards the coordinated molecule through a channel of  $\pi$  symmetry. We see from the plots of the hole states that simultaneously a small amount of charge is transferred back towards the metal through a  $\sigma$  channel. This is due to the increased coupling between unoccupied  $\pi$  orbitals of the coordinated molecule but decreased coupling of the occupied  $\sigma$  orbitals of the coordinated molecule to the metal after ionization as pointed out in section 3.

As examples for excited ion states we show the electron redistribution upon electron excitation for two states. To map out electron distributions the equivalent-core ground state has been subtracted from the excited states. We have calculated the plots for those states that lead to large overlap with the frozen state. The largest contributing determinant, according to eq. (3), to the most intense satellites results from the HOMO-LUMO excitation in the core-ionized complex. The character of these orbitals is shown in fig 9. The HOMO can be looked at as the bonding combination of the  $1\pi_g N_2$  orbital and a metal d orbital, while the LUMO is the antibonding combination of the same orbitals (see section 3). The distribution of atomic-orbital coefficients on the  $N_2$  moiety constituting the molecular orbitals of the ion is very similar to the distribution in coordinated CO [43]. The corresponding orbitals for the Ni-CO system have been included in fig 9 for comparison

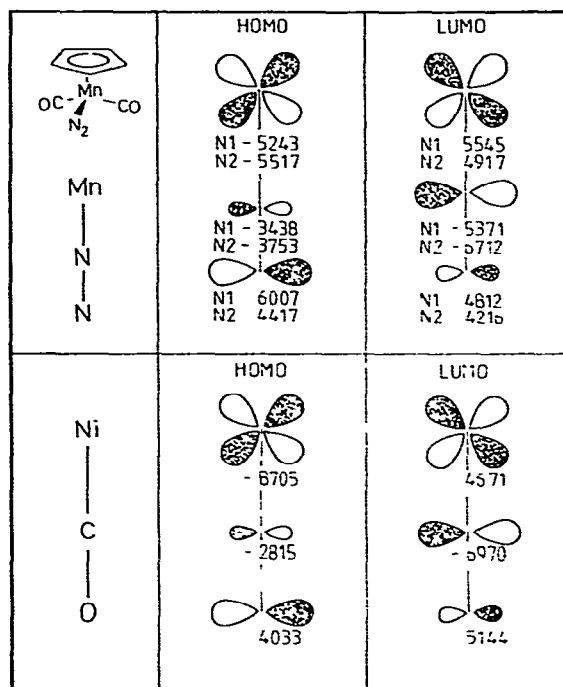


Fig 9 Schematic representation of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital of  $(C_2H_4)(CO)_2MnN_2^-$  in the region of the metal- $N_2$  bond. The HOMO and LUMO of  $NiCO^-$  upon C1s ionization are shown for comparison [43].

[43] The unoccupied linear combination has a rather large coefficient on the ionized center, while the occupied linear combination has a larger coefficient on the non-ionized nitrogen atom. Therefore upon excitation charge is transferred towards the ionized center. It is interesting to note that through the excitation a considerable charge transfer comes from the non-ionized nitrogen. This is clearly seen in the first plot for one of the intense satellites. The second nitrogen loses  $0.1 e$ , while the ionized center gains  $0.04 e$  with respect to the equivalent-core ground state. A very similar situation is found for the other excited states below 16 eV excitation energy as exemplified. The state above 16 eV excitation energy belongs to the  $1\pi_u-1\pi_g^*$  excitation in free  $N_2$ . For comparison we show in fig. 10 the calculated spectrum of free  $N_2$ . The intensity of this state is rather low, but its

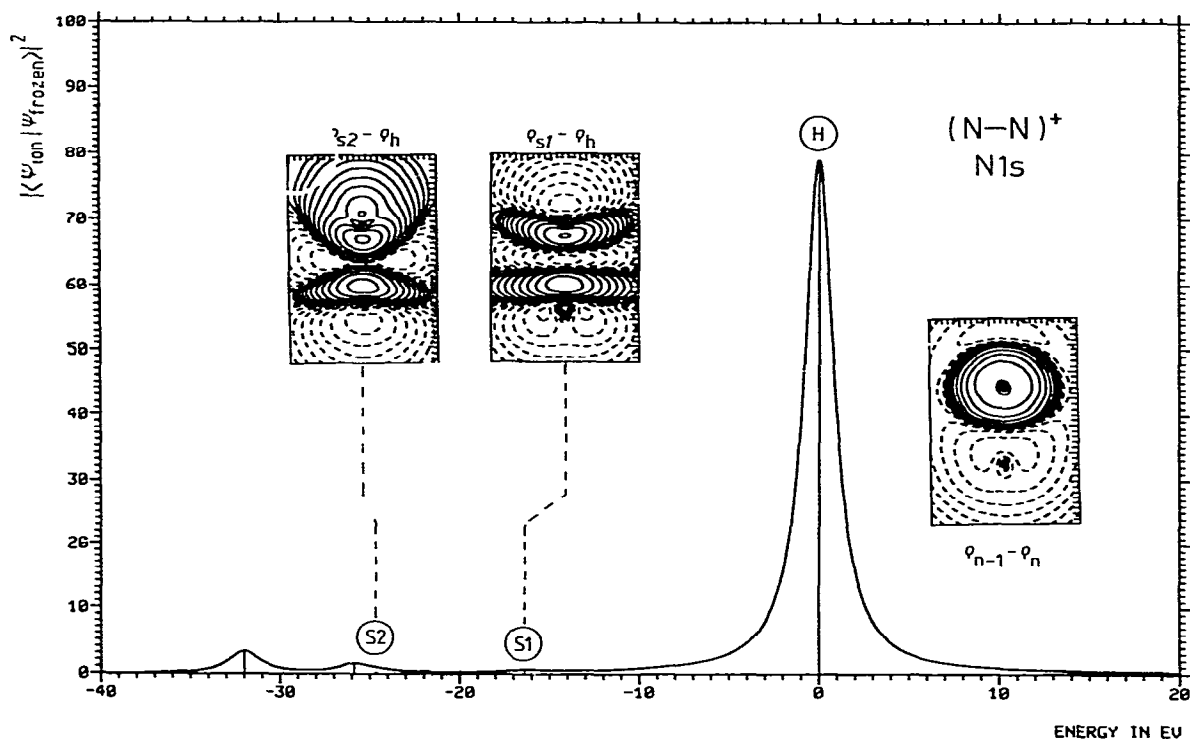


Fig 10 Calculated N1s spectrum of free  $N_2$  using only those doublet spin combinations where the valence excitation can be described by a singlet state [5]

energy is close to the observed peak

The discussion for the hole and excited hole states of the nitrogen further separated from the metal center proceeds very much in the same way. The calculated (see fig 6b) reduced satellite intensity in the case of this  $N_2$  ionization can be traced back to the smaller overlap of determinants created from the HOMO-LUMO excitation and the frozen ion state. As seen in fig. 9 the distribution of atomic coefficients in the HOMO and the LUMO for this ionization is slightly different from the one found for the ionization of the metal adjacent nitrogen. In particular, the coefficients on the  $N_2$  moiety are more balanced in the occupied bonding combination, while the unoccupied antibonding combination has a large coefficient on the metal adjacent nitrogen. An excitation into this orbital therefore does not contribute to a screening of the hole on ionized nitrogen. This rationalizes the calculated differences in satellite intensity and re-

laxation energy between the two inequivalent nitrogen core holes

## 5. Conclusions

From our study we draw the following conclusions.

(a) The photoelectron spectrum of the N1s electrons of a coordinated nitrogen molecule bound within a finite complex exhibits strong satellite structure similar to nitrogen adsorbates on transition-metal surfaces.

(b) The intensities of the satellites relative to the main lines for the coordinated nitrogen molecule are larger than for coordinated carbon monoxide. The excitation energy is larger than in the case of carbon monoxide.

(c) The experimental spectrum can be repro-

duced by a configuration-interaction calculation using LCAO MO SCF wavefunctions on the basis of the equivalent-core approximation. The two inequivalent nitrogen atoms in the coordinated system lead to ion states that are energetically shifted relative to each other, with the nitrogen further separated from the metal at lower binding energies. Ionization of the metal adjacent nitrogen leads to more intense satellite structure than the ionization of the nitrogen atom further separated from the metal. This can be rationalized by one-electron considerations involving the HOMO and LUMO of the two equivalent-core-ion ground states. The larger excitation energy of the satellites in coordinated nitrogen systems with respect to coordinated CO can be traced back to strong contributions of doubly excited states due to the weaker bonding in  $N_2$  coordinated systems.

(d) The spectrum of the finite complex shows all the characteristics of the photoelectron spectra of nitrogen adsorbed on transition-metal surfaces. The analysis presented lends support to an interpretation of the core spectra of adsorbed nitrogen in terms of the ionization of two inequivalent nitrogen atoms rather than in terms of substrate band structure. It supports a "surface-molecule" concept for the interpretation of photoelectron spectra even for weakly chemisorbed molecules.

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