The Raman Spectrum of Boron Trifluoride Gas

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The Raman spectrum of BF₃ was photographed using a purified preparation obtained from
the thermal decomposition of C₆H₅N₂BF₆. Of the lines observed, that with the frequency
888 cm⁻¹ is certainly, and the band at 439–513 cm⁻¹ is probably due to BF₃. 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, 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., SO₂) as was shown by the presence of at least one Raman line
of silicon tetrafluoride in the photographs. The infra-red spectrum of BF₃ has been determined
by Professor Bailey et al., 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 ν₄.
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 BF₃ was prepared by the thermal de-
composition of benzene diazonium fluoborate (C₆H₅N₂BF₄). 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 SiF₄. Since strong sulfuric
acid is not present during the formation of BF₃ (gas) there is little likelihood that SO₂ 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 SO₂. The volatile compounds, C₆H₅F, BF₃, N₂,
resulting from the decomposition of the diazonium salt were passed through two traps cooled with
solid CO₂, and one cooled to −100° (CHCl₃, 31 percent +C₂HCl₃, 69 percent cooled to freezing
point with liquid air) before being condensed with liquid air. The first three traps served to
remove C₆H₅F, and the BF₃ was collected in the liquid-air trap. After pumping off the N₂, the
BF₃ 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 BF₃, but any volatile product formed was
small and was, for the most part, frozen out in the −100° trap. An amount of BF₃ 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 2537Å 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 forma-
tion 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
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 cm\(^{-1}\) found by Anderson, Lassettre and Yost and assigned to the isotopic doublet, \(v_3\), 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 cm\(^{-1}\) line assigned to 2 \(v_2\) by Anderson, Lassettre and Yost was not found; two faint Hg lines at 1376 and 1405 cm\(^{-1}\) were found and may be responsible for the previous result.

The only line that is certainly present in the Raman spectrum of BF\(_3\) is the strong one at 888 cm\(^{-1}\). The band at 439–513 cm\(^{-1}\) is probably due to 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. Their bands at 1448 and 1501 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 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 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.\(^4\)