

## The Raman Spectrum of Boron Trifluoride Gas

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The Raman spectrum of  $\text{BF}_3$  was photographed using a purified preparation obtained from the thermal decomposition of  $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4$ . Of the lines observed, that with the frequency  $888\text{ cm}^{-1}$  is certainly, and the band at  $439\text{--}513\text{ cm}^{-1}$  is probably due to  $\text{BF}_3$ . The Raman frequencies and the infra-red results of Bailey *et al.* are assigned to the fundamental modes of vibrations.

IN a former paper by Anderson, Lassettre and Yost<sup>1</sup> on the Raman spectra of the boron halides, the assignment arrived at for boron trifluoride was stated to be a tentative one. This was due to the fact that, in spite of efforts to avoid it, the boron trifluoride was contaminated with silicon tetrafluoride (and possibly small amounts of other impurities, e.g.,  $\text{SO}_2$ ) as was shown by the presence of at least one Raman line of silicon tetrafluoride in the photographs. The infra-red spectrum of  $\text{BF}_3$  has been determined by Professor Bailey *et al.*,<sup>2</sup> and the results were not in complete agreement with those of the Raman spectrum, the most important difference being the lines assigned to the isotopic doublet  $\nu_3$ . In order to resolve, if possible, these difficulties and discrepancies, the experiments on the Raman spectrum were repeated and with special attention given to the preparation of pure material.

The  $\text{BF}_3$  was prepared by the thermal decomposition of benzene diazonium fluoborate ( $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4$ ).<sup>3</sup> This compound was prepared from purified materials, and at the stages where hydrofluoric acid was involved, platinum dishes or paraffin coated beakers were used to avoid contamination with  $\text{SiF}_4$ . Since strong sulfuric acid is not present during the formation of  $\text{BF}_3$  (gas) there is little likelihood that  $\text{SO}_2$  is present. It is to be emphasized that fluorides formed in reactions requiring concentrated sulfuric acid contain small quantities, 0.1 percent or less, of  $\text{SO}_2$ . The volatile compounds,  $\text{C}_6\text{H}_5\text{F}$ ,  $\text{BF}_3$ ,  $\text{N}_2$ ,

resulting from the decomposition of the diazonium salt were passed through two traps cooled with solid  $\text{CO}_2$ , and one cooled to  $-100^\circ$  ( $\text{CHCl}_3$ , 31 percent  $+\text{C}_2\text{HCl}_3$ , 69 percent cooled to freezing point with liquid air) before being condensed with liquid air. The first three traps served to remove  $\text{C}_6\text{H}_5\text{F}$ , and the  $\text{BF}_3$  was collected in the liquid-air trap. After pumping off the  $\text{N}_2$ , the  $\text{BF}_3$  was allowed to vaporize into an evacuated storage flask. Apiezon grease was used on all stopcocks and was found to be slightly attacked by the  $\text{BF}_3$ , but any volatile product formed was small and was, for the most part, frozen out in the  $-100^\circ$  trap. An amount of  $\text{BF}_3$  sufficient to give a final pressure of 75 pounds gauge was condensed in a quartz Raman tube which was then sealed off. A water-cooled mercury arc, operated with a current of 150 volts and 8 amperes, and burning in quartz was used as a source of 2537A radiation.

When first exposed to the arc the contents of the tube clouded up slightly in a few minutes. On standing, the cloud or precipitate settled, and further illumination did not result in the formation of any more of it. The amount of precipitate was so small that it could hardly be seen on the tube walls. The exposures, with Eastman 50 plates, varied from 28 to 73 hours. Comparison spectra of the mercury arc were taken at the end of each exposure before turning off the arc. Enlargements of the plates were made on process film, and contact prints were made of the latter on extreme contrast Velox paper. Such prints are very convenient for examining a spectrum for faint or diffuse lines. The iron arc comparison spectrum was photographed on both sides of each Raman spectrum.

The results are presented in Table I. The

<sup>1</sup> Anderson, Lassettre and Yost, *J. Chem. Phys.* **4**, 703 (1936).

<sup>2</sup> Bailey, Hale and Thompson, *J. Chem. Phys.* **5**, 275 (1937); *Proc. Roy. Soc.* **161**, 107 (1937).

<sup>3</sup> Balz and Schiemann, *Ber.* **60**, 1186 (1927). These authors describe the compound  $\text{C}_6\text{H}_5\text{N}_2\text{BF}_4$ ; Mr. Henri Lévy of this laboratory is the first to suggest and use the method described above for preparing pure  $\text{BF}_3$ .

numbers in parenthesis adjoining the frequency values are estimated intensities. The assignments refer to the nomenclature and diagrams given in the former paper, by Anderson, Lassettre and Yost.

The lines 1037 and 1100  $\text{cm}^{-1}$  found by Anderson, Lassettre and Yost and assigned to the isotopic doublet,  $\nu_3$ , were found here in the spectrum of the Hg arc. These lines did not appear in the comparison spectrum of Anderson, Lassettre and Yost but were plainly present in the Raman spectrum; it appears from this and other results that the relative intensity of an Hg line in the scattered spectrum may be greater than in a direct exposure of the arc. The explanation may lie in the sensitizing effects arising from continuous fluorescence present in the scattered spectrum. The 1395  $\text{cm}^{-1}$  line assigned to 2  $\nu_2$  by Anderson, Lassettre and Yost was not found; two faint Hg lines at 1376 and 1405  $\text{cm}^{-1}$  were found and may be responsible for the previous result.

The only line that is certainly present in the Raman spectrum of  $\text{BF}_3$  is the strong one at

TABLE I. *The Raman spectrum of  $\text{BF}_3$  (g).*

FREQUENCY IN $\text{CM}^{-1}$	REMARKS
888 (10) 439 to 513 (2)	$\nu_1$ Band corresponds to band at 415 to 465 found by A.L.Y. and assigned to $\nu_4$ . Barely possible that it is due to quartz.
769 to 854 (1)	Band may correspond to 783 of A.L.Y., and explained as resonance between $\nu_1$ and 2 $\nu_4$ . Presence in Hg arc doubtful.
723 (0)	
745 (0)	
1126 (0)	Possibly in Hg arc though not plainly.
1143 (0)	
1448 (0)	Might be in Hg arc. Bailey found 1448 and 1501 in infra-red and assigned them to isotopic doublet, $\nu_3$ .
1481 (00)	

TABLE II.

FREQUENCY IN $\text{CM}^{-1}$	ASSIGNMENT
888	$\nu_1(1)$ , Symmetrical or swelling vibration. <i>R</i> . Forbidden in <i>IR</i> .
722	$\nu_2(1)$ , <i>B</i> atom moves to plane of <i>F</i> atoms. <i>IR</i> . Forbidden in <i>R</i> .
694	
1448	$\nu_3(2)$ , Isotopic doublet, <i>IR</i> ; not certain in <i>R</i> .
1501	
439 to 513	$\nu_4(2)$ , Broad band in <i>R</i> .

888  $\text{cm}^{-1}$ . The band at 439–513  $\text{cm}^{-1}$  is probably due to  $\text{BF}_3$ , since it appears in experiments that differ both in technique and method of preparation of the compound.

The final assignment of the frequencies obtained from the Raman spectrum and infra-red to the fundamental modes of vibration can now be made with moderate assurance that it is correct. The scheme shown in Table II is in complete agreement with that arrived at by Bailey, Hale and Thompson.<sup>2</sup> Their bands at 1448 and 1501  $\text{cm}^{-1}$  are resolved and it seems correct to consider them as an isotopic doublet. They have chosen to resolve analytically the rather broad band at 722  $\text{cm}^{-1}$  into two and then ascribe the two to a second isotopic doublet. This seems a questionable procedure in general, but in this case the result is possibly correct. The numbers in parentheses give the degeneracies; *IR* and *R* refer to the infra-red and Raman spectrum, respectively. The  $\text{BF}_3$  molecule is known to have the *F* atoms at the corner of an equilateral triangle with the *B* atom in the center and in the same plane.<sup>4</sup>

<sup>4</sup> H. Lévy and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 2085 (1937).