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Calculation of L X-ray Emission Energies and Intensities in PO_4^{3-} and ClO_4^-

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Central-atom L X-ray emission (L XE) energies and intensities are calculated for PO_4^{3-} and ClO_4^- with use of the self-consistent-field $X\alpha$ scattered-wave MO method. Central-atom 3d orbitals are found to make contributions to the L XE intensities which are much larger than suggested by their orbital populations. Central-atom 3d-orbital participation also strongly influences XE spectral energies calculated by using the transition-state approach although its effect on ground-state orbital energies is quite small. Thus, XE provides a sensitive measure of the relatively small amount of 3d-orbital participation in these materials.

Introduction

The question of d-orbital participation in the bonds formed by the elements in the third period of the periodic table has received considerable attention since it was first suggested by Cruickshank.[1] Nonetheless, there is still considerable disagreement concerning the importance of such d-orbital participation.[2-4] This paper does not consider this question in general but rather addresses the specific issue of the effect of d-orbital participation upon central-atom L X-ray emission energies and intensities in the tetrahedral oxyanions PO_4^{3-} and ClO_4^-.

Urch[5] has noted that the existence of a feature at high energy in the metal XE spectra of such materials can be most reasonably explained in terms of d-orbital participation in their molecular orbitals of e and t_2 symmetry. Recently Cl L XE spectra have been obtained for a number of Cl-containing oxyanions[6] in order to determine the extent of d-orbital participation, and the results have been compared with those obtained from theoretical calculations.[7,8] Assuming common radial functions for the 3s and 3d orbitals, Henke et al.[6] found that the angular terms in the matrix elements for valence orbital to M 2p orbital transitions caused the intensity generated by a 3d electron to be only two-fifths as great as that for a 3s electron. On the basis of this assumption, they estimated Cl L intensities from calculated orbital populations.[7,8] They found this approach to significantly underestimate the relative intensity of the highest energy peak, arising from the orbitals with Cl 3d character. However, the relative intensities of the Cl Kβ XE spectral peaks had previously been calculated quite accurately by using one of these wave functions.[7] It has recently been shown[9] for SF_6 that the assumption of equal S 3s and S 3d L XE radial transition intensities is incorrect and gives results in error by almost a factor of 3. In addition, the neglect of transition intensity arising from ligand 2p admixture in both the valence orbitals and the nominal S 2p core was also shown to significantly affect the results.[9] Another complication in the prediction of XE intensities, not considered in the SF_6 calculation, is the effect of orbital relaxation attendant upon core hole creation. Such relaxation effects have been accurately described for many materials by using the transition-state procedure[10] within the self-consistent-field $X\alpha$ scattered-wave MO method.[11]

Table I. Calculated and Experimental Energies (eV) and Relative Intensities in PL XE of PO_4^{3-}

	calcd[a]			exptl		
orbital	*E*	Δ*E*	*I*	*E*	Δ*E*	*I*[b]
$3t_2$, 1e	133.1, 132.6	5.2[c]	1.69	126.3	6.5	1.15
$2t_2$	130.8	3.1	0.02			
$2a_1$	127.7	0.0	1.00	119.8	0.0	1.0
$1t_2$	118.2	−9.5	0.22	110.2	−9.6	0.65
$1a_1$	116.0	−11.7	0.63	106.9	−12.9	

[a] From transition-state calculations. [b] Obtained by block counting the areas under the experimental peaks in ref 17. [c] Intensity-weighted average.

Computational Method

SCF–$X\alpha$ calculations have been previously performed on ClO_4^- [12] and PO_4^{3-},[13] and calculated relative orbital energies were shown to be in good agreement with photoemission data. We have repeated the calculations for ClO_4^- using the bond distance, statistical exchange factors (α), and sphere radii parameters determined as optimium in ref 12. For PO_4^{3-} we used the parameter choice favored by Weber[13] (i.e., touching rather than overlapping sphere radii), but we adopted a P–O distance of 1.51 Å, a more typical value for orthophosphates[14] than that used in ref 13. Maximum *l* values for partial waves were 3 on the outer sphere, 2 on the central atom, and 1 on oxygen.

We have also calculated central-atom L XE energies and intensities for a transition state with half an electron removed both from the metal 2p orbital and from the valence orbital being studied. Spontaneous X-ray emission intensities are calculated with the use of the method described by Noodleman,[15] which has previously been applied successfully to the calculation of visible and UV relative absorption intensities. Since the potential gradient formalism used in this method employs the cube of the transition energy in the calculation of transition probabilities, it may well be more accurate for the XE case, where the percentage energy errors are considerably smaller, than for the case of optical spectra. The intensity of spontaneous emission is proportional to the absolute transition probability for absorption times the fourth power of the transition energy. Since the percent variation in ML XE energies is quite large, this factor has an important effect upon relative intensities.

Results

Direct Calculations of L XE Energies and Intensities. Orbital energies obtained for the ground state of ClO_4^- are identical with those of ref 12. The highest occupied orbital is the O 2p nonbonding $1t_1$. Below it lie the $3t_2$ and 1e orbitals,

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(1) D. W. J. Cruikshank, *J. Chem. Soc.*, 5486 (1961).
(2) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).
(3) P. J. Hay, *J. Am. Chem. Soc.*, **99**, 1003 (1977).
(4) E. E. Ball, M. A. Ratner, and J. R. Sabin, *Chem. Scri.*, **12**, 128 (1978).
(5) D. S. Urch, *J. Chem. Soc. A*, 3026 (1969).
(6) B. L. Henke, R. C. C. Perera, and D. S. Urch, *J. Chem. Phys.*, **68**, 3692 (1978).
(7) J. A. Connor, I. H. Hiller, V. R. Saunders, and M. Barber, *Mol. Phys.*, **23**, 81 (1972).
(8) H. Johansen, *Theor. Chim. Acta*, **32**, 273 (1974).
(9) H. Ågren, J. Nordgren, L. Selander, C. Nordling, and K. Siegbahn, *Phys. Scri.*, **18**, 499 (1978).
(10) J. C. Slater, *Adv. Quantum Chem.*, **6**, 1 (1972).
(11) K. H. Johnson, *Adv. Quantum Chem.*, **7**, 143 (1973).
(12) J. G. Norman, Jr., *Mol. Phys.*, **31**, 1191 (1976).
(13) J. Weber, *Chem. Phys. Lett.*, **40**, 275 (1976).
(14) A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Clarendon Press, Oxford, England, 1975, p 689.
(15) L. Noodleman, *J. Chem. Phys.*, **64**, 2343 (1976).

0020-1669/80/1319-3328$01.00/0

Table II. Calculated and Experimental Energies (eV) and Relative Intensities in Cl L XE of ClO_4^-

	calcd[a]			exptl[b]		
orbital	*E*	ΔE	*I*	*E*	ΔE	*I*
$3t_2$, 1e	203.0, 202.9	8.2	4.3	200.1	7.2	3.9
$2t_2$	198.1	3.7	0.02			
$2a_1$	194.8	0.0	1.0	192.9	0.0	1.0
$1t_2$	186.0	−8.8	0.63	182.7	−10.2	1.1
$1a_1$	179.6	−15.2	2.57	174.7	−18.2	5.9

[a] From transition-state calculations. [b] Reference 6.

which are basically nonbonding but have some central-atom 3d character. Below them are the central-atom–O 2p bonding orbitals $2t_2$ and $2a_1$, and deeper lie the $1t_2$ and $1a_1$ orbitals, which are mostly O 2s in character with some central-atom s or p admixture. According to dipole selection rules, the only orbitals giving features in the Cl L XE spectrum will be those having a_1, e, or t_2 symmetry. It is well established[5,6] that the high-energy peak in the L XE spectra of PO_4^{3-} and ClO_4^- arises from the 1e and the $3t_2$ orbitals. The next peak in the spectrum arises from the $2a_1$ orbital, which is strongly bonding between the central atom and O with substantial central-atom 3s character. The lowest energy L XE peak is generally associated with the $1a_1$ orbital. However, this peak is broad, and some of its intensity may be attributable to the $1t_2$ orbital, which possesses some central-atom 3d character.

The various XE and X-ray photoemission (XP) spectra of the PO_4^{3-} ion have been discussed by Kosuch et al.[16] The PL XE spectrum which they employ is that recorded by Wiech[17] for $AlPO_4$. The $AlPO_4$ spectrum was picked since this material showed no decomposition under the X-ray beam and its spectrum did not differ greatly from the spectrum of other phosphates.

In Table I we compare calculated and experimental energies and relative intensities in the PL XES of PO_4^{3-}. Calculated transition energies are about 10 eV larger than the experimental energies while the spectral width is reproduced with an error of less than 3 eV. We have calculated relative XES intensities by evaluating absolute transition probabilities for the orbitals of the XE transition state and multiplying them by the fourth power of the transition-state eigenvalue differences. The P 2p orbital was allowed to delocalize onto the ligands. Results presented for PO_4^{3-} in Table I are in reasonable agreement with experiment. We correctly predict the ($1e + 3t_2$) peak to be more intense than the $2a_1$ peak by a modest margin. The high calculated intensity for the $1t_2$ peak suggests that the PL XE spectrum would be better interpreted by a decomposition of the broad, low-energy peak into two components.

Analogous results for the ClO_4^- calculations are presented in Table II. Agreement of calculated and experimental energies is similar to that for phosphate. Henke et al.[6] have presented evidence indicating that part of the apparent $1a_1$ peak intensity actually arises from shake-up satellites and from decomposition products. Inspection of the calculated and experimental intensities in Table II suggests that about one-third of the apparent $1a_1$ peak intensity may derive from such sources with the rest coming from Cl 3s character in the $1a_1$ orbital.

We observe that the ratio of the calculated ($1e + 3t_2$) peak intensity to that of the $2a_1$ peak increases by about a factor of 2–3 in going from PO_4^{3-} to ClO_4^-, in reasonable agreement with experiment. This arises from a substantial increase in d-orbital participation in ClO_4^- compared to that in PO_4^{3-}.

Table III. Total Numbers[a] of Electrons within the Central-Atom Atomic Sphere for Ground-State Molecular Orbitals of PO_4^{3-} and ClO_4^-

	1e	$3t_2$	$2a_1$	$1t_2$	$1a_1$
PO_4^{3-}	0.08	0.20	0.41	0.06	0.29
ClO_4^-	0.22	0.46	0.34	0.23	1.08

[a] Total numbers are summed over degeneracy; e.g., the 1e orbital holds 4 electrons, of which only 0.08 is within the central-atom sphere for PO_4^{3-}.

Table IV. Variation of Relative ML XE Intensities for Different Calculations on ClO_4^-

		localized 2p hole emissn intens		delocalized Cl 2p hole emissn intens,
orbital	pop. ratio × $(\Delta E/\Delta E_{2a_1})^4$	ground state	transitn state	transitn state
1e	0.15	0.91	1.25	1.68
$3t_2$	0.31	2.29	2.58	2.60
$2a_1$	1.0	1.0	1.0	1.0
$1a_1$	2.36	1.98	2.50	2.57

There is also a dramatic increase in the relative intensity of the $1a_1$ peak in going from phosphate to perchlorate. This is associated with an increase in the amount of Cl 3s character in the $1a_1$ orbital as compared to that in the $2a_1$ orbital in the perchlorate. The numbers of electrons contained within the metal atomic spheres in the various molecular orbitals (the equivalent of an orbital population in an LCAO–MO calculation) are shown in Table III and verify this result. Thus, the qualitative differences in the relative intensities of L spectral peaks between PO_4^{3-} and ClO_4^- may be understood on grounds of orbital populations alone. Nonetheless, an inspection of Tables I–III establishes that the orbital populations cannot quantitatively predict the relative peak intensities.

Effect of Approximations on L XE Intensities. The effects of various approximations upon the calculated emission intensities are illustrated in Table IV for the 1e, $3t_2$, $2a_1$, and $1a_1$ orbitals of ClO_4^-. Assuming equal radial dependencies for the Cl 3s and 3d orbitals leads to an absolute transition probability proportional to $P_{3s} + {}^2/_5P_{3d}$, where P_i is the number of electrons with given *l* value within the metal sphere. Relative emission intensities obtained by using this approach are shown in the first column of Table IV. Direct calculation of the transition probabilities from the orbitals in the ground state and XE transition states generates the emission intensities in columns 2 and 3. Our final results allow the Cl 2p orbital to be delocalized onto the ligands and are shown in column 4 (these are the same as the results given in Table II). We see that the assumption of identical radial components of the transition probability for all 3s and 3d functions gives a very serious error in the relative $(1e + 3t_2)/2a_1$ intensity. Thus, the small d-orbital participation calculated makes a much greater contribution to the L XE intensity than is suggested by the model of Henke et al.[6] Conversely, the amount of d-orbital participation needed to explain the observed relative intensity for the ($1e + 3t_2$) peak is smaller than suggested by the Henke et al. model (by about a factor of 6).

Calculations were also performed in which d functions were excluded from the central atom. Such calculations give zero L XE transition probability to the 1e and $3t_2$ orbitals when the Cl 2p orbital is not allowed to delocalize to the ligands. Even when such delocalization is allowed, the transition probability remains essentially zero. This result is, of course, expected. However, we also observe a large and unexpected effect of 3d-orbital participation on the transition energy. In the ground state of ClO_4^- the exclusion of Cl 3d functions destabilizes the 1e orbital with respect to the $1t_1$ orbital by

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(16) N. Kosuch, E. Tegeler, G. Wiech, and A. Faessler, *Chem. Phys. Lett.*, **47**, 96 (1977).

(17) G. Wiech, *Z. Phys.*, **216**, 472 (1968).

only about 0.6 eV, but d function exclusion in the Cl 2p ← 1e transition-state calculations leads to a transition energy of 207.2 eV, more than 4 eV larger than the value of 202.9 eV obtained when d functions are included (Table II). Thus, the inclusion of d functions on the metal is also important in describing the electronic relaxation attendant upon core hole creation which is needed to obtain the correct transition energy.

In addition to the major effect of 3d-orbital participation upon the L XE intensities, small effects arising from other approximations were also observed. We find that orbital compositions and computed oscillator strengths are somewhat changed in going from the ground state of the oxyanion to the XE transition state. For ClO_4^- the Cl 3d character in the 1e orbital increases from 5.5 to 6.4% while the Cl 3s character in the $2a_1$ orbital drops from 16.8 to 14.9% and rises in the $1a_1$ orbital from 50.9 to 57.9. Since Cl-centered orbitals will be stabilized in the L XE transition state, the Cl 3d orbital is expected to be pulled down toward the O 2p, resulting in more Cl 3d–O 2p covalent mixing, while the Cl 3s is pulled further below the O 2s, reducing the Cl 3s–O 2s covalent mixing. Percentage changes in oscillator strengths between the ground and transition states closely match those in orbital population, as illustrated in Table IV. Thus, core hole creation seems to have only a modest effect upon intensities although it strongly modifies energies (e.g., the Cl 2p ← 1e orbital eigenvalue difference increases from 189.7 eV in the ground state to 202.9 eV in the transition state).

Allowance for delocalization of the "Cl 2p" orbital onto the oxygens in the XE transition state increases the intensity of the Cl 2p ← 1e transitions by about one-third but modifies the other transition intensities (including that to the $3t_2$ orbital) by only a few percent. This effect therefore has only a modest influence on the relative emission intensities from the 1e, $3t_2$, and $2a_1$ orbitals.

The remaining discrepancies between calculated and experimental relative intensities may arise from either the limitations of the SCF–Xα scattered-wave method and/or the neglect of the crystalline environment. Since the discrepancy is substantially larger for PO_4^{3-} than for ClO_4^-, the latter factor may be the more important. It is also probable that PO_4^{3-} would be a better model for an ionic phosphate like Na_3PO_4 than it is for $AlPO_4$, whose spectrum yielded the experimental intensities given in Table I.

Conclusion

The SCF–Xα method yields L XE energies and intensities in semiquantitative agreement with experiment for PO_4^{3-} and ClO_4^-. Qualitative trends in peak intensities may be predicted from an inspection of orbital compositions. However, quantitative calculation of the spectral intensities requires the consideration of different radial functions for central-atom 3s and 3d orbitals. In addition to its effect upon transition intensity, 3d-orbital participation is found to strongly modify transition energies.

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Electron Transfer in Mixed-Valent Diferrocenylacetylene and [2.2]Ferrocenophane-1,13-diyne

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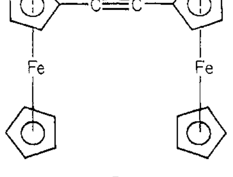
The preparation and characterization of triiodide salts of mixed-valent and dioxidized diferrocenylacetylene and [2.2]-ferrocenophane-1,13-diyne are reported. Iron-57 Mössbauer data show that the mixed-valent salt of diferrocenylacetylene is localized, whereas the mixed-valent salt of [2.2]ferrocenophane-1,13-diyne is delocalized. The latter salt is also shown to be delocalized on the EPR time scale. A criterion based on the appearance of the perpendicular C–H bending bands in the infrared spectrum is developed to tell whether a given mixed-valent ferrocene is delocalized or not on the vibrational time scale. Results are given for mixed-valent salts of [2.21ferrocenophane-1,13-diyne, biferrocene, 1′-acetylbiferrocene, and bis(fulvalene)dicobalt(II,III)(1+). The dioxidized triiodide salt of diferrocenylacetylene is shown to exhibit an antiferromagnetic interaction where μ_{eff}/Fe decreases to 1.39 μ_B at 4.2 K. And finally, insight about the mixed-valent phenomenon in fused ferrocenes is gained by a correlation of g-tensor anisotropy with the magnitude of quadrupole splitting observed.

Introduction

In 1974, Cowan and co-workers reported[2] the electrochemical generation of the mixed-valence ion of a diferrocenylacetylene (I). They found that there is a 130-mV separation between the two one-electron half-wave oxidation potentials of I. The mixed-valence monocation of I has an intervalence transfer (IT) electronic absorption band at 6410 cm^{-1} (ϵ = 670). A later report[3] from the same workers showed that [2.2]ferrocenophane-1,13-diyne (II) exhibits two reversible one-electron oxidation waves with a separation of 355 mV. A relatively intense (ϵ = 3100) IT band is seen at 5680 cm^{-1} for the mixed-valence monocation of II. The EPR spectrum of this same mixed-valence ion in a methylene chloride glass at



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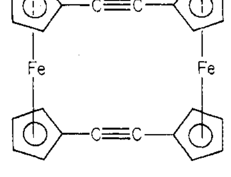

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[1] A. P. Sloan Foundation Fellowship, 1976–1978.

[2] LeVanda, C.; Cowan, D. O.; Leitch, C.; Bechgaard, K. *J. Am. Chem. Soc.* **1974**, *96*, 6788.

[3] LeVanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

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