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An SCF XαSW study of the electronic structure and X-ray and photoelectron spectra of Fe(II) and Fe(III) hexacyano complexes in a cluster approach

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The electronic structure of the hexacyano complexes $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ as clusters of the cyanide complex salts has been calculated by the SCF XαSW method. Theoretical photoelectron, X-ray emission and absorption spectra have been constructed. The contribution of the resonance emission to the X-ray emission spectra has been estimated. On the basis of detailed comparison of the theoretical and experimental spectra an assignment of the fine structure of the spectra has been proposed.

Key words: Photoelectron and X-ray spectra — $[Fe(CN)_6]^{n-}$ — SCF XαSW — Resonance emission — Spin-polarization

Introduction

Cyanide complex salts of alkali earth and alkali metals are typical solid state coordination compounds of transition metals with strong field ligands in which the coordinate bond formation occurs through σ-donation and π-back donation [1]. Because of their relatively simple structure these compounds are widely used as model system in the theoretical studies of the electronic structure of coordination compounds. There have been numerous experimental and quantum-chemical studies of the electronic structure of hexacyanide complex salts. X-ray photoelectron (PE) [2-7], X-ray emission (XE)Fe$L\alpha$ [4, 7, 8], C$K\alpha$ [4, 9], N$K\alpha$ [7], and Fe$K\beta_5$ [7, 8, 10-12] spectra have been reported. Quantum-chemical non-empirical calculations have been performed using self-consistent field (SCF) methods: Hartree–Fock–Roothaan (HFR) [6], Xα discrete variational (XαDV) [13] methods, Xα scattered wave (XαSW) method with touching [14–18] and overlapping [19] atomic spheres and with generalized partitioning scheme (XαSWGP) [20]. The results of all these calculations are rather contradictory. Especially much disagreement is found between the HFR and Xα data. Moreover, the comparison with experiment has been done, as a rule, only for the ionization potentials and not for the PE and XE spectra themselves. Taking into account that there are only two to three maxima in the experimental spectra of the valence levels of the hexacyano complexes while their MO number is equal to 14, such a comparison is clearly inadequate to pick out the correct theoretical results and to obtain a reliable information on the detailed electronic structure of complexes.

A more comprehensive test of the quality of a quantum-chemical calculation can be, in our opinion, a comparison, on a common ionization potential scale, of the full sets of X-ray and PE spectra reflecting, in the one-electron model, the structure of occupied and unoccupied valence MO's. As far as we know, no such a comparison has been reported in the literature for the hexacyano complexes of Fe(II) and Fe(III). Therefore, in the present study we made an attempt to develop a good-quality XαSW model of the electronic structure of the hexacyano complexes of iron on the basis of such a comparison between theory and experiment and proposed an assignment of the fine structure of their PE and X-ray spectra. We also present an analysis of some aspects of chemical bonding in the complexes and various mechanisms of the fine structure formation of their spectra, in particular, resonance emission, relaxation and spin-polarization.

Computational details

Our calculation were performed for octahedral (point symmetry group O_h) hexacyano anions $[Fe(CN)_6]^{n-}$ as clusters of the solid state ferro- and ferricyanide complex salts with $n = 4$ and 3, respectively, using the SCF XαSW [21, 22] method with the exchange factors α taken from [23]. The maximum values of 1 used in the partial wave expansion were equal to 3, 2 and 1 for the outer (out), Fe and the ligand atom spheres, respectively. The atomic sphere radii (Table 1) were determined using Norman procedure [24] with touching spheres of Fe and C which proved to be useful in the case of transition metal carbonyl complexes [25, 26]. We also performed a calculation of a free cyanide ion CN^- using the atomic sphere radii take from the calculation of the ferrocyano anion.

It should be noted that we also tried some other ways for the choice of the atomic sphere radii [14–18] but it was only the above method, analogous to [19], that gave a satisfactory description of the full set of the PE and X-ray spectra of the complexes. The effect on the cluster of all other ions of the crystal was taken into account by the use of a positively charged Watson sphere [27] with a radius equal to that of the outer sphere and a charge $n+$. The boundary conditions were also chosen in another way which was as follows. Using the procedure [28] and the structural data for the salts $Cs_2MgFe(CN)_6$ [29] and $Cs_2LiFe(CN)_6$ [30]

Table 1. Molecular geometry, atomic sphere radii (a.u.), degrees of overlapping (DO)[a] and virial relations $(-2T/V)$

Paramerer	$[Fe(CN)_6]^{4-}$	$[Fe(CN)_6]^{3-}$	CN^-
R_{Fe-C}	3.647 [35]	3.641 [30]	
R_{C-N}	2.194 [35]	2.170 [30]	2.194
b_{Fe}	2.069	2.066	
b_C	1.578	1.575	1.578
b_N	1.603	1.578	1.603
b_{out}	7.444	7.411	2.688
$DO_{Fe-C}(\%)$	0	0	
$DO_{C-N}(\%)$	45	45	45
$-2T/V$	1.0011	1.0012	0.9996

[a] $DO_{A-B}=[(b_A+b_B)/R_{A-B}-1]\cdot 100\%$, where b_A, b_B are the sphere radii of the atoms A and B; R_{A-B} is the distance between the atoms A and B

crystals the shifts of the potentials corresponding to the sum over the "muffin-tin" averaged electrostatic potential contributions from the non-cluster ions were calculated for each atomic sphere. However, the results of an XαSW calculation obtained with these potential shifts only slightly differed from those of the Watson sphere calculation. Therefore, in the following only the Watson sphere data is used. The ionization potentials, I_i, and the transition energies, ω, were calculated using the Slater transition state approach [31]. For the ferricyano anion $[Fe(CN)_6]^{3-}$ having one open $2t_{2g}^5$ shell the spin polarization effects were taken into account by spin-polarization computation. The intensity distribution in the valence region of the PE spectra were calculated according to the independent atom model proposed by Gelius [32] using the partial charges in the atomic spheres, $Q_l^{\alpha i}$, instead of the atomic orbital populations. The photoionization cross sections of the atomic shells were those of a Dirac-Slater calculation [33]. The absolute oscillator strengths of the dipole one-electron diagram transitions $k \to i$ or $i \to k$ (k is an inner level) in the X-ray spectra were calculated in a "length" form using the orbital wave functions of the cluster ground state. It can be shown that they are proportional, to a sufficient accuracy, to the respective orbital charges in the atomic spheres, $Q_l^{\alpha i}$. We have also calculated the energies and the intensities of the XE satellites due to the resonance emission using the approach [34]. The theoretical X-ray and PE spectra were obtained by summarizing over the Lorentzian and Gaussian lines, respectively, using calculated intensities and experimental widths. The spin-orbital interaction was nowhere taken into account.

Electronic structure and spectra

The structure of the valence MO *region*

The XαSW valence MO diagrams for the free CN^- ligand and the hexacyano iron complexes are shown in Figs. 1-3 together with their experimental and theoretical spectra. One-electron transitions from the valence MO's to the unoccupied inner Fe 1*s*, Fe $2p_{3/2}$, C1*s* and N1*s* levels of singly ionized clusters give rise to the diagram lines in the Fe $K\beta_5$, Fe$L\alpha$, C$K\alpha$ and N$K\alpha$XE spectra,

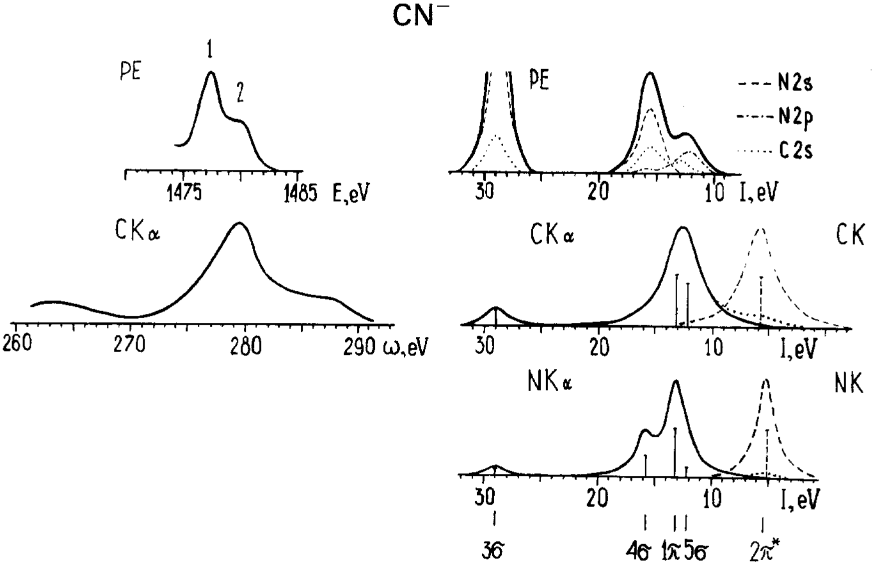
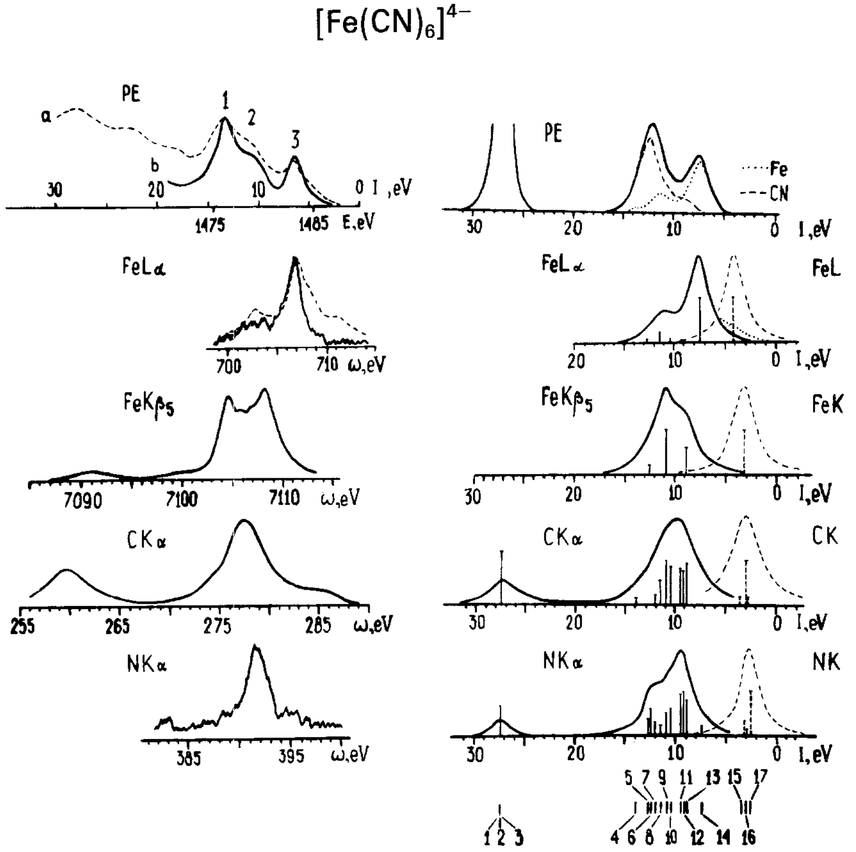


Fig. 1. Experimental and theoretical spectra of the cyanide anion CN⁻. Experimental spectra: PE Al*Kα* [7] and XE CK_α [4] of the salt KCN. *E* is the electron energy, *ω* is the photon energy

respectively. One-electron transitions from these inner levels to the vacant MO's give rise to the discrete part of the XA spectra. In the left-hand parts of these figures are shown the experimental spectra aligned using the inner level ionization potentials [4, 7, 11]. The experimental PE and XE Fe*Lα* spectra were lined up with their $2t_{2g}$ maxima. Unfortunately, no N*Kα* emission spectra for CN⁻ and $[Fe(CN)_6]^{3-}$ seem to have been reported in the literature. In the right-hand parts of the figures are shown theoretical PE and XE spectra (solid lines) and theoretical XA spectra (dashed lines). In order to illustrate the contribution of the resonance emission to the XE spectra the vacant orbital regions of the latter are shown by dotted lines (resonance emission is taken into account) and solid lines (resonance emission being neglected). The dotted and dashed lines under the theoretical PE spectra represent the contributions from the metal and ligands AO's, respectively.

Let us first describe the electronic structure of the complexes in the traditional manner, in terms of the simplest one-electron MO LCAO scheme. The valence σ-MO's of the complexes are formed due to the interaction of the $4s(a_{1g})$, $3d(e_g)$ and $4p(t_{1u})$ metal AO's with the σ-MO's of the six CN⁻ ligands (a_{1g}, e_g, t_{1u}). The π-MO's of the complexes result from the interaction of the $3d(t_{2g})$ and $4p(t_{1u})$ AO's of iron with the π-MO's of the six ligands (t_{1g}, t_{2g}, t_{1u}, t_{2u}). It can be seen from Figs. 1-3 that the experimental PE and XE spectra of the free and the coordinated ligands are very close to each other. From this fact it was suggested [4] that the changes in the electronic structure of the CN⁻ ligands upon their coordination by the iron atom are very small and a model of the electronic structure of the complexes and an interpretation of the fine structure of their spectra have been proposed which are as follows. The highest occupied MO is

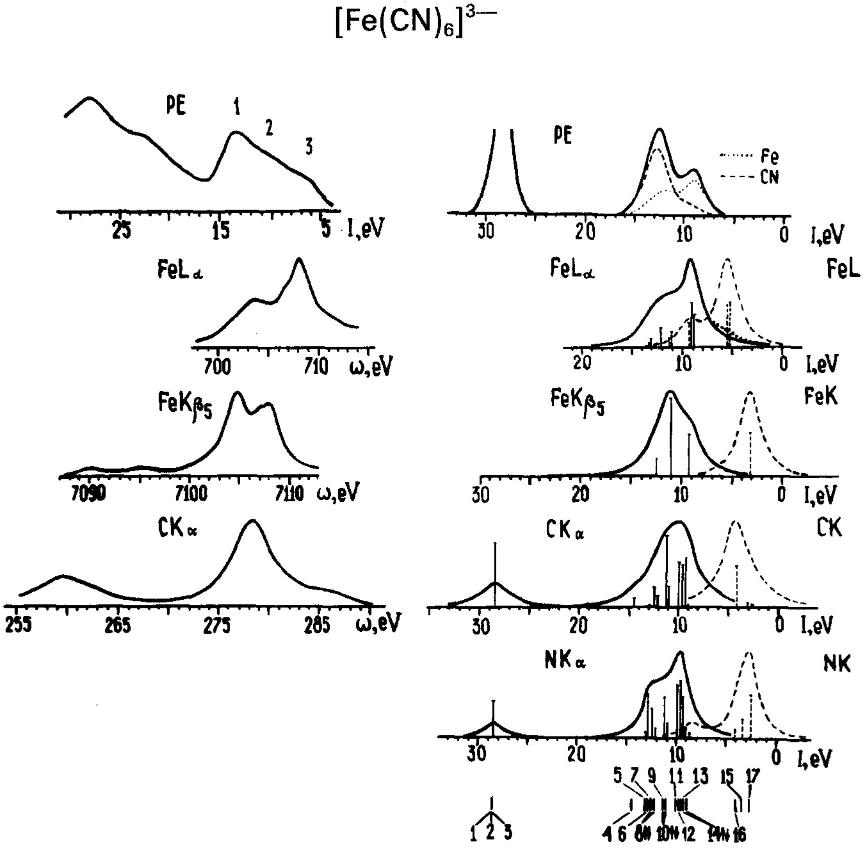


1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$1a_{1g}$	$1t_{1u}$	$1e_g$	$2a_{1g}$	$2e_g$	$2t_{1u}$	$3a_{1g}$	$3e_g$	$3t_{1u}$	$1t_{2g}$	$1t_{2u}$	$1t_{1g}$	$4t_{1u}$	$2t_{2g}$	$5t_{1u}^*$	$4e_g^*$	$3t_{2g}^*$

Fig. 2. Experimental and theoretical spectra of the ferrocyano anion $[Fe(CN)_6]^{4-}$. The experimental spectra: Al*K*αPE (scale *b*); XE Fe*L*α (*solid line*), N*K*α of the salt $Na_4Fe(CN)_6$ [7]; Mg*K*αPE of the salt $Li_4Fe(CN)_6$ (scale *a*); XE Fe*L*α (*dashed line*), C*K*α [4] and Fe*K*β_5 [11] of the salt $K_4Fe(CN)_6$

the $2t_{2g}$ one composed predominantly by the 3*d* metal AO. Ionization of this MO gives rise to the low-energy peak 3 of the PE spectrum and the intense right-hand maximum of the XE Fe*L*α spectrum. All other MO's are mainly composed of the symmetry adapted orbitals of the ligands and correspond to the remaining maxima 1 and 2 of the PE spectrum which in this region is almost completely identical to that of the free CN^- ligand. This interpretation is in good agreement with the results of our theoretical calculations of the electronic structure and the spectra of the complexes.

The chemical bonding occurs through electron density transfer from the ligand to the metal via a system of two σ-orbitals, $2e_g(4\sigma)$ and $3e_g(5\sigma)$, and one π-orbital



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$1a_{1g}$	$1t_{1u}$	$1e_g$	$2a_{1g}$	$2e_g$	$2t_{1u}$	$3a_{1g}$	$3e_g$	$3t_{1u}$	$1t_{2g}$	$1t_{2u}$	$1t_{1g}$	$4t_{1u}$	$2t_{2g}$	$5t_{1u}^*$	$4e_g^*$	$3t_{2g}^*$

Fig. 3. Experimental and theoretical spectra of the ferricyano anion $[Fe(CN)_6]^{3-}$. The experimental spectra: Mg*Kα* PE of the salt $Li_3Fe(CN)_6$ [4]; XE Fe*Lα* and C*Kα* [4] of the salt $K_3Fe(CN)_6$. On the *right* the theoretical spectra are shown with spin-polarization effect taken into account

$1t_{2g}(1\pi)$. Given in the parentheses are the MO's of the free CN^- ligand from which these MO's of the complex were formed. Due to this mechanism the $2e_g$, $3e_g$ and $1t_{2g}$ MO's show themselves in the Fe*Lα* emission spectrum as the second (left-hand) maximum. As can be seen from the relative intensities of the emission lines this bonding mechanism is dominated by σ-donation. The π-acceptor mechanism occurs through the highest occupied $2t_{2g}$MO and can be regarded as back donation of the electronic density from the metal to the vacant antibonding $2\pi^*$ orbitals of the CN^- ligands. As can be seen from the theoretical C*Kα* and N*Kα* XE spectra this transferred density localizes on the nitrogen atoms. On the whole, we can state a satisfactory agreement between theory and experiment (except for $K\beta_5$ spectra) and, consequently, the correctness of the employed

SCF XαSW model of the electronic structure of the hexacyano complexes of iron, i.e. the procedure used for the choice of the atomic sphere radii. We now turn to analyzing the reasons for the observed differences between the theoretical results and the experiment. The most significant deviation concerns the size of the energy gap between the ligand levels and the metal higher occupied MO $2t_{2g}$ for which the theory gives an underestimated value. This results in a decreased separation of the 1 and 2 maxima and the "smearing" of the middle maximum 2 of the PE spectra and an underestimated energy difference of the two maxima of the XE Fe*Lα* spectrum. Since the XαSW model used here has led to good results with the neutral molecular carbonyl complexes of the type $Cr(CO)_6$ [25, 26] and our SCF XαSW eigenvalues ε_i for the ground state of the Fe(II) hexacyano anion are practically the same as the SCF XαDV ones given in [13] (see Fig. 4) we are not inclined to consider this computational defect as being due to the "muffin-tin" averaging of the potential. We think that this deficiency of the theory is inherent in the nature of the one-particle Xα approximation.

For high-symmetry molecules or clusters of solids this approximation leads to underestimated ionization potentials for the inner levels of the ligands and the valence MO's both of which are delocalized throughout the whole complex mainly due to the space symmetry requirements [36–38]. Both the former and the latter have the same characteristic feature- they consist of weakly overlapping AO's of only one type of the ligand atoms. In the complexes under study such a situation takes place for the 1s levels of the ligands and for two groups of MO's: $1a_{1g}$, $1e_g$, $1t_{1u}$ and $2a_{1g}$, $2e_g$, $2t_{1u}$ genealogically associated with the 3σ and 4σ orbitals of the six ligands. It is the second group of the valence orbitals resulting from the 4σ orbitals of the nitrogen lone-pairs which are of the most interest for us. According to the results [37, 38] it can be expected that neglecting the symmetry requirements in the calculations of the ionization potentials, i.e. the adoption of the localized picture of the ionization will increase the ionization potentials of these orbitals by about 3 eV, in full agreement with experiment.

Not unfrequently, mostly in the calculations of the large cluster of solids where the self-consistent procedure is hazy, especially for the excited states, the eigenvalues ε_i of the ground state are used as the ionization potentials. Interestingly, that in this case the effect of the above mentioned deficiency of the Xα approximation on the eigenvalues ε_i is greatly reduced and practically disappears when using the ε_i values of a non-self-consistent calculation of the ground state of the cluster. This is illustrated in Figs. 4 and 5.

Figure 4 shows the MO diagrams for the ferrocyano-anion $[Fe(CN)_6]^{4-}$ obtained by various Xα procedures. To simplify the analysis the first three MO diagrams from the left were lined up with their $2t_{2g}$ orbitals with the fourth diagram obtained by the SCF XαSW method. Therefore, the vertical energy scale refers only to the three last MO diagrams. Comparison of the self-consistent eigenvalues ε_i(SCF XαSW) with the ionization potentials I_i (SCF XαSW) shows that the use of ε_i instead of I_i does increase the energy gap between the metal $2t_{2g}$ and the ligand orbitals. Comparison of the self-consistent results for ε_i (SCF XαSW) with the non-self-consistent ones (NON-SCF XαSW) indicates that giving up

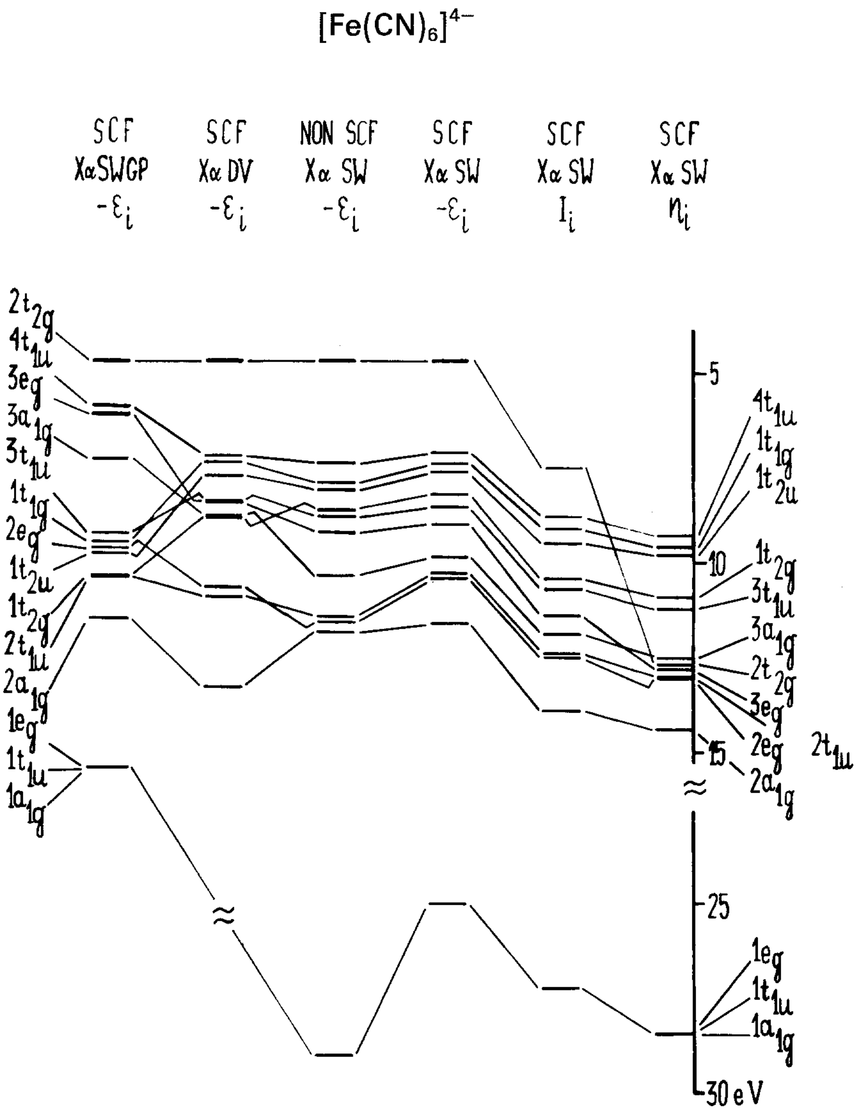


Fig. 4. MO diagram for the ferrocyano anion $[Fe(CN)_6]^{4-}$. ε_i are Xα eigenvalues of the ground state; I_i are ionization potentials taking into account the relaxation effect; η_i are ionization potentials in the frozen Xα orbital approximation. For comparison, data from other Xα methods, Xα DV [13] and Xα SWGP [20] are also given

the self-consistent procedure leads to still further increase in this energy gap and it is these two groups of the cluster MO's $1a_{1g}$, $1e_g$, $1t_{2u}$ and $2a_{1g}$, $2e_g$, $2t_{2u}$ related with the 3σ and 4σ ligand orbitals that become significantly more lowered then the rest of the MO's, in full agreement with experiment.

For comparison, Fig. 5 shows theoretical spectra obtained on the basis of non-self-consistent and self-consistent data. It can be seen that apart from the $K\beta_5$ emission

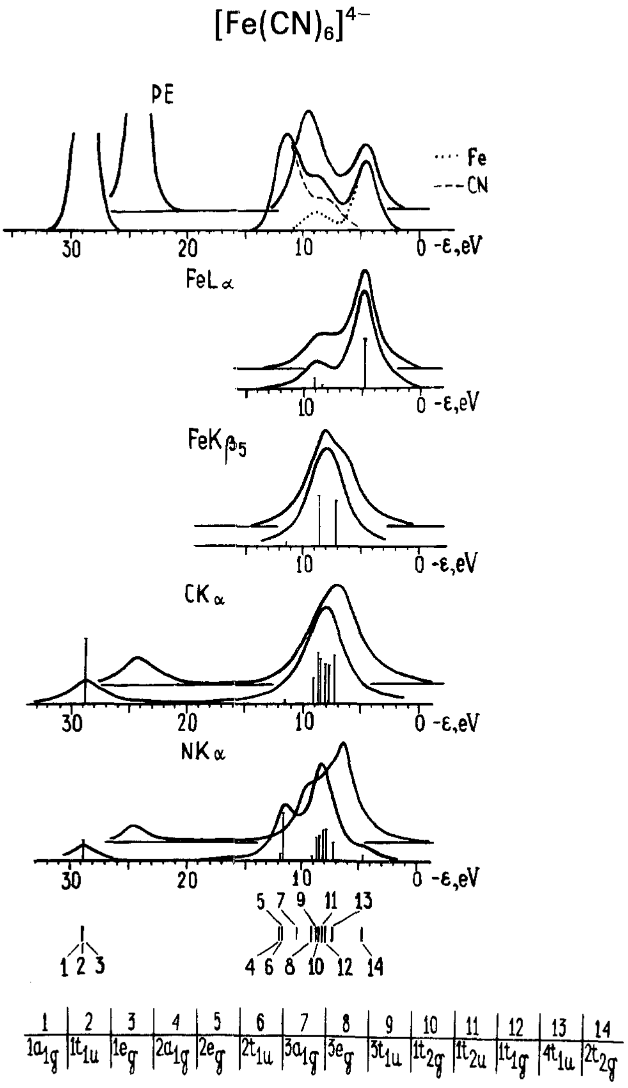


Fig. 5. Theoretical spectra of the ferricyano anion [Fe(CN)$_6$]$^{4-}$. *Upper* and *lower lines* represent SCF and NON SCF XαSW results, respectively. The energy scale corresponds to SCF, and the *vertical lines* to NON-SCF results

spectra, the non-self-consistent spectra are in better agreement with the experiment than the self-consistent ones: the distance between maxima 1 and 3 has increased and a new maximum 2 appeared in the PE spectrum; the splitting of the maxima in the metal and ligand XE spectra has also increased. This result is of great practical value since it permits us to obtain reliable data without performing time-consuming self-consistent calculations. In conclusion, we must point to the fact that there is strong disagreement between our SCF XαSW data and the SCF XαDV [13] ones, on the one hand, and the results obtained by the

SCF XαSWGP [20] and the HFR [6] methods, on the other hand, which appears to be due to computational errors in [6, 20].

Resonance emission

The calculations show (see Figs. 1-3) that the C$K\alpha$, N$K\alpha$, Fe$L\alpha$ XE spectra of the free CN$^-$ anion and the iron hexacyanides have an appreciable contribution from resonance emission, i.e. re-emission of an excited electron from the lower vacant MO's (these MO's are marked by asterisks). More exactly, by the resonance emission is meant the resonance elastic scattering of X-ray photons, a process in which (in the one-electron approximation) an electron excited by an X-ray photon with the energy ω from an inner level k to an unoccupied molecular level ν returns back emitting another photon having the same energy ω. To calculate the relative intensity of the re-emission lines in an XE spectrum an approach has been developed [34] where the non-trivial problem of calculating the total ionization cross-section of the inner level k is solved by applying a one-particle version of the known sum rule for the absolute oscillator strengths and by neglecting the dependence of the exciting X-ray intensity on the energy ω.

The contribution of the resonance emission to the XE spectra of CN$^-$ and the iron complexes shown in Figs. 1-3 by dots has been calculated within the framework of this approach. It can be seen that the resonance emission mechanism partially explains the appearance of the short-wave satellites in the XE spectra, i.e. satellites in the region of small ionization potentials. These results are in agreement with those obtained in [25, 26] for $3d$ metal carbonyl complexes.

X-ray absorption spectra

In addition to the resonance emission or re-emission, the vacant MO's of the complexes show themselves in the most direct manner in the XA spectra. The discrete part of the XA spectra of the compounds under study is formed as a result of the first three transitions to the vacant $5t_{1u}^*$, $4e_g^*$ and $3t_{2g}^*$ MO's (see Figs. 2, 3). Since no corresponding experimental XA spectra were available to us the theoretical spectra should be regarded only as a prediction. The presence of a hole in the $2t_{2g}$ orbital of the Fe(III) complex gives rise to the additional maxima in the FeL and NK absorption spectra and therefore the emission and absorption spectra overlap here. The lowest unoccupied MO of the complexes, $4a_{1g}^*$, consisting mainly of the Fe 4s AO does not appear in the XA spectra. The discrete part of the K absorption spectra of the free CN$^-$ is formed by the transitions of the 1s electrons to the antibonding unoccupied orbital $2\pi^*$. It should be noted that according to the law of energy conservation the maxima of the XA spectra coincide with the corresponding resonance emission peaks of the XE spectra as illustrated in Figs. 1-3.

Many-electron effects

Let us now consider some mechanisms by which the many-electron interactions affect the X-ray and PE spectra. We will concentrate only on the main lines of the PE spectrum corresponding to the one-electron ionization of the orbitals and the diagram lines of the XE spectra which are due to the one-electron transitions. The many-electron effects accompanying the ionization of the orbitals can be divided to a good approximation into two types: the relaxation effects and the correlation effects proper. While a consistent calculation of the correlation effects can be only achieved by using the many-body formalism, configuration interaction or Green's function methods the relaxation effects can be calculated within the framework of the SCF method provided that the self-consistent procedure is performed for each state separately. This modification of the SCF method is called ΔSCF.

For estimation of the relaxation effects in the Xα method it is useful to employ the ionization potentials of the frozen Xα orbital approximation [36, 39-41]

$$\eta_i = E_i^0 - E_0,$$

where E_0 is the energy of the complex in the ground state and E_i^0 is the energy of the complex with a hole in the ith one-electron level calculated using the MO's of the ground state. Then the contribution of the relaxation to the orbital ionization potential can be obtained as the difference of the frozen orbital ionization potential and the ΔSCF ionization potential I_i

$$\Delta I_i^{\text{rel}} = I_i - \eta_i.$$

It is well known that in the transition metal complexes the ionization from the MO's with considerable contributions of the metal *nd* orbitals is accompanied by very strong many-electron relaxation effects which often lead to a change in the valence MO's ordering. This effect is illustrated in Fig. 4 for the complex $[\text{Fe(CN)}_6]^{4-}$: whereas in the frozen Xα orbital approximation the $2t_{2g}$ MO was only the sevenths from above the relaxation effect makes it the first. For this reason the relaxation effect was taken into account in all calculations of the spectra (Figs. 1-3).

One of the ways of partially accounting for the correlation effects is to use spin-polarized SCF methods. Our calculation showed that in the diamagnetic Fe(II) complex the spin-polarization effects are negligible. The presence of the unpaired electron in the Fe(III) complex increases this effect to a value of 0.5 eV for the $2t_{2g}$ orbital. Nevertheless this value is still small and therefore it does not affect markedly the spectra resulting only in a "smearing" of their fine structure, in accord with experiment.

Conclusions

From the results of our studies of the cyano complexes of iron the following conclusions can be made. X-ray and PE spectra are connected in the most direct manner with the results of the quantum-chemical calculations: the ionization potentials and the partial charges or populations. The full set of theoretical X-ray and PE spectra is, in our opinion, a very good means for representing graphically the results of quantum-chemical calculations. The full set of X-ray and PE spectra is also well suited for testing a quantum-chemical theory, selecting an adequate electronic structure model and developing a calculational procedure. In the present case of the XαSW method it is the procedure of selecting the atomic sphere radii. With the properly chosen atomic sphere radii (Norman's radii) the Xα SW method is capable of describing, with a satisfactory degree of accuracy, those aspects of the electronic structure of the coordination compounds which are reflected in the X-ray and PE spectra of the valence orbitals. This method can give sufficiently correct results already at the stage of non-self-consistent calculations which is favourable when using a cluster approach to the description of the electronic structure of solids.

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