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MOLECULAR SPECTROSCOPY

X-ray Absorption Study of the Local Electronic and Atomic Structure of the Ferrohexacyanide Anion $Fe(CN)_6^{4-}$

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Abstract – The near fine structure of *K* spectra of nitrogen and carbon atoms and of $L_{2,3}$ absorption spectra of iron and potassium atoms in a solid-state ferrohexacyanide $K_4Fe(CN)_6$ is studied by the method of the quantum yield of the external photoelectric effect with an RSM-500 X-ray spectrometer–monochromator and bremsstrahlung from an X-ray tube with a tungsten cathode. The resonant features of the spectra obtained and of the Fe*K* spectrum known from the literature are identified within the framework of the extended quasi-molecular approach using a comparative analysis of the absorption N*K* and C*K* spectra of the complex $Fe(CN)_6^{4-}$ anion and free HCN molecule and also general quantum-chemical considerations about the nature of the chemical bond Fe–6(CN) in the complex in order to take into account the effect of this interaction on the formation of a general spectrum of the resonance excited states of the complex. As a result of the analysis performed, all form resonances are identified based on transitions of core electrons to vacant molecular orbitals (MO), the symmetry of these MOs and their energies relative the highest filled MO of the complex are determined, and the region of spatial localization of each resonance is found. It is established that the lowest vacant MO of the complex is mainly formed from the antibonding 2π orbitals of CN^- ligands. By treating π and σ resonances strongly localized at ligands as a result of splitting of the $1s \longrightarrow 2p$ atomic resonance in the absorption *K* spectra of nitrogen and carbon atoms caused by the anisotropic molecular field of the CN^- anion, the interatomic distance d(C–N) = 1.09 Å, which is ambiguously estimated from other experimental methods, is found for the $Fe(CN)_6^{4-}$ complex from the values of splitting $\Delta E(\pi - \sigma)$ in spectra of HCN and H_3CNO_2 molecules and this complex.

INTRODUCTION

X-ray absorption (XRA) spectra of simple molecular compounds of atoms of the second periodic group illustrate the fundamental relation between their near fine structure (NFS) and such characteristics of their electronic and atomic structure as the energy and symmetry of free electronic states, interatomic distances, the chemical state (the effective charge) of an absorbing atom, its coordination, and the symmetry of the atomic environment [1 - 19]. This relation is based on the established physical regularities of formation of the NFS in XRA spectra, according to which the absorption bands dominating in the near-threshold spectral region appear due to the capture of *K* electrons by vacant MOs during XRA and the formation of the metastable states of the "*K*-ionized molecule + photoelectron" system (so-called form resonances), which are strongly localized in the molecular region.

The form resonances observed during scattering of X-ray photoelectrons are related to features of the potential relief of the molecular system. Therefore, it is reasonable that such resonant effects are retained with minor changes in spectra of polyatomic systems (large molecules and solids) containing individual fragments or structural groups (quasi-molecules) of atoms of the second periodic group [7, 15, 20 - 27]. It is obvious that quasi-molecular form resonances are the source of unique information on the local atomic and electronic structure of such polyatomic systems, which can be obtained from an analysis of the NFS in XRA spectra. However, obtaining this information from experimental data is considerably hindered because of the lack of reliable semiempirical methods of quantitative analysis of the NFS in XRA spectra of complex chemical compounds of various classes. The most progress in this field can be probably achieved using the quasi-molecular approach based on a comparative analysis of the NFS in spectra of a quasi-molecule and a free molecule of a similar structure (if possible, isoelectronic and isostructural) [21 - 24, 28 - 30]. In this case, in order to interpret in detail the resonance structure in the NFS in spectra of a quasi-molecule, one has to take into account its interaction with the environment in a polyatomic system [24 - 27]. Such an approach was successfully used, in particular, in a study of the NFS in XRA spectra of atoms of the second periodic group, which form in crystals the planar molecular oxyanions AO_n^{m-} surrounded by a coordination polyhedron consisting of simple monatomic cations [25 - 27].

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The aim of this paper is to elucidate the usefulness of the quasi-molecular approach to studying the NFS in XRA spectra of more complex polyatomic systems where molecular anions of the second periodic group surround cations of the 3*d* metal thus forming a large complex molecular anion. We studied a solid potassium ferrohexacyanide $K_4Fe(CN)_6$. The choice of this complex compound was determined mainly by the fact that one can expect strong resonant effects in the NFS in XRA spectra of the cyan anion CN^- in this polyatomic system because the latter dominate in spectra of free molecules HCN [31, 32], N_2 [1 - 3, 33], and CO [33], which are isoelectronic with the cyan anion. This complex compound was also chosen because there are no partially filled orbitals among its high-lying valence MOs [34, 35], which provides the singlet nature of the X-ray excited states resulting in a more simple interpretation of the NFS in its XRA spectrum. Finally, note that, previously, only the NFS in the absorption Fe*K* spectrum of potassium ferrohexacyanide was studied [36 - 39].

Table 1. Positions (in eV) of the NFS lines in XRA spectra of potassium ferrohexacyanide

Band	N*K* spectrum	C*K* spectrum	$KL_{2,3}$ spectrum	FeL_3 spectrum
A	399.6	286.6		
B	403.3	289.0		713.3
C	407.0	293.0		
a			296.2	
b			297.2	
a			298.9	
b			299.8	
c			302.7	
D	413.8			
E	417.2			
F	423.6	311.5		

EXPERIMENTAL

X-ray absorption study of solid potassium ferrohexacyanide $K_4Fe(CN)_6$ was performed by the method of quantum yield of the external X-ray photoelectric effect [40] using an RSM-500 X-ray spectrometer-monochromator with a 600 lines/mm diffraction grating coated with gold and having a radius of curvature $R = 6$ m [41]. By using bremsstrahlung from an X-ray tube with a tungsten cathode, the NFS of the absorption spectra in the region of *K*-ionization thresholds for carbon and nitrogen atoms and in the region of $L_{2,3}$-ionization thresholds for potassium and iron atoms were obtained with a resolution of $\Delta E = 0.8$ eV (C*K*, N*K*, and $KL_{2,3}$ spectra) and $\Delta E = 1.2$ eV (the $FeL_{2,3}$ spectrum). The origin of the C*K* and N*K* spectra was additionally studied a resolution of 0.3 and 0.4 eV, respectively. The NFS spectra were calibrated using characteristic X-ray lines CrL_α (21.64 Å; second order of diffraction), FeL_l (20.15 Å; second order of diffraction), TiL_l (31.36 Å), TiL_α (27.42 Å), CoL_l (18.292 Å), and FeL_α (17.59 Å) [42]. Other details of the method for investigating the NFS in the region of the N*K*- and C*K*-absorption edges are described in our papers [1, 2, 5, 43].

RESULTS AND DISCUSSION

X-ray spectra of potassium ferrohexacyanide obtained in this paper are presented in Figs. 1 and 3, and the positions of lines in the NFS spectra are given in Table 1 (the lines denoted according to the discussion below).

Potassium ferrohexacyanide is a monoclinic crystal with an island structure containing as structural units the stable polyatomic groups, complex $Fe(CN)_6^{4-}$ anions in which the iron atom is surrounded by six CN^- molecular anion ligands [44, 45]. The interaction of this octahedral complex with potassium cations K^+ in a crystal is purely ionic, while the chemical coordination bond inside the complex is mainly covalent and is effected by way of (i) the donor–acceptor transfer of the electronic density from cyan anions CN^- to the iron atom through bonding σ MOs (σ bonding) and (ii) the reverse dative transfer of the 3dπ electron density from a central atom of the Fe complex to a vacant antibonding 2π MO of ligands (delocalized π bond) [46, 47]. However, despite so complex a nature of the chemical bond in the complex, the X-ray analysis of filled valence MOs in NaCN and $Fe(CN)_6^{4-}$ shows only comparatively small changes in the electronic structure of the cyan anion when passing from ionic sodium cyanide to the hexacyanide iron complex [34, 48]. Taking this into account, we begin the discussion of the XRA spectra obtained for the $Fe(CN)_6^{4-}$ complex from the NFS in the N*K*- and C*K*-absorption spectra of ligands (Fig. 1 and Table 1).

We first compare XRA spectra obtained for the cyan anion in the complex with corresponding spectra of a free HCN molecule [31, 32], which is isoelectronic with the CN^- anion. However, note first that the C*K* absorption spectrum of the ligand in potassium ferrohexacyanide (Fig. 1, curve *2*) is overlapped with the $L_{2,3}$ absorption spectrum of potassium atoms (the *a-c* structure in the 295 - 307-eV region). One can see this from a comparison with the $L_{2,3}$ spectrum of the potassium atom in a KNO_3 crystal (Fig. 1, curve *5*). As a result, the NFS in the C*K* spectrum of the complex contains less lines (*A*, *B*, *C*, and *F*) than the *K* spectrum of the nitrogen atom (Fig. 1, curve *1*).

Comparison of the NFS in spectra of CN^- ligands (Fig. 1, curves *1* and *2*) and corresponding spectra of

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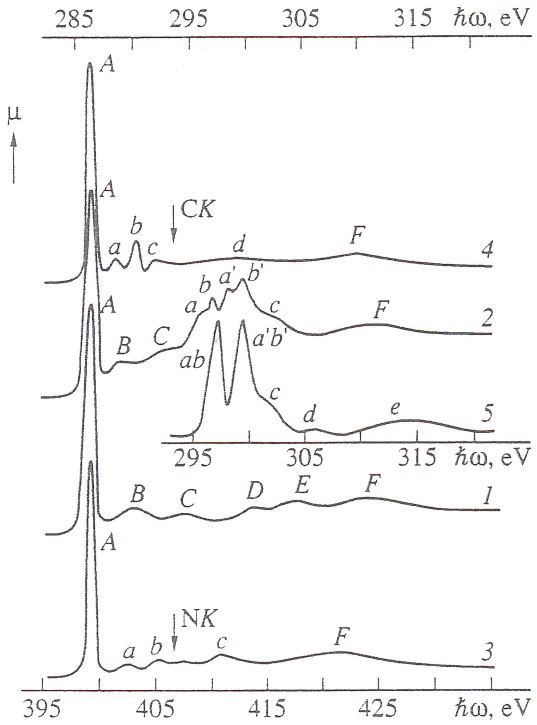


Fig. 1. The near fine structure of absorption *K* spectra of (*1*) nitrogen and (*2*) carbon atoms in $K_4Fe(CN)_6$. The spectra are matched in the energy scale using X-ray electronic data [34, 35] about relative positions of *K* levels of nitrogen and carbon atoms in potassium ferrohexacyanide crystal (113.0 eV). Absorption *K* spectra of (*3*) nitrogen and (*4*) carbon atoms in a free HCN molecule (the arrows show corresponding *K* ionization thresholds) [31, 32] and (*5*) the absorption $L_{2,3}$ spectrum of the potassium atom in KNO_3 are presented for comparison.

the isoelectronic HCN molecule (curves *3* and *4*) clearly shows that all absorption spectra exhibit a characteristic narrow intense peak *A* and a low-intensity broad band *F*, which only slightly change in passing from the molecule to the anion. In the case of HCN, these most interesting details of the NFS are related to the transitions of the *K* electrons in the nitrogen and carbon atoms to the excited states of the molecule (form resonances of the π and σ symmetry [31, 32]), which are strongly localized in the region of the stable CN group. Our previous studies of the nature of similar molecular resonances in XRA spectra of the N_2 molecule, which is isoelectronic to HCN and CN^-, indicated that they are related to the atomic $1s \longrightarrow 2p$ resonance, which is split by the anisotropic field of the linear atomic group into $2p\pi$ and $2p\sigma$ components [9, 10, 12 - 17]. Although these form resonances are most adequately described with the help of vacant MOs containing corresponding contributions of free $2p$ states of atoms of the second periodic group, such an approach nevertheless proves to be clearer and rather convenient for an analysis of the differences (for different polyatomic systems) in such parameters of the atomic and electronic structure of the total quasi-molecule as the interatomic distance, $2p$ partial effective charge of the absorbing atom, etc. Thus, the value of the energy splitting $\Delta E(\pi - \sigma)$ of the atomic resonance, which characterizes the anisotropy of the molecular potential, is substantially determined by the value of the interatomic distance and, hence, can be used to measure the latter. In such a quasi-atomic description of molecular form resonances in XRA spectra, the type of the dependence of $\Delta E(\pi - \sigma)$ on the interatomic distance d (between the absorbing atom and its nearest neighbors) is clear: the splitting of the atomic $1s \longrightarrow 2p$ resonance will increase with decreasing d. Analysis of a great number of experimental results showed that, in the first approximation, the dependence of $\Delta E(\pi - \sigma)$ on d is close to linear [49].

Taking into account the above discussion, it is reasonable to assert that the excited states related to the *A* and *F* bands in XRA spectra of $Fe(CN)_6^{4-}$ are quasi-molecular form resonances of the π and σ type strongly localized on CN^- ligands, which only slightly change upon chemical bonding of cyan anions with the iron atom. The most substantial change in these π and σ components of the atomic $1s \longrightarrow 2p$ resonance splitting when passing from HCN to ferrohexacyanide anion is a noticeable increase in the value of $\Delta E(\pi - \sigma)$. In N*K* spectra, $\Delta E(\pi - \sigma)$ changes from 21.1 (HCN [31, 32]) to 24.0 eV [$Fe(CN)_6^{4-}$], while in *K* spectra of carbon this quantity increases from 21.5 [31, 32] to 24.9 eV, although the accuracy of the latter value is probably smaller because of the overlap of the C*K* and $L_{2,3}$ absorption spectra of potassium atoms. We will use these results to quantitatively estimate d(C–N) in the ferrohexacyanide anion. For this purpose, we plot the dependence $\Delta E(\pi - \sigma)$ on d(C–N) (Fig. 2) based on the structural data about d(C–N) (HCN: 1.158 Å [50], C_2N_2: 1.162 Å [51]; H_3CNO_2: 1.489 Å [52, 53]) and the value of $\Delta E(\pi - \sigma)$ from N*K* absorption spectra (HCN 21.1 eV [31, 32]; C_2N_2: 20.4 eV [32]; H_3CNO_2 5.25 eV [19]). Using this dependence and the value $\Delta E(\pi - \sigma) = 24.0$ eV from the N*K* absorption spectrum of the $Fe(CN)_6^{4-}$ anion, we found d(C–N) ≈ 1.09 Å for $K_4Fe(CN)_6$.

Let us compare our estimate with the data obtained by other methods. Unfortunately, in this case, we have no clear knowledge. The average length of the d(C–N) bond in $Fe(CN)_6^{4-}$ measured by X-ray diffractometry is equal to 1.029 Å [54], while, according to the neutron diffraction analysis [44], this distance is equal to 1.1608 Å. Analysis of the far fine structure (EXAFS) of the Fe*K* absorption spectrum of the ferrohexacyanide anion yields the value of d(C–N) = 1.0955 Å measured as the difference between interatomic distances d(Fe–N) and d(Fe–C) [37], while the authors of a similar study [38] consider, based on an additional comparison of the experimental and calculated NFS in the Fe*K* absorption spectrum, more reliable the results of the

bove neutron diffraction study. A considerable spread n compared values of d(C–N) does not allow us to etermine the degree of reliability of our estimate of (C–N) = 1.09 Å, which, as one can readily see, proves o be close to the average of values obtained by other xperimental methods.

Considering the obtained value of d(C–N) as an estimate, we can nevertheless state that, in passing from the HCN molecule to the complex $Fe(CN)_6^{4-}$ anion, the bond length reduces noticeably from 1.158 Å in HCN to ~1.09 Å in the hexacyanide anion because the difference in energies $\Delta E(\pi - \sigma)$ of the $\pi 2p$ and $\sigma 2p$ form resonances in K spectra of nitrogen and carbon substantially increases. This decrease in the bond length in cyan anions upon their coordination by the iron cation suggests that the chemical state of the atomic CN group in HCN and $Fe(CN)_6^{4-}$ is different. This is confirmed by X-ray diffraction analysis, which demonstrates a decrease in the distance $\Delta E(NK–CK)$ between the NK and CK levels when passing from the HCN molecule (113.44 [31, 32], 113.3 eV [55]) to the $Fe(CN)_6^{4-}$ complex (113.0 [34, 35]; 113.1 [56]; 113.3 eV [57]). It is obvious that this change in the chemical state of the cyan anion should be manifested in the NFS of the spectra under study. One can see from Fig. 1 that corresponding spectra of HCN and $Fe(CN)_6^{4-}$ have a different structure in the region between slightly changing π and σ form resonances (the A and F bands). These changes in the region of the NK and CK spectra can be reasonably related to the influence of the iron cation on the X-ray absorption of CN^- anions in the $Fe(CN)_6^{4-}$ complex. In this case, one can try to assign low-intensity B, C, D, and E absorption bands to the X-ray transitions to vacant MOs of the complex, which reflect the chemical binding of the Fe^{2+} cation with CN^- anions.

To identify these absorption bands, we consider the NFS for all XRA spectra of the complex $Fe(CN)_6^{4-}$ anion (Fig. 3). All the spectra are matched in energy. To do this, we used the following X-ray data [34, 35] on positions of inner levels in $K_4Fe(CN)_6$: $\Delta E(FeL_3–CK)$ = 423.9 eV and $\Delta E(FeL_3–NK)$ = 310.9 eV, and also a tabulated value (6403.84 eV) of the $K_{\alpha 1}(K–L_3)$ line energy for a metal [42] taking into account its shift $\Delta E(FeK_{\alpha 1})$ = –0.69 eV in $K_4Fe(CN)_6$ [58]. We took as the origin of the common energy scale the position of the higher filled $2t_{2g}$ MO of the complex corresponding to the main peak α in the FeL_α emission spectrum [34, 35] (Fig. 3, the dashed line) at the energy of 707.1 eV. The $FeL_{2,3}$ spectrum obtained in our paper exhibits two rather intense absorption bands separated by the distance of 13.3 eV, which is close to the value of the spin–doublet splitting of the $L_{2,3}$ level of the iron atom $\Delta E(FeL_2–FeL_3)$ = 13.0 eV [59]. Therefore, for consideration, we present in Fig. 3 only the L_3 component (the B band) of the $FeL_{2,3}$ absorption spectrum of the complex.

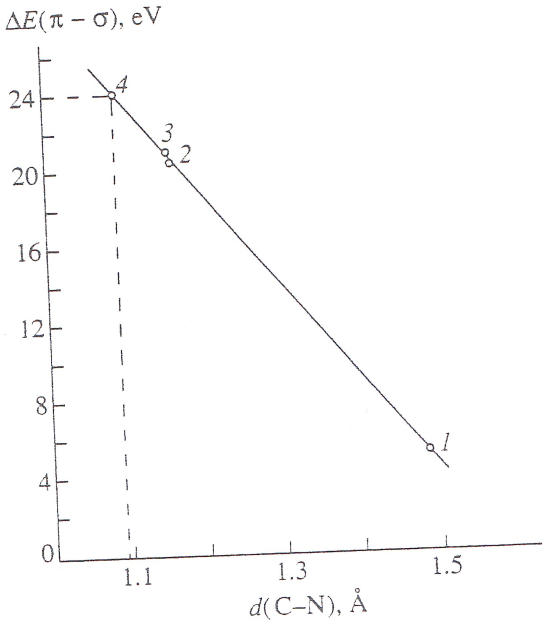


Fig. 2. Determination of the interatomic distance d(C–N) in $Fe(CN)_6^{4-}$. (*1*) H_3CNO_2: d(C–N) = 1.489 Å [52, 53], $\Delta E(\pi - \sigma)$ = 5.25 eV [19]; (*2*) C_2N_2: d(C–N) = 1.162 Å [51], $\Delta E(\pi - \sigma)$ = 20.4 eV [32]; (*3*) HCN: d(C–N) = 1.158 Å [50], $\Delta E(\pi - \sigma)$ = 21.1 eV [31, 32]; (*4*) $K_4Fe(CN)_6$: d(C–N) = 1.09 Å, $\Delta E(\pi - \sigma)$ = 24.0 eV. The values of $\Delta E(\pi - \sigma)$ are taken from the NK absorption spectra.

A comparison of the NFS in all spectra of $Fe(CN)_6^{4-}$ in the region of E < 15 eV shows a clear correlation of positions of the A, B, and C absorption bands, which are differently manifested in different spectra. According to our quasi-molecular approach, this experimental fact appears to be quite reasonable: all spectra reflect, taking into account the selection rules, the same system of the excited states of the polyatomic $Fe(CN)_6^{4-}$ complex, which are localized at the whole complex or at its separate parts. These strongly localized states, which appear during multiple or resonance scattering of low-energy (X-ray or photo-) electrons by the potential of the polyatomic system, can be treated as a result of electron capture (in the case of the NFS in XRA spectra, X-ray photoelectrons) by vacant MOs of the polyatomic system, i.e., of the formation of metastable excited states (quasi-molecular form resonances.)

We will try to identify the lower vacant MOs of the ferrohexacyanide anion, which are related to the A, B, and C absorption bands, using a comparative analysis of the NFS in $Fe(CN)_6^{4-}$ and general information on the nature of chemical bond in this complex. It was mentioned above that the chemical binding in $Fe(CN)_6^{4-}$ occurs through σ and π bonds between the iron cation and ligands. Let us take into account for the moment only the π bond, which is formed due to interaction of

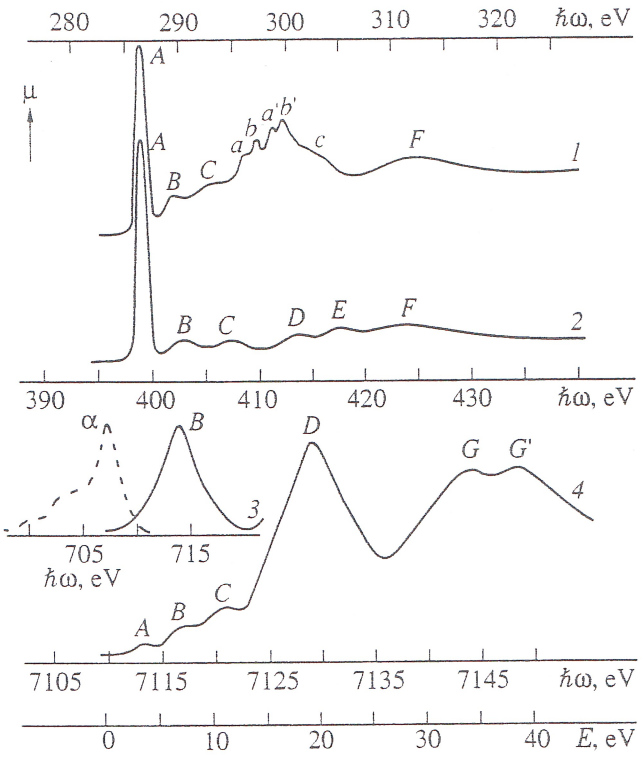


Fig. 3. The near fine structure in X-ray absorption spectra of complex $Fe(CN)_6^{4-}$ anion. (*1*) The C*K* spectrum; (*2*) the N*K* spectrum; (*3*) the FeL_3 spectrum; (*4*) the Fe*K* spectrum [36]. The spectra are matched in the energy scale using X-ray electronic and spectral data for $K_4Fe(CN)_6$: $E(FeL_3–CK)$ = 423.9 eV and $E(FeL_3–NK)$ = 310.9 eV [34, 35]; $EFeK_{\alpha 1}(K–L_3)$ = 6403.84 eV, metal [42]; $\Delta EFeK_{\alpha 1}$ = –0.69 eV, $K_4Fe(CN)_6$ [58]. The position of the higher filled $2t_{2g}$ orbital to which corresponds the main peak α at 707.1 eV in the FeL_α emission spectrum (the dashed curve) [34, 35], is taken as the origin of the common energy scale.

the $3d\pi$ states of iron with the bonding 1π MO and antibonding 2π MO of CN^- anions [46, 47, 60, 61]. Because the $Fe(CN)_6^{4-}$ complex has the O_h symmetry group, the π orbitals of six CN^- ligands form four triply degenerate group MOs t_{1g}, t_{1u}, t_{2g}, and t_{2u}. The 3*d* states of the iron cation in the octahedral complex are transformed, in turn, in the irreducible representations t_{2g} and e_g [35], and, therefore, the π interaction between a complexing atom and ligands occurs in this case by the transfer of the electron density over the MO of the t_{2g} symmetry only, while the remaining group MOs of the π type (t_{1g}, t_{1u}, t_{2u}) prove to be antibonding if they are not involved in the formation of the σ bond.

The scheme of formation of the MO of the π type for the $Fe(CN)_6^{4-}$ complex constructed taking into account the analysis of the NFS is presented in Fig. 4. Figures 1 and 3 show that the first absorption *A* band is related to the transitions of N*K* and C*K* electrons to vacant 2π states of ligands (group MOs $2t_{1g}$, $3t_{1u}$, and $2t_{2u}$), which are not involved in the formation of the π bond between the iron cation and the cyan anion. Although these antibonding MOs are mainly localized at ligands, one of them, $3t_{1u}$, is probably manifested in the Fe*K* absorption spectrum as a weak *A* band. The intensity of the allowed $Fe1s \longrightarrow 3t_{1u}$ dipole transition is determined by the contribution of the 4*p* states of iron, which is possible only for the MO of the complex of this symmetry because *p* states of the central atom are transformed in the octahedron in the irreducible representation t_{1u} [35]. Thus, a weak *A* band in the Fe*K* spectrum suggests that the 4*p* states of the iron atom only weakly involved in the formation of this MO.

The type of the next vacant state responsible for the *B* band in the NFS of the complex can be determined quite easily because this is the only state that is definitely manifested in the L_3 spectrum. Taking into account that the intense allowed dipole transition in this spectrum is the $2p \longrightarrow 3d\,(2t_{2g}, 2e_g)$ transition, we can definitely conclude that this MO should have the e_g symmetry because another MO ($2t_{2g}$), having a large contribution of the Fe3*d* states, is the higher filled MO of the complex. The crystal field theory applied to the octahedral complexes describes these MO of the t_{2g} and e_g symmetry as components of the 3*d* states of the transition-metal atom, which are split by the value of $\Delta = 10D_q$ by the octahedral field of ligands [46, 62]. In this case, the quantity Δ is considered one of the most important parameters of the complex. In the Fe*K* spectrum, this excited state appears due to a weak quadrupole $Fe1s–3de_g$ transition. The analog of the *B* band in spectra of ligand atoms probably results from a weak contribution of the 2*p* states of the carbon and nitrogen atoms to the MO of the $2e_g$ symmetry: σ orbitals of the complex involving 2*s* and $2p_z$ states of the ligand atoms are transformed in this irreducible representation (and also in a_{1g} and t_{1u}) [35]. Based on the band intensity in different spectra, one can state that the $2e_g$ orbital is mainly localized at the iron cation.

Taking into account the above assignment of the first two absorption bands, it is reasonable to relate the third *C* band to the transitions of inner electrons to the $3t_{2g}$ orbital (Fig. 4), which, according to its manifestations in the NFS in various spectra, is delocalized over the entire complex.

Let us compare our results with the results of other theoretical and experimental studies of the electronic structure of $Fe(CN)_6^{4-}$. Note first that neither theoretical calculation known to us [47, 56, 60, 61, 63] give for the complex the sequence of lower vacant MO that was obtained in our paper. The most important difference of our results is the conclusion that the lower vacant state of the complex is essentially formed by vacant 2π orbitals of ligands. However, according to theoretical calculations, the lower vacant MO in $Fe(CN)_6^{4-}$, as in other

octahedral complexes, is the orbital of the e_g symmetry formed mainly from the $3de_g$ states of the iron atom. In turn, the statement that the higher filled MO and lower vacant MO in $Fe(CN)_6^{4-}$ are the components of splitting (t_{2g} and e_g) of the $3d$ states of the iron cation in the octahedral field of CN^- ligands is the main result of the application of rather imperfect crystal field theory to complexes of the $3d$ metals [46, 62]. In this approach, the parameter characterizing the chemical bond in the complex is the magnitude of splitting $\Delta = 10D_q = E(3de_g) - E(3dt_{2g})$, which, in turn, determines the energy of the main low-energy absorption band of the complex in the optical region. According to [61], $\Delta = 3.84$ eV (31000 cm^{-1}) for $Fe(CN)_6^{4-}$. However, we obtained in this study a substantially larger value of the distance between $3dt_{2g}$ and $3de_g$ components, 6.0 - 7.3 eV, according to different absorption spectra (6.2 eV, from the emission and absorption L spectra directly related to $3d$ components; Table 2), while the first absorption A band ($2t_{1g}$, $3t_{1u}$, $2t_{2u}$ MOs) is located by 3.5 - 3.6 eV higher than the higher filled MO, which agrees well with the energy of the optical transition (3.84 eV) [61]. The nonzero intensity of the $2t_{2g} \longrightarrow (2t_{1g}, 3t_{1u}, 2t_{2u})$ optical transition can be reasonably explained by the above-mentioned admixing of the $4p$ states of iron to the $3t_{1u}$ orbital, resulting in the allowed dipole $3d \longrightarrow$ $4p$ transition.

By comparing positions of lower vacant MOs determined for $Fe(CN)_6^{4-}$ from different spectra (Table 2), we see that they agree quite well with each other, taking into account the low accuracy of measuring the absolute positions of the B and C absorption bands due to their low intensity compared to the intense D band (the FeK spectrum) and intense $L_{2,3}$ absorption of potassium atoms (the A - C bands in the CK spectrum). Recall that the X-ray excited states of a polyatomic molecule or complex, which are formed due to transitions of core electrons from different shells or atoms to the same MO, generally have different energy positions (as a rule, within 1 eV) relative the vacuum level or the higher filled MO, which depend on the type of the X-ray vacancy [64 - 66]. Therefore, it follows from the above that the assignment of the A, B, and C absorption bands performed for all spectra is well substantiated.

Let us now take into account the effects of a stronger chemical binding Fe^{2+}–$6(CN)^-$, which provides in the spectrum of free states of the complex the presence of high-energy σ orbitals that are formed from $3de_g$, $4sa_{1g}$, and $4pt_{1u}$ states of the iron cation and group σ orbitals (a_{1g}, t_{1u} and e_g) of ligands, which in turn are mainly formed from filled (3σ) and vacant (4σ) MOs of CN^- anions (Fig. 5). Consideration of more deeply lying filled (2σ, 1σ) MOs of ligands does not result in important changes in the spectrum of free molecular states of the complex.

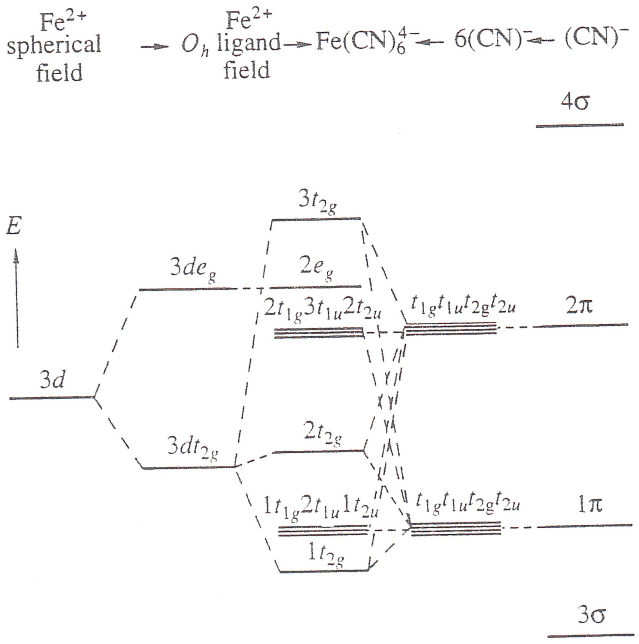


Fig. 4. Scheme of formation of MOs that provide the π interaction in the $Fe(CN)_6^{4-}$ complex. MOs are numbered taking into account σ orbitals (Fig. 5).

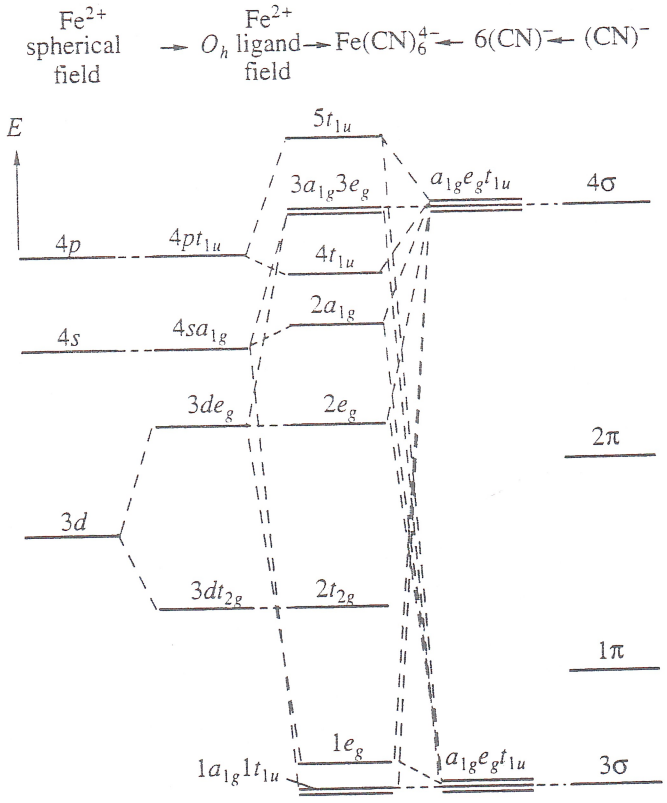


Fig. 5. Scheme of formation of antibonding σ orbitals in the $Fe(CN)_6^{4-}$ complex, which are responsible for the resonance absorption in the high-energy part of the NFS in the XRA spectrum of the complex.

Table 2. Results of the assignment of the NFS in XRA spectra of the $Fe(CN)_6^{4-}$ complex and energies (in eV) of the excited states of the complex (relative the higher filled $2t_{2g}$ MO) obtained from different spectra

Absorption band		*A*	*B*	*C*	*D–E*	*F*	*G–G'*
Excited state, MO		$2t_{1g}$, $3t_{1u}$, $2t_{2u}$	$2e_g$	$3t_{2g}$, $2a_{1g}$	$4t_{1u}$	$3a_{1g}$, $3e_g$	$5t_{1u}$
MO localization region		Ligands	Iron cation	Complex	Complex	Ligands	Complex
MO energy	N*K* spectrum	3.6	7.3	11.0	17.8; 21.2	27.6	
	C*K* spectrum	3.6	6.0	10.0		28.5	
	FeL_3 spectrum		6.2				
	Fe*K* spectrum [36]	3.5	7.2	11.4	18.7		34.6; 38.6

Note first that consideration of the σ binding does not change the assignment of the *B* band in the NFS of the complex as related to the transitions of the core electrons to the $3de_g$ state of the iron cation. Moreover, it was noted above that the involvement of this MO in the σ bonds in the complex allows one to explain the presence of this band in spectra of ligand atoms. The next vacant σ orbital of the complex is probably the $2a_{1g}$ orbital related to the 4*s* states of the iron cation and σa_{1g} orbitals of ligands. This state can be manifested in dipole transitions in spectra of ligand atoms due to possible admixing of the $2p_z$ states of nitrogen and carbon atoms, and also in quadrupole transitions in the Fe*K* spectrum. Therefore, the *C* band, which was previously assigned to the transitions to the $\pi 3t_{2g}$ state, can be alternatively assigned to the transitions to the $2a_{1g}$ orbital of the complex.

Among vacant σ orbitals of the $Fe(CN)_6^{4-}$ complex, the $4t_{1u}$ and $5t_{1u}$ orbitals are manifested most clearly. They are related to the intense *D* and *G–G'* absorption bands in the Fe*K* spectrum (Fig. 3, curve *4*), which result from the allowed dipole transitions of the Fe1*s* electrons to the vacant molecular states $4t_{1u}$ and $5t_{1u}$ of the complex with large contributions from the Fe4*p* states. Between these antibonding MOs of the complex, the vacant molecular states $3a_{1g}$ and $3e_g$ are located, which are essentially vacant 4σ orbitals of CN^- anions. They are observed (the *F* band) in *K* absorption spectra of carbon and nitrogen atoms only (Fig. 3, curves *1* and *2*). Note that the position of the *F* band in the N*K* and C*K* spectra coincides with that of the deep dip between *D* and *G–G'* bands in the Fe*K* absorption spectrum. We can offer an interesting physical explanation of this experimental fact returning to the description of the NFS within the framework of processes of resonance (multiple) scattering of X-ray photoelectrons by anions surrounding an absorbing atom. The dipole *K* absorption of the iron cation is accompanied by the formation of *p* photoelectrons, which come out from an atom absorbing photon mainly along coordinate axes. In turn, the latter determine the orientation of CN^- anions in the $Fe(CN)_6^{4-}$ complex. Therefore, *p* photoelectrons coming out from the iron cation will be scattered by carbon and nitrogen atoms, which form the CN^- anion. If the energy of photoelectrons is sufficiently high (>50 eV), the electrons will scatter independently and singly by carbon and nitrogen atoms, resulting in the appearance of corresponding EXAFS oscillations in the Fe*K* absorption spectrum [37, 38]. For low energies of photoelectrons, the diatomic CN^- group will scatter as a whole, resulting in the manifestation of resonance features of the CN^- anion in the scattering spectrum of *p* photoelectrons of the iron cation and, respectively, in the NFS of the Fe*K* absorption spectrum. Indeed, in the absence of the hexacyanide environment around the iron atom, its *K* spectrum above the ionization threshold represents a smooth monotonically decreasing *p* continuum [60]. The presence of six surrounding CN^- groups results, as one can see from Fig. 3, in the redistribution of the oscillator strengths in the near-threshold region of the Fe*K* absorption spectrum: the yield of *p* photoelectrons sharply decreases for the energy close to the energy of the 4σ resonance in CN^-, while this yield increases in neighboring energy regions, indicating the formation inside the octahedron, consisting of CN^-, of the quasi-stationary states (form resonances), which are related to the *D* and *G–G'* absorption bands in the *K* spectrum of the iron atom.

Note that the possibility of manifestation in the NFS in XRA spectra of resonance effects in the vicinity of the absorbing atom was repeatedly suggested earlier [7, 65], and attempts were made to take into account these effects in theoretical analysis of the NFS in XRA spectra of some polyatomic systems [18, 24, 67]. However, our paper appears to be the first study where the resonance effects in the environment were definitely observed in experimental spectra.

In conclusion of the quasi-molecular analysis of the NFS in XRA spectra of the $Fe(CN)_6^{4-}$ complex, we note that a weak *E* band in the N*K* absorption spectrum remains to be assigned within the framework of this approach. This band (rather than the *D* band) may be related to the $2a_{1g}$ molecular state of the complex.

However, the E band (or the D band) in the NK spectrum is more likely to be related to the two-electron excitations that were observed in NK and CK spectra of a free HCN molecule [32, 33].

CONCLUSION

The X-ray absorption study of solid potassium ferrohexacyanide $K_4Fe(CN)_6$ demonstrated the prospects of applying the extended quasi-molecular approach in the empirical analysis of the NFS in XRA spectra of polyatomic systems containing individual fragments or structural groups (quasi-molecules) of atoms of the second periodic group. As applied to the $Fe(CN)_6^{4-}$ complex with molecular CN^- ligand anions, this approach, based on a comparative analysis of the NK and CK absorption spectra of the complex and a free HCN molecule, and also on general quantum-chemical considerations about the nature of the Fe^{2+}–$6(CN)^-$ bond, allowed us to quite completely and uniquely assign the NFS in all XRA spectra of the complex based on the transitions of core electrons to vacant MOs. As a result, we obtained valuable information on the local electronic and atomic structure of the complex, namely, on its symmetry, energies of vacant MOs in the regions of spatial localization, and the interatomic distance d(C–N). The most important and original result is experimental verification of the influence of form σ resonances in CN^- ligands on the process of formation of the NFS in the K absorption spectrum of the iron atom (the central atom of the complex) and the conclusion about the relation of the lower vacant state of the complex to the antibonding 2π states of CN^- ligands. The results obtained demonstrate the wide possibilities of X-ray absorption spectroscopy for experimentally studying the local electronic and atomic structure of substances.

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