

Figure 9. Absorption spectrum of glucose predicted by combining the spectra of the individual chromophores.

COH chromophore. Again the graphically calculated spectrum predicts the measured spectrum of tetrahydropyran-2-methanol (Figure 5) satisfactorily.

The success in constructing spectra in this manner indicates that the COH chromophore is independent and interacts little with the ring oxygen chromophore when the two are separated by at least two carbon

atoms. In contrast, one can try to generate the spectrum of 2-hydroxytetrahydropyran by combining the spectrum of tetrahydropyran with the spectrum of the COH chromophore. The result (similar to the calculated spectrum of tetrahydropyran-2-methanol, Figure 8) does not resemble the measured spectrum of 2-hydroxytetrahydropyran. This indicates that the COH and ring oxygen interact strongly here.

Finally it is of interest to try to predict the as yet unmeasured spectrum of a sugar in the vapor phase. We chose glucose which in our approximation should have an absorption spectrum identical with the other seven diastereomers in their cyclic six-membered ring form. The predicted spectrum, given in Figure 9, is calculated by combining the spectrum of 2-hydroxytetrahydropyran plus the spectra of four COH groups. The $\sigma\sigma^*$ transitions of the saccharides will differ from those of the model compounds in that the saccharides will have more CO and OH transitions and fewer CH transitions. In this case the basic cyclic compound should have been 2-hydroxy-5-methyltetrahydropyran but the spectrum of this compound should not differ markedly from the spectrum of 2-hydroxytetrahydropyran.

Valence Level Studies of $\text{Cr}(\text{CN})_6^{3-}$, $\text{Mn}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ by X-Ray Photoelectron Spectroscopy

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Abstract: The X-ray photoelectron spectra of the valence regions of the molecular ions $\text{Cr}(\text{CN})_6^{3-}$, $\text{Mn}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ have been measured from spectra of salts containing these ions. The results have been compared with the photoelectron spectrum of the cyanide ion itself and with expectations from theoretical studies of the ions. The salient feature in some of the spectra is the $2t_{2g}$ level, arising from metal 3d and half ligand orbitals in $\text{Fe}(\text{CN})_6^{4-}$.

The cyanide complexes of the first transition series have received very large amounts of attention, both theoretical and experimental. This attention is due to the fact that they are relatively simple, symmetrical compounds and that, more importantly, they serve as a model of the low spin, strong crystal field complex.^{1,2}

We have studied the valence electron levels of a number of iron series cyanide complexes, and of a related compound, by X-ray photoelectron spectroscopy. This technique reveals a different aspect of the electronic structure and, we believe, clarifies our understanding of these compounds.

Before discussing our experiments, we remind the reader of some salient features of previous work on the cyanides. We cannot hope to survey so vast an area of research in a short introduction, so we emphasize merely those studies which are germane to the ground-

state electronic structure of the cyanide complexes. In these areas, we emphasize general conclusions and data which may be compared with our results.

Most of the large amount of optical spectroscopic work on cyanides has involved examination of ligand field transitions and, thus, involves moving electrons between occupied and unoccupied orbitals. Some work on ligand-to-metal charge-transfer transitions has appeared, however. In these transitions one moves electrons between two orbitals, both of which may be occupied in the ground state. The data, thus, have some direct relevance to ground-state electronic structure. An extensive discussion of the optical spectra of cyanides, based upon Gaussian analysis of spectra at room temperature and at 77°K and upon approximate calculations, has been given by Gray and Alexander.³

According to them, the first $L \rightarrow M$ charge-transfer

(1) J. H. van Vleck, *J. Chem. Phys.*, **3**, 807 (1935).

(2) L. Pauling, *J. Amer. Chem. Soc.*, **53**, 1367 (1931).

(3) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968).

transition, assigned to the orbital change $3t_{1u} \rightarrow 2t_{2g}$, falls in energy from some $40,000 \text{ cm}^{-1}$ in $\text{Cr}(\text{CN})_6^{3-}$ to $23,500 \text{ cm}^{-1}$ in $\text{Fe}(\text{CN})_6^{3-}$. They also identify several other $L \rightarrow M$ charge-transfer transitions, which follow the same trend.

In general, Alexander and Gray conclude that the charge-transfer band energies depend largely on the energy of the metal t_{2g} orbitals, the ligand orbitals involved being largely invariant in energy. They also find that the positions of charge-transfer bands, and thus of metal t_{2g} levels, change very little in changing the oxidation state of a given metal. They interpret this to mean that the metal has about the same net charge in the two oxidation states.

Another experimental tool which provides information on the placement of some of the ligand levels in complexes is X-ray emission spectroscopy. Koster has applied this technique to several iron series cyanides.⁴ The $K\beta$ X-ray spectrum of a transition-metal atom or ion consists of a strong line, called $K\beta_{1,3}$, due to the transition $3p \rightarrow 1s$, and various satellites. One of these satellites, called $K\beta_5$, the most intense, may be interpreted as a cross-over transition between a ligand $2p$ level and the metal $1s^5$ or in a molecular orbital picture as a transition of an electron from one of the filled molecular orbitals of the complex to the metal $1s$.⁶ Taking the latter point of view, one concludes that, if $K\beta_5$ is to be dipole allowed, the electron must arise from a t_u orbital in an octahedral complex. Of the t_u orbitals in hexacyanide complexes, the most likely candidate is $3t_u$. Composed essentially of lone pair σ orbitals on CN^- , it should have the best overlap with the metal $1s$.

Taking the point of view we have just outlined, the $K\beta_{1,3} - K\beta_5$ splitting yields the energy difference between the metal $3p$ level and a t_u level, probably $3t_u$. These prove to be 37.6, 43.8, 49.2, and 49.8 eV in $\text{Cr}(\text{CN})_6^{3-}$, $\text{Mn}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, and $\text{Fe}(\text{CN})_6^{3-}$, respectively.

Two other spectroscopic techniques yield information of interest to us about the ground state of cyanide complexes. Mössbauer studies revealed, some time ago, that the isomer shifts of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ are nearly the same.⁷ Sugano and Shulman subsequently showed that these data could be understood and integrated with the orbital reduction factors of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Mn}(\text{CN})_6^{4-}$ by assuming that the charge on Fe in the two cyanides was essentially the same, due to a great increase in back-donation in the Fe^{3+} complex over the Fe^{2+} complex.⁸

The evidence of magnetic resonance on the ground state electronic structure of the hexacyanides is rather mixed. The early work of Bleaney and coworkers⁹ on ferricyanide and manganicyanide, mentioned above, led to orbital reduction factors which put substantial unpaired spin density on the ligands. Direct evidence for the ligand spin density has been lacking, however. Kuska and Rogers searched for anisotropy in the ^{13}C

hyperfine tensor of $\text{Cr}(\text{CN})_6^{3-}$ and found none.¹⁰ They and others¹¹ have also sought evidence for substantial ligand spin density of π type in pentacyanonitrosyl complexes, again without success. Furthermore, the ^{13}C nuclear magnetic resonance of several hexacyanides has been examined,¹² without revealing any notable π -type ligand spin density. On the other hand, Thornley¹³ has reexamined the theory underlying the orbital reduction factor in low-spin d^5 complexes and has concluded that the π covalency should be larger than the estimate of Bleaney and O'Brien.

We may summarize much of the information we have just outlined, and express a widely held point of view on cyanide complexes, by saying that π bonding, especially with the unfilled cyanide π^* levels, is important in cyanide complexes. In the case of the iron cyanides, varying amounts of π^* interaction tend to equalize the charges between $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$. One must note, however, that experiments which are sensitive to π -type ligand spin density have not revealed any appreciable spin transfer, which should accompany charge transfer, in $\text{Cr}(\text{CN})_6^{3-}$ or in the pentacyanonitrosyls. The data on $\text{Fe}(\text{CN})_6^{3-}$ are a little hard to interpret, since some of the π orbital spin densities are negative,¹² but the net spin density in all ^{13}C π orbitals is only about $0.12 e^-$.

The only extensive series of calculations on iron series hexacyanides has been that of Alexander and Gray.³ We shall have occasion to display some of their level schemes, which were calculated in the Wolfsberg-Helmholz approximation, later along. They find that the π bonding between metal and cyanide is large, so that the filled t_{2g} levels of the complexes are about half metal $3d$ and half ligand π orbitals.

We turn now to a brief consideration of the study of valence levels by X-ray photoelectron spectroscopy and of previous work in this area.

There are two factors which are to the detriment of X-ray photoelectron spectroscopy, as compared with uv photoelectron spectroscopy,¹⁴ as a tool in the study of valence levels. These are poor resolution, due at least in part to the X-ray line width, and poor sensitivity, due to the fact that photoelectric cross sections become very small far above onset. These disadvantages are, however, outweighed by certain advantages of the technique. These advantages have appeared in various pioneering works in the field. First, X-ray photoelectron spectroscopy can be applied to study the valence levels of solid samples.¹⁵⁻²¹ One may thus examine systems which cannot be prepared as gaseous species, such as diamond,¹⁵ ionic crystals,¹⁶ and molecular ions.¹⁷⁻²¹

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(18) R. Prins, *Chem. Phys. Lett.*, **19**, 355 (1973).

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(21) R. Prins and T. Novakov, *Chem. Phys. Lett.*, **16**, 86 (1972).

Second, the intensities of valence-level photoelectron features lend themselves to a simple interpretation involving molecular orbital coefficients and cross sections for photoelectric emission from the various atomic orbitals which comprise the molecular orbital.²²

In other words, the various atomic orbitals contribute incoherently to the molecular orbital photoelectric cross section. This fact has been exploited most completely by Gelius,²² who studied molecules in the gas phase, but it has been used to a certain extent in discussions of spectra from solids also.^{20,21} In favorable cases, it allows one to deduce molecular orbital coefficients from X-ray photoelectron spectra.

In order to analyze the intensities of valence level features in the X-ray photoelectron spectrum one needs atomic cross sections for the various orbitals at the photon energy of the X-radiation, as one sees from the preceding paragraphs. The atomic photoeffect has interested atomic physicists for many years and is very well understood. An excellent review of the effect has appeared recently.²³ The interests of atomic physicists tend to be somewhat different from ours, however, and their data and calculations tend to stress total cross sections at rather widely spaced photon energies. Thus, the data we need are not always readily available. Indeed, although a calculation of cross sections for each subshell of each element at kilovolt spacings of energy has been made, the results have not been published.²⁴ One may proceed in several ways to get the information one needs. First, Gelius has published ratios of cross sections for 2s and 2p levels of the first row elements and of a few other elements.²² These are values which allow one to fit the observed intensities in various simple molecules, using molecular orbital calculations of high quality. The results seem to be reliable, on the whole.

Second, Jørgensen has published a large number of relative intensities of photoelectron lines, taken from experimental spectra.²⁵ One may use these to deduce atomic orbital cross sections.

One may, of course, measure photoelectron intensities of levels in selected compounds and use these to construct his own relative cross sections. We have measured a rather large number of cross sections for atom-like orbitals from simple solids. Of interest for the work we report here are the 3d cross sections in the iron series. We have measured these from the simple fluorides. We find 3d cross sections of 2.2, 1.8, 5.3, 6.4, and 6.7 for Ti, V, Cr, Mn, and Fe, respectively, relative to O 2p. Using the same reference, we find the K 3s cross section to be 20.1. We have used these, and Gelius' C and N cross sections, in the work reported here.

Experimental Section

All spectra were taken using the Varian-IEE 15 electrostatic focussing spectrometer equipped with a high-intensity magnesium anode. Sample preparation was accomplished by brushing a thin layer of the sample onto adhesive tape, ensuring complete coverage of the tape. Commercially available potassium and sodium salts were used in all cases. All samples were left in the spectrometer

until the pressure reached the desired 2×10^{-6} mm range to ensure complete dehydration of all hydrated samples.

Some pains were taken to be sure the spectra did not contain features due to contaminants. The metal $2p_{1/2}$ - $2p_{3/2}$ region of each compound was scanned before and after the valence region to monitor sample stability. No notable differences were found in these spectra suggesting that no appreciable sample decomposition is taking place. In order to check for gross contamination, we compared the integrated intensity of the potassium 3p photoelectron line, which appears near 18 eV, with the integrated intensity of the features between 0 and 10 eV. Since these latter are due almost entirely to CN^- (the metal 3d electrons, although they have a substantial cross section, are numerically insignificant), the intensity ratio should scale with the ratio of CN^-/K^+ , to a good approximation. This check was satisfactory in all the spectra we report.

We attempted to obtain absolute binding energies by depositing a thin layer of gold onto the sample and calibrating the potassium 3p line against the $4f_{5/2}$ line of gold which was taken to have a binding energy of 87.0 eV.^{3,26} The K 3p line of the valence region spectrum was then taken to have the same binding energy as the K 3p line of the sample with the gold layer. The rest of the spectrum was calibrated accordingly. This procedure was repeated several times for each compound, yielding consistent results. This technique was used because the gold conduction band obscures the spectrum at low binding energy, where important valence levels are found. The binding energy of the ferrocyanide t_{2g} orbitals obtained in this manner, however, was found to be 0.0 eV. This suggests that although the results are consistent, the method does not yield correct absolute binding energies for this series of compounds.

Another method that was tried was that of depositing a thin layer of carbon on the sample and again calibrating the K 3p line against the carbon 1s level whose binding energy was taken as 284.0 eV.^{16,27} It must be pointed out that this is not the contaminant vacuum carbon which is taken to have a binding energy of 285.0 eV. Again this procedure yields the same results as the gold suggesting that in both methods the sample and standard are in electrical contact; *i.e.*, their Fermi levels are the same. Their vacuum levels, however, are different resulting in the above discrepancy with respect to the $2t_{2g}$ orbitals of ferrocyanide. The difficulty with calibration does not affect the relative binding energies within a given ion, of course. It results in an uncertainty of, perhaps, some 1-2 eV in comparing different ions. This uncertainty can be reduced in comparison of the various ions of charge -3. In these systems, the K 3p level should always have the same binding energy with respect to vacuum because the Madelung potential should not vary. We can, thus, compare levels of different ions of trivalent metals by adjusting binding energies to make the K 3p levels coincide. The measured binding energies of K 3p are 17.2, 17.5, 17.0, and 17.3 eV in $Cr(CN)_6^{4-}$, $Mn(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, and $Co(CN)_6^{3-}$, respectively.

The photoelectron spectra of most of the compounds we studied, which were potassium salts, were dominated by strong features near 34 and 17 eV, due to the 3s and 3p levels of K^+ . Since the X-radiation contains satellites, the photoelectron spectra also contain satellites of each feature. The satellites of the potassium 3s and 3p features tend to obscure features due to the anions, so we subtracted the satellites from the spectra. In order to do this, we measured the position and intensity of each satellite line appearing in a spectrum of the Au 4f level and of the F^- 1s level (in NaF). We measure two satellites, spaced 8.70 and 10.60 eV from the main line. They have intensities, relative to the main line, of 0.082 and 0.051. We prepared a simple computer program to subtract the satellites of the K^+ 3s and 3p lines from our spectra. *All the spectra we report, though otherwise raw data, have been so subtracted.*

Results

The X-ray photoelectron spectrum of the valence region of KCN appears in Figure 1. We observe a rather broad line centered at approximately 24 eV. This we associate with photoemission from the 3σ molecular orbital of CN^- whose parentage is largely carbon and nitrogen 2s with substantial 2p character.²⁸

(26) D. J. Hiratowich, J. Hudis, M. L. Perlman, and R. C. Regámi, *J. Appl. Phys.*, **42**, 4882 (1971).

(27) K. Siegbahn, *et al.*, *Nova Acta Regiae Soc. Sci. Upsal. Ser. IV*, **20**, 53 (1967).

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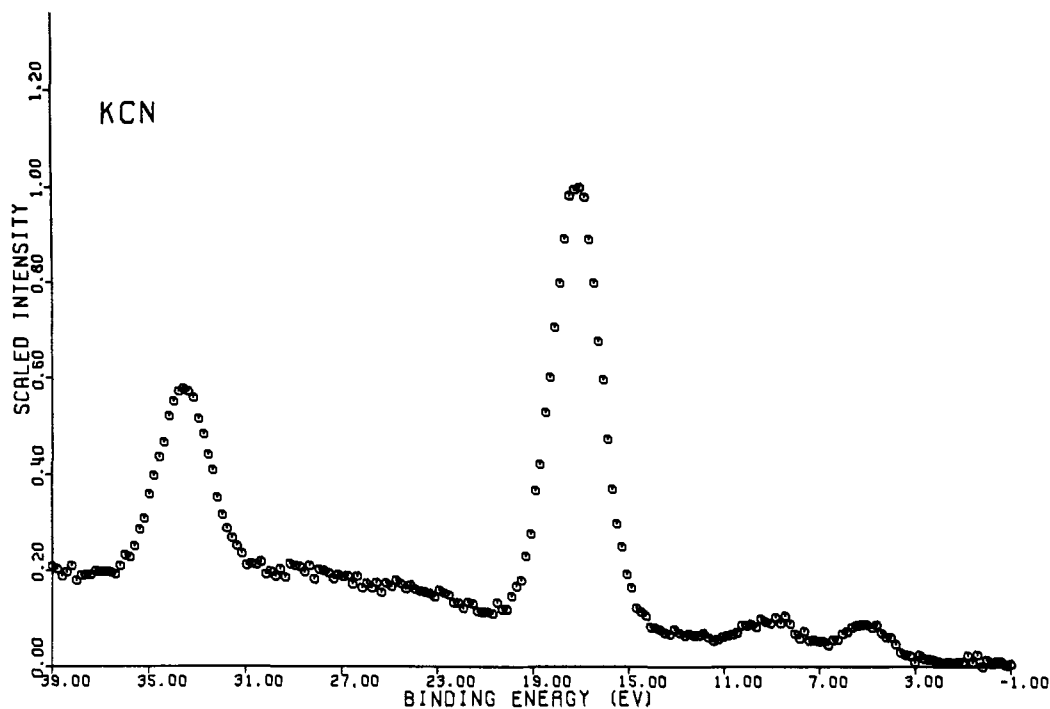


Figure 1. X-Ray photoelectron spectrum of the valence region of KCN excited with Mg $K\alpha$ radiation.

The feature at 9 eV we attribute to the 4σ molecular orbital while that at 5 eV is the result of photoemission from the 5σ and 1π molecular orbitals. The latter two orbitals are predicted to be separated by a few tenths of an electron volt by the calculation of Clementi and Klint.²⁹ Under the experimental conditions then, we would not be able to resolve these two lines. The experimentally measured intensities of these lines appear in Table I. This table also lists the results of the Cle-

Table I. Energy and Intensity Data for KCN

Binding energy		Intensity	
Exptl	C and K	Exptl	MO anal
3σ 24–25	25.4	Broad	1.0
4σ 8.9	9.25	1.0	0.8
5σ } 5.2	5.2 }	1.0	0.74 }
1π } 5.3	5.3 }		0.23 }

menti-Klint calculation as well as expected intensities predicted by a simple molecular orbital analysis using Fenske's functions.²⁸ Since we were not able to calibrate our spectra, we cannot report absolute binding energies. However, we may compare energy separations, and the experimental values in Table I should not be interpreted as absolute values but only as relative values. The data show that where comparison is possible the agreement between theory and experiment is encouraging.

Figure 2 shows the X-ray photoelectron spectra of two d^6 ions, ferro- and cobalticyanide. Again we note the very intense potassium 3p feature at approximately 17 eV. The 23–25-eV region of both compounds shows a rather broad feature which we again associate with the CN^- 3σ molecular orbital. According to MO theory, the CN^- 4σ , 5σ , 1π , and $1\pi^*$ molecular orbitals

interact with the metal 3d, 4s, and 4p to form the molecular orbitals of the complex, which we observe in the 2–9-eV region. Centered near 8.5 eV is a feature which retains the essential characteristics of the CN^- 4σ molecular orbital. Both the 3σ and 4σ MO's are C–N bonding orbitals, and the fact that they are relatively unaffected by complex formation shows that the extent of their participation in metal bonding is rather limited. The remaining feature between 2 and 8 eV is associated with the remaining molecular orbitals resulting from complex formation. The fact that in this region the distinct 5σ , 1π feature of CN^- is completely smeared suggests that it is these two cyanide orbitals which participate strongly in bond formation.

The cyanide ligand is known to be a strong crystal field ligand so that all of the complexes under consideration are in the low spin state. The lowest binding energy feature clearly seen in the ferrocyanide spectrum we associate with the $2t_{2g}$ molecular orbitals. The equivalent feature in cobalticyanide appears at a higher binding energy as expected since the additional positive charge in cobalticyanide stabilizes the $2t_{2g}$ orbitals relative to ferrocyanide. In each case the t_{2g} orbitals are completely filled.

Figure 3 shows the photoelectron spectra of ferri-, mangani-, and chromicyanide which are d^5 , d^4 , and d^3 systems, respectively. Once again we observe the usual features associated with the CN^- 3σ and 4σ molecular orbitals distinctly. In addition we also note a gradual increase in intensity in the 5-eV region as we go from chromi- to ferricyanide, and in ferricyanide a rather distinct shoulder appears on the low binding energy end of the spectrum. This obviously suggests that the binding energy of the $2t_{2g}$ level rises steadily from chromicyanide to cobalticyanide. One should, however, keep in mind that there is more than one final state in photoemission from d^4 and d^5 systems and that the initial and final states may differ in interelectronic

(29) E. Clementi and D. Klint, *J. Chem. Phys.*, **50**, 4899 (1969).

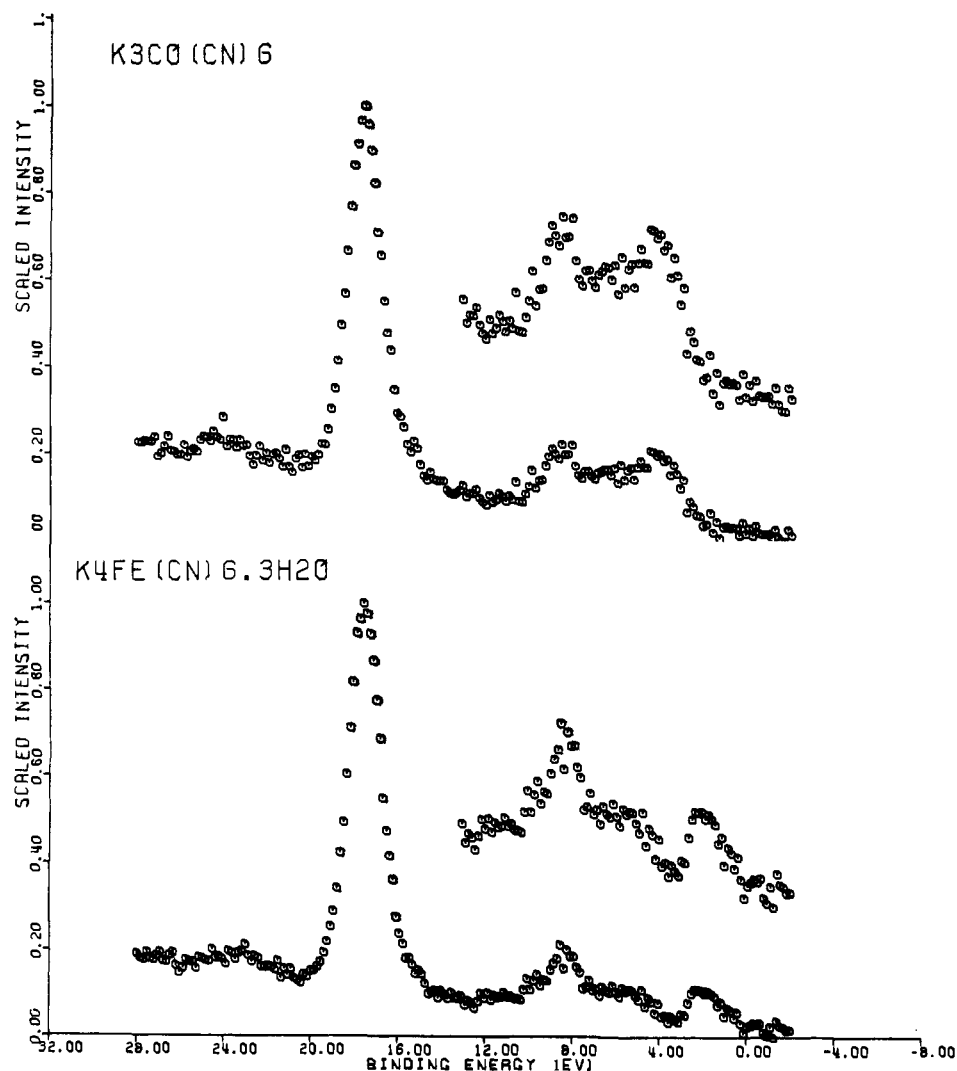


Figure 2. X-Ray photoelectron spectra of $K_4Fe(CN)_6$ and $K_3Co(CN)_6$ excited with Mg $K\alpha$ radiation.

repulsion, so that the observed binding energy does not reflect the orbital energy of the t_{2g} level. Finally, it may be that the electronic structures of the initial and final states differ, so that Koopman's theorem does not hold. We discuss these three matters in the next section.

As we discussed earlier, Koster and Mendel have studied the X-ray $K\beta$ emission spectra of these compounds and have found $K\beta_3$ - $K\beta_5$ splittings of 37.6, 43.8, 49.8, and 49.2 eV, respectively. As we have mentioned we believe these $K\beta_5$ lines to originate from the valence t_{1u} orbital(s), probably $3t_{1u}$, having ligand 2p character, which arise from 5σ and 1π MO's of CN^- . We have measured the binding energies of the metal 3p level in each one of these compounds, and using Koster's above-cited values for ($K\beta_5$ - $K\beta_{1,3}$) we located the orbital(s) from which the $K\beta_5$ line originates. This was found to be in the center of the valence region between 5 and 6 eV in each compound as indicated by the arrows in Figure 3. Even though this result points to the $3t_{1u}$ orbital, it is not possible to determine with certainty whether it is only the $3t_{1u}$ orbital involved or whether it is a result of the 1,2 and $3t_{1u}$ orbitals. This is because the width at half maximum of the $K\beta_5$ line is approximately 10 eV and the calculated³ separation between the 1 and $3t_{1u}$ orbitals is no more than 4 to 5 eV.

We have also studied the photoelectron spectrum of sodium nitroprusside, which appears in Figure 4. The nitroprusside ion contains ferrous iron, formally, but much evidence indicates a strong interaction between the metal and nitrosyl grouping in the nitrosyl complexes.³⁰⁻³⁴ As one sees, the spectrum of $Fe(CN)_5NO^{2-}$ is much different from that of $Fe(CN)_6^{4-}$ in that the feature assigned to the t_{2g} level in ferrocyanide is absent in nitroprusside.

Discussion

We begin by estimating the role of final state effects in the spectra of the various ions. We are especially interested to know what effect these might have on the features associated with the t_{2g} levels. Such effects are of two kinds. First, photoemission from the ground states of d^5 and d^4 ions yields several final states. Thus, in the case of ferricyanide, which we shall discuss, the initial state, d^5 ${}^2T_{2g}$, yields four final states: d^4 ${}^3T_{1g}$,

(30) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc., London*, 668 (1962).

(31) J. Lewis, *Sci. Progr. (London)*, 47, 506 (1959).

(32) G. Johansson and W. N. Lipscomb, *Acta Crystallogr.*, 11, 594 (1959).

(33) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.*, 11, 599 (1958).

(34) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 2, 1043 (1963).

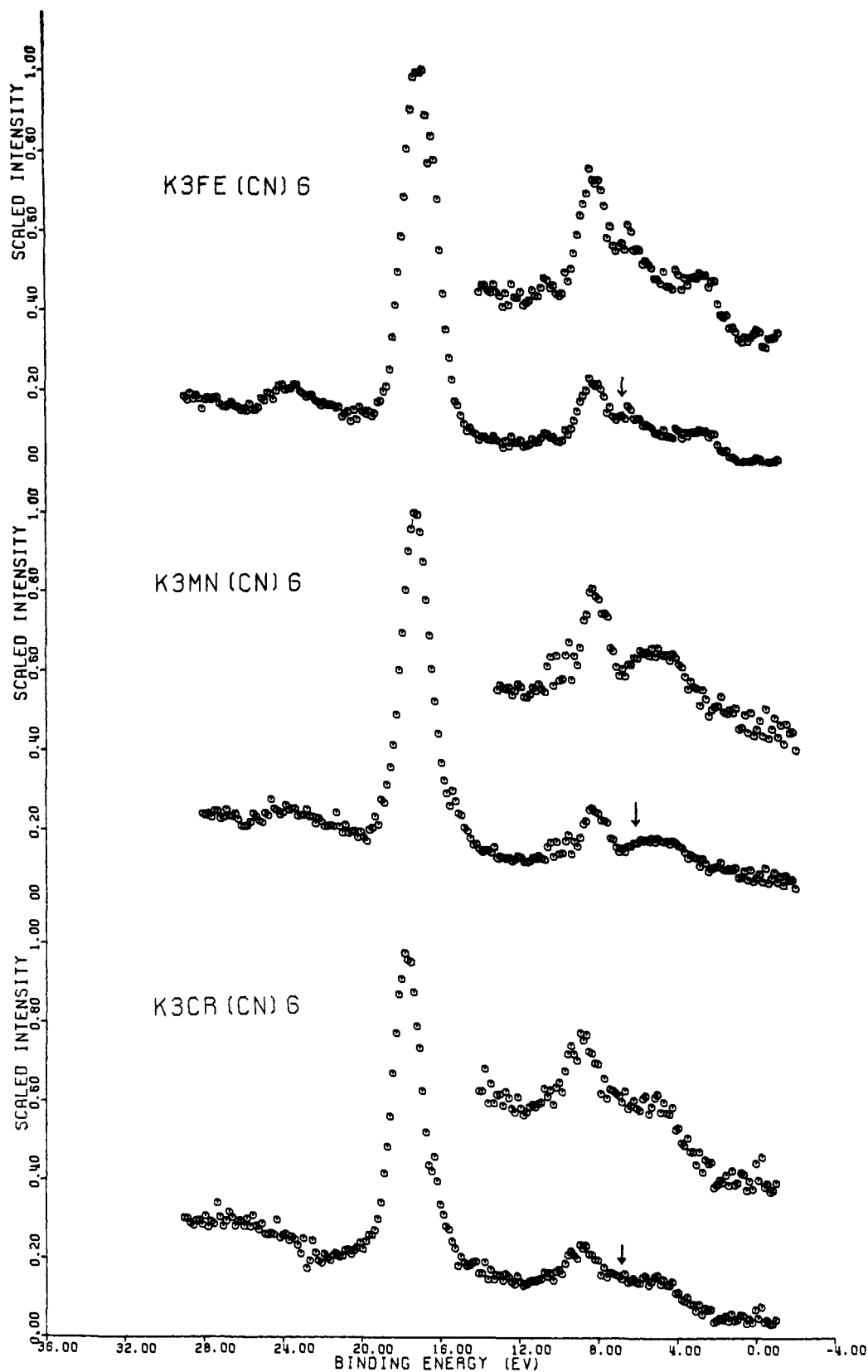


Figure 3. X-Ray photoelectron spectra of $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, and $K_3Fe(CN)_6$ excited with Mg $K\alpha$ radiation.

$d^4 \ ^1A_{1g}$, $d^4 \ ^1E_g$, $d^4 \ ^1T_{2g}$. Second, ejection of a t_{2g} electron may cause substantial changes in the electronic structure of the ion. The first effect has been discussed, for different systems, by Wertheim and coworkers.³⁵

(35) G. K. Wertheim, R. L. Cohen, A. Rosencwaig and H. J. Guggenheim, *Phys. Rev. B*, **8**, 813 (1973).

The second has been discussed by various workers. Signorelli and Hayes discuss a somewhat similar problem.³⁶

Consider first the population of several final states. We discuss ferricyanide because in this ion a feature

(36) A. J. Signorelli and R. G. Hayes, *Phys. Rev. B*, **8**, 81 (1973).

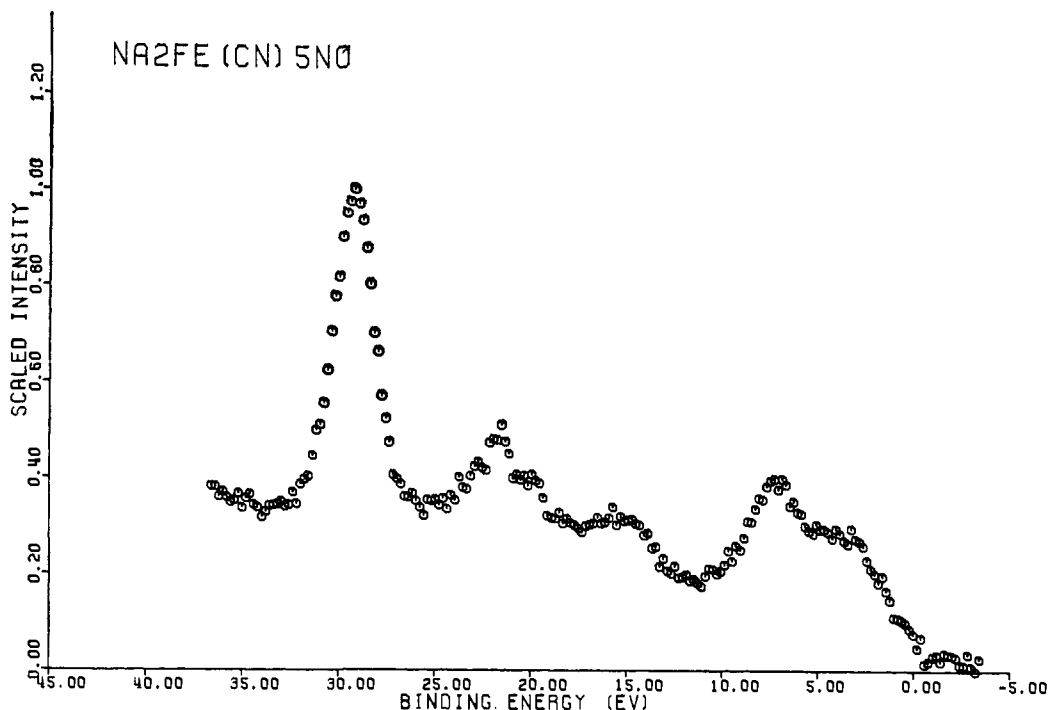


Figure 4. X-Ray photoelectron spectrum of $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ excited with Mg $K\alpha$ radiation.

attributable to the $2t_{2g}$ levels appears. The probability of population of a given term of $(t_{2g})^4$ is proportional to the degeneracy of the term, as may be seen from the coefficients of fractional parentage.³⁷ Thus, 9/15 of the intensity arising from photoemission from t_{2g} levels shows up in $(t_{2g})^4$ ${}^3T_{1g}$ and 6/15 in $(t_{2g})^4$ ${}^1A_{1g}$, 1E_g , ${}^1T_{2g}$ combined.

The excitation energies of the various states of $(t_{2g})^4$, relative to ${}^3T_{1g}$, may be gotten from a calculation on $(t_{2g})^2$.³⁸ We find that 1E_g and ${}^1T_{2g}$ lie together at $(6F_2 + 40F_3)$ and ${}^1A_{1g}$ lies at $(15F_2 + 100F_4)$. Taking $F_2 = 1200 \text{ cm}^{-1}$ and $F_4 = 100 \text{ cm}^{-1}$, we find these energies to be 11,200 and 28,000 cm^{-1} , respectively, or 3.47 and 1.39 eV. Thus, the shoulder we see in ferricyanide should be attributed to ${}^3T_{1g}$ and have 9/15 the intensity of the t_{2g} levels. The rest of the intensity should be some 2 eV away, buried in the features due to CN^- . Thus, the shoulder we see should have about one-half the intensity of the t_{2g} line seen in ferrocyanide ($5/6 \times 9/15$, to be exact). One cannot estimate this intensity from the spectrum, but $1/2$ is certainly closer than $5/6$.

We consider next the effects to be expected from a change of electronic structure in the final state of the system. We shall, once again, consider photoemission from a $2t_{2g}$ level. We shall also, for simplicity, suppose that, in the initial state, the t_{2g} levels are essentially pure metal d orbitals. The latter assumption is not necessary. In the final state, which has one t_{2g} electron less and, thus, a greater charge, it may well be that the t_{2g} levels originally associated with the metal become admixtures of ligand and metal functions. Furthermore, the various e_g levels will change in composition, the more bonding, filled ones experiencing an increase

in metal 3d amplitude. We shall, for simplicity, restrict ourselves to a discussion of the effects on the spectrum of changes in the e_g orbitals, supposed to consist of one filled pair, called ψ_e^b , and an empty pair ψ_e^a . The discussion will reveal the salient features of the effect on the spectrum of changes in electron structure of the complex upon photoemission. Initially, we have ψ_e^b filled and ψ_e^a empty. We write $\psi_e^b = (1 - \lambda^2)^{1/2}\psi_e^L + \lambda\psi_e^M$, with ψ_e^L and ψ_e^M the ligand and metal orbitals of e_g symmetry. In the final state we have $\psi_e^{b'} = (1 - \lambda'^2)^{1/2}\psi_e^L + \lambda'\psi_e^M$, with $\lambda < \lambda'$. The ground state of the final species will be $[\psi_e^{b'}]^4$ but, since $\lambda \neq \lambda'$, there will also be some probability of obtaining the state $[\psi_e^{b'}]^3\psi_e^{a'}$. If then, photoemission is accompanied by redistribution of electron density, one expects satellites on the photolines from various levels. The change outlined above yields a satellite on the t_{2g} line of relative intensity $[\lambda(1 - \lambda'^2)^{1/2} - \lambda'(1 - \lambda^2)^{1/2}]^2 / [(1 - \lambda^2)^{1/2}(1 - \lambda'^2)^{1/2} + \lambda\lambda']^2$. The satellite will be separated from the main line by the energy difference between the bonding and antibonding e_g states, some 6.5 eV in ferrocyanide.

Changes in the compositions of the various t_{2g} levels themselves on photoemission can be expected to yield effects similar to those discussed above, but they are somewhat harder to work out because the various t_{2g} levels of interest are already filled, or partly filled.

It is possible to search for satellites only on the t_{2g} photoline of ferrocyanide and on the $4s$ photoline of the various cyanides. Such satellites are not prominent (for a situation in which satellites are prominent, see ref 36), so we conclude that a discussion of the spectra based on Koopmans' theorem should be fruitful.

One wishes to compare our data with the predictions of molecular orbital calculations, among other applications. In order to do this, one needs to convert observed binding energies of the t_{2g} levels to the energy of the center of the configuration. The orbital energies

(37) J. S. Griffith, "The Irreducible Tensor Method," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(38) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 10.

have an averaged interelectronic repulsion built into them. The average in question is over occupation of all the d levels (through the VOIP). So one needs the contributions of interelectronic repulsion to the energies of the initial and final states of each complex, measured with respect to the average energy of d^n and d^{n-1} . These quantities are not hard to obtain, at least to a fair approximation. Basch, Viste, and Gray³⁹ have tabulated the average energies of the d^n configurations with $n = 3-6$, with respect to the atomic ground state. These were obtained from experimental data on neutral atoms but should serve our purposes, since the Slater-Condon parameters are not especially strong functions of charge. One may calculate the average energy of d^2 with respect to the 3F ground state in terms of Slater-Condon parameters, using well-known formulas for the term energies of d^2 .⁴⁰ The energies of the strong-field ground states with respect to the atomic ground states in terms of Slater-Condon parameters are available.⁴¹ Using these data, we have calculated the average energies of the various d^n configurations with respect to their strong-field ground states. We have assumed that $F_2 = 1000 \text{ cm}^{-1}$ and $F_4 = 100 \text{ cm}^{-1}$ in all cases, a good enough approximation for our purposes. The results appear in Table II. Table

Table II. Average Energies of d^n Configurations with Respect to Their Strong Field Ground States and Differences in This Energy between Successive Configurations

n	E_{av} , eV	Δ , eV
2	0.55	
3	4.75	4.20
4	2.50	-2.25
5	-0.28	-2.78
6	3.07	+3.35

II also shows the difference in such energies between configurations differing in one d electron, such as d^3 and d^2 , in the column labeled Δ . These numbers have the significance that the observed binding energy, between the lowest terms of the initial and final configurations, is equal to the Wolfsberg-Helmholtz binding energy plus Δ , if the system is largely ionic (so the Slater-Condon parameters used are roughly appropriate). As we shall see presently, the systems at hand are not largely ionic, so some allowance must be made for this. We shall take a simple approach which should isolate the salient effect of covalency on our results. We shall scale the interelectronic repulsion parameters by the d-orbital amplitudes of the MO's. In the case at hand these amplitudes are near 0.5, so we may scale each value in Table II by 0.5.

Finally, before examining our data, we must ask why the line arising from the 3σ orbital is so broad and, thus, appears weak both in CN^- and in the metal cyanides. We cannot answer this in detail but can only suggest that the 3σ hole state has an exceptionally short lifetime due to processes which fill it from higher orbitals. Another possibility is that the line we see is a broad Franck-Condon envelope, due to a large change in geometry between CN^- and the 3σ hole state. Such

(39) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).

(40) E. U. Condon and W. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, London, 1970, p 202.

(41) C. J. Ballhausen, ref 40, Chapter 10.

a large change is likely, since the 3σ orbital is an important bonding orbital. We cannot distinguish between these possible explanations. A similar broadening, although much less severe, is seen in the X-ray photoelectron spectrum of N_2 in the gas phase.⁴²

The salient features of the spectra which we have obtained are the invariance of the 3σ and 4σ orbitals of CN^- to complex formation, which is expected on the basis of their binding energy, and the appearance of resolved features due to the $2t_{2g}$ levels, which are largely metal d functions. The cyanide 5σ and 1π levels, and perhaps other levels of the metal and the ligands, are clearly involved in bonding, but one can do little with the region of the spectrum in which they fall because the resolution is too poor.

We can estimate the composition of the $2t_{2g}$ levels in ferrocyanide because, in this complex, the feature due to $2t_{2g}$ is resolved well enough to allow us to estimate its intensity relative to K 3p. This proves to be 15:1. We have measured the Fe 3d cross section from FeF_3 and have related this to the K 3p cross section. The K 3p cross section is 2.11 times the Fe 3d cross section. If the $2t_{2g}$ level were entirely Fe 3d we should then find K 3p to be only 8.44 times as strong as $2t_{2g}$. The $2t_{2g}$ level must, then, have quite a large ligand amplitude, composed of carbon and nitrogen 2p orbitals. These orbitals have small cross sections, so they make the $2t_{2g}$ cross section smaller. The C 2p and N 2p cross sections are nearly the same and are equal to 0.07 times the Fe 3d cross section. Using this, we find that the $2t_{2g}$ is 56% Fe 3d, ignoring overlap.

One may reach the same conclusion about the $2t_{2g}$ orbitals from our data by other routes. For instance, if one assumes that the composition of the cyanide 4σ orbital is the same in the complexes as in free cyanide and that the Fenske-Hillier calculations²⁹ represent the 4σ orbital well, one may use the intensities of the 4σ and $2t_{2g}$ features in ferrocyanide to draw the same conclusion about the composition of $2t_{2g}$.

One may attempt a comparison in some detail between our results and the Wolfsberg-Helmholtz calculations. The energy level schemes calculated for a number of complexes appear in Table III. As one sees, the binding energies of the various levels are all calculated to be too high by some 9 eV. Shifting of all calculated binding energies by this amount results in a

Table III. Valence Level Structure of Cyanide Complexes According to the Calculations of Alexander and Gray^b

	Cr(CN) ₆ ³⁻	Fe(CN) ₆ ³⁻ ^a	Fe-(CN) ₆ ⁴⁻ ^a	Co(CN) ₆ ³⁻ ^a
1a _{1g}	17.58	18.34	18.31	18.58
1t _{2g}	17.45	17.14	16.85	16.88
1t _{1u}	16.57			
1e _g	15.96			
2t _{1u}	14.74			
2e _g	13.31			
1t _{2u}	13.27			
1t _{1g}	13.25			
2a _{1g}	13.84			
3t _{1u}	12.67			
2t _{2g}	10.01	11.24	10.91	11.68

^a Levels not shown differ from the corresponding levels of Cr(CN)₆³⁻ by less than 0.2 eV. ^b Binding energies in eV.

(42) K. Siegbahn, *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1970, p 62.

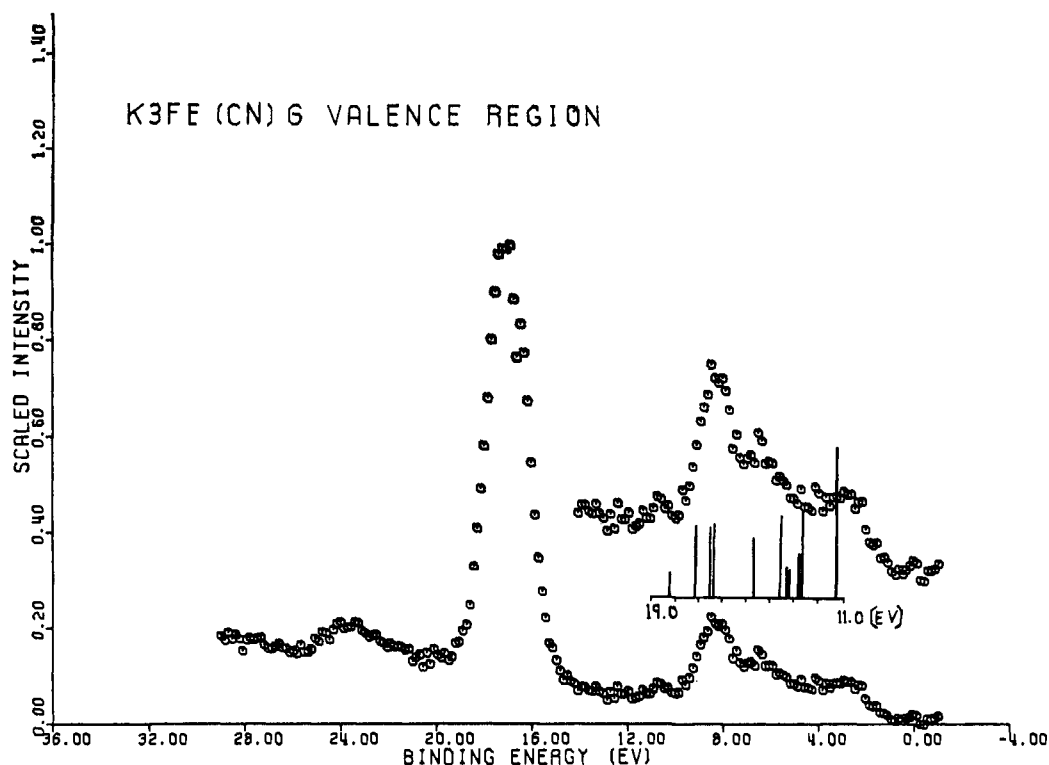


Figure 5. Comparison of the valence region of $K_3Fe(CN)_6$ with the calculated spectrum using the wave functions of Alexander and Gray.

reasonable fit, in the sense that the spread of calculated energy levels approximates the experimental spread. It is difficult to make a more detailed comparison because this would entail calculating the cross sections to be expected of the various orbitals. In such a calculation one may use the various atomic orbitals which were used in the calculation, or one may use the results of a better set of atomic orbitals, perhaps even experimental atomic orbital cross sections. We have reconstructed the spectrum expected from $Fe(CN)_6^{3-}$ using experimental atomic orbital cross sections. The results appear as Figure 5. As one sees, the agreement with the observed spectrum is reasonably good.

The binding energy of the $2t_{2g}$ is predicted to rise monotonically in the series of trivalent ions as one goes across the transition series and to fall by 0.78 eV as one goes from the trivalent $Co(CN)_6^{3-}$ to divalent $Fe(CN)_6^{4-}$. In point of fact, the binding energy falls by 1.7 eV going from cobalticyanide to ferrocyanide. The predicted trend of binding energies of the $2t_{2g}$ level is not reflected in the data. According to predictions, the $2t_{2g}$ level of $Co(CN)_6^{3-}$ should be more tightly bound than that of $Fe(CN)_6^{3-}$ by 0.45 eV and than that of $Cr(CN)_6^{3-}$ by 1.67 eV. The observed position of features from the $2t_{2g}$ levels obviously do not correlate well with this prediction, since the feature from $Cr(CN)_6^{3-}$ is more tightly bound than that from $Co(CN)_6^{3-}$ and is buried in the regions of the spectrum arising from cyanide levels. Correction of the observed binding energies to the centers of the configurations does not help. Since the corrections for $Co(CN)_6^{3-}$ and $Fe(CN)_6^{3-}$ are substantial, but of opposite sign, the corrected energies are far apart, much farther than the observed energy difference. The observed binding energies of the t_{2g} levels indicate a slow decrease in the binding energy of the lowest term across the series.

The spectrum of $Fe(CN)_5NO^{2-}$ differs sharply from that of $Fe(CN)_6^{4-}$ in that one does not see a feature similar to the $2t_{2g}$ level of $Fe(CN)_6^{4-}$ in the spectrum of $Fe(CN)_5NO^{2-}$. In point of fact, such a feature should be split into two features in the low-symmetry pentacyanonitrosyl. This suggests that the iron in $Fe(CN)_5NO^{2-}$ is not to be considered to be divalent, but to have a valency more like three or perhaps more. This agrees qualitatively with much other information.

Fenske-Hillier calculations on $Fe(CN)_5NO^{2-}$, and on numerous other pentacyanonitrosyls, have been published by Fenske and DeKock.²⁸ Their results come out at about the right energy, but they still have the levels arising from Fe 3d some 2.5 eV above the uppermost level arising from CN^- , thus too loosely bound.

Conclusions

It is clear, in general, that valuable information can be obtained from X-ray photoelectron spectroscopic studies of compounds which are as complex as the transition metal hexacyanides. In our studies, we have shown that, on the whole, the energy shifts of levels originating as CN^- levels are quite a bit less than has been predicted. Clear effects of metal bonding on the CN^- levels are seen; however, but they are hard to interpret quantitatively.

Judging from the data on ferrocyanide, the Wolfsberg-Helmholz calculations of Gray and Alexander fare well in dealing with the orbital composition of the hexacyanides, at least with the least-bound level. They are less satisfactory in predicting binding energies, as is often the case with calculations of the Hückel type.

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