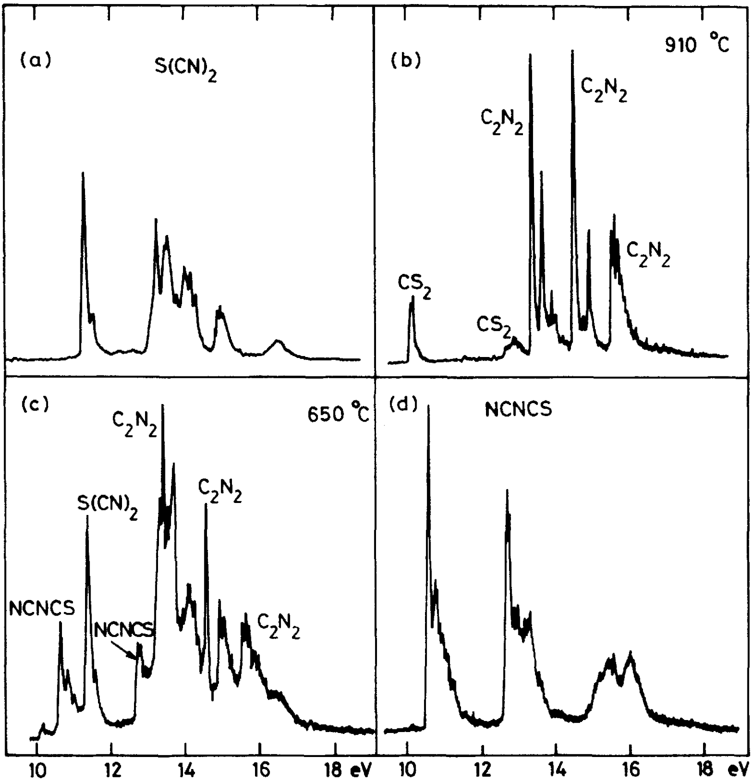

Figure 7 *(a) The p.e. spectrum of* $S(CN)_2$. *(b) The p.e. spectrum of* $S(CN)_2$ *pyrolysed at* 910 °C. *(c) The p.e. spectrum of* $S(CN)_2$ *pyrolysed at* 650 °C. *(d) The p.e. spectrum obtained by revaporizing* NCNCS *from a sample produced under the conditions of (c) and trapped*[9]

overlooked some other important reaction pathways. In the next sections similar situations are discussed, some of which show the rôles reversed in that the p.e. technique has spearheaded microwave detection.

3 Studies of Semistable Molecules

A. Thiocarbonyls and Selenocarbonyls.—It was work on some small thiocarbonyls which originally highlighted the value of joint microwave and photoelectron experiments as general readily applicable techniques for detecting moderately unstable species. There must have been many attempts in the past to make sulphur analogues of formaldehyde, acetaldehyde, and acetone. Indeed Noller[10]

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[10] C. R. Noller, Chemistry of Organic Compounds', W. B. Saunders Co., Philadelphia, 1957, p. 282.

notes that 'the odour of thioacetone is so obnoxious that Baumann and Fromm had to abandon their work because of the protests of the City of Freiburg'. This anecdote conjures up a vision of the smell wafting gently over the city fathers as they, holding their noses, march towards the laboratory to find Baumann and Fromm working without a fume cupboard and oblivious to the odour.

The present work has its origins in a number of experiments. During flash photolysis experiments on dimethyl peroxide aimed at the detection of the methoxy-radical, MeO, the spectrum of formaldehyde $H_2C{=}O$ was detected (unpublished results). Subsequent experiments aimed at detecting the sulphur analogue, $H_2C{=}S$, by photolysing MeSSMe proved unsuccessful because the S—S bond was more difficult to break photolytically and the electronic transition sought is very weak. Some experiments by Callear *et al.*[11] did, however, detect a transient spectrum at around 2100 Å. The first clear spectroscopic identification was made by Johnson *et al.*[12] using flow pyrolysis of MeSSMe and microwave detection. The value of photoelectron spectroscopy, which is also a low pressure (1—50 μHg) technique, for detecting such molecules became clear after experiments on CS produced by a discharge in CS_2[13-15] as well as experiments on H_2CS.[16] Lifetime data for CS had previously been obtained by Dyne and Ramsay[17] and the microwave spectrum by Kewley *et al.*[18] The *synergistic* value of combining the two techniques was evidenced by work on F_2CS, a molecule which had originally been made by Middleton, Howard, and Sharkey[19] by pyrolysing the dimer $(CF_2S)_2$. Several attempts to detect the microwave spectrum by myself and others had failed although the molecule was isolable. Subsequent photoelectron detection of the species in a flow-pyrolysis system[20] showed that the molecule was readily formed by this technique and, using an essentially identical set-up and optimized conditions for production, the microwave spectrum of F_2CS was finally observed.[21] The spectrum was very weak because the dipole moment μ (on which rotational intensity depends as μ^2) was only 0.08 Debye. In addition F_2CS reacts very quickly (in the metal waveguide microwave cell) with adsorbed water to form HF, F_2CO, HFCO, and OCS, whose lines are very strong. The flow technique flushes the cell and after a while the strong lines of by-products can be almost eliminated allowing the search for weak lines to proceed efficiently. A very similar two pronged approach finally succeeded in detecting the elusive mixed halide BF_2Cl, which is in fact isoelectronic with CF_2S. Photoelectron experiments showed clear evidence for the mixed

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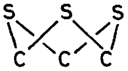
[11] A. B. Callear, J. Connor, and D. R. Dickson, *Nature*, 1969, **221**, 1238.
[12] D. R. Johnson, F. X. Powell, and W. H. Khirchhoff, *J. Mol. Spectrosc.*, 1971, **39**, 146.
[13] G. H. King, H. W. Kroto, and R. J. Suffolk, *Chem. Phys. Letts.*, 1972, **13**, 457.
[14] N. Jonathan and M. Okuda, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 67.
[15] D. C. Frost, S. T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, 1972, **17**, 153.
[16] H. W. Kroto and R. J. Suffolk, *Chem. Phys. Letts.*, 1972, **15**, 545.
[17] P. J. Dyne and D. A. Ramsay, *J. Chem. Phys.*, 1952, **20**, 1055.
[18] R. Kewley, K. V. L. N. Sastry, M. Winnewisser, and W. Gordy, *J. Chem. Phys.*, 1963, **39**, 2856.
[19] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 1965, **30**, 1375.
[20] H. W. Kroto and R. J. Suffolk, *Chem. Phys. Letts.*, 1972, **17**, 213.
[21] A. J. Careless, H. W. Kroto, and B. M. Landsberg, *Chem. Phys.*, 1973, **1**, 371.

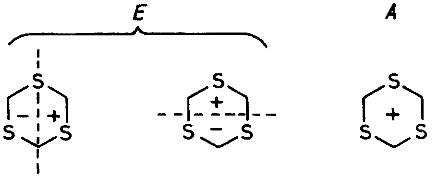
species BF_2Cl and $BFCl_2$ in BF_3–BCl_3 mixtures,[22] and reproducing the flow conditions using microwave detection resulted in the observation of some very weak lines of BF_2Cl which proved very difficult to detect.[23]

The studies on CS, CH_2S, and F_2CS, all of which were known compounds, showed how well microwave and photoelectron techniques could be used to mutual benefit and in particular should enable the detection of new molecules—most obviously new thiocarbonyls. In general, attempts to prepare the smaller thiocarbonyls result in the production of trithianes which are ring trimers, $(R_2CS)_3$. For instance, the reaction of acetaldehyde, CH_3CHO, with H_2S in acid solution yields 1,3,5-trimethyltrithiane $(CH_3CHS)_3$ which has a crown shaped skeleton (1).



(1)

This compound is sufficiently volatile to allow its photoelectron spectrum to be observed Figure 8a. The sulphur *p* orbitals overlap to give rise to *E* and an *A* highest occupied molecular orbitals with the nodal characteristics [(2)–(4)].



(2) (3) (4)

The degenerate combination is less bonding, possessing a node, and gives rise to the broad first IP at 8.39 eV. The more bonding *A* orbital is more stable and is associated with the second IP at 8.91 eV. The intensities are roughly 2:1, in line with the degeneracies. On pyrolysis this spectrum is completely eliminated and replaced by the more simple spectrum of monomeric $CH_3CH{=}S$[24] as shown in Figure 8b. The spectrum of CH_3CHS has a single peak at 8.98 eV which can be assigned to ionization from a single sulphur lone-pair orbital and a second band at 10.87 eV which corresponds to ionization from the C=S π bonding orbital. The spectra given in Figures 8a and b show how efficient and complete is the formation of the monomer from the trimer. On the

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[22] H. W. Kroto, M. F. Lappert, M. Maier, J. B. Pedley, M. Vidal, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1975, 810.

[23] H. W. Kroto and M. Maier, *J. Mol. Spectrosc.*, 1977, **65**, 280.

[24] H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Letts.*, 1974, **29**, 265.

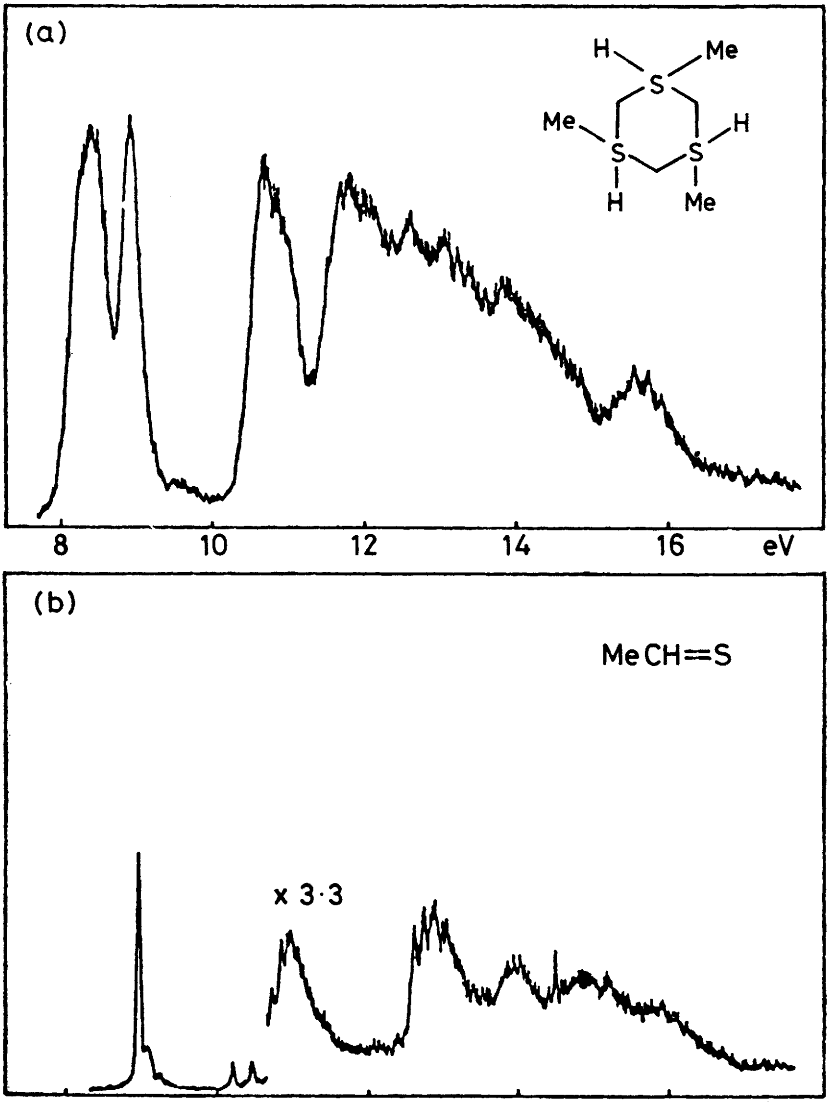

Figure 8 (*a*) *The p.e. spectrum of* $(CH_3CHS)_3$. (*b*) *The p.e. spectrum of monomeric* $CH_3CH{=}S$ *produced by pyrolysing the trimer at* 600 °C. *The first and second bands correspond to ionization of electrons from the n*(S) *and* π(C=S) *orbitals respectively*[24]

basis of these experiments a microwave search for CH_3CHS was carried out successfully[25] and the spectrum of the $J = 3 \leftarrow 2$ transition is shown in Figure 9. The pattern has the classic structure of a bunch of centrally placed $K_A \neq 1$ lines flanked by two $K_A = 1$ lines. Here the $K_A = 1$ lines are split by methyl group internal rotation tunnelling into doublets. From these splittings the barrier height $V_3 = 6.578\,\mathrm{kJ\,mole^{-1}}$ was determined.

In a similar way the photoelectron and microwave spectra of $(CH_3)_2CS$ were observed in the pyrolysis of the trimer $(Me_2CS)_3$.[24]

These experiments were refined still further in an attempt to detect thioketene $CH_2{=}C{=}S$. Some evidence for this species as an intermediate had been presented previously by Howard during the pyrolysis of $Me_3SC{\equiv}C{-}H$.[26] In our experiments[27,28] this species was positively identified by microwave spectroscopy in the pyrolysis of $(Me_2CS)_3$ at 1000 °C. Krantz and Laureni[29] also detected this molecule by i.r. spectroscopy by a neat route involving the pyrolysis of the thiadiazole, $\overline{CH{=}CH{-}S{-}N{=}N}$. Krantz and Laureni also detected $CH_2{=}C{=}Se$ by an analogous route.[30] This route is more efficient and has allowed photoelectron spectra to be observed.[31,32] The microwave spectrum of CH_2CSe has also been studied using this route[33].

As well as thioketene, a second new species was identified when thioacetone trimer was pyrolysed at 1000 °C. This was finally identified as propenethial, $CH_2{=}CHCH{=}S$,[34] which had formed by skeleton rearrangement from thioacetone. This molecule had originally been identified by Bailey and Isogawa[35] in the pyrolysis of diallylsulphide $(CH_2{=}CHCH_2)_2S$ from which it is more efficiently produced.

Some preliminary experiments aimed at developing analogous selenocarbonyl species have been carried out. These are much more difficult to handle (i) because there is an ever-present tendency for elemental Se to deposit and (ii) there is a psychosomatic response at the mere hint that such experiments are being carried out. Before the latter problems halted the present work the microwave spectrum of selenoacetaldehyde CH_3CHSe was detected and studied[36] and some circumstantial photoelectron evidence for CH_2Se obtained. Some synthetic studies of $(CH_2Se)_3$ have been discussed[37] and these methods were modified, with difficulty, to make $(MeCHSe)_3$ which was successfully pyrolysed to produce CH_3CHSe. This species was found to be much less stable and more difficult to

[25] H. W. Kroto and B. M. Landsberg, *J. Mol. Spectrosc.*, 1976, **62**, 346.
[26] E. G. Howard, *Chem. Absr.*, 1962, **57**, 13617*f*.
[27] K. Georgiou, H. W. Kroto, and B. M. Landsberg, *J. Chem. Soc., Chem. Commun.*, 1974, 739.
[28] K. Georgiou, H. W. Kroto, and B. M. Landsberg, *J. Mol. Spectrosc.*, 1979, **77**, 365.
[29] A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, 1974, **96**, 6768.
[30] A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, 1977, **99**, 4843.
[31] H. Bock, B. Solouki, G. Bert, and P. Rosmus, *J. Am. Chem. Soc.*, 1977, **99**, 1663.
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[33] B. Bak, O. J. Nielsen, and H. V. Svanholt, *Chem. Phys. Lett.*, 1978, **53**, 374.
[34] K. Georgiou and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 1.
[35] W. J. Bailey and M. Isogawa, *Polym. Prep. Am. Chem. Soc., Div. Polym. Chem.*, 1973, **14**, 300.
[36] M. Hutchinson and H. W. Kroto, *J. Mol. Spectrosc.*, 1978, **70**, 216.
[37] H. J. Bridger and R. W. Pittman, *J. Chem. Soc.*, 1950, 1371.

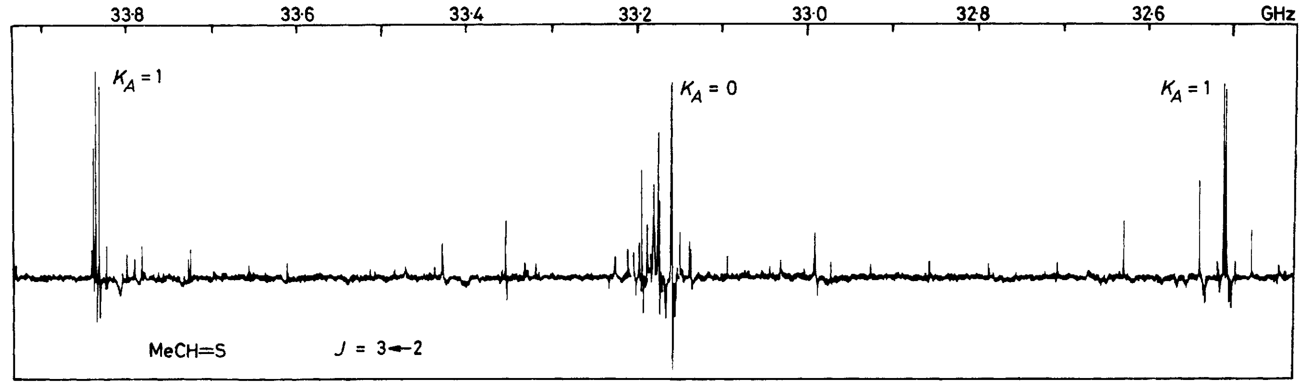

Figure 9 *The* $J = 3 \leftarrow 2$ *microwave transition of* $CH_3CH{=}S$.[25] *The outer* $K_A = 1$ *lines are split into doublets by the effects of methyl group internal rotation. The central group consisting of the* $K_A = 0$ *and* $K_A = 2$ *lines are also split by these effects. The other lines belong to torsional satellites*

detect than CH_3CHS. Attempts to produce selenoacetone compounds appear to lead to the deposition of elemental Se.[38]

Data on various thio- and seleno-carbonyls have been collected together in Table 1.

Table 1 *Collected data for thio- and seleno-carbonyls*

	r(C=S) r(C=Se) /Å	μ/Debye	*Ionization Potentials*/eV	*Other data*
$CH_2{=}S$	1.611[12]	1.6474[12]	9.34 11.78[16]	
$CH_3CH{=}S$	1.610[25]	2.33[25]	8.90 10.87 12.74[24]	V_3 = 6578 J mole^{-1} [25]
$(CH_3)_2C{=}S$	—	—	8.60 10.46 12.40[24]	V_3 = 5440 J mole^{-1} [24]
$CH_2{=}CHCH{=}S$	1.61[34]	2.61[34]	—	r(C=C) = 1.341[34] r(C—C) = 1.46 Å
$F_2C{=}S$	1.59[21]	0.080[21]	10.45 11.34 14.87[20] 17.65	∠(FCF) = 107.1° [21] r(C—F) = 1.315 Å
$CH_2{=}C{=}S$	1.554[28]	1.02[28]	8.9 11.3 12.1[31]	r(C=C) = 1.314 Å[28]
$CH_3CH{=}Se$	1.758[36]	—	—	V_3 = 6859 J mole^{-1} [36]
$CH_2{=}C{=}Se$	1.702[33]	0.9[33]	8.7 10.7 11.6[32]	r(C=C) = 1.313[33]

B. Sulphidoboron and Selenidoboron Species.—A family of molecules related to HCN can be assembled and the resulting cube would have HCN, HBO, and CO along the isoelectronic top edge. The second layer beginning with HC≡P, together with the third layer, is shown in Figure 10. The isoelectronically related molecule HB=O has not been detected spectroscopically although the halide ClB=O has been observed by Kawaguchi, Endo, and Hirota in an O_2–BCl_3 discharge.[39] HBS, the sulphur analogue of HBO, was detected by Kirk and Timms in the products of a high temperature reaction (*ca.* 1000 °C) between H_2S and crystalline boron using a mass spectrometer[40] and further confirmation has come from microwave work by Pearson and McCormick[41,42] and photoelectron work.[43,44] In Figure 11 the spectrum observed using a fast-flow photoelectron instrument (of the type developed at Southampton by Dyke, Jonathan, and Morris[45]) is shown.[46]

The original detection of HB=S initiated a programme to produce substituted analogues by various sensible, though unsuccessful, routes such as the thermal elimination of HCl from BCl_2SH. Finally, a simple modification of the original Kirk and Timms route to HBS was attempted which at the time did not seem likely to be fruitful. In the event it worked beautifully. In the first experiment

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[38] D. S. Margolis and R. W. Pittman, *J. Chem. Soc.*, 1957, 799.

[39] K. Kawaguchi, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.*, 1982, **93**, 381.

[40] R. W. Kirk and P. L. Timms, *Chem. Comm.*, 1967, 18.

[41] E. F. Pearson and R. V. McCormick, *J. Chem. Phys.*, 1973, **58**, 1619.

[42] E. F. Pearson, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.*, 1974, **60**, 1761.

[43] H. W. Kroto, R. J. Suffolk, and N. P. C. Westwood, *Chem. Phys. Letts.*, 1973, **22**, 495.

[44] T. P. Fehlner and D. W. Turner, *J. Am. Chem. Soc.*, 1973, **95**, 7175.

[45] J. M. Dyke, N. Jonathan, and A. Morris, *Electron Spectrosc.*, 1979, **3**, 189 (Academic Press).

[46] T. A. Cooper and H. W. Kroto, to be published.

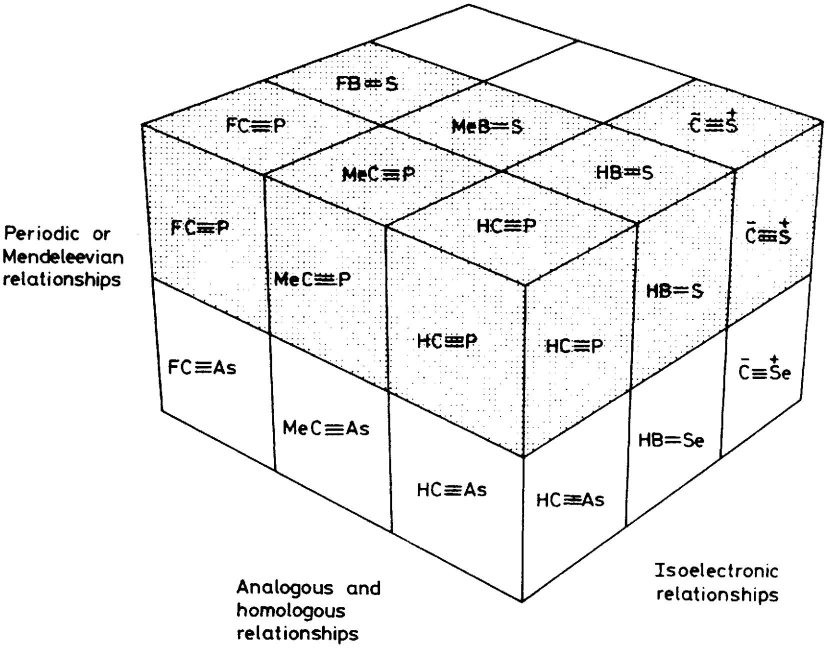

Figure 10 *The* $HC{\equiv}N$ *cube with the top layer removed. All the molecules shaded in the second-row layer have been studied in the work discussed in this review*

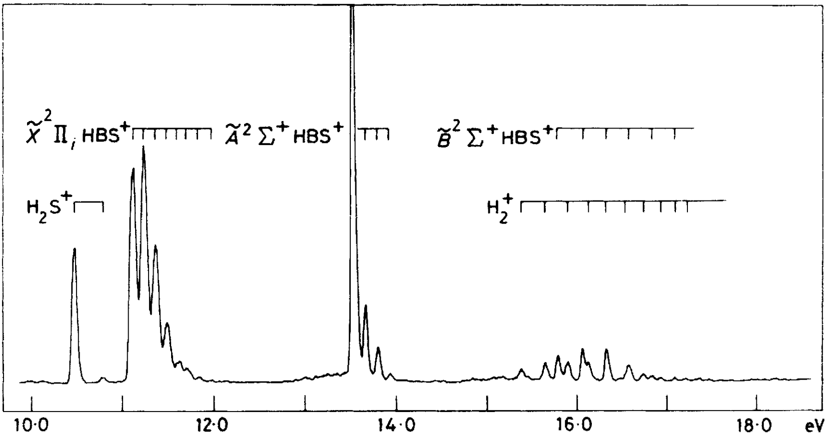

Figure 11 *The p.e. spectrum of* $HB{=}S$ *detected during fast flow pyrolysis of* H_2S *over solid boron*[46]

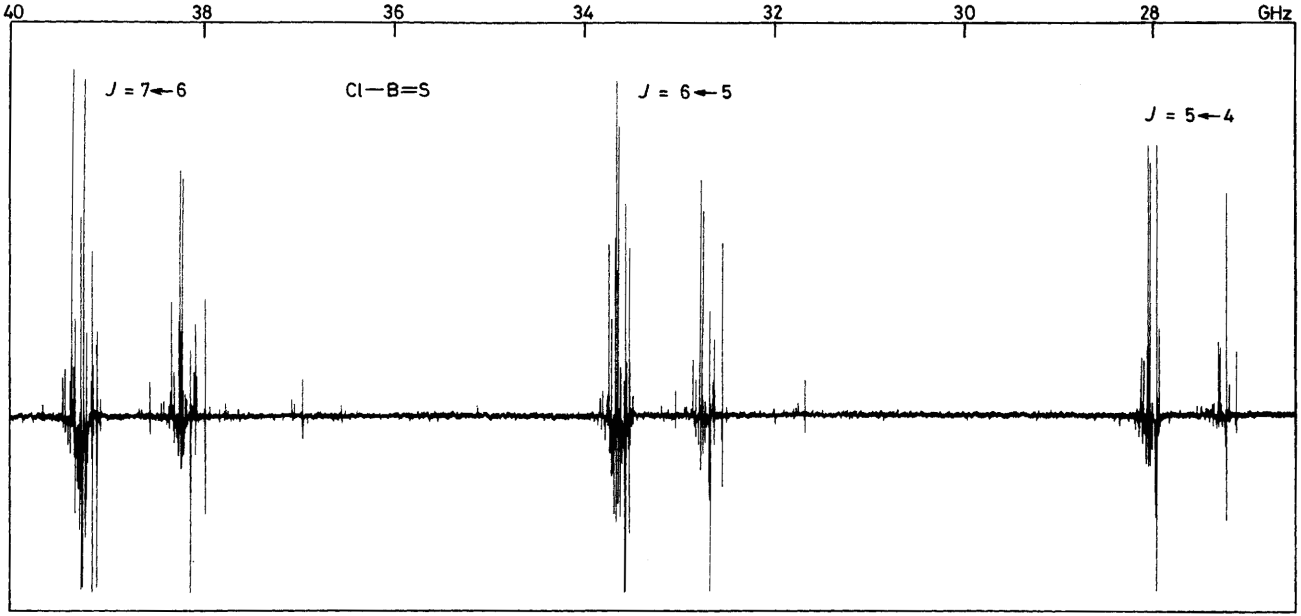

Figure 12 *The wide band scan of* ClB=S.[49] *There are 12 possible isotopic variants involving* ^{35}Cl, ^{37}Cl, ^{10}B, ^{11}B, ^{32}S, ^{33}S, *and* ^{34}S. *Lines of all twelve appear in the spectrum together with associated vibrational satellites. As the most abundant species* ^{35}Cl^{11}B^{32}S *and* ^{37}Cl^{11}B^{32}S *give rise to the most prominent lines each J transition appears to be split into two bunches. The higher frequency bunch associated mainly with* ^{35}Cl *variants, the lower frequency bunch with* ^{37}Cl *variants. The intensities bear a very poor relationship with abundance due to modulation effects*

the reaction of MeSSMe with crystalline boron at *ca.* 1000 °C was investigated and the new molecule $CH_3B{=}S$ was readily identified by microwave measurements.[47,48] Of course, with hindsight, a logical mechanism can be formulated such as equation (11)

$$CH_3SCH_3 \xrightarrow{\Delta} CH_3S\cdot \xrightarrow[B]{\Delta} CH_3SB \longrightarrow CH_3BS \qquad (11)$$

where the electron deficient boron surface is attacked by $CH_3S\cdot$ radicals following the readily accomplished thermal breakage of the S—S bond. The feasible CH_3SB species may then isomerize to the more stable methyl sulphidoboron, $CH_3B{=}S$. The process is probably more complex than this, involving solid products. Photoelectron studies have not detected this species, indicating that in this case the process produces very small amounts of CH_3BS which is detected because microwave spectroscopy is very sensitive to symmetric tops with large dipole moments ($\mu = 2.573$ Debye).

These experiments led naturally on to the study of the halides by essentially the same technique using disulphur dihalides, equation (12).

$$X_2S_2 \xrightarrow[B]{1000\,°C} XB{=}S\ (X = Hal) \qquad (12)$$

In Figure 12 the microwave spectrum of ClBS[49] is shown. Here the wide band scan shows the profusion of isotopic transitions which can be used to obtain accurate structural data. The photoelectron spectrum of ClBS is shown in Figure 12. In the original photoelectron work on HBS[43] and ClBS[50] a modified Perkin Elmer P.S.16 spectrometer was used which allowed only modest flow rates to be achieved. With very fast flow rates the much improved data in Figures 11 and 13[46] are obtained which indicate that reaction (12) yields a remarkably high conversion rate in these cases. This really seems quite surprising considering all the other possible reactions that might be expected to occur.

This work has been extended to the detection of monomeric FBS and BrBS by both photoelectron[46,51] and microwave spectroscopy.[46] The trimers of the sulphidoboron species are quite well known, and in fact, some interesting results on the FBS system have been obtained using combined microwave, photoelectron, and mass spectrometric techniques. These have shown that under the right conditions the spectra of FBS, $(FBS)_2$, and $(FBS)_3$ can be identified in the gas phase.[51] Such species can be formed by high temperature reactions involving SF_4–B, SF_6–B, or BF_3–B_2S_3 as well as the F_2S_2–B.[51]

The sulphidoboron data are collected together in Table 2 and the photoelectron data correlated in Figure 14.

This work has recently been extended to the bottom layer of Figure 10 by the detection of ClBSe[52] using a modification of reaction (12) in which Cl_2Se_2

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[47] C. Kirby, H. W. Kroto, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1978, 19.
[48] C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 1.
[49] C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 130.
[50] C. Kirby, H. W. Kroto, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 3766.
[51] T. A. Cooper, C. Kirby, H. W. Kroto, and N. P. C. Westwood, to be published.
[52] T. A. Cooper, M. A. King, H. W. Kroto, and R. J. Suffolk, *J. Chem. Soc., Chem. Commun.*, 1981, 354.

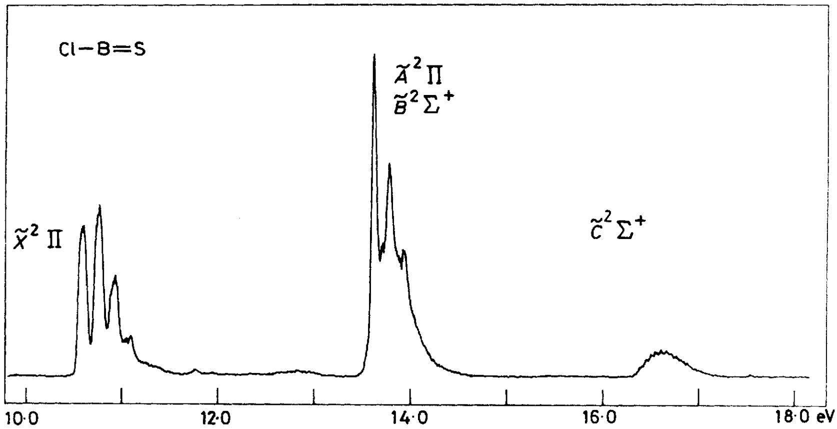

Figure 13 *The fast flow p.e. of* ClB=S.[46] ClBS *is produced by passing* Cl_2S_2 *over solid boron at* 1100 °C *and this spectrum indicates that the resulting vapour phase product is essentially pure* ClBS. *Note that the* 2nd *and* 3rd *ionization potentials coincide closely*

Table 2 *Spectroscopic data on sulphidoboron and selenidoboron species*

Species	r(X—B)/Å	r(B=S)/Å	μ/Debye	*Ionization Potential*/eV	*Ref.*
HB=S	1.169	1.599	2.098	11.1 13.55 15.84	41—44
FB=S	1.284	1.606	1.086	10.9 14.2 17.2 19.62	46, 51
ClB=S	1.681	1.606	1.45	10.57 13.55 13.63 16.36	49, 50
BrB=S	1.831	1.608	—	10.42 12.77 13.43	46
CH_3B=S	1.535	1.603	2.573	—	48
ClB=Se	1.664	1.751	—	—	52

is passed over B at 1100 °C. The spectrum is much more difficult to detect than that of ClBS. This is the first example of a selenidoboron compound and there is no obvious reason why other analogues should not be detectable.

C. Carbon–Phosphorus Multiple Bonds.—*Phospha-alkenes and Phospha-alkynes.* In 1961 Gier at Du Pont showed that phosphaethyne, HC≡P, the phosphorus analogue of HCN is produced when PH_3 is passed through a carbon arc discharge.[53] Subsequently Tyler at NRC studied the microwave spectrum[54] and the optical spectrum with Johns and Shurvell.[55] The existence of this molecule immediately suggested various possible consequences. Could analogues be made and might there be an associated chemistry parallel to that of the nitriles? The chemistry of the C≡P group might be equally, if not even more,

[53] T. E. Gier, *J. Am. Chem. Soc.*, 1961, **83**, 1769.
[54] J. K. Tyler, *J. Chem. Phys.*, 1964, **40**, 1170.
[55] J. W. C. Johns, H. F. Shurvell, and J. K. Tyler, *Can. J. Phys.*, 1969, **47**, 893.