# Photoelectron Spectra of the Halides of Elements in Groups III, IV, V and VI

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# Photoelectron spectra of the halides of elements in groups III, IV, V and VI

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Photoelectron spectra of the halides of B, C, N, P, As, S, Se, Te and U are reported and interpreted in terms of molecular orbital structure. The experimental criteria which are used to identify the orbitals are briefly discussed. It is shown how the orbitals of the halides of the elements of different groups are related and how the additional electrons of molecules containing higher group atoms are accommodated in outer orbitals in a building up process somewhat analogous to that which occurs in atoms.

## INTRODUCTION

The photoelectron spectra of molecules reveal their orbital structure in a very direct manner. It is found that in much the same way as the 'aufbau' principle enables the electronic structure of atoms to be understood in terms of the filling up of closed shell groups of electrons, a similar process operates for filling the orbitals of molecules. This has been shown to hold for simple diatomic and triatomic systems in which molecules such as $N_2$, CO, BF and $CO_2$, $N_2O$ represent closed shell structures in linear symmetry. Departure from linearity occurs for $NO_2$ and the resulting modifications to the orbital shells are well understood for triatomic molecules. The object of the present paper is to extend our information on orbital structure from triatomic to planar and bent tetra-atomic, tetrahedral, pentatomic and octahedral molecules. To do this we start with planar molecules of the type $AB_3$ of which the boron trihalides form the simplest examples.

## THE BORON TRIHALIDES

The spectra of the trihalides of boron taken with the 584 Å line of helium are shown in figure 1 which indicates also the assignments and gives schematic pictures of the orbitals. The 304 Å line was used to observe $2a_1'$ of boron trifluoride. Assuming the symmetrical planar configuration ($D_{3h}$) and omitting halogen s orbitals the orbital order (inner to outer) is found to be $2a_1'$, $2e'$, $1a_2''$, $1e''$, $3e'$, $1a_2'$. The only doubt concerns the relative order of $1a_2'$ and $3e'$. Mean vertical ionization energies for the orbitals are given in table 1. The grounds on which the assignments are made are as follows. Taking first $BF_3$, there is little doubt about the assignment of $2a_1'$ (21.4 eV) to a mainly 2s(B) orbital and we only wish to remark on how little it appears to contribute to the bonding at the atomic separations existing in the molecule as judged from the sharpness of the band and the absence of vibration structure on ionization.

The next innermost ionization is from the $2e'$ orbital which is the main in-plane bonding orbital. The bands corresponding to these orbitals in $BF_3$ and $BCl_3$ are good examples of Jahn–Teller contours. The vibrational structure envelopes to be expected from a transition between a non-degenerate electronic state (A) and a Jahn–Teller (J.T.) degenerate state (E) have been calculated for different changes of vibrational frequencies by Longuet-Higgins, Opik, Pryce & Sack (1958). A useful review giving some examples taken from solid state physics has been written by Sturge (1967). Briefly the contour is that of the sum of two overlapping bands which have the same origin and the same total ($I$, $\nu$) area but with one of these bands being spread out over a larger frequency range than the other. The consequence of this is that the envelope shows two maxima the intensity of the higher frequency maximum being less than that of the lower one as is required to maintain the total area of the second, more extended, band equal to that of the first. In $BF_3$ the vibrational pattern has a separation of *ca.* 700 $cm^{-1}$ corresponding to the symmetrical valence vibration $\nu_1(a_1')$ for which the value in

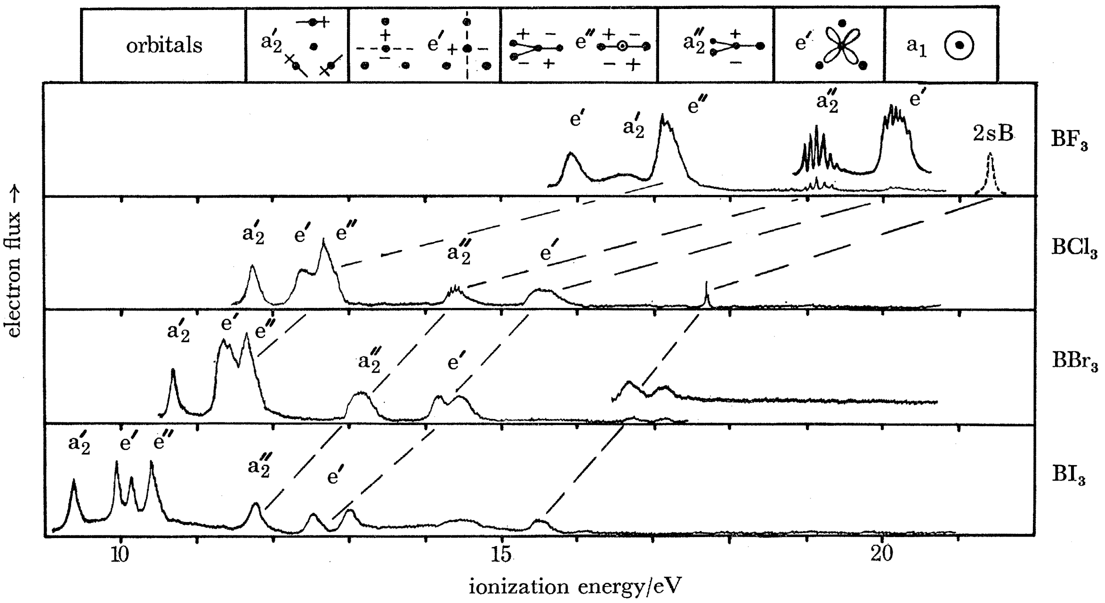

FIGURE 1. Photoelectron spectra of the boron trihalides.

TABLE 1. IONIZATION ENERGIES OF THE BORON TRIHALIDES

| $BF_3$ | $BCl_3$ | $BBr_3$ | $BI_3$ | assignment |
|---|---|---|---|---|
| 16.68 | 11.73 | 10.68 | 9.40 | $1a_2'$ |
| 15.95 | 12.38 | 11.36 | 9.90 | $3e'$ |
| | | 11.46 | 10.11 | |
| 17.13 | 12.65 | 11.70 | 10.40 | $1e''$ |
| 17.21 | | 11.75 | 10.50 | |
| 17.30 | | | | |
| 19.06 | 14.40 | 13.15 | 11.72 | $1a_2''$ |
| 20.14 | 15.52 | 14.17 | 12.44 | $2e'$ |
| | 15.70 | 14.48 | 12.94 | |
| 21.4 | 17.71 | 16.70 | 15.2? | $2a_1'$ |
| | 17.75 | 17.10 | | |

Tables give band maxima and in some cases the ionization energies of associated structure.

the neutral molecules is 888 $cm^{-1}$. In $BCl_3$ the separation is *ca.* 330 $cm^{-1}$ compared with 471 $cm^{-1}$ in the neutral molecule. In both $BBr_3$ and $BI_3$ these bands are doubled and the vibrational structure is too small to be resolved. The doubling is to be attributed to the splitting of the degeneracy by the large spin orbit coupling prevailing in the heavier atoms. Splittings of 0.31 and 0.50 eV are observed for these bands in $BBr_3$ and $BI_3$ respectively. These values are close to the s.o. coupling coefficients of the atoms.

The next lower band corresponds to a smooth vibrational pattern of a single frequency difference which again corresponds to the $\nu_1(a_1')$ vibration reduced from its neutral state value.

In $BF_3$ the mean observed difference is 670 $cm^{-1}$ and in $BCl_3$ it is 440 $cm^{-1}$. This band undoubtedly corresponds to the $a_2''$ orbital since it has the relative intensity of a non-degenerate band and does not exhibit J.T. splitting in $BF_3$ or $BCl_3$ or s.o. splitting in $BBr_3$ and $BI_3$. It is rather similar to the $a_{2u}$, $(\pi_1)$ orbital in benzene but has relatively more bonding character since it shares an empty p$\pi$ orbital on the boron atom. Vibrational differences of about 260 $cm^{-1}$ are observed for this band in $BBr_3$, corresponding to a value of 279 $cm^{-1}$ for $\nu_1(a_1)$ in the neutral molecule. Those of $BI_3$ could not be resolved.

Of the three outer orbitals, the innermost of these can be identified as 1e″ because of its intensity, its expected non-bonding character, the absence of s.o. splitting in $BBr_3$ and $BI_3$. This octahedral e″ orbital should show neither s.o. nor J.T. splitting in planar centro-symmetric molecules for the following reasons. Both these phenomena are equivalent alternative manifestations of residual angular momentum, the one electronic and the other nuclear, i.e. s.o. and J.T. splitting respectively. In the latter case the nuclei assume a distorted configuration in much the same way as the weights of the balancing mechanism of a spin drier change their positions when an off-axis part of the load is removed. The residual angular momentum of the molecular ion when an electron is removed from a degenerate orbital must be equal and opposite to that possessed originally by the ionized electron in the neutral molecule. Because the motions of an electron above and below the molecular plane in an e″ orbital are equal and opposite, the removal of this electron from a planar centro-symmetric molecule does not produce any angular momentum change. Another important example of this situation occurs for the analogous $e_{1g}$ $(\pi_{2,3})$ orbital of benzene which as we shall show in a forthcoming paper exhibits no J.T. splitting. Further proof of the assignments of the e″ orbitals will be given later when it will be shown that all the orbitals of the boron trihalides can be traced through into the spectra of $HCX_3$, $NX_3$, $PX_3$ and $AsX_3$, i.e. even when planarity is lost and the e″ band does acquire a splitting.

The identification of the remaining two bands is somewhat less certain. On simple overlap grounds one might expect $a_2'$, which is built from the out-of-phase combination of the three in-plane pX orbitals, to be outermost. However, the possibility that repulsion of 3e′ by 2e′ might push 3e′ above $a_2'$ must be considered. In fact the 304 Å spectrum of $BF_3$ shows the first band to be comparable in intensity with 1e″ and the intermediate band to be much weaker, thus suggesting that 3e′ is outermost. However, while this appears to be the case for $BF_3$ and similar orbitals in $PF_3$ and $AsF_3$ (see later), it is not the case for the other halides. The most convincing argument for the identification of the outer orbitals starts with the bromide and the iodide. In both of these 3e′ should show spin-orbit splitting of the same order of magnitude as that observed in their 2e′ valence orbitals, i.e. about 0.3 and 0.5 eV respectively. In the bromide the separation between the first and second band is about 0.68 eV and this is considered to be too large to be due to spin-orbit coupling. Hence the first band must be $1a_2'$ and, the 3e′ identified as the stronger band following it with peaks at 11.35 and 11.45 eV. A similar argument for identifying the first band as $1a_2'$ holds even more strongly for the chloride. Although in the case of the iodide the separation of 0.50 eV for the first two bands might possibly be due to spin-orbit coupling, it is considered that this is too large. By analogy with the bromide and chloride the first band of the iodide, is identified as $a_2'$, the second and third bands at 9.90 and 10.11 eV being assigned to the two s.o. components of 3e′. This interpretation has the advantage that the spin-orbit splitting in 3e′ for both the bromide and the iodide, is uniformly less than that observed in the 2e′ state where its large value probably arises from mixing with nsX.

## THE HALOGEN DERIVATIVES OF METHANE

### *Bromomethanes*

We shall first discuss the bromomethanes since for these molecules there is virtually no mixing in the ionized states, i.e. the ionization potentials of the pπ bromine electrons are low enough so that they have little interaction with other electrons in orbitals of similar symmetry and there is no interaction between high Rydberg states of the former with low Rydberg states of the latter. The successively substituted bromomethanes form a most interesting example of how, when hydrogen is replaced by a heavier atom such as a halogen atom the additional electrons are accommodated in hitherto unfilled outer orbitals, the orbitals of the initially resident electrons being only slightly modified in the process.

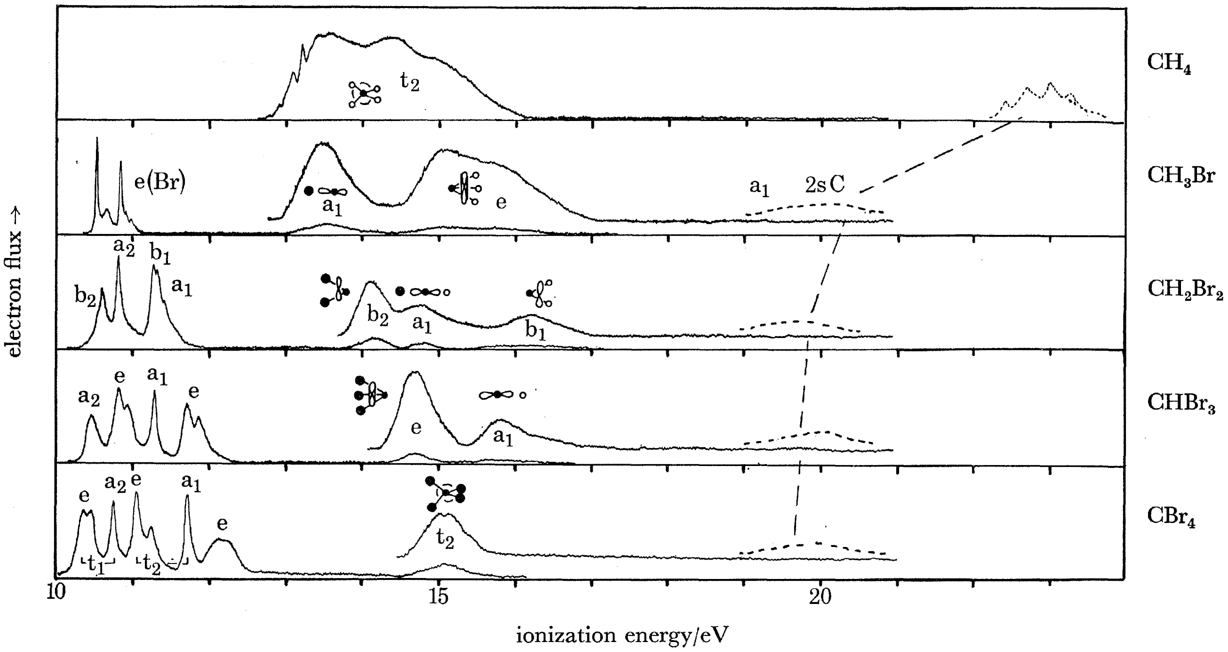

FIGURE 2. Photoelectron spectra of the bromomethanes.

TABLE 2. IONIZATION ENERGIES OF THE BROMOMETHANES (eV)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $CH_3Br$ | 19.9 $a_1$; | 15.08 e; | 13.49 $a_1$; | 10.86, 10.54 e | | | |
| $CH_2Br_2$ | 19.7 $a_1$; | 16.25 $b_1$; | 14.75 $a_1$; | 14.12 $b_2$; | 11.28 $b_1+a_1$; | 10.82 $a_2$; | 10.61 $b_2$ |
| $CHBr_3$ | 19.8 $a_1$; | 15.81 $a_1$; | 14.71 e′; | 11.88, 11.72 e″; | 11.28 $a_1$; | 10.95, 10.81 e′; | 10.47 $a_2$ |
| $CBr_4$ | 19.7 $a_1$; | 15.15 $t_2$; | 12.24, 12.11 e; | 11.73, 11.28, 11.07 $t_2$; | 10.76, 10.48, 10.39 $t_1$ | | |

The photoelectron spectra with assignments and schematic orbitals are shown in figure 2. Values of peak ionization energies are given in table 2. It is assumed that the s electrons of the halogens play little part and the highest ionization potential corresponds to the 2s(C) orbital which is labelled $2a_1$. The orbital structure of methane, namely $(a_1)^2\ (t_2)^6$ is well understood and the highest ionization energy in its photoelectron spectrum corresponds to the $a_1$(2s, C) orbital giving a band with a pattern of $\nu_1(a_1)$ vibrations of frequency *ca.* 2000 $cm^{-1}$ as compared with the neutral state value of 2914 $cm^{-1}$. The onset is at 22.4 eV and the peak at 23.0 eV. Ionization from the $t_2$ shell occurs over the region 13–16.5 eV (Baker, Baker, Brundle & Turner 1968). This band has a J.T. contour and although only the first part of it has discrete structure, the differences observed of *ca.* 1200 $cm^{-1}$ for the lower of the J.T. states probably correspond to the $\nu_2$(e) deformation vibration which has a frequency of 1526 $cm^{-1}$ in the ground state.

### *Methyl bromide*

In methyl bromide the $2a_1$ band moves to lower ionization energies as expected through the influence of the bromine atom. Although the band retains some evidence of structure it is rather diffuse and the pattern is no doubt complicated by superposition of CBr and CH vibrations. The next highest band occurs between 14.5 and 17 eV. It has a characteristic J.T. contour and is identified with the e($CH_3$) orbital being derived from the splitting in $C_{3v}$ symmetry of $t_2(CH_4)$ into $e + a_1$. The band next to it peaking at 13.5 eV and having the smooth contour of a singly degenerate orbital is assigned to the $2a_1$ (CBr) orbital. The greater breadth of bands which arise from $CH_n$ orbitals relative to those arising from $CX_n$ bonding orbitals is due to the greater spread of the ground state vibrational wavefunction associated with the high zero-point energy of vibrations involving hydrogen atoms. Neither of the bands e and $2a_1$ show discrete structure which indicates that the life-times of the ionized states are very short. The mass spectrometric photoionization studies of Kraus, Walker & Dibeler (1968) which show the appearance of $CH_3^+$ at 12.77 eV supports this explanation of the absence of structure. The two sharp bands occurring just below 11 eV are clearly due to the ionization from the e orbital of the $(p\pi)^4$Br non-bonding electrons and show the expected spin-orbit separation as in HBr (Lempka, Passmore & Price 1968). Although the vibrational patterns accompanying ionization to these two $^2E_{\frac{3}{2},\frac{1}{2}}$ states are relatively weak they show interesting differences. The main vibration band accompanying the first band ($^2E_{\frac{3}{2}}$) has a frequency of *ca.* 1240 $cm^{-1}$ interpreted as $\nu_2(a_1)$ symmetrical $CH_3$ deformation vibration, 1305 $cm^{-1}$ in the ground state. It also has a much weaker band at a separation of 800 $cm^{-1}$ which must be associated with the $\nu_6$(e) vibration which has a value of 952 $cm^{-1}$ in the ground state. On the other hand, the strongest sub-band of $^2E_{\frac{1}{2}}$ has a separation of only 560 $cm^{-1}$ from the main band and must be assigned to $\nu_3(a_1)$ the CBr stretching vibration which is 611 $cm^{-1}$ in the ground state. The 1240 $cm^{-1}$ $\nu_2(a_1)$ also occurs but somewhat more weakly than in the $^2E_{\frac{3}{2}}$ band. It thus appears that the e orbitals are oriented in the trigonal $CH_3$ field, possibly 'in' and 'perpendicular to' an XCH plane. Even in $CH_3I$ there is a small difference between the two vibrational patterns of the $^2E$ states. These differences are progressively increased in going to the bromide and the chloride.

### *Methylene bromide*

$CH_2Br_2$ (electron configuration—$(2a_1)^2(1b_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(2b_1)^2(1a_2)^2(3b_2)$ omitting s electrons of Br and taking the orbital which is symmetrical with respect to reflexion in the $CH_2$ plane as $b_1$ in $C_{2v}$ symmetry).

The substitution of the second bromine atom completely splits the degeneracy of the $(t_2)^6$ bonding orbitals on the carbon atom. The bands peaking at 16.25, 14.75 and 14.12 are clearly associated with the $1b_1(CH_2)$, the $3a_1(H_2CBr_2)$ and the $2b_2(CBr_2)$ orbitals respectively as indicated in figure 2. These bands show no well-marked vibrational structure, a feature related to the rapid dissociation of the ion states. The progressively narrowing band spread as the orbital changes from being mainly hydrogen atom bonding to mainly bromine atom bonding is as expected from the previous discussion. The band occurring around 20 eV is derived from $2a_1$(2sC). It is without structure and shifted to lower ionization energy relative to the corresponding band in methane.

The bands occurring in the range 10 to 11 eV are due to the non-bonding bromine electrons and arise from in-plane and out-of-plane, in-phase and out-of-phase combinations of p orbitals just as in an $AX_2$ molecule. From considerations of overlap they are expected to correspond to $4a_1$, $2b_1$, $1a_2$ and $3b_2$ orbitals in order of decreasing ionization energy, the order of $1a_2$ and $3b_2$ being uncertain. Their relative positions can be affected by interaction with other orbitals in the molecule. For example, repulsion by an inner orbital of the same symmetry would tend to lower the ionization energy of an orbital. On the other hand, an $a_1$ orbital can be strongly affected and its ionization energy raised by replacing the hydrogen by fluorine atoms. The spectrum of $Br_2CF_2$ shows that the highest of these four bromine orbitals is pulled in much more strongly than the other three by the fluorine thus confirming its assignment to an $a_1$ orbital. Theoretical calculations to be published later support a configurational order $4a_1$, $2b_1$, $1a_2$, $3b_2$. In addition, it should be mentioned that the diffuseness of the two higher energy bands is probably due to mixing of Rydberg states with those of inner orbitals of the same symmetry. When the latter are pulled in by fluorine substitution the $4a_1$ and $2b_1$ bands become sharper.

*Bromoform* $(2a_1)^2\ (3a_1)^2\ (2e)^4\ (3e)^4\ (4a_1)^2\ (4e)^4\ (1a_2)^2$

In bromoform, $C_{3v}$ symmetry is regained and the $(t_2)^6$ orbitals around the central carbon atom split into $(2e)^4$ $(CBr_3)$ and $3a_1^2(CH)$. We shall use ′ and ″ symbols in the following discussion on bromoform to indicate that the orbitals are derived from the e′ and e″ orbitals of planar $AX_3$ molecules. As expected 2e′ is at lower energies and has roughly twice the intensity of the $a_1$ band. It should have J.T. or s.o. splitting of about 0.2 eV, but this is lost in the diffuse structure of the band. The twelve non-bonding pπBr electrons fall into orbitals 3e″, $4a_1$, 4e′ and $1a_2$ in decreasing order of binding. It is evident that the degeneracy is completely split, six bands of comparable intensity being obtained. Their assignment is made by: (1) comparing the bands with those of $CBr_4$ of which $HCBr_3$ forms a subgroup of lower symmetry, (2) by comparison with the associated set of orbitals in $BBr_3$, (3) by observing which band, shifts on fluorine substitution (i.e. in $FCBr_3$) and so assigning the $a_1$ orbital, and (4) by comparison of the spin-orbit splittings with those expected theoretically. The pair at 11.72 and 11.88 eV are 3e″. They are related to 1e″ in $BBr_3$ and follow through unchanged in character but with slightly increased binding to 1e in $CBr_4$. They appear to relate also to the $3a_1$, $2b_1$ pair in $CH_2Br_2$. The contour of this 3e″ band indicates J.T. splitting in that the second component is broader and has a lower peak value but probably a common origin with the first component. It is predicted to have zero s.o. splitting and in fact if the splitting were of this type the two bands would be expected to have equal heights but different origins. The sharp band at 11.28 eV is assigned to $4a_1$ because of its single character and the fact that it suffers a relatively large shift on substituting the hydrogen by a fluorine atom. The pair at 10.81 and 10.95 eV we assign to 4e′ corresponding to 3e′ in $BBr_3$. Its contour indicates J.T. splitting but this appears to be modified in $FCBr_3$ where it splits into two sharp bands. While in $FCBr_3$ the e fluorine orbitals strongly repel the valence 2e′ $(CBr_3)$ orbitals, this repulsion is not passed on to the 3e″ orbitals because of their perpendicular orientation. The lowest band in $HCBr_3$ (at 10.47 eV) we attribute to $1a_2$ from overlap considerations.

*Carbon tetrabromide* $(2a_1)^2\ (2t_2)^6\ (1e)^2\ (3t_2)^6\ (1t_1)^6$

In the case of $CBr_4$ we have arrived at a similar analysis to that given by J. C. Green *et al.* (this volume p. 111) though for different reasons. It differs from the conclusions of some authors

(Bassett & Lloyd 1969) who consider that repulsion between $2t_2$ and $3t_2$ pushes $3t_2$ above $1t_1$ in $CX_4$ molecules in spite of the fact that $t_1$ has the greater number of nodal surfaces due to the head to tail arrangement of its pπ orbital combination. In addition to the arguments given by Green *et al.* for placing $3t_2$ inside $t_1$ we wish to point out that $3t_2$ is derived from $4a_1+4e$ in $HCBr_3$. It is clear by comparison of the spectra that the band at 11.28 eV in $HCBr_3$ which is identified as $4a_1$ is shifted to 11.7 eV in $CBr_4$ retaining its $a_1$ character and forming with the bands at 11.07 and 11.28 eV ($4e'$ in $HCBr_3$) the components of the $3t_2$ orbital. Likewise in replacing the hydrogen of $HCBr_3$ by a bromine atom the incoming e orbital of Br combines with the outer $a_2$ orbital to give the $t_1$ set for which the lower symmetry components are $e+a_2$. Thus although in the building up of the electronic structures of the halogenated methanes there is always repulsion between valence orbitals and non-bonding orbitals of the same symmetry, this never seems large enough to change the ordering expected from considerations of overlap. We seem to differ from Green *et al.* on the interpretation of the spin-orbit splitting which appears to us from comparisons with corresponding bands of $BX_3$ and $HCX_3$ to be localized between the two lower energy components of the $t_1$ and $t_2$ systems rather than between the first and the third, the positions of the third components being largely determined by orbital overlap.

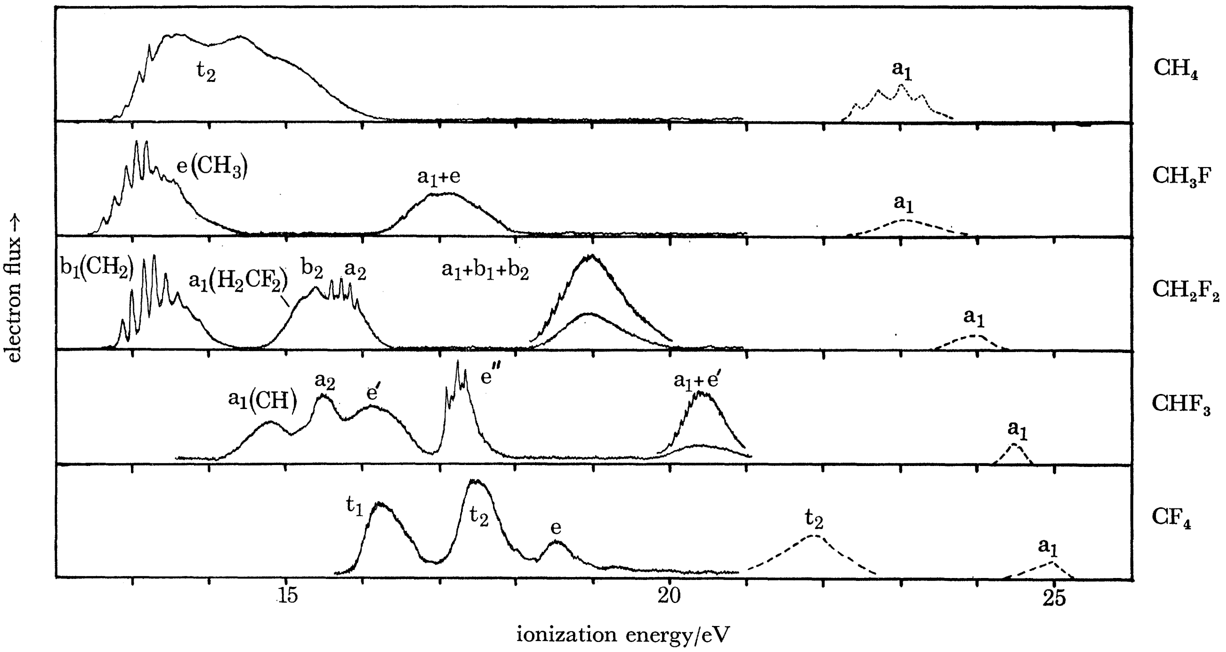

FIGURE 3. Photoelectron spectra of the fluoromethanes.

## The fluoromethanes

### *Methyl fluoride*

Spectra of the fluoromethanes are shown in figure 3. The orbitals corresponding to $2a_1$ (mainly 2s of carbon) and several others have energies greater than 21 eV and have been recorded by using 304 Å irradiation. For methyl fluoride the $2a_1$ (2sC) band has a broad maximum at 23.4 eV being shifted slightly to higher energies from its analogue in methane for which the maximum is at 23.0 eV. The broad band in the range 16 to 18 eV corresponds to a superposition of the $3a_1$(CF) band and one corresponding to the e(F) orbitals. The latter ionized state is greatly modified by a repulsive curve associated with the former. This is a situation exactly similar to that in HF which has been described by Lempka *et al.* (1968), the main difference being that the interaction is much stronger in methyl fluoride due to the fact that the ionization potential of $CH_3$ is less than that of H. It has the effect of appreciably lowering the ionization energies of some of the non-bonding pπ(F) electrons in all the fluoromethanes below that in the free F atoms. We shall not discuss it further here and only note the fact that this unstable state of the ion at 16 to 18 eV dissociates into $CH_3^+ + F$ (Krauss *et al.* 1968). The remaining band occurs between 12.6 and 14 eV and clearly corresponds to the valence $e(CH_3)$ orbital and has the corresponding J.T. contour. Its pattern is very interesting in this respect since it is one of the few examples where the vibrational structure is partially retained in the second J.T. peak. The vibrational pattern starts at 12.59 eV with a progression of bands having a separation interval of *ca.* 1120 $cm^{-1}$. This corresponds to the $\nu_2(a_1)$ $(\delta CH_3)$ vibration which has a value of 1475 $cm^{-1}$ in the ground state. Its hydrogen dependence has been confirmed by comparison with the spectrum of $CD_3F$. At 13.3 eV the regularity and sharpness of the pattern alters and differences of 1600 $cm^{-1}$ no doubt associated with weakened CH stretching occur. This is to be correlated also with the appearance of $CH_2F^+$ at 13.37 eV in mass spectroscopic photoionization studies (Krauss *et al.* 1968). It is a most interesting example of how the distortions in J.T. splitting can be demonstrated by the combination of photoelectron and mass spectroscopic studies.

TABLE 3. IONIZATION ENERGIES OF THE FLUOROMETHANES (eV)

| | | | | | | |
|---|---|---|---|---|---|---|
| $CH_3F$ | 23.4 $a_1$; | 17.06 $a_1+e$; | 13.04 e | | | |
| $CH_2F_2$ | 23.9 $a_1$; | 18.97 $b_2+a_1+b_1$; | 15.58 $a_2$; | 15.40 $b_2$; | 15.25 $a_1$; | 13.29 $b_1$ |
| $CHF_3$ | 24.4 $a_1$; | 20.50 $a_1+e$; | 17.25 $e''$; | 16.16 $e'$; | 15.50 $a_2$; | 14.80 $a_1$ |
| $CF_4$ | 25.1 $a_1$; | 21.95 $t_2$; | 18.50 e; | 17.47 $t_2$; | 16.23 $t_1$ | |

### *Difluoromethane*

In the spectrum of difluoromethane the $a_1(2sC)$ band moves to 23.5 eV (vert.). This is followed by an intense broad band peaking at 19.0 eV and consisting in part of a regular pattern of slightly diffuse bands with a separation of 670 $cm^{-1}$ which appears to be the $\nu_1(a_1)(CF_2)$ stretching frequency reduced from its value of 1000 $cm^{-1}$ in the ground state. This band probably corresponds to a mixture of bands arising from $a_1(F_2)$, $b_1(F_2)$ and $b_2(CF_2)$ orbitals. (Note that the $a_1(H_2CX_2)$ and $a_1(X)$ orbital order is inverted in fluoro relative to the other methanes since fluorine is the only halogen with an ionization potential greater than that of hydrogen.) In order to preserve a consistent scheme of orbital development from the orbitals in $H_2CF_2$ and $HCF_3$ to the $t_2$ valence orbital of $CF_4$ at 21.95 eV, it is necessary to have three orbitals in the range 18 to 22 eV with symmetries $a_1$, $b_1$ and $b_2$ for $H_2CF_2$ and two of symmetries $a_1$ and e for $HCF_3$ from which $t_2(CF_4)$ can be generated. Although we do not resolve the 18.5 to 19.8 eV band of $H_2CF_2$ into three bands its intensity when recorded on a slotted grid system with 584 and 304 Å irradiation (Price 1968) is such as to require it to arise from three orbitals. Spectra of $Cl_2CF_2$ and $HClCF_2$, which have the same $CF_2$ orbital character in this energy range, have corresponding bands of the same high intensity and in the case of $HClCF_2$ the band is split into two with maxima at 18.7 and 19.7 eV the latter being twice as strong as the former. Likewise in $HCF_3$ although the strong band in the range 20 to 21.4 eV is not clearly separated into its $a_1$ and e components, it is split in the spectra of $ClCF_3$, $BrCF_3$ and $ICF_3$ into a lower energy band corresponding to the $a_1$ orbital followed by a band of twice the intensity corresponding to the e orbital. This separation arises from the attraction of the

$a_1$ orbital by the substituted halogen which simultaneously repels the e orbital. The separation of $a_1$ from $b_1$ and $b_2$ in $HClCF_2$ has a similar explanation and the failure to separate in $CCl_2CF_2$ and $Br_2CF_2$ probably arises from the repulsion of the $a_1(X_2CF_2)$ orbital by the $a_1(X_2)$ orbital which is formed in these molecules between the *two* chlorine or the *two* bromine atoms. (We have recorded the spectra of a large number of mixed halogeno methanes and shall be publishing them separately.)

The next system of difluoromethane occurs between 14.7 and 16.2 eV. It is composed of three overlapping band systems. The high energy hump peaking at 15.7 eV has a well-defined vibrational pattern with differences of *ca.* 980 $cm^{-1}$ possibly corresponding to $CH_2$ deformation vibrations and others of *ca.* 500 $cm^{-1}$ corresponding to $CF_2$ deformation vibrations. As will be seen later this type of pattern carries through to the derived orbital in $HCF_3$ (band from 17.1 17.6 eV) and again we draw attention to the similarity with the halogen acids namely that whereas little vibrational structure accompanies the ionization of the non-bonding electrons of I, Br and Cl, pronounced vibrational structure is associated with the ionization of non-bonding fluorine electrons. Similar interactions between non-bonding and bonding potential energy surfaces of the same symmetry are again probably responsible for this phenomenon.

The lower energy features in the 14.7 to 16.2 eV range are two structureless bands with maxima at 15.25 and 15.40 eV which overlap both themselves and the discrete region around 15.7 eV. These three systems with maxima at 15.25 15.40 and 15.7 eV must represent mainly $a_1(H_2CF_2)$, $b_2(F_2)$ and $a_2(F_2)$ orbital ionization respectively apart from configuration interaction effects, since $b_2+a_2$ are required to form the e band in $HCF_3$ at 17 eV, the $a_1$ band becoming the $a_2$ band in fluoroform at 15.4 eV. These assignments are required by our analysis of fluoroform and carbon tetrafluoride to be discussed later and supported also by comparison with similar bands appearing in $Cl_2CF_2$ and $Br_2CF_2$.

In addition to the above arguments for the existence of a split of nearly 4 eV between the in-phase $a_1b_1$ and the out-of-phase $a_2b_2$ non-bonding (F) orbitals of $H_2CF_2$ in contrast to the heavier halides where the splitting is only about 1 eV, we make the following general observation. In all $AB_2$ molecules whether linear or bent where B is a first row atom (e.g. in $NO_2$, $CO_2$, $N_2O$, $SO_2$, etc.) the splitting is found to be about 4 eV. Its magnitude when B is a second row element (e.g. in $SCl_2$, $CS_2$, etc.) is only about 1 to 2 eV and comparable with that found in the heavier methylene halides. Similar comparison can be made between in-phase and out-of-phase orbital combinations even for diatomic molecules where the splittings are much larger for NO, $O_2$ and $F_2$ than for $S_2$, $Cl_2$ and $Br_2$.

The lowest energy band of difluoromethane peaking at 13.2 eV has the simple intensity contour of a band arising from a single non-degenerate orbital and is undoubtedly to be associated with the $b_1(CH_2)$ orbital. It consists of a regular vibrational progression with a vibrational interval of 1120 $cm^{-1}$ corresponding to the $CH_2$ deformation vibration of 1508 $cm^{-1}$ in the ground state (Glockler & Leader 1939).

### *Fluoroform*

In the case of fluoroform the innermost orbital $a_1(2sC)$ appears as a broad band with a maximum at 24.4 eV being progressively shifted to higher energies relative to methyl and methylene fluoride with the increasing fluorine substitution. It is followed by a very broad intense band peaking at 20.5 eV which as discussed in the previous section must represent the $a_1(F)$ and $e'(CF_3)$ orbitals. There is a long progression of about ten vibrational peaks superimposed on the low energy side of this band with a mean separation of 480 cm$^{-1}$ probably corresponding to a $\nu_6(a_1)$ symmetrical $CF_3$ valence vibration which has the value 696 cm$^{-1}$ in the ground state. This part of the band must correspond to $a_1(F)$ from the manner in which it splits off from the higher energy portion when Cl, Br or I is substituted for the hydrogen. It correlates with $a_2''$ in $BF_3$ and the remaining high energy portion which represents two thirds of the total intensity is $e(CF_3)$ correlating with $2e'$ in $BF_3$.

The band peaking at 17.25 eV is e(F). It arises from the non-bonding F orbitals and correlates with $2e''$ in $BF_3$. It shows vibrational structure with main differences of 1040 cm$^{-1}$ which may correspond to the ground state $\nu_2(e)$ (1500 cm$^{-1}$) CH deformation frequency and subsidiary differences of 560 cm$^{-1}$ probably correlating with the 698 cm$^{-1}$ $\nu_3(a_1)$ $CF_3$ ground state vibration. The next two bands peaking at 16.16 and 15.50 eV do not have discrete vibrational structure. They are identified as $e'(F)$ and $a_1(F)$ on grounds of shape and intensity and the need to correlate with the bands of the other fluoromethanes and boron trihalides into a consistent orbital derivation scheme. Their order relative to their analogues in $BF_3$ ($e'$ and $a_2'$) is interchanged but is the same as that in the other boron trihalides. The final band at 14.68 eV is again structureless. It is identified as $a_1(CH)$ because it disappears in going to $CF_4$.

### *Carbon tetrafluoride*

The $a_1(2sC)$ band and the $t_2(CF_4)$ valence bands are found to have maxima at 24.95 and 21.95 eV respectively using 304 Å irradiation and are progressively shifted to higher energies relative to their analogues in $HCF_3$. That at 22.1 eV shows vibrational structure with differences of 640 cm$^{-1}$ corresponding to $\nu_1$ (904 cm$^{-1}$ in ground state). It is interesting to note that in replacing H by F in $HCF_3$ to form $CF_4$ the $a_1(F)$ orbital fuses with the $e(CF_3)$ to form the $t_2(CF_4)$ valence orbital and the $a_1(CH)$ orbital fuses with the $e'(F_3)$ to give the $t_2(F_4)$ orbital. In the other halides $a_1(CH)$ fuses with $e(CX_3)$ to give the valence $t_2(CX_4)$. The $e''$ of $HCF_3$ at 17.2 eV moves to 18.50 eV to form $e(F_4)$ in $CF_4$. The $e'(F_3)$ of $HCF_3$ at 16.16 eV fuses with $a_1(CH)$ to give the $t_2(F_4)$ of $CF_4$ at 17.47 eV and $a_2(F_3)$ at 15.50 eV accepts the incoming e(F) at 17.42 eV to form $t_1$ at 16.32 eV.

The analysis of the orbital structure of the fluoromethanes given above is based entirely on empirical grounds. It is satisfying that it is in very good agreement with the results of recent calculations which were subsequently communicated to us by C. R. Brundle and D. Neumann.

## *The chloromethanes*

### *Methyl chloride*

The inner orbitals are clearly identifiable as $a_1(2sC)$ at 21.5 eV (max.), $e(CH_3)$ showing J.T. splitting at (14.8 to 16.5 eV), and $a_1(CCl)$ at 14.42 eV (max.). No vibrational structure is observed in any of these bands in agreement with the appearance of $CH_3^+$ at 13.87 eV in mass photoionization spectroscopic studies (Krauss *et al.* 1968). The non-bonding e(Cl) orbitals corresponding to the $^2\Pi_{\frac{3}{2},\frac{1}{2}}$ states of HCl are however affected by some interaction with the $e(CH_3)$ states. This no doubt occurs through the overlap of the higher Rydberg states approaching the e(Cl) ionization limit with the lower ones of those going to the $e(CH_3)$ ionization. While the first $^2E_{\frac{3}{2}}$ state at 11.28 eV does not seem to be affected and appears as a single strong peak, the second $^2E_{\frac{1}{2}}$ shows a vibrational pattern of $\nu_2(a_1)$ ($CH_3$ deformation) with a value of 1000 cm$^{-1}$ as compared with 1355 cm$^{-1}$ in the ground state. Weaker peaks accompany the main peaks at separations of 500 cm$^{-1}$ from them. They probably correspond to $\nu_3(a_1)$ (CCl).

### *Methylene chloride*

The $a_1$(2s, C) band of this molecule has a broad maximum around 20.3 eV. The bonding ($p^6$) orbitals are split in the manner characteristic of methylene halides into three distinct orbitals giving bands with maxima at 16.77, 15.94 and 15.30 eV corresponding to the orbitals $b_1(CH_2)$, $a_1(H_2CCl_2)$ and $b_2(CCl_2)$ respectively. These bands do not exhibit vibrational structure indicating that the ionized states have very short life times. The states arising from ionization of the non-bonding Cl electrons, namely, $b_2$, $a_2$, $b_1$ and $a_1$ in increasing order of overlap, are affected by Rydberg interactions with electrons in bonding orbitals as discussed for methyl chloride. The relevant bands occur in the range 11.2 to 12.5 eV. The outermost of these shows a vibrational progression of three peaks at 11.32, 11.40 and 11.48 eV. Their separation of about 640 $cm^{-1}$ probably corresponds to $\nu_1(a_1)$ $CCl_2$ stretching vibrations (700 $cm^{-1}$ in the ground state) as might be expected from the ionization of the $1b_2(CCl_2)$ orbital. A broad tail to this band extending from 11.5 to 11.8 eV probably accounts for the $a_2$ orbital. The peak at 12.2 eV may well be interpreted as $2b_1$ and the following tail as $2a_1$. Substitution of fluorine for hydrogen did not help to elucidate this system.

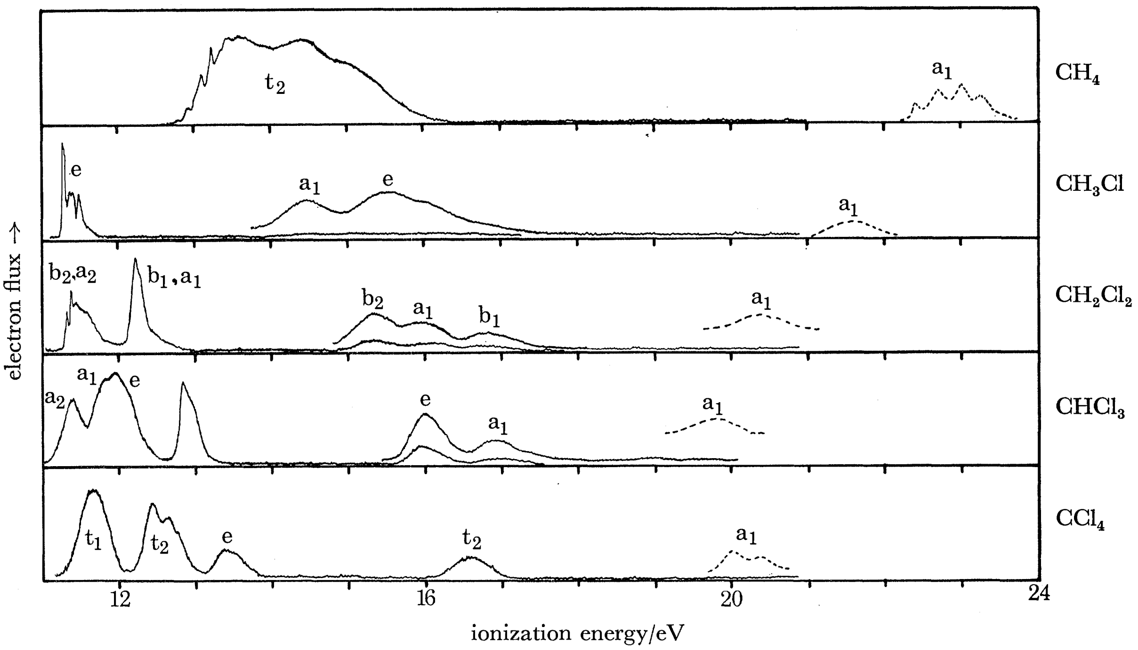

FIGURE 4. Photoelectron spectra of the chloromethanes.

TABLE 4. IONIZATION ENERGIES OF THE CHLOROMETHANES (eV)

| | |
|---|---|
| $CH_3Cl$ | 21.5 $a_1$; 15.40 e; 14.42 $a_1$; 11.30, 11.32 e |
| $CH_2Cl_2$ | 20.3 $a_1$; 16.77 $b_1$; 15.94 $a_1$; 15.30 $b_2$; 12.22 $a_1+b_1$; 11.40 $b_2+a_2$ |
| $CHCl_3$ | 19.8 $a_1$; 16.96 $a_1$; 15.99 e′; 12.85 e″; 12.01 e′; 11.91 $a_1$; 11.48 $a_2$ |
| $CCl_4$ | 20.0 $a_1$; 16.58 $t_2$; 13.50, 13.37 e; 12.78, 12.65, 12.44 $t_2$; 11.69 $t_1$. |

### *Chloroform*

The inner orbitals of chloroform, namely $1a_1$(2s, C), $2a_1$(CH) and $e(CCl_3)$ are readily identified as corresponding to structureless bands with maxima at 19.8, 17.0 and 16.0 eV respectively. The orbitals from the non-bonding $Cl_3$ electrons e″, e′, $a_1$ and $a_2$ are assigned by their intensities to peaks at 12.85, 12.01, 11.91 and 11.48 eV respectively. The only difficult assignment was that of $a_1$ which is a small hump on the low energy side of e′. However, on substituting a fluorine for the H atom this band is drawn over in $FCCl_3$ on to the high energy side of the system by virtue of its $a_1$ symmetry. Four bands are then clearly seen with the intensities expected from their degeneracies and in the inner-to-outer order $a_1$, e″, e′, $a_2$.

### *Carbon tetrachloride*

The inner orbitals $a_1$(2s, C) and $t_2$(CCl) are identified as bands with maxima at 20.0 and 16.58 eV. Of the non-bonding orbitals the band at 13.4 eV is clearly e because of its lower intensity and J.T. shape. The next with its peak at 12.44 eV is identified as $t_2$ for many reasons. It is slightly split having subsidiary peaks at 12.65 and 12.78 eV which cannot be of vibrational origin. Since theory shows that splitting is greater for $t_2$ than $t_1$ the sharper peak at 11.69 eV is accordingly assigned to $t_1$. The above assignments fit in with the general correlation scheme for the orbitals of the chloromethanes.

## *The iodomethanes*

### *Methyl iodide*

The spectrum of methyl iodide shows the inner orbitals $a_1$(2s, C), e($CH_3$) and $a_1$(CI) as structureless bands having maxima at 19.6, 15.2/14.4 and 12.5 eV respectively, the e($CH_3$) band being easily recognized by its J.T. contour and its breadth. The non-bonding I electrons appear as the sharp peaks at 9.54 and 10.16 eV agreeing exactly with the spectroscopically determined ionization potentials of the $^2E_{\frac{3}{2}}$ and $^2E_{\frac{1}{2}}$ states (Price 1936). The weak accompanying vibrational peaks have separations of 1260 $cm^{-1}$ and undoubtedly correspond to the $\nu_2(a_1)CH_3$ deformation vibration almost unchanged from its value of 1251 $cm^{-1}$ in the neutral molecule. Extremely weak peaks at 480 and 750 $cm^{-1}$ separations similarly correspond to the CI vibrations $\nu_3(a_1)$ and $\nu_6(e)$ which have ground state values of 533 and 880 $cm^{-1}$ respectively.

### *Methylene iodide*

The inner orbitals $a_1$(2s, C), $b_1(CH_2)$, $a_1(I_2CH_2)$ and $b_2(CI_2)$ of methylene iodide appear as structureless bands with maxima at 19.5, 15.5, 13.7 and 12.8 eV respectively. The non-bonding orbitals $a_1$, $b_1$, $a_2$ and $b_2$ are identified with the relatively sharp bands of roughly equal areas peaking at 10.56, 10.21, 9.76 and 9.46 eV. It is possible that part of the breadth of $2b_2$ is due to some interaction with $1b_2$. Indications of vibrational structure of about 160 $cm^{-1}$ interval possibly due to $CI_2$ vibrations accompanies all the bands.

A most important feature arises from the comparison of the results of the vacuum ultraviolet absorption spectra of $CH_2I_2$ with its photoelectron spectrum. Whereas good Rydberg series are obtained converging on $(2a_1)^{-1}$ and $(2b_1)^{-1}$ at 10.21 and 10.56 eV respectively (W. C. Price & Y. Tanaka, unpublished work) no such series are found for the $2a_2$ (9.76 eV) and $2b_2$(9.46 eV) orbitals. A similar situation occurs in the u.v. spectra of $O_2$ and NO where no Rydberg series have yet been found going to the ground states $O_2^+$ and $NO^+$ and a further example of this occurs for several of the orbitals of $SF_6$ which are discussed later. Electrons in such orbitals acquire their oscillator strengths through autoionizing–dissociative processes which occur in the ionization continuum and can thus be seen by photoelectron spectroscopy but not as Rydberg bands in optical spectroscopy. The explanation appears to be that if strong autoionization occurs just above the ionization threshold, oscillator strength is stolen from the high Rydberg bands by the autoionization process. The breadth of the two lowest i.p. bands in the photoelectron spectrum of $CH_2I_2$ indicates that they are both affected in this way.

Unfortunately it has not been possible to complete the iodomethane series by obtaining the spectra of $HCI_3$ and $CI_4$ because of the low volatility of these compounds.

We have also obtained the spectra of the chlorides of silicon, germanium, titanium, tin and lead and the fluorides of silicon and germanium but as these are being reported by Green *et al.* (this volume) with those interpretation we agree, we now pass on to the halides of the group V elements.

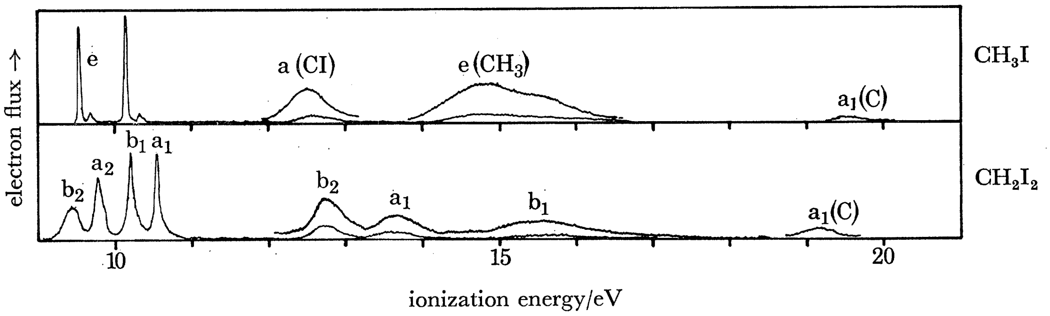

FIGURE 5. Photoelectron spectra of methyl and methylene iodides.

TABLE 5. IONIZATION ENERGIES OF THE IODOMETHANES (eV)

| | |
|---|---|
| $CH_3I$ | 19.6 $a_1$; 14.80 e; 12.50 $a_1$; 10.16, 9.54 e |
| $CH_2I_2$ | 19.5 $a_1$; 15.46 $b_1$; 13.67 $a_1$; 12.75 $b_2$; 10.56 $a_1$; 10.21 $b_1$; 9.76 $a_2$; 9.46 $b_2$ |

## THE TRIFLUORIDES AND TRICHLORIDES OF NITROGEN, PHOSPHOROUS AND ARSENIC

The spectra of these fluorides are given along with those of boron trifluoride and fluoroform in figure 6. They are plotted together in this way in order to trace the movement of the orbitals as more electrons are put into the system. The two outer electrons which these molecules have, in addition to those possessed by boron trifluoride, go into an outer $3a_1$ orbital corresponding to the bonding CH orbital in fluoroform (max. 14.8 eV) and to non-bonding orbitals in $NF_3$, $PF_3$ and $AsF_3$ giving bands with maxima at 13.75, 12.25 and 13.0 eV respectively. The increase in the ionization potentials of these orbitals in going from $PF_3$ to $AsF_3$ is to be associated with the increased polarizability of the heavier atom which will tend to stabilize the ion. The only anomoly in the relative order of the orbitals in this diagram is the inverted order of $2e'$ and $a_2$ in fluoroform. From considerations of overlap $a_2$ is expected to lie above $2e'$. However, in all other trifluorides it appears that $1e'$ (valence) repels $2e'$ so that this orbital lies above $a_2$. The order of these orbitals is reversed in the trichlorides (see below) and accords with that expected from overlap.

The spectra of the corresponding trichlorides is given in figure 7. There is little doubt about the $3a_1$ orbital being associated with the maxima of the first bands at 10.7 eV for $NCl_3$, 10.52 eV for $PCl_3$ and 10.84 eV for $AsCl_3$. The breadth of these bands both in the fluorides and the chlorides indicates that there is a considerable increase in the apical angle on ionization. In the case of $PF_3$ and $PCl_3$ the band envelopes obtained for the first Rydberg bands of these molecules are centred at 1300 and 1500 Å respectively (Humphries, Walsh & Worsop 1963). They have comparable half-widths of about 0.5 eV. The corresponding term values are also similar, namely 2.7 eV for $PF_3$ and 2.24 eV for $PCl_3$, their values suggesting $3p \rightarrow 4s$ excitation for these bands. The vibrational structure indicated in the vacuum ultraviolet spectra is also

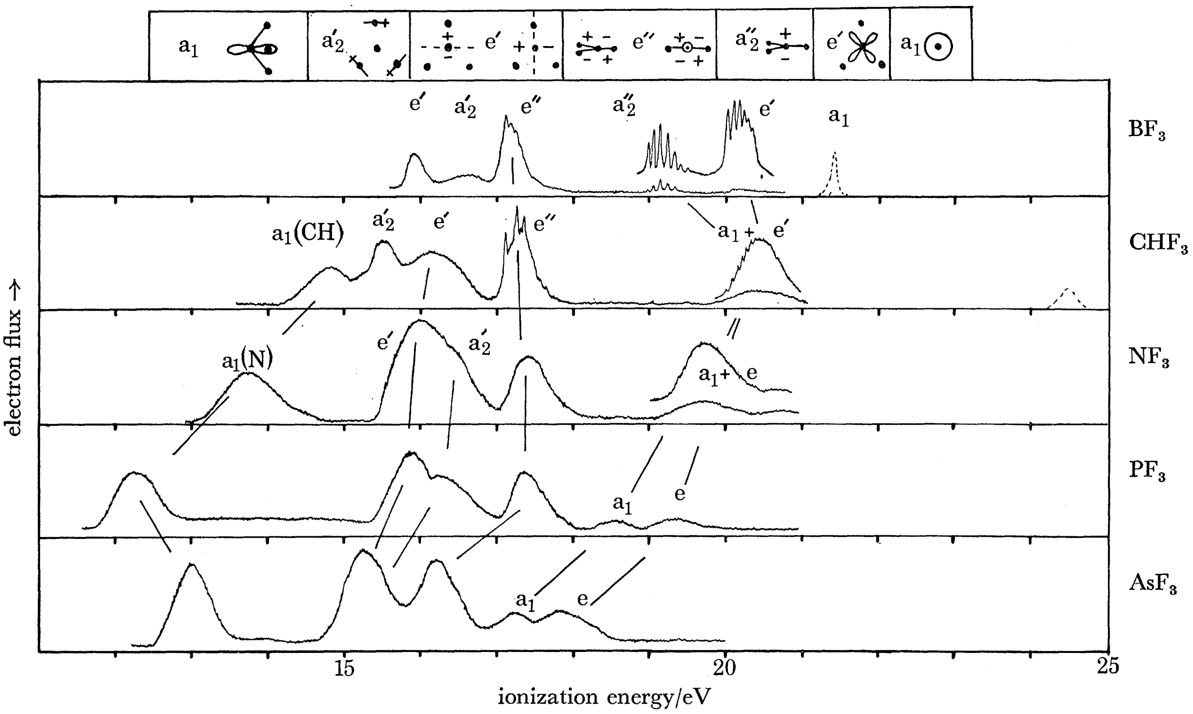

FIGURE 6. Photoelectron spectra of the trifluorides of B, CH, N, P and As.

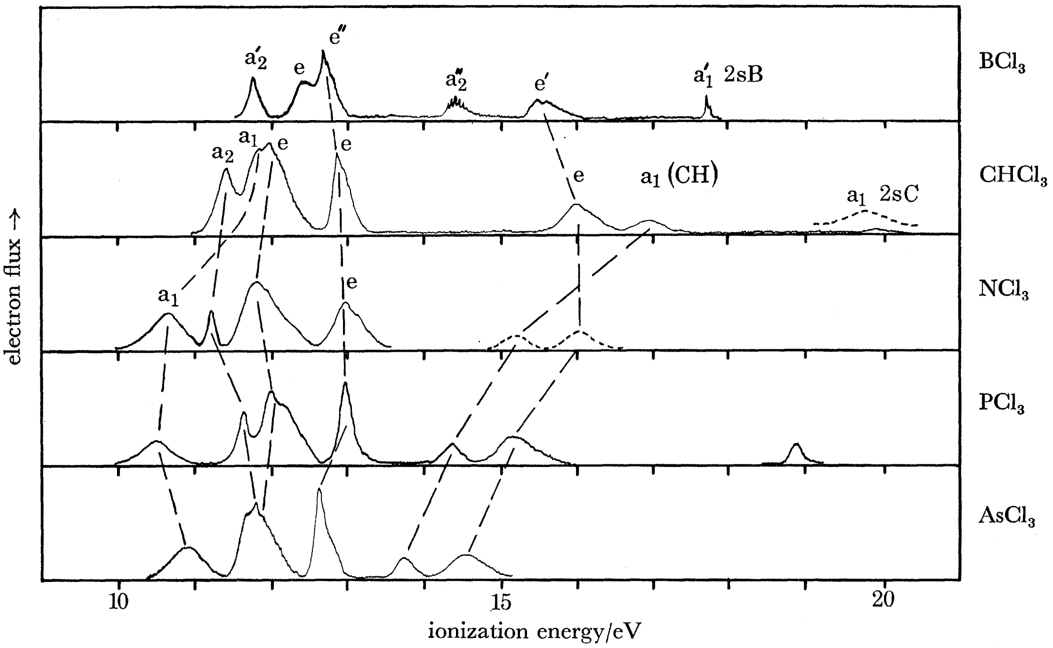

FIGURE 7. Photoelectron spectra of the trichlorides of B, CH, N, P and As.

present in our higher resolution spectra though not indicated in figures 6 and 7. It corresponds to frequencies of about 500 cm$^{-1}$ for the fluorides and 250 cm$^{-1}$ for the chlorides, these values probably corresponding to the $AX_3$ symmetrical bending mode.

A very interesting feature of the chlorides is the way the $a_2$ orbital can be picked out in all the spectra as a sharp narrow band in conformity with the contour to be expected for the small overlap of an orbital with many nodal surfaces. With the possible exception of $BCl_3$, it is clear that $a_2$ lies above 2e′ the order of these two orbitals being reversed from that in the triflorides, where except for fluoroform, 2e′ appears to have a lower ionization energy than $a_2$. Another interesting feature is the movement of the $2a_1$ orbital in this series which is indicated in figure 7.

Table 6. Ionization energies of the trifluorides of N, P and As (eV)

| | | | | | | |
|---|---|---|---|---|---|---|
| $NF_3$ | 19.73 $a_1$; | 17.40 e; | 15.95 e+$a_2$; | 13.73 $a_1$ | | |
| $PF_3$ | 19.31 e; | 18.51 $a_1$; | 17.35 e; | 16.29 $a_2$; | 15.89 e; | 12.28 $a_1$ |
| $AsF_3$ | 17.82 e; | 17.22 $a_1$; | 16.21 e; | 15.24 e+$a_2$; | 13.00 $a_1$ | |

Table 7. Ionization energies of the trihalides of P and As (eV)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $PCl_3$ | 18.85 $a_1$; | 15.22 e; | 14.24 $a_1$; | 12.97 e; | 12.01 $a_2$; | 11.71 e; | 10.52 $a_1$ |
| $AsCl_3$ | $a_1$; | 14.64 e; | 13.80 $a_1$; | 12.59 e; | 11.75 e+$a_2$; | 10.89 $a_1$ | |

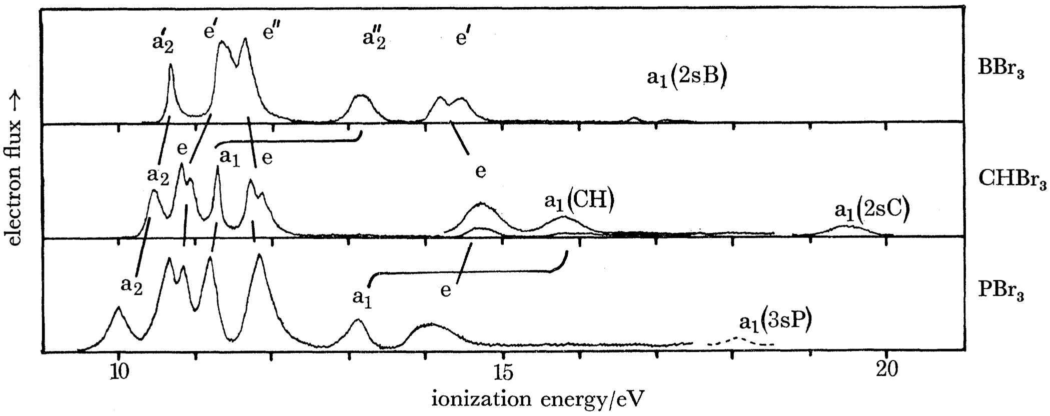

Figure 8. Photoelectron spectra of the tribromides of B, CH and P.

## The tribromides

The only simple tribromides of which we have obtained spectra are $BBr_3$, $HCBr_3$ and $PBr_3$. The orbital correlations are marked on the spectra (figure 8). It is interesting to see how similar are the spectra associated with the non-bonding $Br_3$ orbitals of $HCBr_3$ and $PBr_3$ (range 10 to 12 eV) and also how the CH bonding orbital in $HCBr_3$ becomes a P non-bonding orbital at lower energies in $PBr_3$ as in the corresponding chloride.

## The tri-iodides

The only tri-iodide for which we have been able to obtain a spectrum is $BI_3$ (see figure 1). Its resemblance to the bromides, particularly with respect to the splitting of the degenerate levels is so striking that it would not be difficult to make reliable predictions for the orbitals energies of iodoform and carbon tetraiodide from those found for the corresponding bromides.

## The hexafluorides of sulphur, selenium, tellurium and uranium

We conclude this article with a discussion of the photoelectron spectra of some hexafluorides (see figure 9). The photoelectron of $SF_6$ is given with the intensities as obtained with 304 Å irradiation since the spectrum obtained with 584 Å irradiation (shown by the broken line) is grossly distorted by autoionization. The spectra of $SeF_6$ and $TeF_6$ (obtained using 584 Å irradiation), are no doubt also somewhat distorted but that of $UF_6$ should not suffer seriously from autoionization since its innermost valence shell ionization energy falls below the irradiating photon energy of 21.2 eV if we disregard 2s, F combinations.

The orbital structure of $SF_6$ in the spd approximation and omitting 2s(F) orbitals is given by Santry & Segal (1967) (misprints corrected by D. W. Davies, private communication)

$$(2a_{1g})^2\ (1t_{2g})^6\ (2t_{1u})^6\ (1t_{2u})^6\ (2e_{1g})^6\ (1t_{1g})^6\ (3t_{1u})^6.$$

Schematic diagrams indicating the main characteristics of the orbitals are given in figure 9. The highest energy band in the spectrum of $SF_6$ is a sharp peak at 26.8 eV which no doubt corresponds to the $2a_{1g}$(3s, S) orbital. This value agrees with the limit of the Rydberg series of window resonances found by Codling (1966). The next maximum at 22.5 eV is broader and is assigned to ionization from the $1t_{2g}$ orbital. (*Note added in proof:* The order of $1t_{2g}$ and $2t_{1u}$ is difficult to establish with certainty. It appears now that $2t_{1u}$ is innermost since this assignment makes its separation from $2a_{1g}$ more comparable with that of corresponding orbitals in $CF_4$. The following text giving reasons for the alternative order has not been altered but figure 9 has been changed.) Codling (1966) reported progressions of absorption bands in the region 600 to 550 Å without giving any detailed analysis of them. In view of the ionization at 22.5 eV we have given further consideration to these bands from which it has become clear that they consist of Rydberg systems each containing 4 to 5 members with a vibrational interval of about 560 cm$^{-1}$. If the first bands of the first two progressions are inserted into a Rydberg formula, an ionization potential of 22.46 is obtained which is in good agreement with the photoelectron value. The first system given by Codling probably corresponds to a transition of the type $2p\sigma_g(F) \rightarrow 4p\sigma_u$ or $4p\pi_u$ and an earlier member is therefore predicted to be around 18.5 eV. This could well be the strong feature at 17.5 eV which shows up in the low-energy electron scattering work of Simpson, Kuyatt & Mielczarek (1966) in which energy loss correlates with optical oscillator strength. A much weaker peak which they observe around 21 eV clearly corresponds to the first Codling system. The Rydberg states are of $(na_{2u})\ (^2T_{2g}) = {}^1T_{1u}$ symmetry and transitions to them from the $t_{2g}$ orbital of the $^1A_1$ ground state are expected to be strong since this is the translational symmetry. The term value is also close to that of 3s(F), namely 4.5 eV, which confirms the fact the orbital is mainly built from 2p(F) orbitals.

Although we do not resolve the vibrational structure of the 22.5 eV band it is clear that the ionized state should have a vibrational pattern similar to that of the Rydberg systems which converge on to it which have an overall width of about 0.2 eV approximately equal to that of the photoelectron band. Under higher resolution than we can at present achieve there is thus not doubt that the p.e. band should be represented by a *simple* progression of vibrational bands with intervals of 560 cm$^{-1}$ which correspond to the $\nu_1(a_{1g})$ symmetrical breathing vibration reduced from its value of 769.4 cm$^{-1}$ in the ground state. The absence of any evidence of J.T. splitting in the Rydberg bands is strong confirmation of the assignment of the orbital to $t_{2g}$ which because it has no angular momentum can cause neither J.T. or s.o. splitting in the molecular ion produced when this orbital is ionized.

The next band in the photoelectron spectrum occurs with a maximum at 19.7 eV and exhibits a rather broad vibrational pattern (*ca.* 1 eV wide) indicating the bonding nature of the orbital. The vibrational intervals are of the order of 0.1 eV but appear to change in a way which suggests J.T. splitting as is also suggested from the somewhat unsymmetrical nature of the band contour. We assign this band to the $2t_{1u}$ orbital mainly because of the strength of the Rydberg band at 15.5 to 16.5 eV with which it can be associated and which is observed in the energy loss spectrum. The term value of about 3.7 eV for this Rydberg band indicates that it is associated with a 3p(S)–4s(S) transition for which the term value of the upper state is about 3.5 eV thus confirming the nature of the orbital suggested in figure 9. The Rydberg state being $(a_{1g})\ (^2T_{1u}) = {}^1T_{1u}$ has the symmetry necessary for it to be strong in absorption.

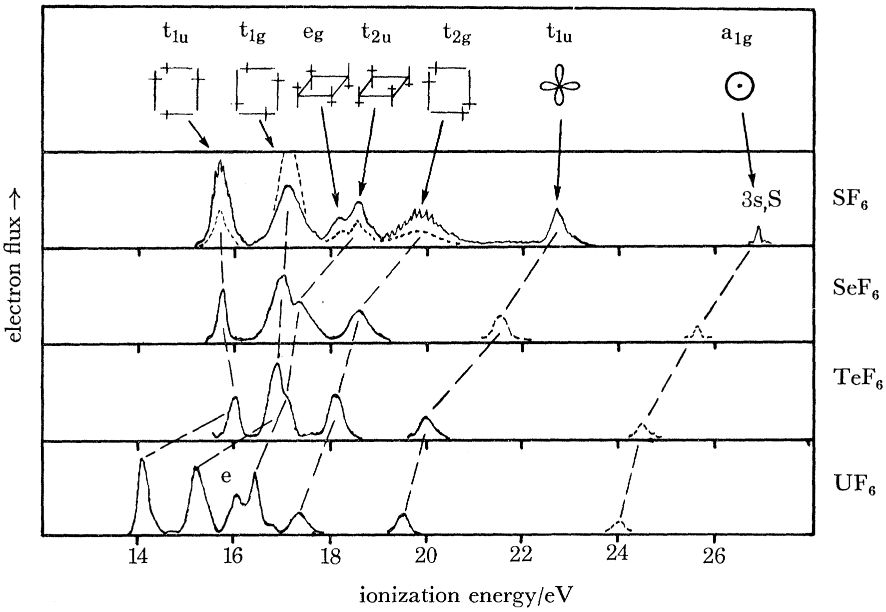

FIGURE 9. Photoelectron spectra of the hexafluorides of S, Se, Te and U.

TABLE 8. IONIZATION ENERGIES OF THE HEXAFLUORIDES OF S AND U (eV)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $SF_6$ | 26.8 $a_1$; | 22.5 $t_{2g}$; | 19.68 $t_{1u}$; | 18.71 $t_{2u}$; | 18.40 $e_{1g}$; | 16.96 $t_{1g}$; | 15.69 $t_{1u}$ |
| $UF_6$ | 23.5? $a_1$; | 19.46 $t_{2g}$; | 17.42 $t_{1u}$; | 16.52 $t_{2u}$; | 16.02 $e_{1g}$; | 15.25 $t_{1g}$; | 14.14 $t_{1u}$ |

The remaining four bands must be associated with orbitals built from 2p(F) combinations. Two of these are readily assigned. That with its peak at 15.69 eV corresponds to ionization from the $3t_{1u}$ orbital since it is to be associated with the strong Rydberg band in the vacuum ultraviolet absorption at 11.7 eV (Nostrand & Duncan 1954) and the intense peak at 11.6 eV in the energy loss spectrum (Simpson *et al.* 1966). The term value of *ca.* 4 eV supports a 2p(F)–3s(F) type transition and a classification of the Rydberg state as $(a_{1g})\ (^2T_{1u}) = {}^1T_{1u}$. This Rydberg band is the only remaining strong band and must therefore be associated with the last unassigned $t_{1u}$ orbital. Some diffuse vibrational structure is present in this system indicating that the lifetime of the ionized state is not inappreciable which is also shown by the relatively low efficiencies of $SF_5^+$ production at the ionization threshold in the mass photometric studies of Dibeler & Walker (1966).

The other band for which the assignment is obvious is that occurring at 18.4 eV. On account of its intensity which is approximately two-thirds of that in the adjacent triply degenerate bands it clearly is of $e_{1g}$ character. The intensity ratio is best seen in the analogous band in $UF_6$. Its Rydberg transition probably corresponds to the weak u.v. absorption at 14.35 eV.

This leaves only the $t_{1g}$ and the $t_{2u}$ orbitals to be assigned and they seem to fit in well with the order given by Santry & Segal (1967). As can be seen from the orbital diagram in figure 9, the atomic orbitals overlap least for $t_{2u}$ which should therefore by a very non-bonding electron. The sharpness of the band at 18.71 eV fits in with assigning $t_{2u}$ to this orbital. Its analogue in $UF_6$ is extremely sharp and close to the ionization potential of atomic fluorine. No Rydberg orbitals exist to which strongly allowed transitions are possible and the only u.v. absorption/electron loss peak with which it can be associated appears to be the very weak peak at 15 eV. This leaves the peak at 11.96 eV to be assigned to $1t_{1g}$ with a possible associated weak Rydberg state at 13.3 eV. This (16.96 eV) band has a remarkably high intensity in its spectrum taken with 584 Å irradiation (also on 736 Å neon irradiation) where it is several times as strong as the bands belonging to other orbitals. However, its intensity becomes comparable with the other bands under 304 Å irradiation. Thus the electron has considerable oscillator strength over a range of several electronvolts above its ionization threshold. The mass photometric studies of Dibeler & Walker (1966) show that this is associated with distortions of the molecular ion resulting in $SF_5^+$ production. In fact an appreciable part of the background in the absorption spectrum above 16 eV must be associated with processes of this nature involving electrons in orbitals for which the oscillator strength of the Rydberg bands is depleted by autoionization processes above the ionization threshold. It is interesting to note that in $SF_6$ the lowest i.p. has little autoionization as judged by $SF_5^+$ production and is associated with a strong first Rydberg band. The second i.p., on the other hand, is associated with enormously strong autoionization just above the threshold and has a correspondingly weak Rydberg absorption.

Spectra of the hexafluorides of Se, Te and U are included in figure 9 in which the correlation of the orbitals is suggested by dashed lines.

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