The He I Photoelectron Spectra of Mixed Boron Trihalides and the Microwave Spectrum of $BClF_2$†

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Summary Although the mixed boron halides $BX_nX'_{3-n}$ cannot be isolated pure, but exist in essentially statistical equilibrium with BX_3 and BX'_3, it is shown that their He I photoelectron (p.e.) spectra, as well as their microwave spectra, can be measured; the p.e. spectra of $BClF_2$ and BCl_2F, and the microwave spectrum, structure, and quadrupole interaction data for $BClF_2$ are described and are supported by *ab initio* SCF MO calculations.

IT has been established that boron trihalides, *e.g.*, BCl_3 and BF_3, rapidly react either in the condensed[1] or in the vapour[2] phase in almost thermoneutral fashion to produce an essentially statistical equilibrium mixture of the four possible halides, BCl_nF_{3-n} (n = 0, 1, 2, or 3). A broadly similar situation holds for the heavier monomeric gaseous Group 3 halides.[3] We now show, that although the pure mixed halides are not isolable, it is nevertheless possible to record their He I p.e. and microwave spectra. These molecules are also small enough to allow good *ab initio* molecular orbital calculations. A combination of such data has considerable bearing on the long controversial problem of bonding in the Group 3 metal halides, especially on the issue of the relative trends in X–B $(p\rightarrow p)\pi$-bonding as between X = F or Cl. We illustrate our results by reference to the BF_3–BCl_3 situation. Reliable molecular structure parameters for three-co-ordinate boron halides were hitherto available only for $MeBF_2$,[4] $HOBF_2$,[5] and H_2NBF_2,[6] although electron diffraction and early *X*-ray data are known for BF_3 and BCl_3.[7]

P.e. spectra were recorded on a Perkin Elmer PS16 instrument with a modified high intensity lamp, attached to a vacuum line and manifold; instrument resolution varied from 20 to 50 meV. Samples of BF_3 and BCl_3 were allowed to mix prior to entry into the target chamber. The Figure

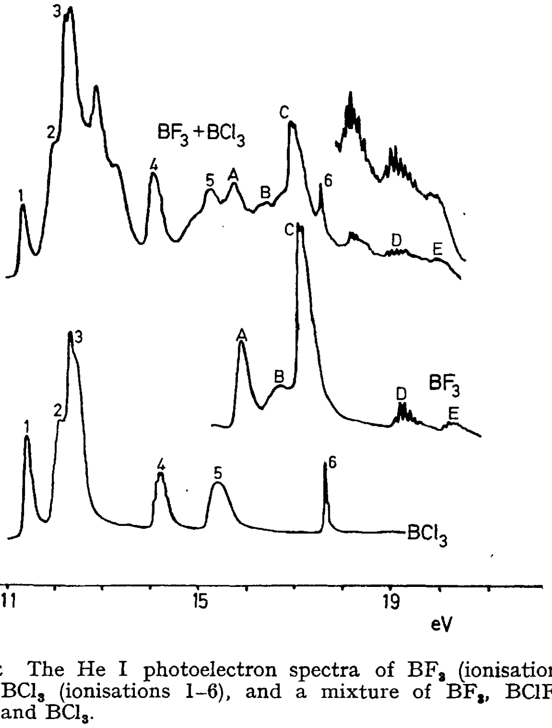

FIGURE The He I photoelectron spectra of BF_3 (ionisations A–E), BCl_3 (ionisations 1–6), and a mixture of BF_3, $BClF_2$, BCl_2F, and BCl_3.

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† No reprints available.

shows the p.e. spectra of pure BF_3[8] and BCl_3,[8] together with that of a 1 : 1 mixture. The spectrum of the mixture shows several new bands, the relative intensities of which could be varied by alternating the composition of the mixture, thus facilitating the identification of the spectra of the two mixed halides. The correlations of Table 1 are based on (i) the above analysis, (ii) good agreement between the first vertical ionisation potentials (i.p.'s) and the previously observed mass spectrometric values,[2] (iii) trends within the series of four compounds, and (iv) comparison of experimental data with *ab initio* SCF MO calculations, particularly helpful in the high i.p. region.

experiments, however, yielded valuable data with regard to the optimum experimental conditions for producing the mixed halides in a low pressure (*ca.* 30 μm Hg) flow system ideal for microwave search experiments. These data, together with the recognition that initial success in detection was very much more likely for the $4_{32} \leftarrow 3_{31}$ and $4_{31} \leftarrow 3_{30}$ lines of $BClF_2$ (in the 26·5—40 GHz range of our spectrometer) than for any other lines, facilitated the assignment of the spectrum. The various problems associated with observing the microwave spectrum of $BClF_2$ are almost identical to those which occurred in the case of F_2CS and were solved in a similar manner.[12]

TABLE 1

Vertical i.p.'s (eV) for the compounds BCl_3, BCl_2F, $BClF_2$, and BF_3 with assignments (calculated values)[a]

BCl_3[b]	BCl_2F	$BClF_2$	BF_3[b]	BCl_3[b]	BCl_2F	$BClF_2$	BF_3[b]
11·62 $1a'_2$ (11·78)							15·95 $1a'_2$ (16·15)
12·28 $3e'$ (12·41)	12·18 $4b_2$ (11·92)						16·65 $3e'$ (16·90)
12·53 $1e''$ (12·28)	12·44 $1a_2$ (12·23)				16·93 $4a_1$ (16·52)	16·93 $3b_2,a_2$ (16·53, 16·70)	
		12·85 $4b_2$ (12·61)					17·10 $1e''$ (16·72)
	13·15 $5a_1$ (12·88)	13·00 $2b_1$ (12·84)		17·7 $2a'_1$ (17·74)			
	13·50 $2b_1$ (13·19)					18·35 $1b_1$ (18·39)	
14·35 $1a''_2$ (14·10)	14·35 $3b_2$ (13·81)				18·5 b_1 (18·17)		
		15·1 $5a_1$ (14·75)			19·00 $2b_2$ (18·58)	? $4a_1$? (18·58)	19·15 $1a''_2$ (18·92)
15·49 $2e'$ (15·27)						? $2b_2$? (19·32)	20·1 $2e'$ (19·93)

[a] Koopmans' i.p.'s scaled by a factor of 0·92. [b] Calculated values from ref. 9.

Ab initio calculations for the molecular orbital energies of $BClF_2$ and BCl_2F (see Table 1, with results[9] on BF_3 and BCl_3) were performed in bases of uncontracted Gaussian type functions,[10] consisting of 7*s* and 3*p* type functions for B and F and 10*s* and 6*p* for Cl. [Earlier calculations[9] using this procedure showed good agreement between the calculated (scaled by a factor of 0·92) and experimental[8] i.p.'s for BF_3 and BCl_3]. For BCl_2F, we used the B–F length (**1·31** Å) found by electron-diffraction in BF_3 and the optimised[9] B–Cl bond length of 1·78 Å, with bond angles of 120°. For $BClF_2$, the geometrical parameters obtained from microwave spectra (see below) were used.

Previous attempts to detect the microwave spectra of the mixed boron halides led to the conclusion that the dipole moments were very small due to the near cancellation of the B–F and B–Cl bond moments[11]; we now estimate, by calculation, that for $BClF_2$ this is 0·1 D. The above p.e.

A 2 : 1 mixture of gaseous BF_3 and BCl_3 was made up in a 1 l flask (total pressure *ca.* 10 cm Hg) and equilibrated for several hours. This mixture was then allowed to flow continuously *via* a needle valve through the cell of a Hewlett-Packard 8460A microwave spectrometer operating between 26·5 and 40 GHz. The pressure in the cell was *ca.* 40 μm Hg. So far only some very weak lines belonging to the most abundant isotopic modification, $^{11}B^{35}Cl^{19}F_2$, have been identified and the assignments and measured line frequencies are given in Table 2. The lines are subject to ^{35}Cl nuclear quadrupole interactions and the resulting splittings have been analysed using a least squares criterion to fit the standard first-order theory.[13] The resulting quadrupole parameters are also given in Table 2, together with line centre frequencies. The latter were then fitted by a least squares rigid asymmetric rotor programme to obtain the rotational constants, also listed in Table 2.

TABLE 2

Line frequencies, rotational constants, and quadrupole parameters of $^{11}B^{35}ClF_2$ in MHz

Assignment	F'–F''	ν_{obs}	ν_{calc}	obs — calc	ν_{centre}	obs — calc
4_{23}–3_{22}	$^5/_2$–$^3/_2$	31590·985	31591·003	−0·019		
	$^{11}/_2$–$^9/_2$	31589·620	31589·583	0·037	31588·107	0·170
	$^7/_2$–$^5/_2$	31586·893	31586·946	−0·053		
	$^9/_2$–$^7/_2$	31585·562	31585·526	0·036		
4_{22}–3_{21}	$^5/_2$–$^3/_2$	33724·521	33724·541	−0·020		
	$^{11}/_2$–$^9/_2$	33722·964	33722·976	−0·012	33721·066	0·011
	$^7/_2$–$^5/_2$	33719·412	33719·447	−0·035		
	$^9/_2$–$^7/_2$	33717·947	33717·882	0·065		
4_{31}–3_{30}	$^5/_2$–$^3/_2$	32368·363	32368·358	0·005		
	$^{11}/_2$–$^9/_2$	32363·330	32363·320	0·010	32360·048	0·020
	$^7/_2$–$^5/_2$	32358·288	32358·280	0·008		
	$^9/_2$–$^7/_2$	32353·246	32353·241	0·005		
4_{32}–3_{31}	$^5/_2$–$^3/_2$	32213·009	32213·054	−0·045		
	$^{11}/_2$–$^9/_2$	32208·168	32208·084	0·084	32204·985	−0·128
	$^7/_2$–$^5/_2$	32203·184	32203·196	−0·012		
	$^9/_2$–$^7/_2$	32198·199	32198·227	−0·026		
5_{24}–4_{23}	$^7/_2$–$^5/_2$	39180·754	39180·735	0·019		
	$^{13}/_2$–$^{11}/_2$	39180·545	39180·499	0·046	39179·710	−0·038
	$^9/_2$–$^7/_2$	39178·844	39178·906	−0·062		
	$^{11}/_2$–$^9/_2$	39178·666	39178·670	−0·004		

$A_0 = 10460 \pm 2$, $B_0 = 4706{\cdot}28 \pm 0{\cdot}10$, $C_0 = 3238{\cdot}98 \pm 0{\cdot}10$ MHz
$\chi_A = 42{\cdot}47$, $\chi_B = 32{\cdot}27$, $\chi_C = 10{\cdot}20$ MHz.

So far only the lines belonging to the most abundant isotopic species have been satisfactorily identified. Thus the assumption has been made that the B–F bond length is 1·325 Å which is close to the values observed in $HOBF_2$ (1·323 Å)[5] and H_2NBF_2 (1·325 Å).[6] This allows a value of 1·71 ± 0·01 Å for the B–Cl bond length and 116·6 ± 0·1 degrees for the F–B–F angle to be derived.

An approximate estimate of 14% π-character in the B–Cl bond can be obtained from the quadrupole asymmetry parameter.[14] This compares with 17% by the above *ab initio* calculation and a Mulliken analysis; the $B2p\pi$–$Cl3p\pi$ overlap population being larger than $B2p\pi$–$F2p\pi$.

It is hoped to increase the sensitivity of our spectrometer by time averaging in order to detect lines belonging to the less abundant isotopic species and also determine the dipole moment. These measurements will allow the geometry to be further refined and yield further information about the electronic structure of the molecule. Many other weak lines appear throughout the spectral range which almost certainly belong to BCl_2F and it is hoped that the spectrum of this molecule can be assigned also and thus complete the series of mixed boron halides.

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