Matrix Isolation Studies of Monomeric Boron Trisulphide†

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The i.r. spectrum of diboron trisulphide isolated in argon and nitrogen matrices is reported. The use of partial isotopic substitution ($^{10}B/^{11}B$ and $^{32}S/^{34}S$) enables the observed bands to be assigned to in-phase and out-of-phase vibrations of two –B=S residues in a non-linear arrangement. This, coupled with mass spectrometric evidence and the assumption of linear S=B–S linkages, show the shape of monomeric B_2S_3 to be based on a planar C_{2v} molecule with a BSB bond angle of *ca.* 120°.

There have been numerous investigations of the boron–sulphur system. Of the mass spectrometric papers, one in 1972 is particularly significant and summarises the literature.[1] In that paper Chen and Gilles demonstrate that the vapours from stoicheiometric B_2S_3 yield principally the molecular ion and state that the vaporisation is congruent.

There have also been optical studies of the vapours using both absorption and emission techniques, as well as matrix isolation spectroscopy. This is discussed in a paper by Brom and Weltner[2] who carried out matrix isolation i.r. studies on the vapours from heated mixtures of boron and zinc sulphide. Although these authors tentatively assigned bands in the 1 400 cm^{-1} region to B_2S_3 they did not observe the expected $^{10}B^{11}B$ isotopomer.

An early electron diffraction investigation[3] of the vapour suggested a planar structure with an S=B–S angle of 180° and a B–S–B angle of 96 ± 5°. It is also interesting to note that in the elegant structural analysis[4] of crystalline B_2S_3 the exocyclic B–S–B bridges have bond angles of 111.5 or 115.2°.

Experimental

Iron(II) sulphide was prepared from the elements by heating:[1] Ag_2S was prepared by the addition of an ammonium polysulphide solution to aqueous silver nitrate solution, followed by filtration and drying at 110 °C.

Boron trisulphide was prepared from the reaction of stoicheiometric amounts of boron and either FeS or Ag_2S. The temperature for reaction varied from 600 to 750 °C, depending on the sample of boron, and the resultant B_2S_3 condensed on the cooler parts of the apparatus as a thin film which could be carefully removed as a sheet.

The i.r. spectrum of the sheet held between CsI plates showed broad bands in the regions of 800 and 1 000 cm^{-1} plus two narrow bands at 1 365 and 1 390 cm^{-1} superimposed on a further broad band at 1 375 cm^{-1}. We were not able to obtain satisfactory mull spectra of B_2S_3.

A quadrupole mass spectrometer was used to examine the vapours. A prominent cluster of peaks was observed centred at *m/z* 120, corresponding to the parent ion $B_2S_3^+$. No other bands of higher *m/z* values were observed up to the instrumental limit of 400.

For the matrix i.r. studies the B_2S_3 (prepared in a separate experiment or *in situ*) was cocondensed with N_2 or Ar (both B.O.C., >99.99%) onto a CsI window cooled to <10 K using an Air Products Displex system AP8S. The samples were normally vaporised at temperatures of *ca.* 600 °C (measured by a sheathed thermocouple) from inductively heated graphite or stainless-steel Knudsen cells. Spectra were recorded on a Perkin-Elmer 225 i.r. spectrometer over the range 4 000—200 cm^{-1}. (No additional bands were seen in experiments where B_2S_3 was prepared separately, transferred to the matrix isolation apparatus under anhydrous conditions, and the whole sample vaporised.)

Boron trisulphide enriched in ^{10}B was prepared from the reaction of iron(II) sulphide with either a chemically homogeneous boron sample or from mixtures of two isotopically distinct samples which had been *manufactured* under closely similar conditions. Preliminary studies showed that the reactivity of boron is dependent on the method of preparation: the temperature of the onset of the reaction of iron(II) sulphide with two different samples of boron may differ by more than 100 °C. Enrichment in ^{34}S was carried out in a similar fashion by reacting enriched sulphur with elemental iron to give the iron(II) sulphide which was then reacted with boron.

Results and Discussion

In all the experiments using natural boron (*ca.* 80% ^{11}B, 20% ^{10}B) four bands of medium to strong intensity were found to occur in the 1 400 cm^{-1} region of the i.r. spectrum of the matrix isolated species. The matrix shifts between argon and nitrogen were, in all cases, less than 5 cm^{-1}. The relative intensities within this sub-group of four bands did not change significantly as a function of the experiment. The frequencies (argon matrix) were 1 331.5, 1 344.7, 1 373.5, and 1 413.0 cm^{-1}.

By varying the $^{10}B:^{11}B$ isotopic ratio it was possible to identify a total of six bands of which four could be unambiguously assigned to the all ^{10}B or all ^{11}B species. The remaining two bands are logically assigned to the corresponding $^{10}B^{11}B$ mixed isotopomers (see Table). No other narrow bands of significant intensity were observed in the frequency range 4 000—250 cm^{-1} apart from those due to matrix isolated impurities H_2O, CO_2, CS_2,[5] and SO_2.

These high-frequency modes observed for boron trisulphide are associated with ν(B=S) vibrations which will be largely uncoupled from other vibrations of the molecule. The situation is similar to that in metal carbonyls where ν(CO) vibrations may be factored out. It is also important to note that the reduced symmetry of the $^{10}B^{11}B$ species allows these vibrations to interact, accounting for the asymmetry in the positions of these bands relative to the parent ^{10}B and ^{11}B isotopomers.

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† *Non-S.I. unit employed:* dyn = 10^{-5} N.

Table. Observed (1 500—1 300 cm^{-1}) and calculated (^{32}S) frequencies for $^{10}B/^{11}B$ isotopomers of B_2S_3

	Antisymmetric (ν_6) parent			Symmetric (ν_1) parent		
Isotopomer	b_1 $^{11}B_2S_3$	a' $^{10}B^{11}BS_3$	b_1 $^{10}B_2S_3$	a_1 $^{11}B_2S_3$	a' $^{10}B^{11}BS_3$	a_1 $^{10}B_2S_3$
Observed ν/cm^{-1} (N_2 matrix)	1 329.0	1 342.5	1 381.75	1 371.0	1 411.0	1 425.0
Observed ν/cm^{-1} (Ar matrix)	1 331.5	1 344.75	1 384.5	1 373.5	1 413.0	1 427.75
Calculated* ν/cm^{-1}	1 331.6	1 344.9	1 384.9	1 373.5	1 415.5	1 430.8

* F(B=S) = 7.298 mdyn Å^{-1}, F(B–S) = 3.865 mdyn Å^{-1}, F(B=S,B–S) = 0.613 mdyn Å^{-1}, F(B–S,B–S) = 0.528 mdyn Å^{-1} (see ref. 6).

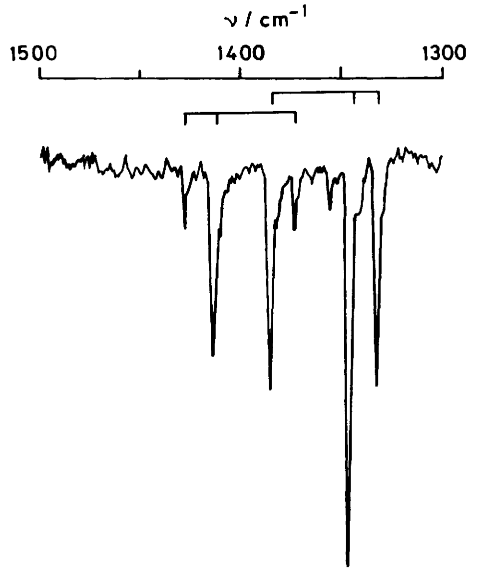

Figure 1. Spectrum of B_2S_3 matrix isolated in argon with a $^{10}B:^{11}B$ ratio of *ca.* 1:1

This has the added interest that it demonstrates that all the vibrations are associated with the isotopomers deriving from one molecular species. A calculation of the $\nu(^{11}B{=}S)$ frequencies from the observed $\nu(^{10}B{=}S)$ frequencies gives agreement to within 4 cm^{-1} merely using the diatomic reduced-mass approximation.

Figure 1 shows the two sets of triplets obtained for B_2S_3 matrix isolated in argon, with a $^{10}B:^{11}B$ ratio of *ca.* 1:1. The intensity ratio within each triplet is *ca.* 1:2:1, as expected for the relative abundances of the isotopomers $^{10}B_2S_3$, $^{10}B^{11}BS_3$, and $^{11}B_2S_3$.

Sulphur isotopic substitution ($^{32}S/^{34}S$), again for *ca.* 1:1 isotopic ratio, showed that two equivalent sulphur atoms were involved in these vibrations. The pure $^{10}B_2S_3$ and $^{11}B_2S_3$ isotopomers give the expected 1:2:1 triplet structure arising from two equivalent sulphur atoms, see Figure 2. (The further doublet splitting on the triplets is not seen at the resolution of our spectra.) In the case of the mixed isotopomers $^{10}B^{11}BS_3$ the modes of vibration correspond largely to movement of either ^{10}B or ^{11}B so that the bands concerned now show a 1:1 doublet structure.

The mass spectrometric data[1] show monomeric B_2S_3 as the principal vapour species under the conditions of our experiment. We therefore adopted a model of B_2S_3 with linear S–B=S and non-linear BSB. Initial calculations suggested that the isotopomer frequencies were insensitive to the BSB bond angle, which is not unexpected. However the angle between the two B=S bonds can be estimated from the relative intensities of the symmetric and antisymmetric B=S stretching frequencies of the C_{2v} parent molecules. In this way we find a BSB bond angle of 124°.

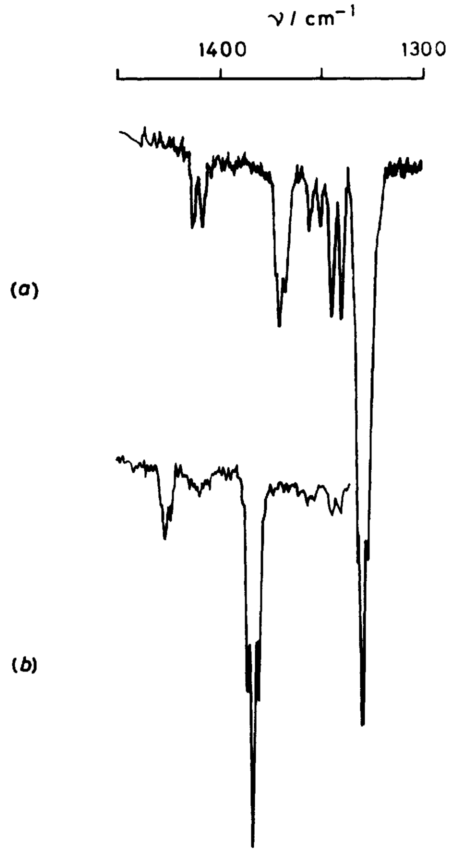

Figure 2. Spectrum of B_2S_3 matrix isolated in argon: (*a*) $^{10}B:^{11}B$ *ca.* 1:4, $^{32}S:^{34}S$ *ca.* 1:1; (*b*) $^{10}B:^{11}B$ *ca.* 25:1, $^{32}S:^{34}S$ *ca.* 1:1

Finally, calculated[6] and observed frequencies in the ν(B=S) region for the $^{10}B/^{11}B$ isotopomers are compared in the Table. The agreement is excellent and the force constants are reasonable. (Calculations based on a dimeric B_4S_6 unit containing a four-membered B–S–B–S ring using interaction constants approximately one-tenth of the primary force constants did not yield frequencies in agreement with those observed.)

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