A Photoelectron Spectroscopic Study of the $(FBS)_n$ System (n = 1—3) †

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The unstable species FBS, $(FBS)_2$, and $(FBS)_3$ are produced in high yield by pyrolysis reactions of various sulphur fluorides over boron. FBS and $(FBS)_2$ can be produced in a direct flow system and $(FBS)_3$ by revaporising a trapped monomer–dimer mixture. He(I) photoelectron (p.e.) spectra are reported for these species, the identities of which are confirmed by *in situ* quadrupole mass spectrometry. *Ab initio* molecular orbital calculations, including perturbation corrections to Koopmans theorem, are consistent with the identifications, assist with the assignments of the p.e. spectra, and provide information on their electronic structures.

Since the initial discovery of thioborane, HBS,[1] and its subsequent characterisation by microwave spectroscopy,[2] several other species containing a B=S double bond have been prepared and studied using a combination of microwave and photoelectron (p.e.) techniques. These complementary techniques serve to establish the optimum conditions for producing these unstable molecules and give information on their molecular and electronic structures.

The original method for producing HBS (H_2S + boron at *ca.* 1 100 °C),[1] used for determining the microwave [2] and p.e. spectra,[3,4] has now been superseded by a more general procedure involving the reaction (1) (X = halide). This route

$$X_2S_2 + B \xrightarrow{1\,100\,^{\circ}C} XB{=}S \qquad (1)$$

has proved superior for the formation and detection of substituted sulphidoboron compounds such as ClBS [5-7] and BrBS [5] which have both been observed by microwave and p.e. spectroscopy, and CH_3BS,[8,9] observed by microwave spectroscopy alone.

This work has now been extended to the fluoro-analogue, FB=S, prepared by a variety of routes and studied by both microwave and p.e. techniques. In p.e. spectroscopy fluorine-containing molecules present some advantages over the heavier congeners; higher vibrational frequencies, perfluoro-shift effects,[10] the possibility of a Koopmans breakdown,[11] and the relative tractability of *ab initio* quantum mechanical methods. During this study it became apparent that the chemistry of the FBS monomer was complicated by the presence of polymeric species such as $(FBS)_2$ and $(FBS)_3$. This is in accord with earlier gas-phase work on the SF_6–B system,[12,13] and also solution chemistry where species such as $(HSBS)_2$, $(HSBS)_3$, $(XBS)_3$ (X = Cl, Br, or I), and various trialkyl/trialkoxy sulphidoboron compounds have been characterised.[14-17] Although microwave spectroscopy is excellent for the detection of small or linear molecules or those with a large dipole moment, species such as $(FBS)_2$ and $(FBS)_3$ are more difficult, possessing too many frequencies and if they are planar ring systems they will not be detectable by microwave due to the absence of a dipole moment. Photoelectron spectroscopy, on the other hand, has the advantage that it detects *all* species present in a mixture, which may be a disadvantage when it comes to analysis.

This paper reports the preparation, detection, identification, and photoelectron spectra of the compounds $(FBS)_n$ (n = 1—3). Identification of the various $(FBS)_n$ species is supported by quadrupole mass spectrometry and *ab initio* quantum mechanical calculations. The geometric and electronic structures of these molecules are discussed.

Experimental

Preparations.—Four methods, (*a*)—(*d*), were used to produce $(FBS)_n$ (n = 1—3); the first three employed the use of gaseous sulphur fluorides in a flow system over heated boron.

Method (*a*). This method leads to the highest yield of FBS and involves reaction (2). Under very fast pumping conditions

$$F_2S_2 + B \xrightarrow{1\,100\,^{\circ}C} (FBS)_n \ (n = 1 \text{ or } 2) \qquad (2)$$

the p.e. spectra yield a rough estimate of the vapour composition as 90% FBS and 10% $(FBS)_2$. Boron chips were obtained from Koch Light. F_2S_2 was synthesised by reaction of AgF with molten flowers of sulphur according to the literature method,[18] stored in an ampoule, and used without further purification. Subsequent p.e. spectra indicated that the sample contained mainly the FSSF isomer,[19] with traces of SSF_2 and SF_4.

Method (*b*). This method employs reaction (3) which also

$$SF_6 + B \xrightarrow{1\,100\,^{\circ}C} (FBS)_n \ (n = 1 \text{ or } 2) \qquad (3)$$

leads to production of FBS and $(FBS)_2$,[12,13] the ratio of the two species depending upon flow rates. The advantage of this method is the stability and ease of handling of SF_6. The disadvantage is the non-stoicheiometric S : F ratio [compared to method (*a*)] which leads to the formation of excess BF_3.

Method (*c*). The reaction (4) also gives FBS and $(FBS)_2$, plus

$$SF_4 + B \xrightarrow{1\,100\,^{\circ}C} (FBS)_n \ (n = 1 \text{ or } 2) \qquad (4)$$

BF_3, similar to reaction (3).

Method (*d*). In principle, reaction (5) [16] should provide a

$$BF_3 + B_2S_3 \longrightarrow (FBS)_n \ (n = 1 \text{ or } 2) \qquad (5)$$

direct route to FBS. In practice this is not a straightforward method since at the high temperature (*ca.* 900 °C) required for reaction, the B_2S_3 sublimes out of the reaction zone. This system therefore cannot be fast pumped easily and only the $(FBS)_2$ species is obtained in the presence of excess BF_3.

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† *Non-S.I. unit employed*: eV = 1.60×10^{-19} J.

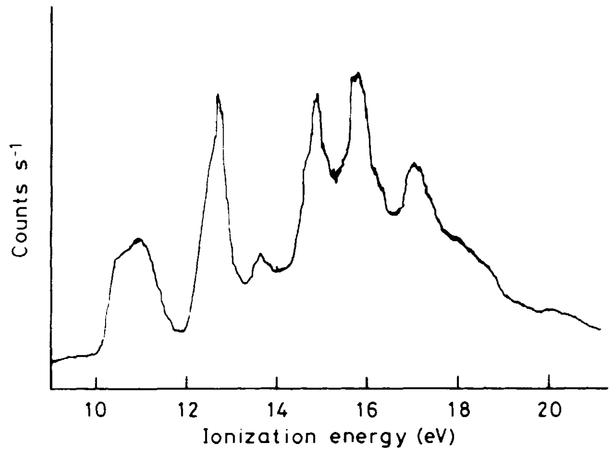


Figure 1. The p.e. spectrum of F_2S_2 used as the precursor for the production of $(FBS)_2$ and FBS, Figures 2 and 4 respectively

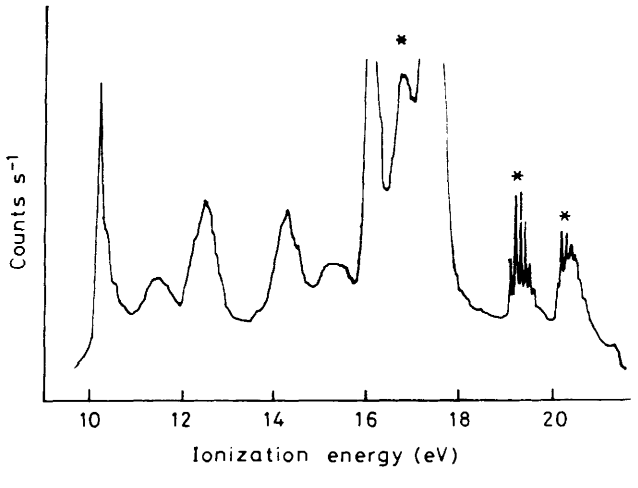


Figure 2. The p.e. spectrum obtained when F_2S_2 (Figure 1) is pyrolysed over boron chips at 1 100 °C in a slow flow system. The peaks between 10 and 16 eV belong mainly to $(FBS)_2$, whereas those above 16 eV belong mainly to BF_3 as indicated by asterisks

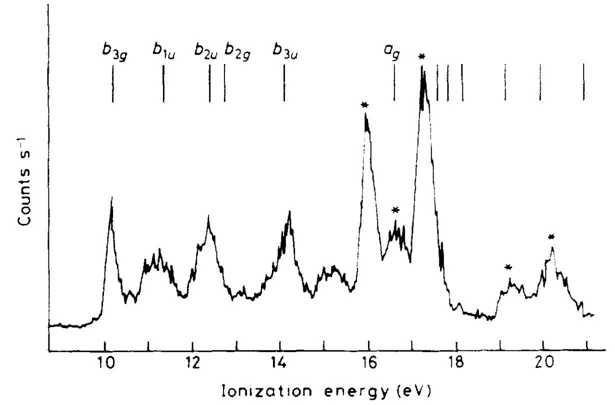


Figure 3. The p.e. spectrum obtained when SF_6 is passed at moderate flow rates over boron at 1 100 °C. Comparison with Figure 2 indicates that the products are very similar to those from the F_2S_2 + B reaction. The positions of the lower ionisation potentials (adjusted by 3 eV, see text) as predicted by a STO-3G calculation for $(FBS)_2$ are indicated. The features with i.p.s above 16 eV belong mainly to BF_3

Physical Measurements and Calculation.—The p.e. spectra were obtained on spectrometers designed for the study of transients; one located at the University of Sussex,[20] and the other located at the University of British Columbia.[21] An *in situ* quadrupole mass spectrometer was also used (EAI 150, modified to reach 300 a.m.u.) which permits mass analysis under identical reaction conditions.

Electronic structure calculations were carried out at, or close to, the experimental geometry for FBS [r(BF) = 1.284, r(BS) = 1.606 Å],[5] and at estimated geometries for $(FBS)_2$ and $(FBS)_3$ (see later). The *ab initio* calculations were performed with the ATMOL set of programs [22] using a minimal basis set, and with the GAUSSIAN 70 and GAUSSIAN 76 programs [23] using the minimal STO-3G and extended 4-31G basis sets. Subsequent application of perturbation corrections to Koopmans theorem [24] provided a definitive assignment of the FBS spectrum. The latter method, employing Rayleigh–Schrödinger perturbation theory, has been shown to provide excellent results for small molecules containing B and F atoms.[25]

Calibration was carried out using the ionisation potentials (i.p.s) of H_2S, Ar, and N_2. Resolution was variable, but generally in the range 25—35 meV.

Results

Figure 1 depicts the p.e. spectrum of F_2S_2 which is primarily, although not entirely, that of the FSSF isomer.[19] Under *slow* flow pyrolysis conditions the spectrum shown in Figure 2 is obtained. Apart from the strong peaks of BF_3 (indicated by asterisks), five distinct new bands appear below 16 eV. These five bands are also detected in slow-flow experiments using SF_4 or SF_6 and boron (Figure 3) and relative intensity comparisons carried out while altering the experimental conditions indicate that they belong to only one species. Quadrupole mass-spectrometric analysis shows a parent peak centred at 124 a.m.u. [$(FBS)_2^+$] with weaker peaks at 105 [$FB_2S_2^+$] and 94 a.m.u. [FBS_2^+], as well as a strong peak at 75 a.m.u. [BS_2^+], and a dominant peak at 62 a.m.u. [FBS^+]. Excess BF_3 is indicated by a peak at 49 a.m.u. [BF_2^+]. A comparison of the measured and calculated i.p.s and correlation with similar molecules (see later) confirm the identity of the species in Figures 2 and 3 as $(FBS)_2$.

In a *fast* flow experiment on the F_2S_2 + B system the spectrum shown in Figure 4(*a*) is observed. Some residual traces of $(FBS)_2$ are present, but the stoicheiometric S : F ratio is probably responsible for the absence of BF_3. Similar spectra are observed in the SF_6–B and SF_4–B systems under fast pumping conditions but BF_3 is also present [Figure 4(*b*)]. The spectrum can be assigned to the FBS monomer by comparison with the p.e. spectra of HBS [3-5] and ClBS,[5,7] and by comparison with the corresponding perfluoro-shifts between HC≡P and FC≡P,[26] isoelectronic with HBS and FBS respectively. The calculations, including those involving perturbation correction to Koopmans theorem, support the assignment to the monomer.

If the products [FBS, $(FBS)_2$ and BF_3] of an SF_6–B reaction are trapped at liquid-nitrogen temperatures and revaporised, after the excess BF_3 has volatilised, the spectrum shown in Figure 5 is obtained. Quadrupole mass spectra confirm the identity of this species as $(FBS)_3$, showing a parent peak centred at 186 a.m.u., and subsequent major fragments at 124 $[FBS]_2^+$, 75 [BS_2^+], and 62 a.m.u. [FBS^+]. The mass spectrometry results for both $(FBS)_2$ and $(FBS)_3$ corroborate earlier

Table 1. Experimental and calculated ionisation potentials (eV) for F–B=S

		Calculated i.p.s					
		Koopmans		RSPT [a]			
Ion state	Experimental i.p.	STO4-31G [b]	ATMOL [c,d]	$\Delta(E^{g.a.})$	$(\Delta E)^{g.a.}$	$\Delta E^{a.g.a.}$ [e]	Scaled
$\tilde{X}^2\Pi$ [f]	10.90 ± 0.01	11.10	10.10	10.73	10.72	10.73	10.86
$\tilde{A}^2\Sigma^+$ [g]	14.20 ± 0.01	14.62	13.28	13.90	13.69	13.76	14.08
$\tilde{B}^2\Pi$	17.2 ± 0.1	20.16	17.76	17.45	17.05	17.25	
$\tilde{C}^2\Sigma^+$	19.62 ± 0.02	22.29	19.73	19.75	19.34	19.56	

[a] Rayleigh–Schrödinger Perturbation Theory. [b] r(B–F) = 1.30, r(B–S) = 1.60 Å. [c] r(B–F) = 1.284, r(B–S) = 1.606 Å. [d] Minimal basis set. [e] $\Delta E^{a.g.a.} = \frac{1}{2}[\Delta(E^{g.a.}) + (\Delta E)^{g.a.}]$. [f] ω = 1 560 ± 60 cm^{-1}. [g] ω = 1 680 ± 40 cm^{-1}.

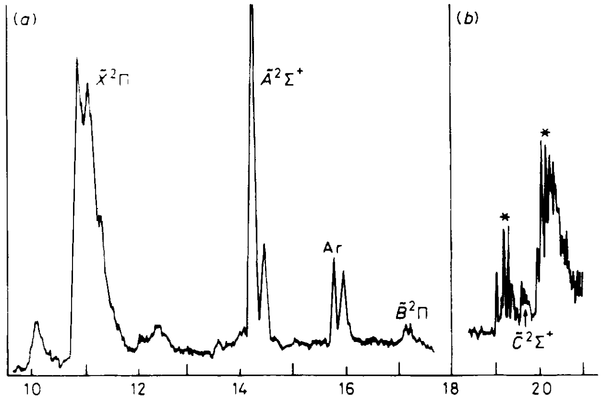


Figure 4. (*a*) The p.e. spectrum of FB=S obtained when F_2S_2 is passed over B at 1 100 °C using a very fast flow system. (*b*) The fourth i.p. of FB=S detected during an SF_6–B pyrolysis reaction (see text). The bands marked with an asterisk belong to BF_3

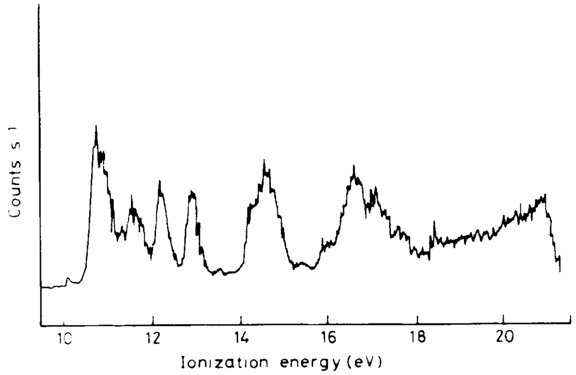


Figure 5. The p.e. spectrum of $(FBS)_3$ obtained when the trapped products of pyrolysing SF_6 over B are revaporised

mass data on the SF_6–B system.[12] No trimer mass peaks are observed in the flow experiments indicating that the $(FBS)_3$ species is not produced in the initial pyrolysis phase, but results on warming the trapped monomer–dimer mixture. The assignment of the p.e. spectrum to a trimer species is also supported by comparison with similar molecules and theoretical calculations, as discussed below.

Table 2. Experimental and calculated i.p.s (eV) for $(FBS)_2$

Band	Observed i.p. [a]	Calculated i.p.[b,c]	Calculated i.p.[c]	Assignment
1	10.10 [d]	10.14	7.14	b_{3g}
2	11.24	11.33	8.33	b_{1u}
3	12.1 [e]	12.42	9.42	b_{2u}
4	12.4 [e]	12.87	9.87	b_{2g}
5	14.1	14.07	11.07	b_{3u}
6	15.2	16.58	13.58	a_g
7	16.0 [f]	—	—	BF_3 [g]
8	16.4 [f]	—	—	—
9	17.1 [f]	—	—	BF_3 [g]
10	19.1 [f]	—	—	—
11	20.1 [f]	—	—	—

[a] Observed vertical i.p.s; ±0.1 eV unless otherwise indicated. [b] Adjusted calculated i.p. [+3.0 eV (see text)]. [c] Calculated i.p. GAUSSIAN 76 STO-3G basis. [d] ±0.02 eV. [e] Two overlapping bands (see text). [f] Calculated (adjusted) i.p.s for bands 7—12: 17.52, 17.76, 18.09, 19.08, 19.86, and 20.88 eV. [g] Main features in this region attributable to BF_3.

Table 3. Experimental and calculated vertical ionisation potentials (eV) for $(FBS)_3$

Band	Observed i.p.[a]	Calculated i.p. [b]	Assignment
1	10.79	7.91	e''
2	11.60	8.31	e'
3	12.21	9.35	a_2''
4	12.93	10.33	a_2'
5	14.30 [c]	12.33	a_1'
6	14.67 [c]	12.68	e'
	16—18 [d]	14.7—18.2 [e]	

[a] Vertical i.p.s correct to ±0.10 eV. [b] GAUSSIAN 76 calculated STO-3G basis for planar structure (see text). [c] Overlapping bands. [d] Complex features: 16.0, 16.6, 17.1, and 17.7 eV; *note*, may also include BF_3 features near 16.0 and 17.1 eV. [e] Calculated i.p.s for bands 7—12: 14.7, 15.0, 15.2, 16.7, 16.8, and 18.2 eV.

The experimentally determined i.p.s are given in Tables 1, 2, and 3, together with the assignments and calculated values. The details of these assignments and the electronic and geometric structures of these molecules are discussed in the next section.

Discussion

FBS *Monomer*.—The p.e. spectrum of the monomeric, linear FBS molecule is predicted to show four i.p.s below 21.2 eV. The ground-state electron configuration and resulting term for FBS are $(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^4$; $^1\Sigma^+$.

The p.e. spectrum (Figure 4) shows the first two ionic states, $^2\Pi$ and $^2\Sigma^+$, clearly as distinct structured bands with coincident adiabatic and vertical i.p.s. The first occurs at 10.90 eV; the second at 14.20 eV. The remaining two bands are more difficult to discern due to the presence of residual $(FBS)_2$ and unfavourable discrimination of the analyser against low-energy electrons. In the SF_6–B experiments where unfavourable discrimination did not occur, overlap by BF_3 caused problems. The weak band at 17.2 eV can be assigned to the third ionic state ($^2\Pi$) and a band at 19.62 eV can be assigned to the fourth ionic state ($^2\Sigma^+$). This assignment is supported by the *ab initio* calculations (Table 1). The perturbation corrections to Koopmans theorem, which, taken to third order, have been shown to be reliable to within 0.3—0.5 eV,[24] confirm the assignment of the $\tilde{B}^2\Pi$ and $\tilde{C}^2\Sigma^+$ states even though they are weak in intensity. The $\Delta(E^{g.a.})$ and $(\Delta E)^{g.a.}$ values are usually taken to be the most reliable, with the scaled values providing the most accurate results for the lowest states of each symmetry.[24,27] Recently, $\Delta E^{a.g.a.}$ (average geometric approximation) values have been shown to provide superior values for vertical i.p.s [28] (see Table 1, where the average deviation from the i.p.s is only 0.18 eV), although the improvement is generally better with large basis sets.

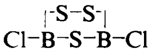
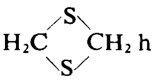
The first band (Figure 4) shows a vibrational progression of three members with a spacing, ω = 1 560 cm^{-1} belonging to ν_1, the B=S stretching vibration. In the ion this frequency is expected to be somewhat lower than the molecular ground-state value due to the loss of the BS π-bonding electron. The vibration may however be more accurately assigned as an asymmetric stretching frequency of the triatomic molecule as appears to be the case in FCP where the C–F and C≡P bonds have almost the same force constant value.[29]

The second band at 14.20 eV has a single intense peak with one or possibly two, much weaker vibrational components (Figure 4) indicating that the frequency of 1 680 cm^{-1} is hardly changed from the molecular value for ν_1. The Franck–Condon contour is consistent with ionisation involving the non-bonding electron in the predominantly lone-pair orbital on sulphur, with significant boron 2*s* and sulphur 3*s* character. Interestingly, the corresponding $^2\Sigma^+$ ionic state in the iso-electronic FCP molecule exhibits a progression, in what can roughly be described as a symmetric stretching mode.[26]

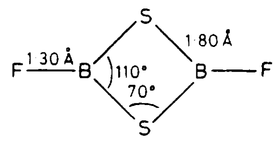
The third i.p. at 17.2 eV is weak despite the fact that it corresponds to a degenerate ($^2\Pi$) state. The low intensity of these bands in FBS, FCP,[26] and FCN [30] is due to the discrimination against low-energy electrons by the analyser, and also possibly to the low cross-section for ionisation of 2*p*(F) electrons with He(I) radiation. In all three cases the π orbital possesses considerable 2*p*(F) character.

The fourth band at 19.62 eV [Figure 4(*b*)] was only observed in the SF_6–B system, but appears between the final two bands of BF_3. The position of this $^2\Sigma^+$ state is accurately predicted by the calculations (Table 1), particularly the $\Delta E^{a.g.a.}$ values. It is strongly B–F bonding in character.

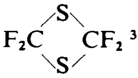
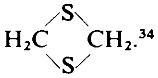
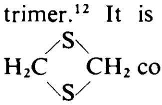
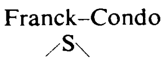
A comparison of the first two ionic states of FBS with the corresponding states of HBS [3–5] shows very similar perfluoro-shifts to those observed for the FCP–HCP system.[26] The $^2\Pi$ state of FBS^+ is destabilised by 0.20 eV, whereas the $^2\Sigma^+$ state is stabilised by 0.66 eV.

$(FBS)_2$ *Dimer*.—There is a paucity of data on dimeric sulphidoboron species. The $(HSBS)_2$ dimer is known in solution [16] and is assumed to have a ring structure with S at the 1 and 3 positions, suggesting a similar structure to that expected for the $(FBS)_2$ dimer. There is some evidence that the related molecules  and  have planar rings.[31,32] Indeed, most substituted 1,3-dithietanes also have planar rings. In addition various trimers of the type $(XBO)_3$ and $(XBS)_3$ have been shown to have planar rings.

For the dimer, the ring structure has been optimised initially at the CNDO/2 level with assumed bond lengths and angles, and with additional refinements performed using the STO-3G minimal basis set internal to the GAUSSIAN 70 and GAUSSIAN 76 programs. The best energy is given for a planar structure with D_{2h} symmetry, (I). The computed orbital energies [12 *p*-based orbitals within the He(I) range] are in good semi-quantitative agreement with experiment and the relative spacings of the i.p.s are well reproduced (Table 2). Since STO-3G calculations tend to give low absolute values we have, in Table 2, added 3 eV to the computed energies to normalise the first i.p. The first six distinct i.p.s then show excellent agreement with experiment. In Figure 3 a correlation of the experimental and adjusted theoretical spectrum is presented. Higher i.p.s of $(FBS)_2$ are also shown (Table 2); these have been observed in a few cases in the absence of overlapping BF_3, albeit with lower signal to noise ratio. The orbital energies calculated for *non-planar* $(FBS)_2$, with bond lengths the same but a dihedral angle (angle between the two FBSS planes) fixed at 120°, correspond poorly with experiment. In addition the total energy is greater than that of the planar structure by 0.038 a.u.



(I)

The p.e. spectrum can therefore be assigned by correlation with the calculations and particularly for the sulphur lone pairs, by comparison with the p.e. spectra of  [33] and .[34] The first band has coincident adiabatic and vertical i.p.s at 10.10 eV, and exhibits a short progression in 1 320 cm^{-1}. The Franck–Condon envelope is as expected if non-bonding electrons are involved, in this case the *p*π orbitals are slightly antibonding across the ring (b_{3g}). The observed vibrational interval is presumably a symmetric B–S stretching frequency, which is unknown for the ground-state molecule; strong bands are observed between 1 050 and 1 250 cm^{-1} for the gas- and solid-phase i.r. spectra of the $(FBS)_3$ trimer.[12] It is interesting to note that the b_{3g} orbital in  corresponds to the sharp second i.p. at 9.43 eV,[34] the highest occupied molecular orbital (8.95 eV) being the S *p*π orbitals symmetric (b_{2u}) across the ring with incorporation of antibonding CH_2 character. This gives a sulphur *p*π separation of 0.48 eV. In $(FBS)_2$ the symmetric sulphur out-of-plane lone pair (b_{2u}) orbital is stabilised by overlapping *p*π character on boron and so, following the calculations, it becomes the third i.p. at 12.1 eV, exhibiting a broader Franck–Condon envelope than the corresponding orbital in . The large separation of the sulphur *p*π orbitals in the $(FBS)_2$ dimer (2.02 eV) is thus a manifestation of the strong *p*π–*p*π overlap in this molecule. Having now considered the relative positions of the cross-ring bonding and anti-bonding sulphur lone-pair *p*π orbitals, the remaining i.p.s, which show no observable fine structure, can be assigned to in-plane ring σ orbitals in accord with the calculations. Thus the second broad band at 11.24 eV is assigned to a b_{1u} orbital.

Calculation suggests that the third i.p. assigned to the b_{2u} symmetric non-bonding lone pair combination and the fourth i.p. associated with a b_{2g} ring bonding B–S σ orbital lie close together and have been assigned to the third band at 12.4 eV. The fourth distinct band at 14.1 eV exhibits a trace of the FBS monomer (sharp peak at 14.20 eV in Figure 3). This band is assigned to the fifth i.p.; ionisation from the b_{3u} orbital which is in-plane B–F and B–S bonding with inclusion of 2*s*(B) character. In many respects this orbital is the dimer equivalent of the $p\sigma$ lone pair in the FBS monomer. The destabilisation of the $p\sigma$ lone pair on bending of the FBS chain is thus roughly compensated by the gain in stability due to ring bonding upon dimerisation. The sixth i.p. at 15.2 eV is assigned by comparison with the calculation, to ionisation from an a_g orbital. Beyond 16 eV the spectrum is masked in most cases by BF_3. Numerical values for the higher i.p.s are given in Table 2 and the correspondence with the calculations is shown in Figure 4. Below 21.2 eV there are 12 orbitals of *p* character predicted. Above this there is, according to calculation, a gap of 6 eV in the inner-valence region.

$(FBS)_3$ *Trimer*.—The $(FBS)_3$ trimer almost certainly has a structure analogous to that of $(HBO)_3$ which has been shown to have a planar ring by electron diffraction.[35] Chlorine- and F-substituted oxoboron species are calculated to have planar ring structures.[36] The $(XBS)_3$ species (X = Cl, Br, or I) are all well known as ring trimers.[16,17,37,38] A crystal structure determination [39] has shown that the tribromo-species is planar with *r*(BBr) = 1.895, *r*(BS) = 1.807 Å, BSB = 109.2, and SBS = 130.7°. *Ab initio* calculations at the STO-3G level were therefore performed assuming a planar (D_{3h}) structure and using the BS dimensions determined in the $(BrBS)_3$ crystal structure, and a B–F bond length of 1.30 Å. The effects of ring puckering were assessed in a calculation with a non-planar geometry (chair form, C_{3v}) with BSB = 108.2° and all other bond lengths and angles remaining the same. The total energy was found to be poorer than for a planar configuration (by 0.0286 a.u.). Planarity has thus been assumed in the assignment of the p.e. spectrum.

The photoelectron spectrum (Figure 5) shows at least six major band envelopes up to 18 eV, followed by a rising background up to the cut-off. Calculation indicates that there are 18 *p*-character orbitals within the He(I) region, making assignment difficult. The values for the i.p.s and a plausible assignment based on the distribution of the calculated and experimental i.p.s is shown in Table 3.

As in $(FBS)_2$, the spacings of the first five bands are well reproduced by the calculations. These indicate that the first intense band at 10.79 eV is doubly degenerate comprising out-of-plane and out-of-phase combinations of sulphur lone pairs (e''). The corresponding bonding combination (a_2'') is predicted as the third i.p. (12.21 eV), thereby giving a separation of 1.42 eV between the sulphur lone-pair combinations. This is larger than the splitting of *ca.* 0.5 eV between the sulphur lone-pair combinations of non-planar 1,2,3-trithiane and its methyl-substituted derivatives [40,41] and is again (as in the dimer case) due to the stabilisation of the a_2'' orbital by overlap with the boron *p* orbitals giving strong $p\pi$–$p\pi$ bonding.

The broad second i.p. at 11.60 eV is assigned to a doubly degenerate in-plane orbital (e') and the fourth distinct band at 12.93 eV to the a_2' in-plane combination of sulphur 3*p* orbitals. The fifth a_1' and sixth e' orbitals can be assigned to the broad band centred at 14.67 eV. This assignment is supported by calculation which indicates that these two i.p.s lie within 0.35 eV and are separated by 2 eV from the i.p.s to either side. Above 16 eV the spectrum becomes even more complicated. Calculation indicates that the i.p.s bunch into two groups; the e'', a_2'', and e' groups lying between 16 and 17.7 eV and the a_2' and a_1' group at *ca.* 18.5 eV. This assignment correlates well with the calculation for a planar molecule. The calculation for a puckered structure gives a poorer fit with experiment particularly for the first four i.p.s.

Conclusions

This study of $(FBS)_n$ (*n* = 1—3) has given an opportunity to investigate a monomer–dimer–trimer system by p.e. spectroscopy similar to that for H_2CS, $(H_2CS)_2$, and $(H_2CS)_3$.[33,40,41] They may be produced relatively pure in the gas phase. In the case of the FBS monomer calculations, which include perturbation corrections to Koopmans theorem, permit accurate assignment of individual i.p.s. No evidence of Koopmans breakdown for FBS is observed although the $\tilde{B}^2\Pi$ and $\tilde{C}^2\Sigma^+$ ionic states show large Koopmans shifts.

The spectra of the dimer and trimer are satisfactorily interpreted using planar models as *ab initio* calculations at the STO-3G level favour planar over non-planar configurations. Analysis of the spectra and a comparison with related molecules indicates considerable π-bonding character in these molecules, also supporting planarity.

Of some interest is the question of the relative stabilities of these molecules, and the mechanism of their formation. In the gas phase the monomer species is only produced in high yield under very fast pumping conditions; otherwise the dimer tends to predominate. Timms [13] has shown that the dimer has a lifetime similar to that of SiF_2. In these experiments the monomer seems to be very short lived and much less stable than HBS or ClBS. The trimer appears to be the most stable and may be formed by disproportionation of the dimer, $3(FBS)_2 \longrightarrow 2(FBS)_3$. The presence of monomer may not be necessary for the formation of the trimer. In these experiments the disproportionation reaction occurs at about −30 °C in contrast to the related reaction involving $(HSBS)_2$ which appears to require heat.[16,17] Low-resolution i.r. spectra have been recorded for solid and gaseous $(FBS)_3$,[12] and although the material appeared stable at 0 °C, it decomposed fairly rapidly above 25 °C giving off BF_3 probably *via* the route, $(FBS)_3 \longrightarrow B_2S_3 + BF_3$, the reverse of a procedure which can produce the dimer. More recent work on the $(ClBS)_3$ and $(BrBS)_3$ species [38] implies that they can be sublimed without decomposition. The calculations used in the assignment indicate that the B–S bond is very polar, *e.g.* for FBS we have B, +0.514 e and S, −0.087 e in line with the observed tendency to form trimeric or even polymeric species. Analogous calculations for the FBO monomer show an even more polar B–O bond; B, +0.985 e and O, −0.559 e, perhaps explaining, despite our efforts, our inability to observe monomeric FBO species.

The question of the initial mechanism of FBS formation over heated boron is not clear. However in earlier work involving HBS,[3] ClBS,[7] and BrBS [5] there was no evidence for trimers, although in some instances complicated spectra were observed. The observation of a trimer in this work suggests that in the $(FBS)_n$ system such species may be involved in monomer formation in the solid–vapour pyrolysis zone.

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