A Study of the Bonding in the Group IV Tetrahalides by Photoelectron Spectroscopy

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Phil. Trans. R. Soc. Lond. A 1970 **268**, 111-130
doi: 10.1098/rsta.1970.0065

Phil. Trans. Roy. Soc. Lond. A. **268**, 111–130 (1970) [111]
Printed in Great Britain

A study of the bonding in the group IV tetrahalides by photoelectron spectroscopy

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The photoelectron spectra excited by helium 21.2 eV radiation in the group IV halides, AB_4, where A = C, Si, Ge, Sn, Ti and B = Cl, Br, have been determined. The ionization potential data are discussed in terms of a simple molecular orbital description of the electronic structures.

Introduction

We have measured, and attempted to interpret the photoelectron (p.e.) spectra of a series of simple inorganic compounds, namely the volatile group IV tetrahalides, AB_4, where A = C, Si, Ge, Sn and Ti, and B = Cl and Br. The ultraviolet p.e. spectra of large polyatomic molecules, where there are many distinct ionizable (valence) electrons, and where vibrational fine structure is unlikely to be resolved, pose considerable assignment problems. It is therefore advantageous to study a series of closely related compounds (see for example, Evans, Green, Green, Orchard & Turner 1969) and acquire the additional evidence regarding trends in the spectra.

Experimental

The measurements were made on the photoelectron spectrometer described by Turner (1968*a*). The vapour of the compound under investigation was fed continuously into the ionization chamber at a pressure below 27 N m^{-2} (200 μmHg). The spectra were calibrated by introducing xenon or argon into the ionization chamber subsequent to the photoelectron measurement of the compound.

The group IV tetrahalides were either obtained commercially or synthesized by direct combination of the elements. The materials were thoroughly purified by standard procedures, particular care being taken to exclude moisture.

Results

The photoelectron spectra are presented in figures 1 to 4 and the ionization potential (i.p.) data are recorded in tables 1 to 4. The tabulated figures (eV) refer to vertical i.p., and therefore their accuracy depends on the sharpness of the p.e. band maxima: in the more favourable cases these i.p. may be quoted to within 0.1 eV. The i.p. data in parentheses relate to partially resolved structure on the sides of the main p.e. bands. The *relative* band areas are given in square brackets. When neighbouring p.e. bands overlap substantially these estimates are very inexact.

Discussion

We shall assign the photoelectron spectra in terms of elementary molecular orbital theory, using Koopmans's theorem to relate i.p. data to orbital electronic structure. According to this approximation (Koopmans 1933), the individual vertical i.p. of *closed-shell* atomic or molecular species may be calculated as the Hartree–Fock energy eigenvalues for the orbitals which are ionized. It has certain deficiencies, and these have been emphasized recently by Richards (1969). However, it remains a sufficiently good approximation for our present purposes.

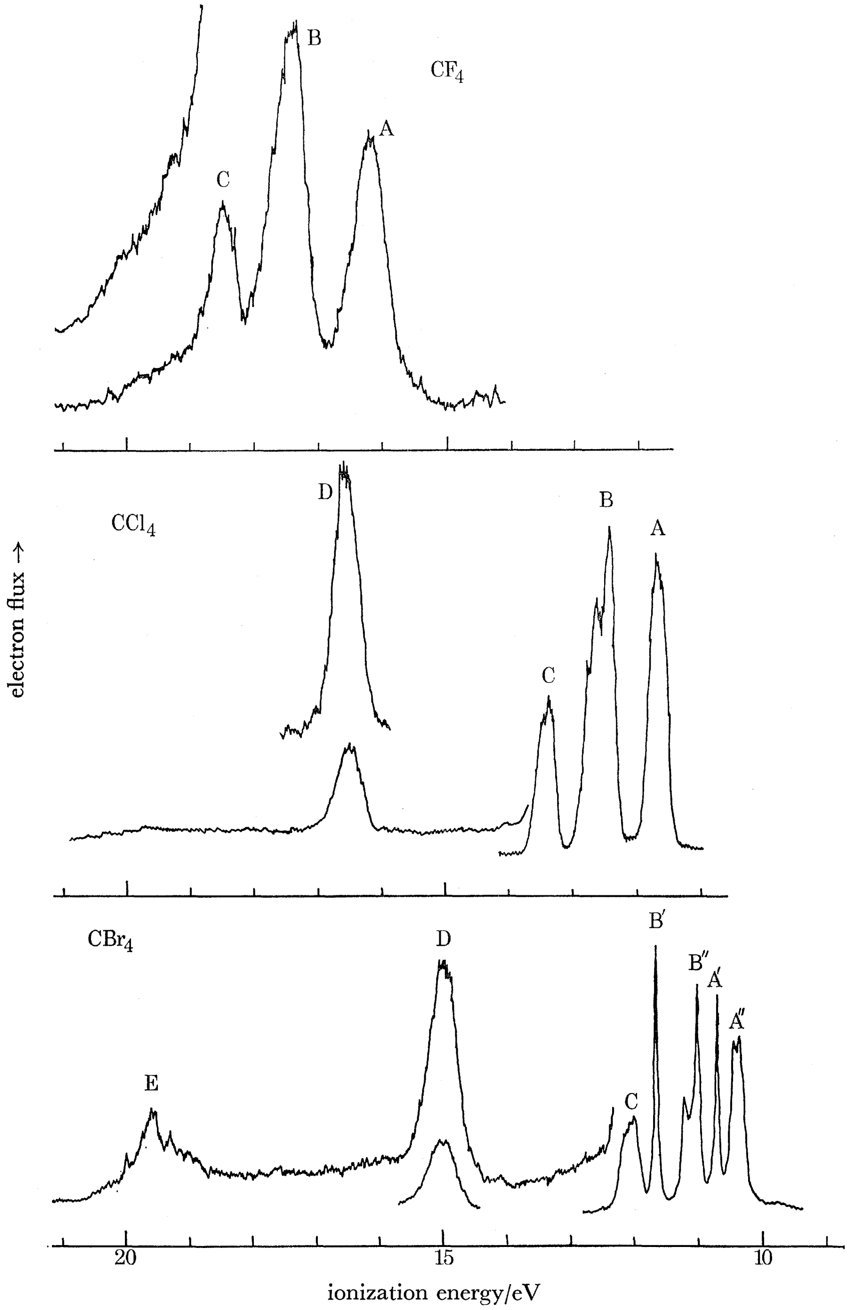

Figure 1. The photoelectron spectra of the carbon tetrahalides.

The assignment of p.e. bands to particular electron levels (or, more precisely, to states of the molecular ion) is often facilitated by the notion that, for the photoionization of orbitals of comparable localization tendencies and similar energy, the integrated p.e. band intensities should reflect the overall spin-orbital degeneracies of the ion states realized (cf. Turner 1968*b*; Turner, Baker, Baker & Brundle 1969). This proportionality of p.e. band area and degeneracy of ion state follows from the theoretical studies of Buckingham, Orr & Sichel (this volume,

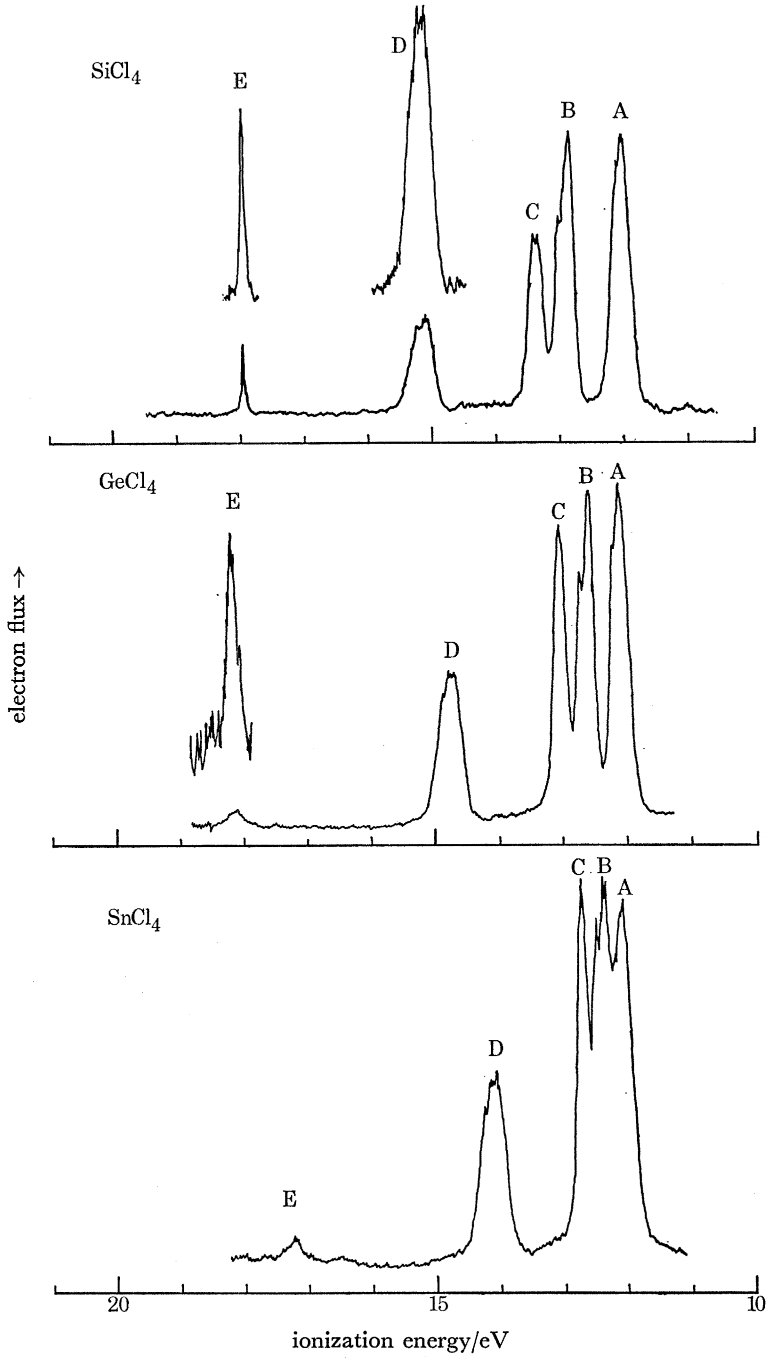

FIGURE 2. The photoelectron spectra of the group IVB tetrachlorides, $SiCl_4$, $GeCl_4$ and $SnCl_4$.

p. 147) if the crucial electric dipole terms are assumed to be equal. We make limited use of this approximate criterion in the analysis below.

(*a*) *The group* IV B *tetrahalides*

We begin with a discussion of the essential features of the orbital electronic structure of a representative tetrahedral AB_4 molecule. Consider the l.c.a.o.–m.o. that may be constructed from a 'chemical' basis set consisting of s and p orbitals on each of the five atoms. The central

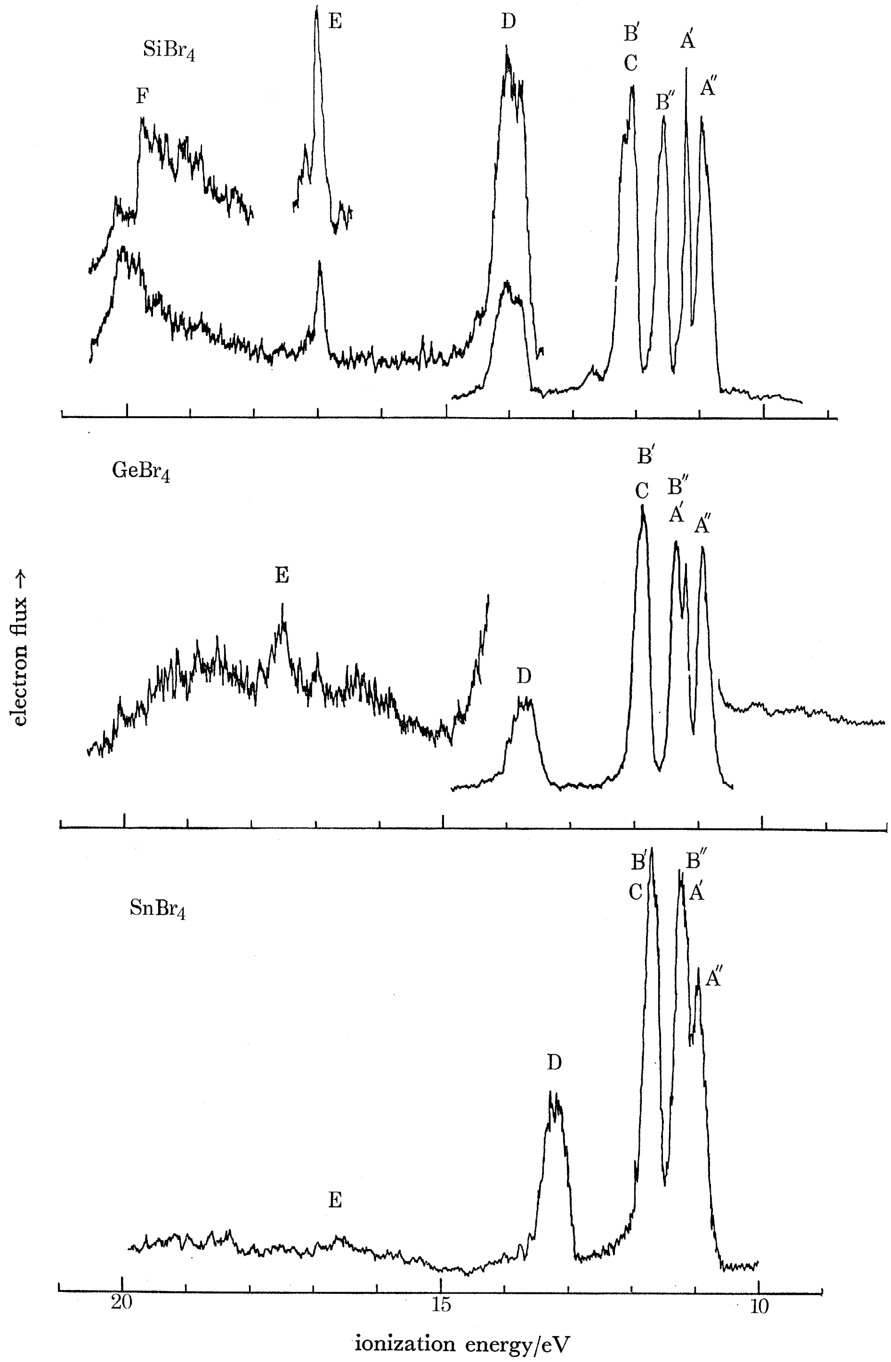

FIGURE 3. The photoelectron spectra of the group IV B tetrabromides, $SiBr_4$, $GeBr_4$ and $SnBr_4$.

atom orbitals, s_A and p_A, transform according to the a_1 and t_2 representations, respectively, of the point group T_d. The remaining four sets of orbitals, s_B and p_B, span representations reducible to a_1+t_2 and $a_1+e+t_1+2t_2$, respectively. The valence electron structure of a group IVB tetrahalide molecule is therefore of the general type,

$$(1a_1)^2\,(2a_1)^2\,(1t_2)^6\,(2t_2)^6\,(3t_2)^6\,(e)^4\,(t_1)^6, \tag{1}$$

where no particular ordering of the levels is implied. On electronegativity grounds we expect the higher energy occupied m.o. to be the $3t_2$ species (composed mainly of halogen p a.o.), together with the non-bonding e and t_1 species (of pure halogen p character). This is a basic feature of the molecular orbital scheme (figure 5), where the Fock integral for the valence a.o., p_A, of the central atom is assumed to be more negative than those of the halogen valence a.o., p_B. The detailed structure of this diagram (which we will show to be consistent with the photoelectron spectra) is based on various model molecular orbital calculations outlined in appendix (A2). The σ, π notation for the halogen p orbitals distinguishes the orbital directed along the A–B vector (p_B^σ) from the pair of orbitals (p_B^π) perpendicular to this direction. An important point illustrated in figure 5, and explained in appendix (A1), is that the symmetry orbitals arising from any particular a.o. species on atom B (s_B, p_B^σ or p_B^π) are substantially

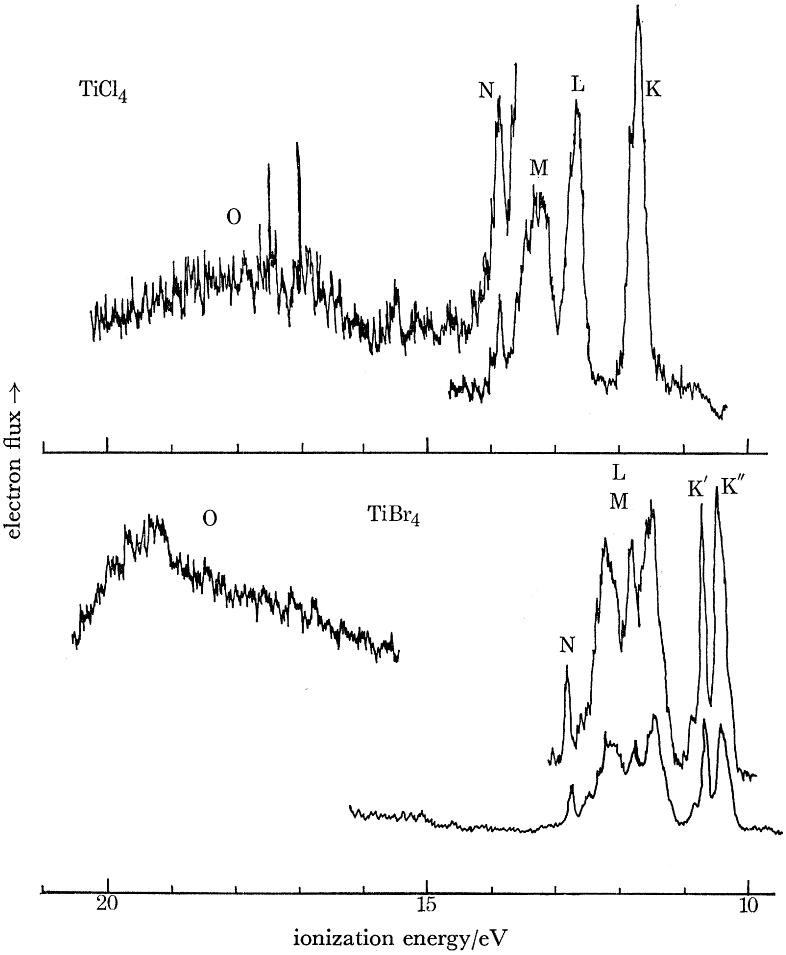

Figure 4. The photoelectron spectra of the titanium tetrahalides, $TiCl_4$ and $TiBr_4$.

differentiated in energy as a result of interactions within the B_4 tetrahedron (see equation (A 7)). Most significantly, the relative energies of the p^{π}_{B} symmetry orbitals become $t_1 > e \geqslant t_2$. This effect may be ascribed, in simple terms, to the fact that in the t_1 combination the overlap of halogen p_{π} a.o. is of unfavourable, negative phase, while this overlap is favourable in the e and t_2 symmetry orbitals. We conclude, in particular, that the t_1 non-bonding (p^{π}_{B}) level must lie above the corresponding e level. The relative energy of the neighbouring t_2 level depends on the nature and extent of the mixing of t_2 (p^{π}_{B}) with central atom p_A and with the t_2 (p^{σ}_{B}) combination.

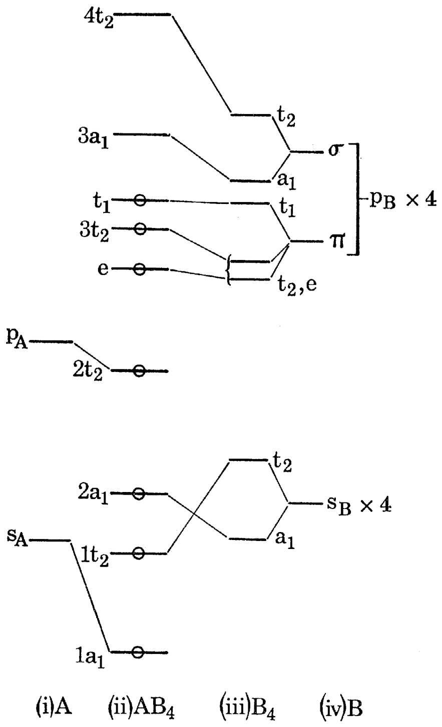

FIGURE 5. Qualitative molecular orbital energy level diagram for the group IV B tetrahalides, AB_4: (i) central atom valence a.o., (ii) molecular orbitals of AB_4, (iii) B_4 symmetry orbitals, (iv) halogen valence a.o.

We now consider some of the less complicated p.e. spectra, such as those of silicon tetrachloride (figure 2) and the carbon tetrahalides (figure 1). The relative areas (tables 1 and 2) of p.e. bands A, B and C in the spectra of CCl_4, CF_4 and $SiCl_4$ lead us to assign these bands to ionizations from triply degenerate (t) and doubly degenerate (e) m.o., respectively. We cannot at this point distinguish between the $3t_2$ and t_1 levels, but this assignment accords with the previous argument that the halogen non-bonding m.o. have relative energies $t_1(p^{\pi}_{B}) > e\,(p^{\pi}_{B})$. The relative areas of bands D and E in the $SiCl_4$ photoelectron spectrum similarly suggest assignment to the $2t_2$ and $2a_1$ m.o., respectively.

A comparison of the CCl_4 and CBr_4 p.e. spectra supports the above assignment of p.e. bands A, B and C, and is helpful as regards the problem of distinguishing the $3t_2$ and t_1 ionizations. We believe that these spectra correspond in the manner indicated in table 1. Thus, while the e p.e. bands (C) have a rather similar appearance, the remaining structure in the high† energy regions of the spectra are quite different. Incipient fine structure of p.e. bands A and B in the

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† We refer to photoelectron bands as of *high* or *low* energy according to their observed positions on the electron *kinetic energy scale.*

CCl_4 spectrum is resolved in the CBr_4 spectrum, where we observe two groups of bands (A and B), each group consisting of a sharp band to low energy (A′ and B′) and a partly resolved doublet to high energy (A″ and B″): the latter bands have approximately twice the area of the former. We attribute the fully resolved fine structure to multiplet splitting of the terms of the CBr_4^+ ion under the strong spin-orbit coupling centred on the bromine atoms. Now only ^2T terms are susceptible to spin-orbit interactions in this way (see appendix (B)). With an a.o. basis of p orbitals, each of the $^2T(t^5)$ terms of the molecular ion should split unsymmetrically into a lower quartet and an upper doublet (just like an atomic $^2P(p^5)$ term): the multiplet splitting is just $\frac{3}{2}\zeta$, where ζ is the appropriate spin-orbit interaction constant for the molecular orbitals (t_1 or t_2). The quartet states transform as U′ in the spinor group T_d^*, while the doublet states arising from $^2T_1$ and $^2T_2$ transform as E′ and E″, respectively. That no multiplet fine structure is observed for band D, which has already been assigned to ionization from the $2t_2$ m.o., is not unexpected for orbitals of predominantly carbon 2p character, spin-orbit coupling in the p-shell of a free carbon atom being extremely small (see table B1).

TABLE 1. PHOTOIONIZATION DATA FOR THE CARBON TETRAHALIDES

p.e. band	CF_4	CCl_4	CBr_4	assignment
A	16.20 [1.6]	11.60 [1.88]	10.40 10.49 } [1.33] A″	t_1 U′
			10.75 [0.58] A′	E′
B	17.36 17.56 17.69 } [2.4]	12.40 12.60 12.75 } [2.58]	11.05 11.23 } [1.31] B″	$3t_2$ U′
			11.69 [0.54] B′	E″
C	18.46 [1.0]	13.40 [1.0]	12.06 [1.0]	e U′
D	—	16.60 [2.0]	15.04 [1.1]	$2t_2$ U′+E″
E	—	—	19.48 [0.4]	$2a_1$ E′

TABLE 2. PHOTOIONIZATION DATA FOR THE GROUP IVB TETRACHLORIDES

p.e. band	$SiCl_4$	$GeCl_4$	$SnCl_4$	assignment
A	12.03 (12.12) } [2.2]	12.12 [1.65]	12.10 } [3.7]	t_1
B	12.85 (13.05) } [2.1]	12.60 (12.75) } [1.55]	12.38 12.50	$3t_2$
C	13.35 13.44 } [1.25]	13.08 [1.15]	12.71	e
D	(15.05) 15.13 15.25 (15.31) } [1.0]	14.7 14.8 14.9 } [1.0]	14.0 [1.0]	$2t_2$
E	17.98 [0.13]	18.0 [0.08]	17.0 [0.07]	$2a_1$

The remaining, partly resolved fine structure (of bands A″ and B″) in the low ionization energy region of the CBr_4 spectrum is almost certainly due to vibronic interactions (see, for example, Sturge 1967) in the molecular ion. The U′ quartet states are in principle susceptible to vibronic perturbations associated with either the e vibrational mode (the ν_2 species) of tetrahedral AB_4, or with either of the t_2 normal modes (the ν_3 and ν_4 species). Such effects can lift the degeneracy of a U′ state, leaving two Kramers doublets. The multiplet terms, E′ and E″, having a simple Kramers degeneracy (see, for example, Griffith 1961), are not affected by vibronic perturbations in this way.

Both types of fine structure observed in the CBr_4 p.e. spectrum provide support for the assignment ventured in table 1, where the first p.e. band system (A) is associated with the t_1 ionizations, and the second band system (B) with the $3t_2$ ionizations. In the first place, the larger multiplet splitting (*ca.* 0.540 eV) for p.e. band B as compared with that of band A (*ca.* 0.315 eV) is intelligible only on this assignment. As explained in appendix (B), the effective spin-orbit coupling constant, ζ_1, for the molecular t_1 shell is of the order $\zeta_1 = \frac{1}{2}\zeta_p$, where ζ_p is the spin-orbit coupling constant for the halogen p orbitals. The corresponding approximation for ζ_2, the effective spin-orbit coupling constant for a t_2 shell, is more complicated (see equation (B 6)), but it is a straightforward matter to show that, for essentially halogen p t_2 m.o., ζ_2 has a maximum value of order ζ_p. Now the first-order multiplet splitting of a $^2T_1$ term is $\frac{3}{2}\zeta_1$, and $\zeta_{4p} = 0.305$ eV for a free bromine atom (see table B 1). The separation of the states $E'(^2T_1)$ and $U'(^2T_1)$ should therefore be of the order of 0.23 eV, while the separation of $E''(^2T_2)$ and $U'(^2T_2)$ can in principle be twice as large, i.e. some 0.46 eV. These estimates, crude though they are, lead us to prefer the assignment of table 1. In particular it is difficult to reconcile the 0.54 eV splitting of p.e. band B with a $^2T_1(t_1^5)$ ion term.†

Also consistent with our assignment of the first two p.e. band systems (A and B) of CBr_4 is the greater splitting (*ca.* 0.18 eV) associated with the secondary fine structure of the second band system, B, as compared with that of the first band system, A (*ca.* 0.09 eV). If, as outlined above, this fine structure arises from vibronic effects, then the $U'(^2T_1)$ state, with a hole in the non-bonding t_1 m.o., should be rather less susceptible to such perturbations than the $U'(^2T_2)$ state.

Having assigned the essential features of some representative p.e. spectra, we now consider our results for the group IV B tetrahalides in a more general way. It will be seen that our conclusions regarding the origin of the different p.e. bands are consistent with the observed trends in this series of spectra.

Comparison of the halides of a given IV B *element*

The ionization energy data for the carbon tetrahalides (table 1) is represented graphically in figure 6. In the particular case of CBr_4 we plot the averages (weighted according to total spin-orbit degeneracy) of the multiplet components of band systems A and B. As can be seen in this figure, the corresponding i.p. for the carbon tetrahalides fall with increasing atomic number of halogen: this effect is also evident in the i.p. data of tables 2 and 3, where the IV B chlorides and bromides, respectively, are compared. In the CX_4 p.e. spectra, the differences between corresponding i.p. for the fluoride and the chloride are much larger than between the chloride and the bromide. These observations support the assignment of p.e. bands A, B and C to ionizations of m.o. of predominantly halogen p character (in fact p_π). Further supporting evidence is provided by the plot in figure 6 of I_p^{av}, the space and spin-randomized i.p. for neutral halogen atoms (Moore 1949, 1952, 1958; Basch, Viste & Gray 1965), which closely parallels each of the plots for p.e. bands A, B and C, and by a closely linear plot of these band positions against Mulliken electronegativity of halogen. The atomic i.p. in figure 6 are only slightly greater than the peak positions of p.e. band C.

We have already discussed the relatively complex relationship between the p.e. spectra of CCl_4 and CBr_4. Spin-orbit interactions are also manifest in the $SiBr_4$ and $GeBr_4$ photoelectron spectra (table 3 and figures 3*a*, *b*), where multiplet splitting of the $^2T_1$ ion term is clearly

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† This point was made by R. N. Dixon at the meeting.

discernible in the first band system. No multiplet structure is observed in the corresponding tetrachlorides (figures 2*a*, *b*). In the case of $GeBr_4$, the higher energy E′ component of $^2T_1$ is very close to the lower energy U′ component of $^2T_2$. The multiplet splitting of the $^2T_2$ ion term must itself be inferred. In $SiBr_4$ and $GeBr_4$ the E″ component of $^2T_2$ has apparently merged completely with the envelope of the ^2E photoelectron band (C). The relative intensities (table 3) of the high energy bands are consistent with this interpretation. As in the case of CBr_4, spin-orbit splitting of the $^2T_2$ term of ABr_4^+ is therefore significantly greater than in the $^2T_1$ ion term. In $SnBr_4$ both doublet states, E′($^2T_1$) and E″($^2T_2$), correspond closely in energy with the quartets, U′($^2T_2$) and U′(^2E), respectively. The form of table 3 is based on these various inferences.

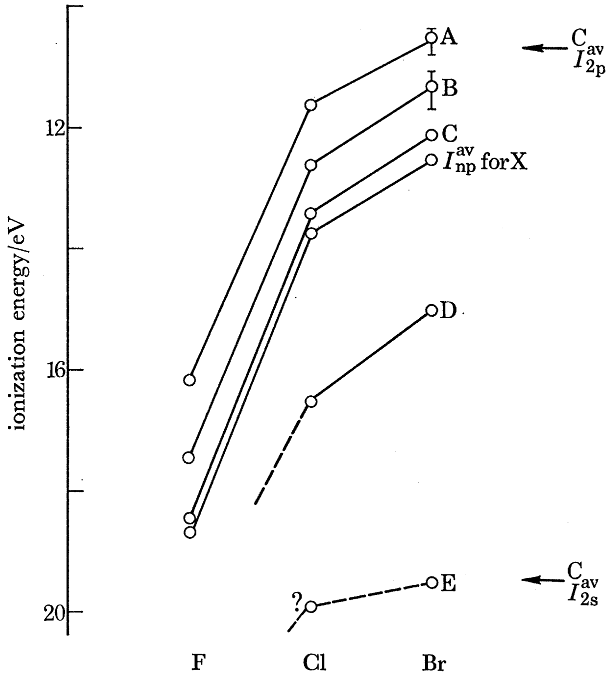

FIGURE 6. A comparison of ionization energy data for the carbon tetrahalides.

TABLE 3. PHOTOIONIZATION DATA FOR THE GROUP IV B TETRABROMIDES

p.e. band	$SiBr_4$		$GeBr_4$		$SnBr_4$		assignment	
A″	(10.8) 10.9	[1.1]	(10.75) 10.85	[1.1]	11.0	[2.3]	t_1	U′
A′	11.17	[0.5]	11.11	[2.0]	11.25		t_1	E′
B″	11.52 (11.63)	[1.0]	11.23				$3t_2$	U′
B′+C	12.05 (12.14) (12.33)	[1.7]	11.89	[2.0]	11.75	[1.7]	$3t_2$ e	E″ U′
D	13.92 (14.06) 14.19 (14.23)	[1.0]	13.63 13.70 (13.9) (14.0)	[1.0]	13.2	[1.0]	$2t_2$	U′+E″
E	17.31	[0.11]	17.6		16.7		$2a_1$	E′
F	*ca.* 20	[0.4]	?		18.2–19.7† ?		$1t_2$	?

† Weak, diffuse band.

Trends in the p.e. spectra down group IVB

In both tetrahalide series, ACl_4 and ABr_4, the p.e. spectra show for the most part a decrease in ionization energy with atomic number of the group IVB atom, A. However, a number of irregularities are apparent (figures 7, 8).

The high-energy p.e. bands A, B and C, are the least sensitive to variation of central atom A, which was to be expected if they indeed concern ionizations from m.o. of predominantly halogen character. Moreover, their ionization energies are of a very similar order to the averaged ionization energies, I_p^{av}, for the neutral halogen atoms (figures 7, 8). The following

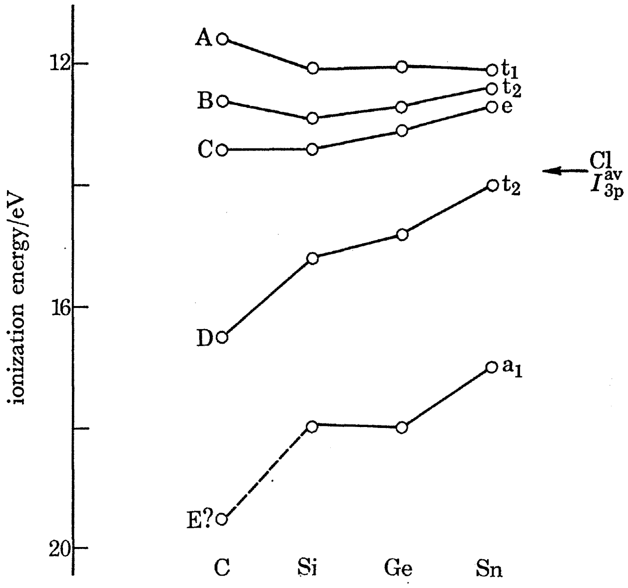

FIGURE 7. A comparison of ionization energy data for the group IVB tetrachlorides.

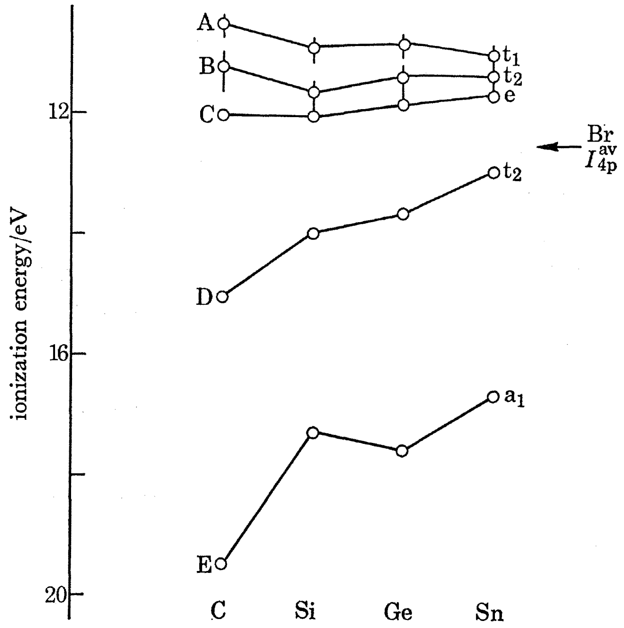

FIGURE 8. A comparison of ionization energy data for the group IVB tetrabromides.

observations regarding these bands seem particularly significant: (*a*) the three bands group more closely together with increasing atomic number of the group IV B atom; (*b*) p.e. band C shifts to higher energy, while band A shifts to lower energy: the behaviour of band B is intermediate.

The first effect may be ascribed simply to diminishing interactions between the halogen atoms as the size of the central atom increases. The p_B^π symmetry orbitals then become less differentiated in energy, i.e. less bonding or anti-bonding. (Similar effects are manifest in the photoelectron spectra of the group IV B tetramethyls which we have recently studied.) At the same time, we see in the tetrachloride series (figures 1*b*, 2*a–c*) a sharpening of the vibrational envelopes of the high energy p.e. bands.

The second observation lends support to this notion: as the interactions between the halogen atoms decrease, the $e(p_B^\pi)$ non-bonding symmetry orbital should become less stabilized, and the $t_1(p_B^\pi)$ non-bonding combination less destabilized. These effects are described in more detail in appendix (A1). The rather irregular variation of the energies of p.e. bands A and C reflects for the most part the non-uniform trend in the size of atom A, and therefore in the halogen–halogen overlap integrals.

The variation in energy of band B is more complex, but this is not surprising since the $t_2(p_B^\pi)$ symmetry orbital interacts with the central atom valence a.o. p_A, and also with the $t_2(p_B^\sigma)$ combination. If the $3t_2$ level in figure 5 related to a non-bonding halogen p_π combination then it would probably lie below the e non-bonding level: and mixing of $t_2(p_B^\pi)$ and $t_2(p_B^\sigma)$ should depress the $3t_2$ level still further. Thus the observed separation of p.e. bands C and B should provide a measure of the interaction between $t_2(p_B^\pi)$ and central atom p_A. It can be seen in figures 7 and 8 that the C–B band separation is largest for the carbon tetrahalides and diminishes overall down group IV B. Also the separation of these two bands decreases with increasing atomic number of halogen. These observations correlate only partly with the known trends in the IV B element–halogen bond energies (see, for example, Cotton & Wilkinson 1966), the atomization energies of the carbon tetrahalides, CX_4, being in fact less than those of the silicon analogues, SiX_4. It may be that the carbon-halogen bonds are particularly weakened as a result of interactions between the halogen atoms.

The low energy p.e. bands, D and E, are much more sensitive to the nature of the central atom A than are the high energy bands discussed above. The irregular form of the plots for these bands (figures 7 and 8) is in fact rather similar to that of the averaged ionization energy plots for the s and p valence shells of the neutral atoms A (figure 9). This supports our contention that band D corresponds to ionizations from $2t_2$ molecular orbitals of predominantly central atom p character. Similarly, it seems likely that the $2a_1$ m.o., which we associate with band E, has appreciable central atom s character.

It should be noted that band D in the p.e. spectra of $SnCl_4$ and $SnBr_4$ displays no well-resolved fine structure despite the large spin-orbit coupling constant for the tin atomic 5p shell (see table B1). Presumably ionization from the strongly bonding $2t_2$ orbital (figure 5) excites sufficient vibration in the molecular ion to obscure the expected U′–E″ multiplet splitting.

The tetrabromides $SiBr_4$, $GeBr_4$ and $SnBr_4$ show further, diffuse structure (F) in the low energy region of their photoelectron spectra. This probably arises from ionization of the $1t_2$ m.o. (figure 5), composed mainly of bromine 4s orbitals.

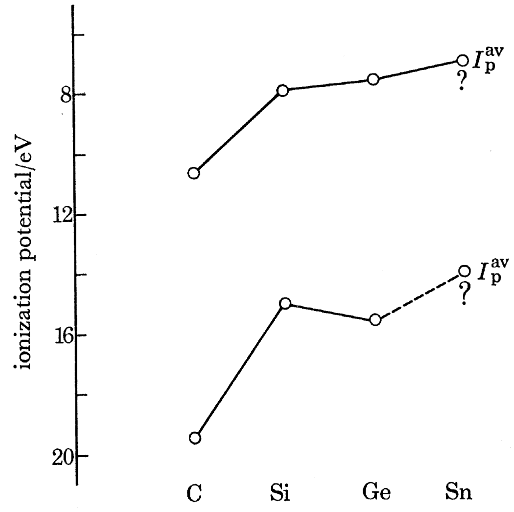

FIGURE 9. The trends in free atom 'average of configuration' ionization energies for the group IVB elements.

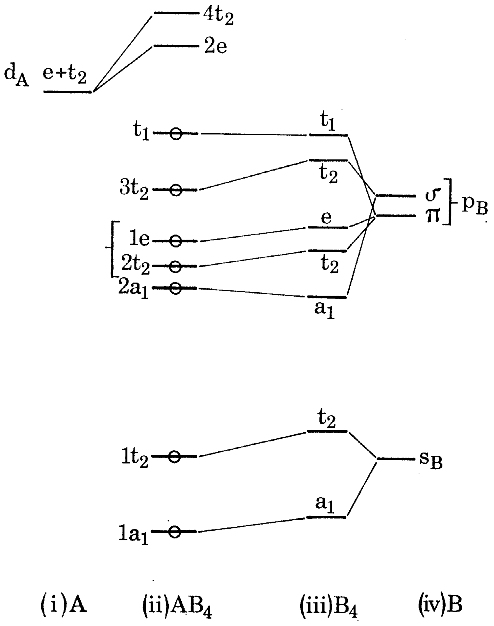

FIGURE 10. Qualitative molecular orbital energy level diagram for the group IVA tetrahalides, AB_4: (i) metal d valence a.o., (ii) molecular orbitals of AB_4, (iii) symmetry orbitals of B_4, (iv) halogen valence a.o.

(b) *The titanium tetrahalides*

The valence electronic structures of the group IVA tetrahalides, while necessarily of the general type (1), are rather different in detail from those of the group IVB tetrahalides. A chemical choice of basis a.o. should include nd orbitals (transforming as $e+t_2$) as the leading valence a.o. of the metal, rather than (n+1) s and (n+1) p, which are normally regarded as of secondary importance. Moreover, the usual expectation is that the Fock integrals for the metal d a.o. (d_A) are more positive than the Fock integrals for the halogen valence a.o., p_B. The l.c.a.o.-m.o. structure of a group IVA AB_4 molecule is therefore of the form given in figure 10, which contrasts sharply with figure 5 for the corresponding IVB species. In particular, the m.o. of majority halogen p character (p^{π}_{B} and p^{σ}_{B}) are now all occupied while those of mainly central atom character are empty. The details of figure 10 are consistent with the p.e. spectra of $TiCl_4$ and $TiBr_4$, and are supported by approximate molecular orbital calculations (see appendix (A 2)).

The photoelectron spectra of $TiCl_4$ and $TiBr_4$ (figure 4) are somewhat more complex, in the high energy region, than those of the group IV B tetrahalides. A distinctive feature of each of these spectra is a weak, but relatively sharp p.e. band (N) at the low energy side of the first group of p.e. bands. The low intensity of this band suggests assignment to ionization from the $2a_1$ m.o., and orbital composed mainly of halogen p_{σ}. One would also expect to encounter in the low energy region ionizations from four other levels, namely $1e$, t_1, $2t_2$ and $3t_2$. However, only three additional bands are in fact observed in the $TiCl_4$ p.e. spectrum. We assume accordingly that the least symmetrical band, M, corresponds to two distinct ionization processes.

TABLE 4. PHOTOIONIZATION DATA FOR TITANIUM TETRACHLORIDE AND TITANIUM TETRABROMIDE

p.e. band	$TiCl_4$	$TiBr_4$	assignment
K	11.7 (11.8) } [1.0]	10.56 [0.65] K″ 10.80 [0.35] K′	t_1 {U′ E′
L	12.66 [0.9]	11.7 (11.8) † 12.0 [2.25]	$3t_2$
M	13.3† [1.1]	(12.25) 12.4	$1e$, $2t_2$
N	13.88 [0.15]	13.08 [0.1]	$2a_1$
O	16.4–19.4‡	18.9–19.7‡	$1t_2$, $1a_1$?

† Relatively broad p.e. band(s) ‡ Weak, diffuse band(s).

Now the first ionizations (band K) almost certainly concern the t_1 electrons, since the t_1 symmetry orbital is non-bonding and markedly destabilized by halogen–halogen interactions (see appendix (A 2)). Our tentative interpretation of the $TiCl_4$ p.e. spectrum is then that advanced in table 4. This assignment is consistent with the one-electron energy level scheme that may be inferred from electronic spectra. For example, Bird & Day (1968), who have analyzed the charge-transfer spectra of various tetrahalide complexes, MX_4^{2-} and MX_4^{-}, where M belongs to the first transition series, conclude that the highest occupied m.o. have the relative energies $t_1 > 3t_2 > 1e$, with a total energy spread of about 2 eV. Molecular orbital calculations by Fenske & Radtke (1968) also yield the latter sequence of levels.

The $TiBr_4$ p.e. spectrum is not sufficiently resolved for a full interpretation to be possible. Its increased complexity is presumably due in large part to the effects of spin-orbit coupling. However, the general correspondence with the p.e. spectrum of $TiCl_4$ is fairly clear (table 4). As observed in the p.e. spectra of the group IV B tetrahalides, the bromide i.p. are uniformly somewhat lower than those of the chloride.

The diffuse structure in the 11.5 to 12.5 eV region of the $TiBr_4$ spectrum (L, M) probably relates to five distinct multiplet terms of the molecular ion—namely, the U′ and E″ multiplet components of each of the two $^2T_2$ states and also the $U'(^2E)$ multiplet term. The relative band areas in table 4 are compatible with this assumption. The multiplet separation of 0.24 eV observed in the first band system (K″ and K′) is of the order expected for a $^2T_1$ term (multiplet splitting $\sim\frac{3}{4}\zeta_{4p}$, see appendix (B)). This lends support to the assignments in table 4.

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The p.e. spectra of $TiCl_4$ and $TiBr_4$ also exhibit weak and extremely diffuse structure in the low energy region (0). This is presumably due to ionization of the $1t_2$, and perhaps also the $1a_1$ levels shown in figure 10.

APPENDIX A. THEORETICAL BASIS OF THE AB_4 M.O. DIAGRAMS

(a) *Effect of halogen–halogen interactions on the energies of the halogen symmetry orbitals*

Consider the symmetry-adapted linear combinations of the valence a.o. of the halogen tetrahedron, B_4. The symmetry orbital constructed from the a.o. species k (s, p_σ or p_π), and transforming as the *m*th component of the irreducible representation Γ_g of the point group T_d, may be written

$$|k_{gm}\rangle = (1+\chi_{gk})^{-\frac{1}{2}} \sum_{k_B} u_{gm,\,k_B} |k_{B'}\rangle, \tag{A1}$$

where

$$\chi_{gk} = \sum_{k_B \neq k_{B'}} \sum u_{gm,\,k_B} u_{gm,\,k_{B'}} \langle k_B | k_{B'} \rangle, \tag{A2}$$

and

$$\sum_{k_B} u^2_{gm,\,k_B} = 1 \tag{A3}$$

$(1+\chi_{gk})^{-\frac{1}{2}}$ is a normalizing factor which corrects for the overlap of orbitals on different halogen atoms, B and B′. The required symmetry orbitals for tetrahedral AB_4 have been tabulated by Ballhausen & Gray (1964), so it is expedient to use the same coordinate systems as these authors. The important overlap functions, χ_{gk}, are presented in table A1.

TABLE A1. THE OVERLAP TERMS χ_{gk} (OF EQUATION (A2)) REQUIRED FOR THE NORMALIZATION OF THE SYMMETRY ORBITALS $|k_g\rangle$ ARISING FROM THE ORBITALS OF ATOM B IN TETRAHEDRAL MOLECULE AB_4

$\lvert k_g\rangle$	χ_{gk}
σ_{a_1}	$2S_\sigma + S_\pi$
σ_{t_2}	$-\frac{1}{3}(2S_\sigma + S_\pi)$
π_e	$\frac{1}{2}(S_\sigma - S_\pi)$
π_{t_1}	$-\frac{1}{2}(S_\sigma + 3S_\pi)$
π_{t_2}	$\frac{1}{6}(S_\sigma + 11S_\pi)$
s_{a_1}	$3S_s$
s_{t_2}	$-S_s$

S_σ and S_π are the optimally directed overlap integrals, $\langle \sigma_B | \sigma_{B'} \rangle$ and $\langle \pi_B | \pi_{B'} \rangle$, respectively. S_s is the overlap integral, $\langle s_B | s_{B'} \rangle$.

The relative one-electron energies (Fock integrals, $F_{k_g k_g}$) for the B_4 symmetry orbitals may be estimated by the following simple model. Let the diagonal Fock matrix elements for the halogen a.o. be written

$$F_{k_B k_B} = \alpha_k \tag{A4}$$

and the off-diagonal elements approximated as

$$F_{k_B l_B} = \langle k_B | l_{B'} \rangle \, \eta_{kl} \tag{A5}$$

where the α_k and η_{kl} are parameters. (One-centre off-diagonal integrals, $F_{k_B l_B}$, are neglected.) The diagonal matrix element for the symmetry orbital $|k_g\rangle$ is then just

$$F_{k_g k_g} = (1+\chi_{gk})^{-1} \, (\alpha_k + \chi_{gk} \eta_{kk}). \tag{A6}$$

If $\alpha_k > \eta_{kk}$, it follows from table A1 that the relative energies of the symmetry orbitals are

$$\left.\begin{aligned} s,\ p_\sigma:&\quad t_2 > a_1, \\ p_\pi:&\quad t_1 > e \geqslant t_2. \end{aligned}\right\} \tag{A7}$$

Note that the differentiation of symmetry orbitals constructed form a given a.o. species follows an approximate baricentre rule. The relative energies of the e (p_π) and t_2 (p_π) combinations depend strictly on the relative magnitudes of the primitive overlap integrals, S_σ and S_π (see table A1), but should normally be $e > t_2$. The relations (A7) can be established in other ways, for example by topological arguments (Schmidtke 1968).

Empirical values of the parameters, α_π and $\eta_{\pi\pi}$, may be obtained by applying equation (A6), in conjunction with Koopmans's approximation, to the ionization energies of the non-bonding halogen p_π electrons (e and t_1). The results of such an analysis for the group IVB tetrahalides are given in table A2. The required overlap integrals, S_σ and S_π, were calculated using the neutral halogen atom analytical s.c.f. functions of Watson & Freeman (1961*a*, *b*), and interatomic distances from Sutton (1958). We note in table A2 that $\alpha_\pi > \eta_{\pi\pi}$, as assumed in the relations (A7). The diagonal element α_π (the *in situ* p_π orbital electronegativity) becomes slightly less negative on descending group IVB, in accordance with the increasing ionic character of the AB_4 species. On the other hand, the parameter $\eta_{\pi\pi}$ becomes more negative, so that the factor $K = \eta_{\pi\pi}/\alpha_\pi$ (cf. Wolfsberg & Helmholz 1952) increases from CX_4 to SnX_4. The silicon tetrahalide parameters are mildly anomalous, and this may be due to a contribution to the bonding from silicon 3d orbitals, one effect of which should be a stabilization of the e molecular orbital. Some support for this conjecture is provided by an analysis of the $TiCl_4$ p.e. data, which yields a particularly large negative value for $\eta_{\pi\pi}$ ($\alpha_\pi = -12.9$ eV, $\eta_{\pi\pi} = -32.2$ eV). In $TiCl_4$ one expects a strong interaction between $e(p_\pi)$ and the titanium $3d_{z^2}$, $3d_{x^2-y^2}$ orbitals.

TABLE A2. SEMI-EMPIRICAL ANALYSIS OF THE LOW ENERGY I.P.† OF THE GROUP IVB TETRAHALIDES

	^2E (obs.)	$^2T_1$ (obs.)	α_π	$\eta_{\pi\pi}$	$^2T_2$ (obs.)	$^2T_2$ (calc.)
CCl_4	13.40	11.60	−13.0	−22.7	12.40	13.8
$SiCl_4$	13.40	12.03	−13.1	−25.85	12.85	13.7
$GeCl_4$	13.08	12.12	−12.8	−22.95	12.60	13.3
$SnCl_4$	12.71	12.10	−12.5	−23.2	12.4	13.1
CBr_4	12.06	10.55	−11.65	−19.1	11.32	12.3
$SiBr_4$	12.1	10.9	−11.75	−21.3	11.7	12.2
$GeBr_4$‡	11.9	10.9	−11.6	−19.9	11.45	11.9
$SnBr_4$	11.75	11.1	−11.5	−20.8	11.45	11.8

† The tetrabromide data relate to the average i.p. for the multiplet bands (weighted according to total spin-orbital degeneracy).

‡ Overlap integrals obtained by interpolation.

We have in turn used the empirical α_π and $\eta_{\pi\pi}$ for the IVB tetrahalides to calculate the ionization energies of the highest occupied t_2 m.o., assuming this to be a pure halogen p_π combination. As shown in table A2, these estimates of the energy of the $^2T_2$ ion term are consistently high, presumably because the $t_2(p_\pi)$ symmetry orbital interacts considerably with the p valence a.o. of the central group IVB atom. This militates against the indiscriminate application of such a model to the photoelectron spectra of a number of compounds we have studied, in particular $C_{2v}AB_2(CH_2X_2)$ and $C_{3v}AB_3(CHX_3, PX_3)$ species, where (for a conventional choice of basis a.o.) there is only one non-bonding halogen p_π combination (namely a_2). However, the model is viable for species such as O_hAB_6 (e.g. SX_6) or $D_{3h}AB_3$ and AB_5 (e.g. BX_3, PX_5).

Derived energy parameters of the type α_k and η_{kl} might find useful application in semi-empirical molecular orbital calculations of large molecules, or to more specialized problems such as the m.o. analysis of the charge-transfer spectra of simple transition metal complexes (see, for example, Bird & Day 1968; Fenske & Radtke 1968). The transference of such parameters may also frequently permit the prediction of the high energy structure in the p.e. spectra of other molecules, or at least substantially aid assignment. For example, let us calculate the low energy i.p. of $TiCl_4$, using for both σ and π chlorine p orbitals the average values, $\alpha = -12.85$ eV and $\eta = -23.6$ eV, obtained from the analysis of the group IVB tetrachloride p.e. data (table A 2). According to equation (A 6) the diagonal Fock integrals for the chlorine symmetry orbitals are

π_{t_1}	σ_{t_2}	π_e	π_{t_2}	σ_{a_1}	
-12.3	-12.9	-13.1	-13.2	-14.1	(eV)

These figures compare quite well with the ionization energy data for $TiCl_4$ (table 4), and strengthen the case for our preferred assignment.

(*b*) *Molecular orbital calculations on* CBr_4 *and* $TiCl_4$†

We have undertaken a number of simple, model molecular orbital calculations on the species CBr_4 and $TiCl_4$ in order to elucidate the essential features of their orbital structures and assist assignment of the photoelectron spectra. These calculations are of the self-consistent extended Hückel type, having some affinity with the method of Fenske, Caulton, Radtke & Sweeney (1966) and Fenske & Radtke (1968). Off-diagonal Fock matrix elements were estimated using the formalism of Basch & Gray (1967). Neutral penetration integrals were treated semi-empirically by the introduction of scale factors for the usual penetration terms. We also explicitly include self-repulsion effects in the atomic valence states (see, for example, Orchard 1969).

The CBr_4 calculations were simplified so that attention is focused on the highest occupied m.o., i.e. those mainly localized on the bromine atoms. Thus we use the elaborate bromine 4s and 4p wavefunctions of Watson & Freeman (1961 *a*), but a simple Slater a.o. (Coulson 1961) for the carbon 2s and 2p orbitals. The required one-centre integrals for carbon were estimated by an analysis of the atomic i.p. data (Moore 1949): the corresponding bromine integrals were however obtained by *ab initio* methods. For all reasonable values of the adjustable parameters scaling the penetration integrals, we obtain m.o. energy levels essentially of the form depicted in figure 5. The interaction between the halogen atoms is, as suggested in the previous section, an important aspect of the problem. The structure of the calculations was such that we have less confidence in the details of the lower part of figure 5 than we have in the upper region. There is strong interaction both between $2p_C$ and $t_2(s_{Br})$ and also between $2s_C$ and $a_1(s_{Br})$. The order $2a_1 > 1t_2$ is probably correct, but the $2a_1$ orbital may possibly be of majority carbon 2s character.

The basis set for the $TiCl_4$ calculations incorporates only 3d a.o. from the metal. However, s.c.f. wavefunctions are employed for both chlorine 3p and 3s orbitals (Watson & Freeman 1961 *b*) and for titanium 3d orbitals (Watson 1959): and all but the penetration terms were evaluated *ab initio*. The results for $TiCl_4$ lead to the m.o. scheme of figure 10. We find that the interaction of $t_2(p^{\pi}_{Cl})$ with $t_2(p^{\sigma}_{Cl})$ and $t_2(d_{Ti})$ is very similar to the interaction between $e(p^{\pi}_{Cl})$ and $e(d_{Ti})$, so that the $2t_2$ and 1e m.o. have closely comparable energies. It should also be mentioned that the $2a_1$ level does not appear below $2t_2$ and 1e in energy if neutral penetration effects are ignored (cf. Fenske & Radtke 1968): but the $2a_1$ level is stabilized quite markedly

† These and related results will be described in detail elsewhere.

when these terms are included. A similar picture emerges from some preliminary calculations on $TiBr_4$.

Certain other details in figures 5 and 10 require explanation. As might be expected, the self-consistent distribution of electron density is such that the halogen p_σ occupancy is less than that of the p_π a.o., and very substantially so in the case of CBr_4. Self-repulsion effects in the halogen valence state thus lead to Fock integrals of relative magnitude $F_{\sigma_B\sigma_B} > F_{\pi_B\pi_B}$. Penetration effects differentiate $F_{\sigma_B\sigma_B}$ and $F_{\pi_B\pi_B}$ in the opposite sense, but in the case of CBr_4 to a considerably lesser degree. In $TiCl_4$ (and in $TiBr_4$) the p_B^σ and p_B^π occupancies are less different so that their Fock integrals are of more similar magnitude.

In each series of calculations it is the halogen $t_2(p_B^\sigma)$ symmetry orbital that interacts most strongly with the central atom valence a.o. (p_A or t_2d_A). The mixing of the $t_2(p_B^\pi)$ combination with central atom orbitals is often less pronounced than the mixing of the halogen valence a.o. themselves. Thus, in the CBr_4 calculations, the $3t_2$ level always falls below the t_1 (non-bonding) level.

APPENDIX B. SPIN-ORBIT INTERACTIONS IN THE TETRAHEDRAL MOLECULAR IONS, AB_4^+

The essential effect of spin-orbit coupling on Russell–Saunders terms, ${}^{2S+1}\Gamma_i$, may be deduced from their transformation properties in the spinor (double) group (see, for example, Griffith 1961). The doublet terms of a tetrahedral molecule span the irreducible representations Γ_j^* of the spinor group T_d^* in the following way:

T_d:	${}^2\Gamma_i$	${}^2A_1$	${}^2A_2$	${}^2E$	${}^2T_1$	${}^2T_2$
T_d^*:	Γ_j^*	E'	E''	U'	$U'+E'$	$U'+E''$

The ${}^2T$ states of the molecular ions, CCl_4^+ etc., are therefore split by spin-orbit interactions into doublet (E' or E'') and quartet (U') multiplet states. Spin-orbit coupling does not however split the ${}^2E$ or ${}^2A$ terms.

The terms of particular interest to us are ${}^2T_1(t_1^5)$, ${}^2T_2(t_2^5)$ and ${}^2E(e^3)$. Let the normalized l.c.a.o. form of the relevant molecular orbitals be

$$|t_2^m\rangle = c_{t_2p}|p_A^m\rangle + c_{t_2d}|d_A^m\rangle + c_{t_2s}|s_{t_2}^m\rangle + c_{t_2\pi}|\pi_{t_2}^m\rangle + c_{t_2\sigma}|\sigma_{t_2}^m\rangle, \tag{B 1}$$

$$|t_1^m\rangle = |\pi_{t_1}^m\rangle, \tag{B 2}$$

$$|e^m\rangle = c_{ed}|d_A^m\rangle + c_{e\pi}|\pi_e^m\rangle, \tag{B 3}$$

where m distinguishes the components of the degenerate irreducible representations. We use the symmetry-adapted linear combinations of the s_B and p_B orbitals listed by Ballhausen & Gray (1964).

To calculate spin-orbit interaction energies we employ the phenomenological hamiltonian, $\mathscr{H}_{s.o.} = \sum_n \hat{h}_{s.o.}(n)$, where n indexes the electrons. Following Misetich & Buch (1964), the one-electron operator, $\hat{h}_{s.o.}$ is assumed to be

$$\hat{h}_{s.o.} = (\sum_N \zeta(r_N)\,\hat{l}_N)\,.\,\hat{s}, \tag{B 4}$$

where $\hat{l}_N$ is the orbital angular momentum operator centred at nucleus N. This expression for $\hat{h}_{s.o.}$ is based on the assumption that the main contribution to spin-orbit coupling energies comes from regions close to the nuclei (since $\zeta(r)$ varies as r^{-3}), and that near any nucleus the electric field is approximately spherical.

It is expedient to make use of the 'hole formalism' (Griffith 1961). Applying the hamiltonian $\hbar_{\mathrm{s.o.}}$ to hole-states of orbital form (B 1) to (B 2), one finally obtains the following diagonal matrix elements of spin-orbit coupling for the many-electron states:

$$\left.\begin{aligned}\langle {}^2\mathrm{T}_2,\ \mathrm{U}'|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{T}_2,\ \mathrm{U}'\rangle &= -\tfrac{1}{2}\zeta_2,\\ \langle {}^2\mathrm{T}_1,\ \mathrm{U}'|\mathscr{H}_{\mathrm{s.o}}|{}^2\mathrm{T}_1,\ \mathrm{U}'\rangle &= -\tfrac{1}{2}\zeta_1,\\ \langle {}^2\mathrm{E},\ \mathrm{U}'|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{E},\ \mathrm{U}'\rangle &= 0,\\ \langle {}^2\mathrm{T}_2,\ \mathrm{E}''|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{T}_2,\ \mathrm{E}''\rangle &= +\zeta_2,\\ \langle {}^2\mathrm{T}_1,\ \mathrm{E}'|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{T}_1,\ \mathrm{E}'\rangle &= +\zeta_1.\end{aligned}\right\} \tag{B 5}$$

The effective spin-orbit coupling constants, ζ_2 and ζ_1, are given by

$$\zeta_2 = c^2_{\mathrm{t_2p}}\,\zeta^{\mathrm{A}}_{\mathrm{p}} - c^2_{\mathrm{t_2d}}\,\zeta^{\mathrm{A}}_{\mathrm{d}} + \tfrac{1}{2}c'_{\mathrm{t_2}\pi}(c'_{\mathrm{t_2}\pi} - 2\sqrt{2}c'_{\mathrm{t_2}\sigma})\ \zeta^{\mathrm{B}}_{\mathrm{p}}, \tag{B 6}$$

$$\zeta_1 = \tfrac{1}{2}(1+\chi_{\mathrm{t_1}\pi})^{-1}\ \zeta^{\mathrm{B}}_{\mathrm{p}}, \tag{B 7}$$

where $c'_{\mathrm{t_2k}} = (1+\chi_{\mathrm{t_2k}})^{-\frac{1}{2}}\,c_{\mathrm{t_2k}}$(cf. Bird & Day 1968), and where $\zeta^{\mathrm{A}}_{\mathrm{p}}$, $\zeta^{\mathrm{A}}_{\mathrm{d}}$ and $\zeta^{\mathrm{B}}_{\mathrm{p}}$ are the spin-orbit coupling constants for the valence orbitals of atoms A and B. In deriving equations (B 6) and (B 7) we neglect cross-integrals of the type $\langle k_{\mathrm{N}}|\zeta(r_{\mathrm{N}})|l_{\mathrm{N'}}\rangle\ \langle k_{\mathrm{N}}|\zeta(r_{\mathrm{N'}})|k_{\mathrm{N}}\rangle$, etc., because of the r^{-3} dependence of $\zeta(r)$. Recent *ab initio* studies of molecular spin-orbit interactions (Walker 1969; Walker & Richards 1969) provide support for this procedure.

The U′ components of ${}^2\mathrm{T}_2$ and ${}^2\mathrm{T}_1$, and ${}^2\mathrm{E}$ itself, mix together under the spin-orbit coupling. The off-diagonal matrix elements are

$$\left.\begin{aligned}\langle {}^2\mathrm{T}_2,\ \mathrm{U}'|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{T}_1,\ \mathrm{U}'\rangle &= \tfrac{1}{4}\,(c'_{\mathrm{t_2}\pi}+\sqrt{2}c'_{\mathrm{t_2}\sigma})\ \zeta^{\mathrm{B}}_{\mathrm{p}},\\ \langle {}^2\mathrm{E},\ \mathrm{U}'|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{T}_1,\ \mathrm{U}'\rangle &= -1/(2\sqrt{2})\,c'_{\mathrm{e}\pi}\,\zeta^{\mathrm{B}}_{\mathrm{p}},\\ \langle {}^2\mathrm{T}_2,\ \mathrm{U}'|\mathscr{H}_{\mathrm{s.o.}}|{}^2\mathrm{E},\ \mathrm{U}'\rangle &= -(\sqrt{3}/\sqrt{2})\,c_{\mathrm{t_2d}}\,c_{\mathrm{ed}}\,\zeta^{\mathrm{A}}_{\mathrm{d}} - (1/2\sqrt{2})\,c'_{\mathrm{e}\pi}(c'_{\mathrm{t_2}\pi}+\sqrt{2}c'_{\mathrm{t_2}\sigma})\ \zeta^{\mathrm{B}}_{\mathrm{p}}.\end{aligned}\right\} \tag{B 8}$$

We can now calculate the ${}^2\mathrm{T}_1(\mathrm{E}'\text{–}\mathrm{U}')$ multiplet separation for each of the group IV tetrabromides. To first order, this is just $\tfrac{3}{2}\zeta_1$. Using the spin-orbit coupling constant for a free bromine atom, $\zeta_{4\mathrm{p}} = 0.305$ eV (see table B 1), and neutral atom s.c.f. 4p wavefunctions for the overlap terms, $\chi_{\mathrm{t_1}\pi}$ (table A 1), we obtain the multiplet splittings given in table B 2. The agreement with the observed separations of the ${}^2\mathrm{T}_1(\mathrm{E}')$ and ${}^2\mathrm{T}_1(\mathrm{U}')$ p.e. bands is reasonably satisfactory given the theoretical approximations and some uncertainty in the experimental data. That the calculated splittings are somewhat low may be due in part to the interaction of ${}^2\mathrm{T}_1(\mathrm{U}')$ with the ${}^2\mathrm{T}_2(\mathrm{U}')$ and ${}^2\mathrm{E}(\mathrm{U}')$ excited states of the ions. Also, the use of Br^- 4p wavefunctions would improve the agreement with experiment.

The calculation of the ${}^2\mathrm{T}_2$ multiplet splittings is more difficult, owing to the relative complexity of equation (B 6). However, the terms in $\zeta^{\mathrm{A}}_{\mathrm{d}}$ should not be significant for the IV B tetrahalides, and the data of table B 1 indicates that, for the lighter IV B elements, the terms in $\zeta^{\mathrm{A}}_{\mathrm{p}}$ may also be safely ignored. Equation (B 6) then reduces to

$$\zeta'_2 = \tfrac{1}{2}c'_{\mathrm{t_2}\pi}(c'_{\mathrm{t_2}\pi} - 2\sqrt{2}\ c'_{\mathrm{t_2}\sigma})\ \zeta^{\mathrm{B}}_{\mathrm{p}} \tag{B 9}$$

(the expression appropriate to a purely halogen p $\mathrm{t_2}$m.o.). The magnitude of ζ'_2 depends on the precise extent of the mixing of the $\mathrm{t_2}(\mathrm{p}^{\sigma}_{\mathrm{B}})$ and $\mathrm{t_2}(\mathrm{p}^{\pi}_{\mathrm{B}})$ symmetry orbitals. If one neglects the overlap between the p orbitals on different halogen atoms, it is easily shown that ζ'_2 has a maximum value of $\zeta^{\mathrm{B}}_{\mathrm{p}}$, for which $c_{\mathrm{t_2}\pi} = \sqrt{\tfrac{2}{3}}$, $c_{\mathrm{t_2}\sigma} = -\sqrt{\tfrac{1}{3}}$. This would correspond to the full restoration of the orbital angular momentum of the p shell of a free halogen atom. Our calculations on CBr_4 do in fact yield this order of mixing for the two t_2 combinations (though there is of course some admixture of carbon 2p).

The extent to which $t_2(p^{\pi}_{B})$ and $t_2(p^{\sigma}_{B})$ are mixed under the one-electron hamiltonian may be gauged by an extension of the model discussed in appendix (A 1). For convenience we abbreviate p_σ as σ, and p_π as π, and for generality we consider the interaction of two symmetry orbitals, $|\sigma_{gm}\rangle$ and $|\pi_{gm}\rangle$ (cf. equation (A 1)). The overlap between these two combinations may be written

Table B 1. Empirical spin-orbit coupling constants (eV) for certain free atoms and ions

C^+	$\zeta_{2p} = 0.005$	F	$\zeta_{2p} = 0.033$
Si^+	$\zeta_{3p} = 0.024$	Cl	$\zeta_{3p} = 0.073$
Ge^+	$\zeta_{4p} = 0.146$	Br	$\zeta_{4p} = 0.305$
Sn^+	$\zeta_{5p} = 0.351$	I	$\zeta_{5p} = 0.628$
Pb^+	$\zeta_{6p} = 1.16$	Ti^+	$\zeta_{3d} = 0.01$

After Dunn (1961), Jørgensen (1962) and Griffith (1961).

Table B 2. The multiplet splitting (eV) of the $^2T_1$ and $^2T_2$ terms of the group IV tetrabromide molecular ions

	$^2T_1$		$^2T_2$		$3t_2$ m.o.	
	obs†	calc‡	obs†	calc‡	$c_{t_2\pi}$	$c_{t_2\sigma}$
CBr_4	0.315	0.263	0.54	0.433	0.970	−0.370
$SiBr_4$	0.325	0.249	0.53*	0.473	0.916	−0.473
$GeBr_4$	0.31	0.245	0.66*	0.470	0.915	−0.451
$SnBr_4$	0.26*	0.239	0.5*	0.450	0.917	−0.439
$TiBr_4$	0.24	0.243	—	—	—	—

† The multiplet splittings are estimated from the peak separations of the multiplet bands (A′ and A″ for $^2T_1$, B′ and B″ for $^2T_2$). The figures indicated * are necessarily very approximate.

‡ The calculations employ the bromine 4p wavefunctions of Watson & Freeman (1961 *a*). The overlap integrals for $GeBr_4$ are estimated by interpolation.

The coefficients given in the right-hand columns relate to normalized t_2 molecular orbitals (assumed of pure bromine 4p composition).

$$\langle\sigma_{gm}|\pi_{gm}\rangle = (1+\chi_{g\sigma})^{-\frac{1}{2}}\,(1+\chi_{g\pi})^{-\frac{1}{2}}\,\chi_{g\sigma\pi}, \tag{B 10}$$

where

$$\chi_{g\;\sigma\pi} = \sum_{\sigma_B}\sum_{\pi_{B'}} u_{gm,\sigma_B}u_{gm,\pi_{B'}}\langle\sigma_B|\pi_{B'}\rangle. \tag{B 11}$$

The interaction of $|\sigma_{gm}\rangle$ and $|\pi_{gm}\rangle$ is described in the usual way (Coulson 1961) by a 2 × 2 matrix equation $(F-ES)\,c = 0$. Now the required F-matrix elements can be obtained from equations (A 4) to (A 6). If we make the particular approximations that $\alpha_\sigma = \alpha_\pi = \alpha$, and that $\eta_{\sigma\sigma} = \eta_{\sigma\pi} = \eta_{\pi\pi} = \eta$, the eigenfunctions are such that the ratio of the coefficients multiplying $|\pi_{gm}\rangle$ and $|\sigma_{gm}\rangle$ is

$$\frac{c_{g\pi}}{c_{g\sigma}} = \langle\sigma_{gm}|\pi_{gm}\rangle\left(\frac{2+\chi_{g\pi}+\chi_{g\sigma}\pm\theta}{\chi_{g\pi}-\chi_{g\sigma}+2\chi^2_{g\sigma\pi}(1+\chi_{g\pi})^{-1}\pm\theta}\right), \tag{B 12}$$

$$\sim \chi_{g\sigma\pi}\left(\frac{2+\chi_{g\pi}+\chi_{g\sigma}\pm\theta}{\chi_{g\pi}-\chi_{g\sigma}\pm\theta}\right),$$

where

$$\theta = [(\chi_{g\pi}-\chi_{g\sigma})^2+4\chi^2_{g\sigma\pi}]^{\frac{1}{2}}.$$

The mixing of $|\sigma_{gm}\rangle$ and $|\pi_{gm}\rangle$ is thus approximately independent of α and η, and a function only of overlap integrals. When $\alpha > \eta$ the negative sign in equation (B 12) yields the eigenfunction of *lower* energy. If $\chi_{g\pi} > \chi_{g\sigma}$ (as in table A 1) this is of $|\pi_{gm}\rangle$ majority character.

In the particular case of the tetrahedral AB_4 species (where $g = t_2$) we have†

$$\chi_{t_2\sigma\pi} = \tfrac{1}{3}2\sqrt{2}\,(S_\sigma - S_\pi). \qquad (B\,13)$$

Equipped with the necessary overlap integrals, S_σ and S_π, we can use equations (B 12) and (B 13) to estimate the effective spin-orbit coupling constant, ζ_2', for a purely bromine 4p $3t_2$ molecular orbital (equation (B 9)). This leads to the calculated $^2T_2$ multiplet splittings ($\frac{3}{2}\zeta_2'$) given in table B 2. The agreement between theory and experiment is comparable with that found for the $^2T_1$ multiplet separations.

We gratefully acknowledge Mr C. Baker's advice and assistance with the measurement of the photoelectron spectra, and his permission to make use of the spectrum of CF_4 (Baker 1969). We also thank Mr S. Evans for his experimental assistance. Finally, we thank Turner and Newall, Ltd, for a Fellowship (to J. C. G.).

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† There are some errors in Tables 8 and 9 (p. 115) of the book by Ballhausen & Gray (1964).