Bonding Studies of Boron and the Group 3—5 Elements. Part XV.[1] He(I) Photoelectron Spectra of Monomeric Group 3 Trihalide, Trimethyl, and Mixed Halogenomethyl Species

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The He(I) photoelectron (p.e.) spectra of *monomeric* Group 3 metal trihalide, trimethyl, and mixed halogenomethyl species, MX_3, $MeMX_2$, Me_2MX, and MMe_3 (X = Cl, Br, or I; M = B, Al, Ga, or In), are analysed. There is close similarity between the p.e. spectra of the heavier Group 3 metal trihalides and those of their boron congeners and this forms the basis for assignments. Aspects of earlier interpretations of the spectra are reassessed in the light of the data now available for the various series. For BMe_3 the BC *e'* orbital is split by a Jahn–Teller effect in the excited state; C–H non-bonding interactions decrease as B is replaced by a heavier metal in MMe_3 and the splitting is obscured in these molecules. For MX_3 the highest observed ionisation potential (i.p.) is the substantially central-atom a_1 which decreases with increasing mass of M. The next in energy is the *e'* which shows an essentially constant and high spin–orbit splitting and thus has little central-atom M character. This is followed by the a_2'' which may give some measure of $X \rightarrow M$ π bonding (greatest for B). It is proposed that the baricentre of the first two i.p.s for each of these molecules provides a measure of their relative Lewis acidity: Al > B ∼ Ga > In.

THE problem of bonding in boron compounds has received considerable attention in this laboratory. For example, first ionisation potentials (i.p.s) were measured by electron impact for a series of trigonal compounds.[2] Later this was extended to a study of the He(I) photoelectron (p.e.) spectra of the series BX_3 and BX_2Y (X, Y = F, Cl, Br, I, NMe_2, or Me).[3] In this paper we report the He(I) p.e. spectra of the monomeric aluminium, gallium, and indium trihalides; assignments are based on analogy with the boron trihalides. He(I) p.e. spectra of the monomeric Ga and In trihalides have recently been published,[4] but our spectra are at higher resolution. Additionally, we present the p.e. spectra of the monomeric trimethyl compounds of B, Al, and Ga, and spectra of some of the mixed B and Al halides Me_nMX_{3-n}, and offer assignments for the highest-occupied molecular orbitals (m.o.s). The spectrum of BMe_3 has recently been described.[5]

At ambient temperature and pressure the gaseous trihalides of the Group 3 elements tend to be dimeric except for the monomeric trigonal boron species BX_3 of D_{3h} symmetry. Likewise, BMe_3 and the mixed halides Me_nBX_{3-n} (n = 1 or 2) are monomeric, planar, and have respectively D_{3h} or C_{2v} symmetry. Numerous structural studies have been reported in support of these propositions,[6] and indicate that the bonding may be described in terms of sp^2 hybridisation at boron and the possibility of $X \rightarrow B$ p_π–p_π bonding for the halides. Analysis of first i.p. data by m.o. theory suggested that, contrary to earlier views, such π bonding decreases in the sequence I > Br > Cl > F and that antibonding interactions between p orbitals on the ligand atoms are significant.[2] The heavier Group 3 trihalides and Al_2Me_6 are dimeric under these conditions, but do exist as monomers at higher temperatures. In a preliminary publication we reported the variable-temperature p.e. spectra of $[\{MX_3\}_m]$ (M = Al or Ga; X = Cl, Br, or I; m = 1 or 2) and established the conditions for obtaining the monomeric species.[7] The most characteristic feature of the chemistry of these monomeric Group 3 compounds is their Lewis acidity. There have been various attempts to measure relative acidities. For example, with respect to ethyl acetate as reference base, acidities decrease in the sequences (*i*) $BBr_3 > BCl_3 \gg BF_3$, (*ii*) $BCl_3 > AlCl_3 > GaCl_3 > InCl_3$, (*iii*) $MBr_3 > MCl_3$, and (*iv*) $BCl_3 > MeBCl_2 > Me_2BCl > Me_3B$.[8] However, using the more bulky amine acceptors the order is often Al > B ∼ Ga > In. In so far as these data may be related to the ground-state electronic properties of the acceptors, the most relevant parameter is the molecular electron affinity which of course is not accessible from p.e. spectra.

EXPERIMENTAL

P.e. spectra were recorded on a Perkin-Elmer PS16 photoelectron spectrometer, fitted with a modified heated inlet system. Spectra were always measured at least in triplicate to establish the accuracy of peak positions. Spectra of AlI_3, $GaBr_3$, GaI_3, and the indium halides were obtained by vaporising the compounds internally. Other compounds were introduced into the spectrometer as vapours by use of a vacuum line. Solid samples were sublimed into a tube fitted with a Rotaflow tap, and the tube sealed off. Where compounds showed a tendency to dimerise, spectra of the pure monomers were recorded with the temperature of the lamp kept high. By alternately lowering and raising the temperature of the lamp it was possible reversibly to obtain monomer and dimer spectra.

P.e. spectra are shown in Figures 1—7 and principal vertical i.p.s are listed with assignments, where this is possible, in Tables 1 and 2. The i.p.s of BX_3 (X = Cl, Br, or I) [3] are included for comparison. The resolution of the instrument was badly affected by the methylaluminium

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[1] Part XIV, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *J.C.S. Dalton*, 1975, 1214.

[2] Part II, M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, and A. Tweedale, *J. Chem. Soc.* (*A*), 1968, 3105; Part III, M. F. Lappert, M. R. Litzow, J. B. Pedley, P. N. K. Riley, T. R. Spalding, and A. Tweedale, *ibid.*, 1970, 2320.

[3] Part IX, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Discuss. Faraday Soc.*, 1972, **54**, 70.

[4] J. L. Dehmer, J. Berkowitz, L. C. Cusachs, and H. S. Aldrich, *J. Chem. Phys.*, 1974, **61**, 594.

[5] W. Fuss and H. Bock, *J. Chem. Phys.*, 1974, **61**, 1613.

[6] *Cf.* 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. S. Nyholm, and A. F. Trotman-Dickenson, Pergamon, 1973, vol. 1.

[7] Part XII, M. F. Lappert, J. B. Pedley, G. J. Sharp, and N. P. C. Westwood, *J. Electron Spectroscopy*, 1974, **3**, 237.

[8] M. F. Lappert, *J. Chem. Soc.*, 1962, 542.

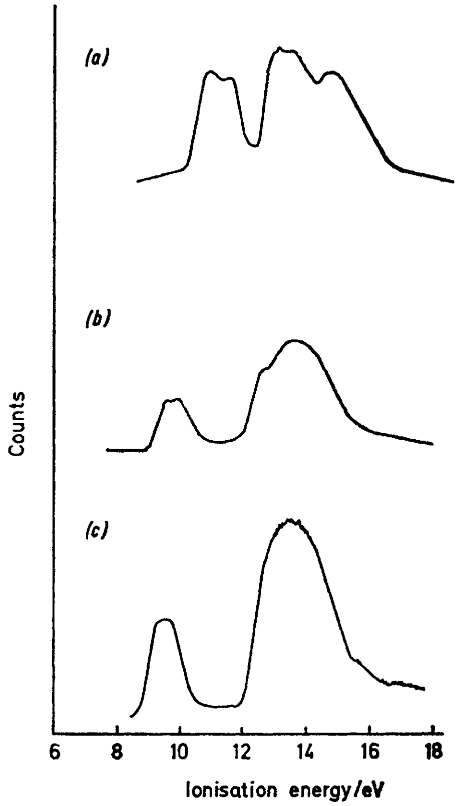

FIGURE 1 He(I) P.e. spectra of (a) BMe_3, (b) $AlMe_3$, and (c) $GaMe_3$

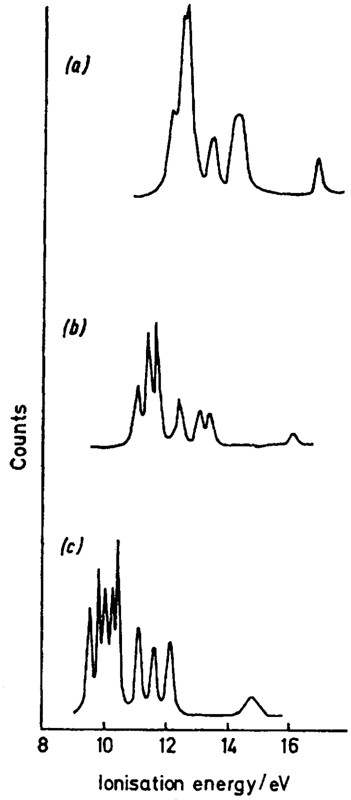

FIGURE 3 He(I) P.e. spectra of (a) $GaCl_3$, (b) $GaBr_3$, and (c) GaI_3

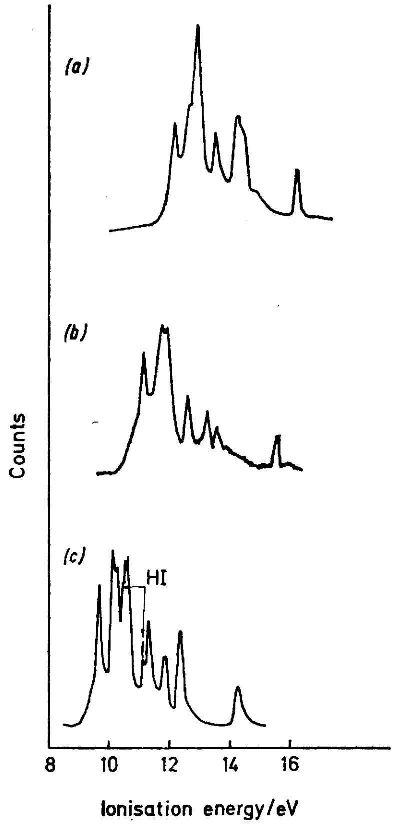

FIGURE 2 He(I) P.e. spectra of (a) $AlCl_3$, (b) $AlBr_3$, and (c) AlI_3

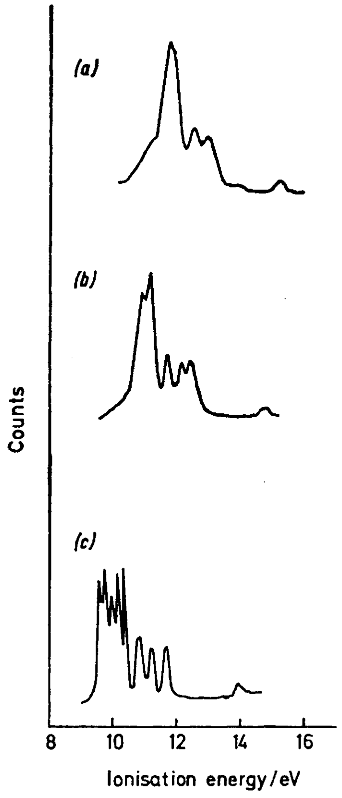

FIGURE 4 He(I) P.e. spectra of (a) $InCl_3$, (b) $InBr_3$, and (c) InI_3

halides, although a working resolution of 45 meV or better was achieved.*

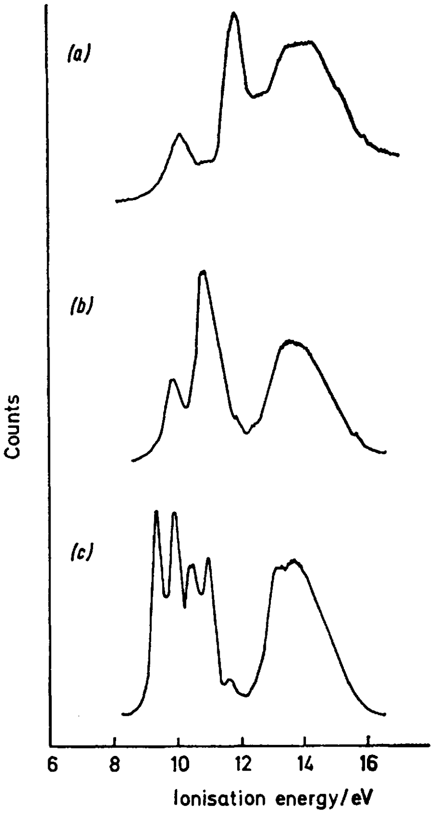

FIGURE 5 He(I) P.e. spectra of (*a*) [$AlClMe_2$], (*b*) [$AlBrMe_2$], and (*c*) [$AlIMe_2$]

Samples of BMe_3, $AlCl_3$, $AlBr_3$, $GaCl_3$, $GaBr_3$, and GaI_3 were obtained commercially. We are grateful for the following: $AlMe_3$, $GaMe_3$, and [Me_2AlI] (Dr. J. D. Smith); [Me_2AlCl] (Professor M. G. H. Wallbridge); Me_2BBr, Me_2BI, and $MeBBr_2$ (Dr. S. S. Krishnamurthy); and $InCl_3$, $InBr_3$, and InI_3 (Dr. M. J. S. Gynane). The following compounds were prepared by literature methods: AlI_3;[9] [Me_2AlBr], [$MeAlBr_2$], and [$MeAlI_2$].[10] All the compounds are air or water sensitive and were sublimed or distilled immediately prior to use. The purity of the compounds was checked by i.r. or n.m.r. spectroscopy.

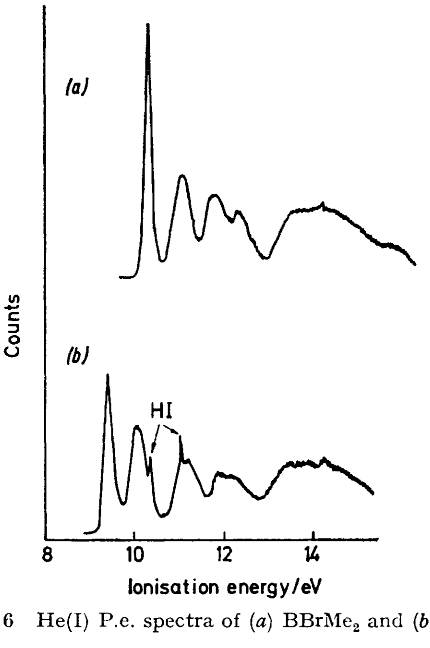

FIGURE 6 He(I) P.e. spectra of (*a*) $BBrMe_2$ and (*b*) $BIMe_2$

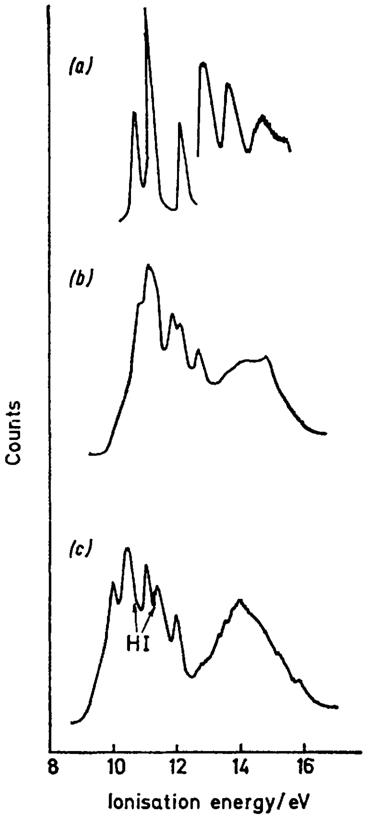

FIGURE 7 He(I) P.e. spectra of (*a*) BBr_2Me, (*b*) [$AlBr_2Me$], and (*c*) [AlI_2Me]

RESULTS

There are few physical data on the monomeric molecules AlX_3. The JANAF Thermochemical Tables [11] do, however, give sufficient results to calculate the relative concentration of monomer to dimer under given conditions and to calculate the energy of dimerisation. No data are available for the monomer–dimer equilibria in the compounds [Me_2AlX] or [$MeAlX_2$]. However, it is possible to calculate the percentage of monomer present at a given temperature and pressure for $AlCl_3$, $AlBr_3$, and $GaCl_3$ using published thermodynamic results,[11,12] and assuming a local pressure of 10^{-3} mmHg in the target-chamber area. The values obtained for the monomer : dimer ratio are shown in Table 3 for 298 (the temperature at which dimer spectra were recorded) and 600 K (the lower temperature limit for monomer spectra). The spectrum of AlI_3 was recorded at 120 °C; the ratio AlI_3: Al_2I_6 is given for this temperature. The data available for

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* 1 eV $\approx 1.60 \times 10^{-19}$ J, 1 mmHg $\approx 13.6 \times 9.8$ Pa.

[9] G. W. Watt and J. L. Hall, *Inorg. Synth.*, 1953, **4**, 117.

[10] A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, 1940, **5**, 106.

[11] JANAF Thermochemical Tables, 2nd edn., U.S. Government Printing Office, Washington, D.C., 1971.

[12] A. W. Laubengayer and F. B. Schirmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1578.

Table 1

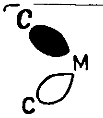
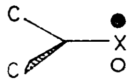
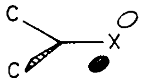
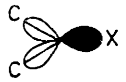
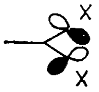
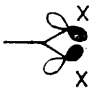
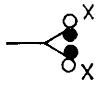
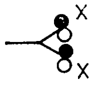
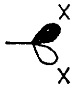
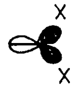
Experimental vertical i.p.s (eV) and assignments for monomeric Group 3 metal trihalides

MX_3	Assigned orbital								
	a_2'	e'		e''		a_2''	e'		a_1'
BCl_3 [a]	11.62	12.28		12.53		14.35	15.49		17.70
$AlCl_3$	12.01	12.47 [b]		12.73		13.33	14.04		15.97
$GaCl_3$	11.96	12.30		12.44		13.20	13.96		16.44
$InCl_3$	11.4 [b]	11.94		12.11		12.82	13.22		15.48
	a_2'	$e''(e_{\frac{1}{2}}, e_{\frac{3}{2}}^{*}), e'(e_{\frac{3}{2}})$		$e'(e_{\frac{5}{2}})$		a_2''	$e'(e_{\frac{5}{2}})$	$e'(e_{\frac{3}{2}})$	a_1'
BBr_3 [a]	10.65	11.30		11.71		13.18	14.20	14.46	16.74
$AlBr_3$	10.91	11.53		11.74		12.37	13.01	13.32	15.23
$GaBr_3$	10.94	11.25		11.52		12.22	12.88	13.19	15.70
$InBr_3$	10.3 [b]	11.13		11.40		11.93	12.43	12.69	14.93
	a_2'	$e'(e_{\frac{1}{2}})$	$e''(e_{\frac{3}{2}})$	$e'(e_{\frac{1}{2}})$	$e'(e_{\frac{5}{2}})$	a_2''	$e'(e_{\frac{5}{2}})$	$e'(e_{\frac{3}{2}})$	a_1'
BI_3 [a]	9.36	9.92	10.10	10.36	10.48	11.74	12.46	12.96	15.39
AlI_3	9.66	10.05	10.18	10.46	10.56	11.24	11.79	12.27	14.10
GaI_3	9.51	9.78	9.97	10.22	10.37	11.00	11.51	11.99	14.57
InI_3 [b]	9.58	9.73	9.97	10.11	10.38	10.86	11.23	11.71	13.96

[a] From ref. 3. [b] Shoulders; estimated vertical i.p.s only.

Table 2

Experimental vertical i.p.s (eV) and assignments for alkyl Group 3 metal halides

Compound	Assigned orbital						
	 b_1	 b_2		 b_1		 a_1	
BMe_3	10.68, 11.24						
$BBrMe_2$	11.84	11.13		10.35		12.37	
$BIMe_2$	11.17	10.12		9.48		11.94	
$AlMe_3$	9.76						
$[AlClMe_2]$	10.25	⟵ 11.85 ⟶					
$[AlBrMe_2]$	9.90	⟵ 10.88 ⟶					
$[AlIMe_2]$	10.49	9.98		9.48		11.00	
	 b_1	 a_1	 a_2	 b_2	 a_1	 b_1	 a_1
BBr_2Me	10.61	⟵ 11.04 ⟶		12.00	12.71	13.48	
$[AlBr_2Me]$	10.65	⟵ 10.96 ⟶		11.63	11.87	12.42	
$[AlI_2Me]$	9.73	⟵ 10.22 ⟶		10.77	11.15	11.69	(*ca.* 12.6)

$GaCl_3$ are incomplete, and no data were found for the indium halides.

Since the compounds $[\{Me_2AlX\}_2]$ have been shown by electron diffraction to be halogen bridged,[13] it is likely that the ratio of monomer to dimer under given conditions is similar to that for the free halide, AlX_3. Thus we conclude that our spectra of $[Me_2AlX]$ contain almost no dimer, since they were recorded under similar conditions to those of the corresponding AlX_3.

Table 3

Monomer : dimer ratios for approximate experimental conditions [a] (using pressure = 10^{-3} mmHg)[b]

Ratio \ T/K	300	400	572	600
$AlCl_3 : Al_2Cl_6$	5×10^{-6}			6.52×10^2
$AlBr_3 : Al_2Br_6$	14×10^{-6}			1.47×10^3
$AlI_3 : Al_2I_6$		8		
$GaCl_3 : Ga_2Cl_6$			4.8×10^4	

[a] Calculated from refs. 11 and 12. [b] Suggested by H. Lempka, Perkin-Elmer, Ltd.

DISCUSSION

The spectra of the trimethyl compounds are considered first. The spectra are shown in Figure 1 and i.p.s are listed in Table 2. The spectrum of BMe_3 has been published previously;[5] we agree with the published results and also consider that the first band corresponds to ionisation from the e' orbital, which is primarily boron–carbon bonding in character. The splitting in this band is evidently due to a Jahn–Teller effect in the excited state. Consistent with this hypothesis, the p.e. spectra of $AlMe_3$ and $GaMe_3$ show a symmetric first band which thus probably corresponds to ionisation from a single orbital, *i.e.* there are no further ionisations in the region. Two further items of evidence support this conclusion. First, we recorded the p.e. spectrum of BMe_3 using either argon or neon discharges and the splitting was still observed. This essentially rules out autoionisation as

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[13] L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287.

a possible cause. Secondly, Murrell and Schmidt[14] observed a similar splitting in the corresponding band in the p.e. spectrum of the closely related molecule isobutane, Me_3CH. The mean i.p. in BMe_3, 10.96 eV, is considerably higher than in $AlMe_3$ (9.76) or $GaMe_3$ (9.76). This indicates that the orbital probably has an appreciable contribution from the p orbitals of the central atom, reflecting the considerably higher atomic i.p. of B compared with Al or Ga. A further notable feature of the spectra is that the cluster of i.p.s above 12 eV becomes increasingly featureless with increase in the size of the central atom. This behaviour may be ascribed to a decreasing through-space interaction between the C–H orbitals. This has been observed before in, for example, the Group 4 tetramethyl compounds;[15] the p.e. spectrum of neopentane shows two distinct symmetry-determined CH levels $1t_1$ and $1e$ which increasingly tend to coalesce for the heavier Group 4 tetramethyl compounds until in $PbMe_4$ a broad featureless band is observed.

No dimer was observed in the spectrum of $AlMe_3$, even with the lamp cold. This is in accordance with mass-spectrometric data,[16] which showed that at the low pressures in the target chamber, even at 30 °C, the species present was almost totally the monomer. Electron-diffraction data[17] have shown the monomeric $AlMe_3$ to have D_{3h} symmetry.

The p.e. spectra of the monomeric Group 3 trihalides will now be considered. The i.p.s are shown in Table 1, and the spectra of AlX_3, GaX_3, and InX_3 are illustrated in Figures 2, 3, and 4 respectively. There is some disparity between our results and those of Berkowitz and his co-workers,[4] especially for $GaCl_3$; this may perhaps be accounted for by the presence of a significant amount of dimer in the earlier work, which showed some ill-defined peaks. The p.e. spectra of AlX_3, GaX_3, and InX_3 bear a strong resemblance to those of the corresponding BX_3 molecules,[3] and this analogy forms the basis of our assignment.

In considering the complete series of compounds, a number of interesting points emerge. Calculations[3,18] indicate that the orbital of highest i.p., a_1', has a considerable amount of central atom s character, which is supported by the observation that for a given halide trends in the highest i.p. closely parallel the i.p.s of the outermost s-atomic orbital (B 15.2, Al 12.1, Ga 13.4, and In 12.5 eV). The orbital of next highest i.p. is the e', which for the bromides and iodides is split by spin–orbit coupling into the $E_{\frac{5}{2}}'$ and $E_{\frac{3}{2}}'$ states in the ion. It is noteworthy that the magnitude of splitting is fairly constant for each series, *ca.* 0.3 eV for the bromides and *ca.* 0.5 eV for the iodides; these values are very close to the atomic spin–orbit values, especially for the bromides. This indicates that the orbital, particularly for the bromides, has little central-atom character. The orbital of next-highest i.p. is the a_2'', which shows a large fall in i.p. from B to Al for all halides but then decreases more gradually to Ga and In. This orbital is substantially responsible for the π bonding in the molecules and the results may indicate that back donation into the central atom is most significant for boron.

As with the lower e' orbital, the splitting of the higher e' and e'' orbitals remains almost constant throughout the spectra of a particular halide. Recent calculations[19] on the spin–orbit-splitting pattern of the ionic states derived from these orbitals indicate that our previous assignments for BBr_3 and BI_3,[3] based on a simpler theory, should be revised. We accept the proposed reassignment. For BI_3 the E' state * of the positive ion is split by first-order spin–orbit coupling into $E_{\frac{5}{2}}'$ and $E_{\frac{3}{2}}'$; the $E_{\frac{3}{2}}'$ state, close in energy to E'', splits the latter (which cannot be split by first-order spin–orbit coupling in a D_{3h} environment) by a second-order spin–orbit interaction. The resulting order of the orbitals (in order of increasing i.p.) is $e_{\frac{3}{2}}\ (e') < e_{\frac{3}{2}}\ (e'') < e_{\frac{1}{2}}\ (e'') < e_{\frac{5}{2}}\ (e')$. For BI_3 this assignment gives good agreement between the observed and calculated splittings. (According to Price and his co-workers,[20] who neglected second-order splitting, an e'' orbital cannot be split by a Jahn–Teller effect in the D_{3h} point group, and so Berkowitz and his co-workers, following their model, were obliged to conclude[4] that the ground state of GaI_3 is pyramidal.) We consider that the explanation *via* a second-order spin-orbit interaction is satisfactory for all the iodides and obviates the necessity of introducing what would be a most surprising result chemically (*i.e.* a pyramidal ground state for a Group 3 MX_3 molecule). The observed splitting pattern is closely reproduced for all the iodides as would be expected for orbitals of predominantly halogen character.

In the case of the bromides, first-order splitting of the E' state causes the $E_{\frac{3}{2}}'$ component to become almost degenerate with the E'' state, which itself undergoes negligible splitting. Thus the E'' ($E_{\frac{3}{2}}$, $E_{\frac{1}{2}}$) and $E_{\frac{3}{2}}$ (e') states are nearly degenerate. This explanation accounts for the fact that only two bands are observed and in part for the relative intensities of the bands. Again it is noted that the splitting does not change greatly from B through to In, consistent with our assignment.

The highest-occupied orbital, a_2', has no central-atom character and is the antibonding combination of the in-plane halogen orbitals. It is tempting to infer information about π back donation into the central atom from

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* In accordance with convention, capital letters refer to states of the positive ion and lower case letters to molecular orbitals.

[14] J. N. Murrell and W. Schmidt, *J.C.S. Faraday II*, 1972, 1709.

[15] S. Evans, J. C. Green, P. J. Joachim, D. W. Turner, and J. P. Maier, *J.C.S. Faraday II*, 1972, 905; R. Boschi, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, *J. Organometallic Chem.*, 1973, **50**, 69.

[16] F. Glockling and R. G. Strafford, *J. Chem. Soc.* (*A*), 1971, 1761; D. B. Chambers, G. E. Coates, F. Glockling, and M. Weston, *ibid.*, 1969, 1712.

[17] A. Almenningen, S. Halvorsen, and A. Harland, *Acta Chem. Scand.*, 1971, **25**, 1937.

[18] Part XVI, M. F. Lappert, J. B. Pedley, G. J. Sharp, and M. F. Guest, *J.C.S. Faraday II*, 1975, in the press.

[19] R. Manne, K. Wittel, and B. S. Mohanty, *Mol. Phys.*, 1975, **29**, 485.

[20] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. Roy. Soc.*, 1970, **A268**, 59.

the i.p. of this orbital, since the i.p. will reflect the residual charge on the halogen atoms; however, it must be remembered that any change in i.p. is a composite of at least three factors, namely (*a*) a decreasing antibonding interaction between the lone pairs as the central atom becomes larger (causing higher i.p.), (*b*) increasing electropositivity with the heavier central atoms causing higher negative charge on the halogen and a lower i.p., and (*c*) π donation of halogen lone pairs into the adjacent central-atom orbital, causing higher positive charge on the halogen and thus a higher i.p. With uncertainty as to the relative weightings of these several factors, conclusions regarding back donation from the changes in i.p. of this orbital must be tentative. It is likely therefore that factors (*b*) and (*c*) are more important relative to (*a*) for Al and Ga than for B and In.

The preceding assignments and analyses of the spectra of the MX_3 and MMe_3 spectra form the basis for the assignments of the spectra of the mixed halogenomethylmetal species. The spectra of those available to us for study are shown in Figures 5—7 and the vertical i.p.s are recorded (with assignment) in Table 2. The species Me_2MX are first considered (Figures 5 and 6). The simplest spectra to interpret are $[Me_2AlCl]$ and $[Me_2AlBr]$. The halogen lone pairs in these molecules are both lower in energy than the b_1 Me_2Al orbital (which has the same form as the e' orbital in $AlMe_3$). Thus the σ (b_1) lone-pair orbital on the halogen is stabilised by interaction with this orbital. The $\pi(b_2)$ lone pair may be stabilised by back donation into the b_2 orbital on the central atom. The lone-pair ionisations are observed in the spectra as a broad band, which in neither compound was resolvable into b_1 and b_2 components. The b_1 (Me_2Al) orbital has a vertical i.p. of 10.2 eV for the chloride and 9.9 eV for the bromide. In both molecules the orbital is evidently stabilised relative to $AlMe_3$ more by the inductive effect of the halogens than it is destabilised by the lone-pair interaction. The spectrum of dimethylaluminium iodide is considerably more difficult to interpret. Here, four approximately equally spaced bands were observed between 9.5 and 11.0 eV. Evidently the σ and π lone pairs are split. A further difficulty is that the energy of an iodide lone pair is fairly close to the i.p. of the e' orbital in $AlMe_3$. Thus it is difficult to predict which is the highest-filled orbital. Furthermore, band shapes are rather similar. Nevertheless the first two bands are rather sharper and more intense than the next two. For this reason we assign the first band (vertical i.p. 9.48 eV) to the $\sigma(b_1)$ lone-pair (destabilised by the b_1 Al) orbital and the second band to the unperturbed $\pi(b_2)$ lone pair. (This may be stabilised by overlap with the p_z atomic orbital on Al.) The third band corresponds to the b_1 C_2Al orbital. Calculation [18] suggests that the symmetric (C_2Al) a_1 orbital in $[Me_2AlCl]$ has an energy between the antisymmetric b_1 orbital and the chlorine lone pairs. This orbital is presumably concealed by the intense lone-pair ionisations in $[Me_2AlCl]$ and $[Me_2AlBr]$. However, it may be observed as the fourth band in $[Me_2AlI]$. It is difficult to predict which of the a_1 orbitals (AlI or C_2Al) will be higher in energy. It is possible that the a_1 orbitals are close since the low-intensity fifth band in $[Me_2AlI]$ was consistently observed.

The spectrum of dimethylboron iodide is rather easier to interpret. Again there are four bands in the low i.p. region. However, the iodide lone-pair energy is now well above that of the Me_2B b_1 orbital, so that the destabilised b_1 lone pair is readily identifiable as the first band at 9.48 eV. The second band, at 10.12 eV, must correspond to the b_2 lone-pair π orbital, indicating that for an iodine atom as neighbour to a boron atom the b_2 orbital on B does not confer significant stabilisation on the corresponding halogen orbital. The third band at 11.17 eV corresponds to the b_1 Me_2B orbital and is, as expected, slightly higher in i.p. than the average of the Jahn–Teller split peaks of the e' orbital in BMe_3, considered earlier. The fourth band may correspond to the a_1 boron–iodine bond orbital, or the symmetric a_1 (C_2B) orbital for reasons discussed above for $[Me_2AlI]$. In dimethylboron bromide we consider the ordering to be the same. The Me_2B (b_1) orbital is further stabilised to 11.84 eV, partly by the greater $-I$ effect exerted by the bromine atom compared with an iodine atom, and partly because the σ lone pair on the bromine is more closely compatible in energy with the b_1 orbital than the corresponding iodine lone pair in dimethylboron iodide.

Finally, the spectra of the species $MeMX_2$ (Figure 7) are considered. In these compounds there is less ambiguity about the ordering of the early bands since the MeM orbital is now an a_1 orbital and presumably considerably lower in energy than the lone-pair orbitals. The first band in each spectrum (in $[MeAlBr_2]$, a shoulder on the first band) corresponds to the b_1 orbital formed by the lone pairs and lies close to the corresponding band in MX_3. The second, intense, band may be identified with the a_2 (π-antibonding lone pair) and a_1 (σ-bonding lone pair) orbitals and the third band with the b_2 (π-bonding) lone-pair orbital. The fourth and fifth bands are more difficult to assign. They must correspond to the a_1 CM orbital and the b_1 antibonding combination of the MBr_2 orbitals (see Table 2). The shapes of the bands in the spectra of $[MeAlBr_2]$ and $[MeAlI_2]$ (Figure 7) are so similar as to imply a strong correlation. If the fifth band in $[MeAlBr_2]$ corresponds to the a_1 orbital this requires a shift of nearly 3 eV from the b_1 orbital in $[Me_2AlBr]$, which is unreasonably high. For this reason we assign the fourth band (at 11.90 eV) to the a_1 orbital and the fifth band to the b_1 orbital, as in Table 2. For $[MeAlI_2]$, our assignment is the same: here the a_1 orbital is at 0.75 eV lower i.p., a shift partially accounted for by the lower $-I$ effect of iodine, but perhaps also by the proximity of the a_1 AlI_2 bonding orbital. The band at 11.00 eV is assigned to the a_1 AlI orbital in $[Me_2AlI]$; the a_1 AlI bonding orbital in AlI_3 occurs at 14.10 eV. By interpolation we infer that the a_1 AlI_2 bonding orbital in $[MeAlI_2]$ is at *ca.* 12.6 eV. A shoulder on the low i.p. side of the unresolved assembly of peaks due to CH_3 ionisations therefore probably corresponds to ionisation from this orbital. A similar argument cannot be applied to [$MeAlBr_2$], since the AlBr orbital is totally obscured in the spectra of [Me_2AlBr].

With the spectra of the pure halides fully assigned, and of the alkylaluminium halides extensively assigned, it is desirable to relate the spectra to chemical properties of the molecules. Since the Lewis acidity of this type of molecule is related to the energy of a vacant orbital [*i.e.* the (predominantly) p_z orbital on the central atom] the problem is rather more complicated than for, say, amines and phosphines where basicity is directly related to lone-pair ionisation energies. A comment on the acidity also requires knowledge of the promotion energy, *i.e.* the change $D_{3h}\rightarrow C_{3v}$ for the different MX_3 and $\overset{+}{L}\overset{-}{M}X_3$ molecules; additionally for boron, the smallest of the Group 3 atoms, steric effects must be considered in interpreting experimental data on relative Lewis-acid strengths.

Bassett and Lloyd suggested that the extent of π bonding in the boron trihalides is related to the differences in energy of the e'' and a_2'' orbitals.[21] This is certainly feasible, but for the bromides and particularly the iodides the situation is complicated by spin–orbit splitting of the $^2E''$ ionic state. The results (Table 4) indicate that the π bonding is anomalously low for the aluminium halides which leads to the conclusion that there is least electron density at the central atom for these. We consider that the values obtained are more closely indicative of the strength of the π interaction between the halogen lone pairs, and do not necessarily provide a measure of the relative π-electron density at the central atom. A better measure of the latter quantity may possibly be obtained by comparing for different halides the baricentres of the first two i.p.s. This value should give a measure of the i.p. of a completely non-bonding lone-pair orbital. Comparison of the values obtained (Table 4) gives for both bromides and chlorides (the values for iodides are spurious due to the large second-order spin–orbit splitting) the order of i.p.s as Al $>$ B $\sim$ Ga $>$ In; the order should reflect the residual charge on the halogen atom and therefore the extent to which donation into the central-atom orbital has occurred.

TABLE 4

Values obtained by (*i*) Lloyd's π-bonding method and (*ii*) our ' pure halogen lone-pair ' method for assessing the extent of back donation

	(*i*) [a] $\Delta e''/a_2''$ (eV)	(*ii*) [b] ' In-plane ' halogen lone-pair i.p. (eV)
BCl_3	1.82	12.06
$AlCl_3$	0.60	12.31
$GaCl_3$	0.76	12.18
$InCl_3$		11.76
BBr_3	1.82	11.24
$AlBr_3$	0.84	11.40
$GaBr_3$	0.97	11.24
$InBr_3$	0.53	10.86

[a] For bromides the $^2E''$ state is almost unsplit. [b] Calculated as: chlorides, baricentre of a_2' and e'; bromides, baricentre of a_2' and e' (the latter is the mean of i.p.s of $^2E_{\frac{5}{2}}$ and the lower of the $^2E_{\frac{3}{2}}$ states).

The order obtained reverses that obtained by the ' π-stabilisation ' method and gives an acceptable order of Lewis acidity for the halides of Group 3 elements. It appears, for these compounds at least, that the ' lone-pair ' i.p. on the halogen atom gives a better measure of the extent of back donation to the central atom.

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[21] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), 1971, 1551.