mation of the amino methyl radical was examined. With γ held fixed at 90°, α optimized again to 0°, a planar radical site, and β to 112°. The rotational barrier is 0.54 eV. Constraining both the carbon and nitrogen to tetrahedral conformations yields a rotational barrier of 0.62 eV, the transoid structure being lower in energy than the cisoid. The origin of the barrier is displayed in Figure 5 where for simplicity we deal with the C_{2v} geometries, both carbon and nitrogen planar. For $\gamma = 0$ interactions 1, between the radical function and the lone pair, and 2, between the CH_2 and NH_2 p-like functions, are strong. However, for $\gamma = 90°$, the NH_2 function interacts with the energetically well separated radical function, interaction 3, and the CH_2 p-like function interacts with the lone pair, 4. Interactions 3 and 4 would be expected to be weaker than 1 and 2. In each conformation we have 4 electrons in bonding orbitals and 3 in antibonding, and the bonding interaction dominates over the antibonding. Consequently, for $\gamma = 0°$, we have stronger interaction and get lower total energy than for $\gamma = 90°$.

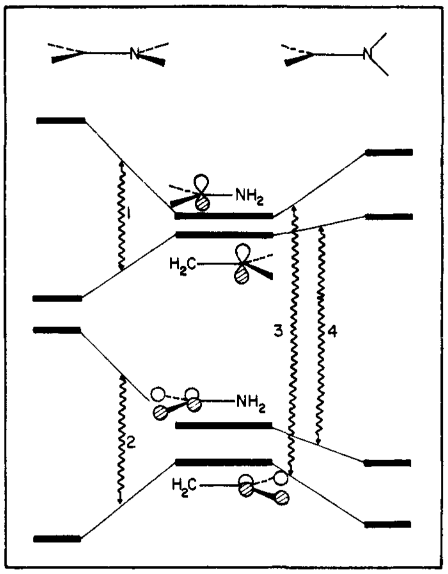

Figure 5. An interaction diagram for the p-like $-CH_2$ and $-NH_2$ localized basis functions, the nitrogen lone pair, and the radical function in the amino methyl radical. On the left the radical is planar and on the right the planes of the NH_2 and CH_2 are perpendicular to each other.

Summary

We may ask which has the greater effect on the electronic structure, the geometry changes or the effects of substitution. In the cases we have looked at, it is not clear. Changing the geometry of the radical site can alter the nature of the lowest excitation but so may the nature of a single substituent.

We have seen that a planar radical structure generally favors the lowest excitation being SOMO → LUMO. Pyramidal radical sites on the other hand lead to the HDOMO → SOMO being lowest. We have found that the effects of π donors or acceptors may modify these trends.

In our calculations, a planar radical site was preferred for donor, acceptor, and unsubstituted model structures. The strength of the preferences was rationalized.

Studies of the Valence Electron Levels of CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, VO_4^{3-}, and FeO_4^{2-} by X-Ray Photoelectron Spectroscopy

Andrew Calabrese and Robert G. Hayes*

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received November 27, 1972*

Abstract: The X-ray photoelectron spectra of the valence regions of the VO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, and FeO_4^{2-} ions are presented. Spectral assignments are made using existing MO calculations in conjunction with available X-ray data. Relative atomic cross sections are used in a semiquantitative discussion of line intensities.

In recent years, photoelectron spectroscopy has become a very useful tool in the study of the electronic structure of molecules, particularly in the investigation of the valence regions of gaseous molecules.[1-3] Irradiation of a sample with monochromatic photons of sufficient energy results in the emission of electrons *via* the photoelectric effect. The kinetic energy imparted to the photoelectrons is a direct measure of the binding energy of the level from which they were ejected. Since there are no formal selection rules for electron emission, the process will occur as long as the incident photon energy is greater than or equal to the binding energy of a particular level. Photoelectron spectroscopy thus allows one to study the entire valence region of compounds regardless of orbital symmetry.

X-Ray photoelectron spectroscopy has also been

---

(1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

(2) M. B. Robin, N. A. Kuebler, and C. R. Brundle, "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 351.

(3) U. Gelius in ref 2, p 311.

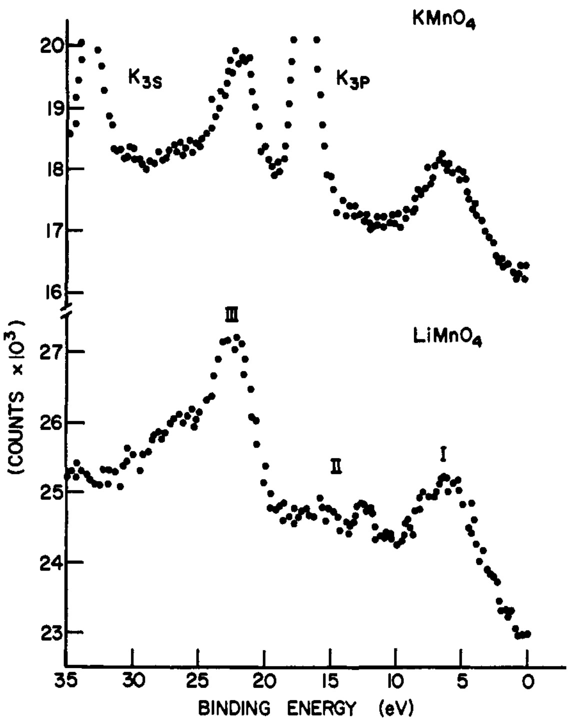

Figure 1. X-Ray photoelectron spectra of the valence region of $LiMnO_4$ and $KMnO_4$ excited with Al Kα radiation.

used by various authors[4–6] in their investigations of the valence region of oxyanions in solids. These spectra have yielded much useful information, despite the poor resolution of X-ray photoelectron spectroscopy, because they yield information about every occupied orbital. We have extended such studies to oxyanions of the first transition series elements VO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, and FeO_4^{2-}.[7] We report here the photoelectron spectra of these oxyanions. The assignment of spectral lines is made on the basis of existing MO calculations and available X-ray data.

Experimental Section

Al Kα radiation was used as the photon source and the electron energies were analyzed in the Varian IEE-15 electrostatic focusing spectrometer. Sample preparation was accomplished by depositing a thin layer of the solid onto adhesive tape. Commercially obtained lithium salts were used in all cases except for the ferrate ion where none was available, and the potassium salt was prepared as described elsewhere.[8] The choice of the lithium salts was made so that the valence region would not be complicated by the photolines of the cation. All samples were anhydrous except $LiMnO_4$, which was left under a vacuum of about 10^{-6} mm for approximately 1 hr to ensure dehydration of the surface layers. All samples were prepared and placed in the spectrometer under an inert atmosphere and the counting was initiated when the chamber pressure was less than 3×10^{-6} mm.

The metal $2P_{1/2}$–$2P_{3/2}$ region of each compound was scanned before and after the valence region. There was no notable difference in either the line shape or line width of any compound except the permanganates. In the spectra of $LiMnO_4$ and $KMnO_4$, a shoulder appeared on the low-energy side of each of the $2P_{1/2}$–$2P_{3/2}$ lines with a separation of 3.9 eV from the main line. We attribute the changes in the spectrum to radiation damage of MnO_4^- and we shall discuss the probable source of the new features presently. Energy calibrations were done using the 1s line of the "vacuum" carbon, which was assigned a binding energy of 285 eV.

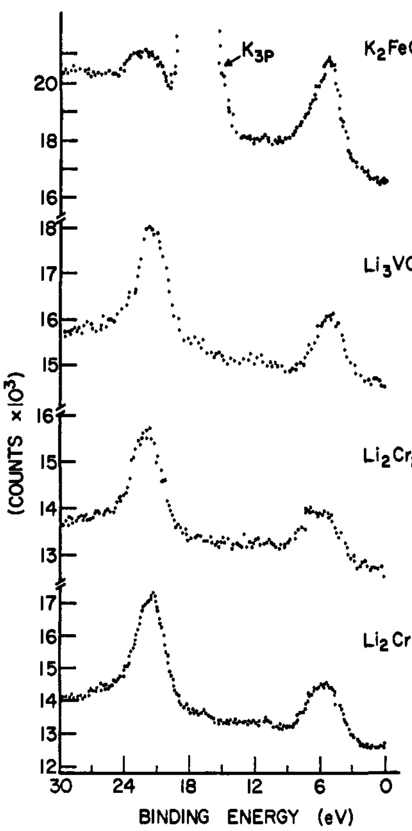

Figure 2. X-Ray photoelectron spectra of the valence region o- Li_2CrO_4, $Li_2Cr_2O_7$, Li_3VO_4, and K_2FeO_4 excited with Al Kα radiaf tion.

Results and Discussion

Various workers[4–6] have observed that the interaction between ions in an ionic crystal is rather small, suggesting that the crystal environment has little effect on the energy levels of the ions. The photolines observed in the valence region can thus be assigned to free ions, and existing MO calculations for the isolated anion may be used in interpreting the spectra. Since MO calculations for most of the ions which we have studied are not available, we will discuss in detail the one ion for which they are, *viz.*, MnO_4^-. Prior to this discussion, let us note (see Figures 1 and 2) that the spectra of all the ions have the same general features, namely a peak at low-binding energy (4–8 eV) and a more intense one at approximately 20 eV. We have labeled these peaks I and III, with the region between them as II, as shown in Figure 1.

Recently two types of calculations have been reported for the MnO_4^- ion, an *ab initio* calculation by Hillier and Saunders[9] and a spin-unrestricted SFC cluster model calculation by Johnson and Smith,[10] henceforth HS and JS, respectively. Table I shows the results of these calculations along with the experimentally mea-

---

[4] M. Barber, J. A. Connor, I. H. Hillier, and V. R. Saunders, ref 2, p 379.

[5] R. Prins and T. Novakov, *Chem. Phys. Lett.*, **9**, 593 (1971).

[6] J. A. Connor, I. H. Hillier, V. R. Saunders, and M. Barber, *Mol. Phys.*, 23, 81 (1972).

[7] While this manuscript was in preparation, a note on the X-ray photoelectron spectra of MnO_4^- and CrO_4^{2-} appeared: R. Prins and T. Novakov, *Chem. Phys. Lett.*, **16**, 86 (1972). Their experimental results resemble ours except that they found $LiMnO_4$ to be stable to irradiation and Li_3VO_4 to be unstable.

[8] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. II, Academic Press, New York, N. Y., 1963, pp 1504–1505.

[9] I. H. Hillier and V. R. Saunders, *Chem. Phys. Lett.*, **9**, 219 (1971).

[10] K. H. Johnson and F. C. Smith, Jr., *Phys. Rev. B*, **5**, 831 (1972).

Table I. Peak Position (eV) in X-Ray PES Spectrum of the Valence Region of $LiMnO_4$ and Calculated Energy Values

Measured		Calculated	
		HS	JS
$1t_1$	4–8	−5.74	−9.28
$6t_2$		−6.63	−10.36
$6a_1$		−7.28	−10.54
e		−11.38	−12.25
$5t_2$		−11.91	−12.44
$4t_2$	21.9		−24.28
$5a_1$			−24.66
$3t_2$	54.5		−57.92
$4a_1$	89.4		−87.52

sured binding energies of the MnO_4^- molecular orbitals. The results of these two calculations vary somewhat with respect to the absolute orbital energies, especially in the case of the outermost orbitals, *viz.*, the $1t_1$, $6t_2$, and $6a_1$. Table II lists the experimental results for the other anions.

Table II. Peak Position (eV) in X-Ray PES Spectra of the Valence Region of Li_2CrO_4, $Li_2Cr_2O_7$, Li_3VO_4, and K_2FeO_4

	CrO_4^{2-}	$Cr_2O_7^{2-}$	VO_4^{3-}	FeO_4^{2-}
$1t_1$, $6t_2$, $6a_1$, e, $5t_2$	3.5–8	3.5–8	3.5–7.5	3.5–8
$4t_2$, $5a_1$	21.9	22.1	22.0	22.5 (broad)
$3t_2$	47.7	48.0	42.6	58
$4a_1$	79.5	79.8	70.6	96.2, 101.4

As one sees from an examination of the spectra and of the calculations, a decision as to the proper assignment of the spectra depends in large part on the assignment of region II. If the HS calculation provides a good description of the ion, one should observe *two levels* in region II, unless the cross sections for these levels are very small. The JS calculation, on the other hand, suggests that five levels are grouped closely. Therefore, one would be inclined to associate region I with five levels and to argue that the JS calculation yields a better set of relative energies of the valence levels of MnO_4^- but poorer absolute values of the energies of valence levels. Several arguments suggest that the second alternative is correct.

The spectra of the lithium salts of most of the ions show no features in region II. Only in the spectra of $LiMnO_4$ do such features appear. But the MnO_4^- ion is susceptible to radiolysis,[11–13] and one has to proceed with some caution. The spectrum of $KMnO_4$, which is expected to decompose more slowly,[12] shows no feature in region II. The problem with $KMnO_4$ is that the K 3p line obscures region II in part.

Our observation on $LiMnO_4$ and $KMnO_4$, and known facts about the radiolysis of permanganates, suggests that MnO_4^- has no features in region II and that the spectrum of $LiMnO_4$ contains features due to radiolysis of MnO_4^-. We have verified this conclusion by examining the Mn 2p and Mn 3p regions of $LiMnO_4$ and of $KMnO_4$ as a function of the duration of exposure to the X-rays. In both cases a feature to lower binding energy grew into spectra of the $2P_{1/2}$, $2P_{3/2}$, and $3P_{1/2,3/2}$ levels. The new feature had a binding energy 3.9 eV less than the binding energy of the original feature in both cases.

One might guess that radiolysis would produce MnO_2 and, indeed, energies of the new features coincide with the energies of the levels measured on a sample of MnO_2.

Although both permanganates decomposed on irradiation, the decomposition of $KMnO_4$ was much less than that of $LiMnO_4$ and the MnO_2 spectrum in $KMnO_4$ was always weak. In $LiMnO_4$, however, we found a substantial fraction of the surface to be MnO_2 after the shortest of irradiation times.

We conclude that region II of each ion is devoid of features. In order to be sure that there are no levels which have a binding energy falling in region II, we have to show that such levels would not have a very small cross section. We can estimate the cross sections of the various levels calculated by CHS because they use the LCAO approximation and Gelius[3] has shown how to obtain molecular cross sections for the X-ray photoeffect in terms of atomic orbital cross sections. The crucial point of Gelius' argument is that the cross section for a molecular orbital is just the sum of the cross sections of each of its component atomic orbitals, weighted by the square of the amplitude of that atomic orbital in the molecular orbital.

The upper three levels ($1t_1$, $6t_2$, $6a_1$) are almost pure O 2p, according to HS. The next two levels, $5t_2$ and 1e, are roughly half O 2p and half Mn 3d. It follows that, even if the Mn 3d cross section is zero, the intensity of $5t_2$ and 1e together should be about 35% that of $1t_1$, $6t_2$, and $6a_1$ together. Thus, they should be detected readily. Furthermore, there is evidence, as we shall argue, that the 3d cross section, σ_{3d}, is, in fact, several times as large as σ_{2p} of oxygen. We conclude that the levels should be detected with ease in the X-ray photoelectron spectrum.

Finally, we may ask if the spectrum itself indicates whether the feature centered near 6 eV contains all five levels or only the upper three. The experimental ratio of the integrated intensity of the feature at 6 eV to that of the feature at 20 eV is 0.5. According to Gelius, σ_{2p}/σ_{2s} for oxygen is 0.112. Since the two orbitals assigned to the feature at 21.9 eV are almost pure oxygen 2s, the intensity ratio of the 6 eV feature to the 20 eV feature should be 0.159 if the 6 eV feature contains only $1t_1$, $6t_2$, and $6a_1$. On the other hand, if the 6 eV feature also contains the $5t_2$ and 1e levels, then the observed intensity ratio can be reproduced if σ_{3d} for Mn is 1.9 times σ_{2p} for O. This is roughly consistent with Jørgensen's observations, based on several compounds,[14] and with our observation[15] in which we have identified a feature in the valence region X-ray photoelectron spectrum of $Fe(CN)_6^{4-}$, which we assign to Fe 3d. Using Gelius' data on cross sections, we find that σ_{3d} of Fe is 3.1 times σ_{2p} of O from our observation. Our data on $Fe(CN)_6^{4-}$ suggest that, in this compound at least, σ_{3d} is larger than that deduced from the data on MnO_4^-, so that the $5t_2$ and 1e levels may contain less 3d amplitude than HS calculate. This, however, may only be clarified in light of further experimental evidence.

---

(11) G. Zimmerman, *J. Chem. Phys.*, **23**, 825 (1955).

(12) S. Yu. Elovich, S. Z. Rojinskii, and E. I. Shmuk, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 469 (1950).

(13) M. LeFort, *J. Chim. Phys. Physicochim. Biol.*, **54**, 782 (1957).

(14) C. K. Jørgensen and H. Berthou, *Discuss. Faraday Soc.*, to be published.

(15) R. G. Hayes, to be published.

We may compare our conclusions with some data on X-ray emission and absorption by some of the oxyanions. Best[16] has reported X-ray emission data from VO_4^{3-}, CrO_4^{2-}, and MnO_4^- ions (the latter two in solution). He has deduced the binding energies of the $3t_2$, $4t_2$, $6t_2$, and $7t_2$ orbitals. Since our photoelectron spectra arise from intramolecular transitions, they are not expected to depend on the surroundings of the ion so that we may use Best's results to confirm our assignments. Best deduces ($3t_2 - 4t_2$) energy differences of 21.2, 27.2, and 33.0 eV for VO_4^{3-}, CrO_4^{2-}, and MnO_4^-, respectively. These compare favorably with our measured values of 20.6, 26.1, and 32.6 eV. For the ($3t_2 - 6t_2$) energy differences Best obtained 37.1, 43.1, and 49.0 eV, which again compare favorably with our measured values of approximately 37.3, 42.3, and 49.4 eV for VO_4^{3-}, CrO_4^{2-}, and MnO_4^-, where we have used the center of peak I as the position of the $6t_2$ MO. Best does not report a value for the $5t_2$ orbital, possibly because the metal 3d parentage is expected to reduce the transition probability considerably. Best also fails to find any binding energies in region II.

Our conclusion concerning the electronic structures of the isoelectronic ions VO_4^{3-}, CrO_4^{2-}, and MnO_4^- is that, based on the analysis of the X-ray photoelectron spectrum of MnO_4^- just presented and on the similarity of the several spectra, all the bonding levels and oxygen 2p lone-pair levels lie within some 2 eV on either side of a binding energy of 6 eV. The compositions of the bonding orbitals must be much as described by HS, since the intensities are much as their calculation would predict.

The ion FeO_4^{2-} has two more electrons than have the other ions. These electrons are unpaired and are expected to reside in orbitals of symmetry e, localized mainly on the metal. As a result of the net spin of the ion, the various binding energies are expected to display exchange splitting.[17,18] These are observed in various ways in the spectrum.

The Fe 3s level, which is a core level, shows an exchange splitting of 5.2 eV, with the intensities of the two peaks in the ratio 1.8 to 1 *vs.* 2 to 1 expected.[17] The surprising thing about this splitting is its size, which is nearly as large as the splittings observed in Fe^{3+} compounds having five unpaired spins. The quantitative interpretation of iron series 3s multiplet splittings is somewhat complicated. The splittings observed in compounds normally thought to be very ionic, such as FeF_3, are only about one-half the calculated free-ion splitting.[17] This has been shown recently[19] to be due to a large amount of electron correlation, resulting in a configuration interaction between the nominal $3s^1\,3p^6\,3d^5$ final state and states such as $3s^2\,3p^4\,3d^6$. The role of such configuration interactions in FeO_4^{2-}, compared to its role in other iron compounds, is difficult to assess.

Exchange splittings apparently play a role also in broadening the feature near 22.5 eV, assigned to $4t_2$ and $5a_1$. Unfortunately, we may say nothing precise about this region of the spectrum because it is overlapped in part by the K 3p line. Some of the levels in the group near 6 eV should also display substantial exchange splittings, but we see no particular evidence for this, presumably because of the overlapping of many levels in this region.

Finally, we might mention that our spectra show a marginal difference between the 6 eV regions of CrO_4^{2-} and $Cr_2O_7^{2-}$, presumably due to splittings of the levels arising from interactions between the units, but we have not attempted to estimate a level scheme for $Cr_2O_7^{2-}$.

Conclusion

Our studies of VO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, and FeO_4^{2-} have shown that all these ions have very similar structures of their valence levels, with all the occupied levels arising from metal 3d and oxygen 2p orbitals appearing within about 2 eV on either side of a binding energy of 6 eV. The intensity of the feature near 6 eV, due to all these levels, compared to the intensity of the levels arising from oxygen 2s orbitals, suggests that there is substantial metal 3d amplitude in some of these orbitals, in agreement with conclusions from the calculation of HS. On the other hand, the spread of orbitals in the region of low binding energy is reproduced somewhat better by the JS calculation.

Acknowledgment. Support of this research by the National Institutes of Health, under Grant HL 13651, is acknowledged gratefully.

---

[16] P. E. Best, *J. Chem. Phys.*, **44**, 3248 (1966).

[17] C. S. Fadley, ref 2, p 281.

[18] J. C. Carver, T. A. Carlson, and L. C. Cain, ref 2, p 803.

[19] D. A. Shirley, private communication.