

ISOTOPIC ASSAY OF BORON-10 IN BORON TRIFLUORIDE BY MOLECULAR SPECTROSCOPIC METHOD

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INTRODUCTION

THE relative abundance of different isotopes of an element can be determined by spectroscopic methods because the wavelengths of the spectral lines corresponding to the different isotopes are different and their intensities are directly proportional to their relative abundances. As the isotopic displacements in the atomic spectra of elements are small, the determination of the relative abundance making use of the atomic spectra requires the use of high resolution instruments like the interferometers or large grating spectrographs. In the case of molecular spectra, however, the isotopic displacements of the bands are often large and in such cases spectrographs of medium dispersion are adequate to separate the isotopic band heads.

Boron-trifluoride gas enriched in ^{10}B is extensively used in neutron counters. During the process of enriching BF_3 , it is necessary to estimate the ^{10}B concentration at different stages. Mass-spectrometric methods could be used but they are not as quick as spectrographic methods and further suffer from memory effects. A spectrographic method was therefore thought to be desirable and has been developed.

To determine the ^{10}B isotopic concentration by the molecular spectroscopic method, it is necessary to obtain a molecular spectrum containing a boron atom which would give an appreciable $^{10}\text{B} - ^{11}\text{B}$ isotope shift. For this purpose, the BF_3 was subjected to different types of excitation, like the high voltage transformer discharge and the high frequency oscillator discharges, and the spectra obtained under these conditions were studied and the results of these studies were reported earlier (Krishnamachari and Vengsarkar, 1963). As mentioned in this report, a microwave oscillator (2450 Mc./sec.) discharge through a mixture of BF_3 and argon was found to give a strong emission spectrum of the BO_2 radical, which is the counterpart of the absorption spectrum obtained by Johns (1961) in the flash photo-

lysis of BCl_3 and oxygen. The emission spectrum of BO_2 could also be obtained equally strongly when krypton or xenon are used in place of argon. Oxygen was not added separately but the trace amounts available either in the gases used or evolved in the discharge tube were sufficient to give a strong BO_2 spectrum. Our identification of the BO_2 emission spectrum has also been independently confirmed by Mathews and Innes (1964). The O-O band at 5457 Å shows a considerable isotope shift ($^{10}\text{BO}_2 - ^{11}\text{BO}_2$) of about 22 cm.^{-1} . Since the spectrum could be obtained with great intensity using very small amounts of BF_3 (about 2 mg.) and also because the isotopic heads could be well separated even on a medium dispersion instrument, it was found suitable for the determination of ^{10}B isotopic concentration in enriched BF_3 samples. The spectra were recorded on a three-prism glass Steinheil spectrograph. The relative intensities of $^{10}\text{BO}_2$ and $^{11}\text{BO}_2$ band heads were measured for known standards (mass-spectrometrically analysed) and the corresponding working curve plotted. The standard deviation obtained from a number of readings varies from 1.7 to 2.7 in the concentration range studied, *i.e.*, 20 to 90 per cent. of ^{10}B .

EXPERIMENTAL

The natural and all the enriched samples were obtained from the Chemical Engineering and Neutron Physics Divisions of our Establishment, in the form of $\text{CaF}_2 - \text{BF}_3$ complex. The complex was heated to 100° C. in a glass tube which was evacuated continuously for about six hours so as to remove all traces of moisture. The temperature was then raised to 250° C. when the complex released the BF_3 gas which was collected in a separate tube.

The BF_3 gas was led into a quartz discharge tube where it was mixed with argon in the ratio of 1:20, the total pressure inside the discharge tube being 4 mm. of Hg. The discharge was excited by means of a Picker-Harting microtherm microwave oscillator of 2450 Mc./sec. and a power output of 100 watts; all the spectra were recorded with 80% of the rated power. Under these conditions an intense greenish discharge was obtained, the spectrum of which was photographed on a Steinheil three-prism glass spectrograph. The relative intensities of the isotopic band heads were determined photographically. The details concerning the spectrographic set-up are given in Table I.

RESULTS

The emission spectrum of BO_2 extends from 4900–6400 Å and consists of red degraded bands at 4900, 5180, 5460, 5800, 6200 and 6380 Å. These bands form a progression of the symmetric stretching frequency in the upper

TABLE I

Spectrograph :	.. Steinheil three-prism glass (with a dispersion of 27 Å/mm. at 5800 Å)
Slit width	.. 30 microns
Exposure	.. 1 to 2 minutes depending on the intensity of the discharge
Plate and Processing	.. Ilford R-40 developed in Kodak D-19 developer for 3 minutes and fixed in F-5 fixer for 10 minutes both at 20° C. Then the plate was washed for half an hour in running water and then dried.
Microphotometer	.. The densities of the R ₁ band heads of ¹¹ BO ₂ at 5456.8 Å and of ¹⁰ BO ₂ at 5450.4 Å are measured with Hilger's non-recording microphotometer H 609.
Plate calibration	.. A 3-amp. d.c. ion arc is exposed for one second with a 7-step rotating step sector (1:2 step ratio) placed in front of the slit.

and lower electronic states with the 5456.8 Å band as the origin band. As analysed by Johns, the spectrum arises due to a transition between $A^2\pi_u - X^2\pi_g$ states. In both the states the molecule is linear. From the vibrational frequencies in the two electronic states, the difference in the zero point energies in the two electronic states comes out as 490 and 511.5 cm^{-1} for the ¹¹BO₂ and ¹⁰BO₂ molecules and the difference between them, which is 21.5 cm^{-1} gives the isotope shift for the O-O band of the system. Since the observed bands, besides the O-O band, involve the symmetric stretching frequency for which there is no boron isotopic effect, the isotope shifts in these bands are about the same as that for the O-O band. Hence the O-O band itself was selected for isotopic assay work because of its greater intensity than the other bands. The variation of relative intensities for the two isotopic heads for four different concentrations is shown in Fig. 1.

Five standards in the range of 20 to 90 per cent. of ¹⁰B, which were mass-spectrometrically analysed, were used for obtaining the working curve. The intensity ratio of the ¹⁰BO₂ and ¹¹BO₂ band heads, plotted against the ratio of the ¹⁰B and ¹¹B concentrations is shown in Fig. 2. For each standard, 18 individual determinations of the relative intensities were made from the

spectra taken on 3 plates of the same make and the standard deviation was calculated from the formula, standard deviation = $\sqrt{\frac{\sum d^2}{(n-1)}}$, where d is the deviation from the mean value and n is the total number of determinations made. The standard deviations corresponding to different concentrations are shown within brackets on the working curve. As seen from Fig. 2, the working curve is a straight line passing through the origin and inclined at 45° to the axes thereby showing that the bands do not suffer from any interference. Thus the present method could be used as an absolute one for the determination of ^{10}B concentration in enriched BF_3 samples.

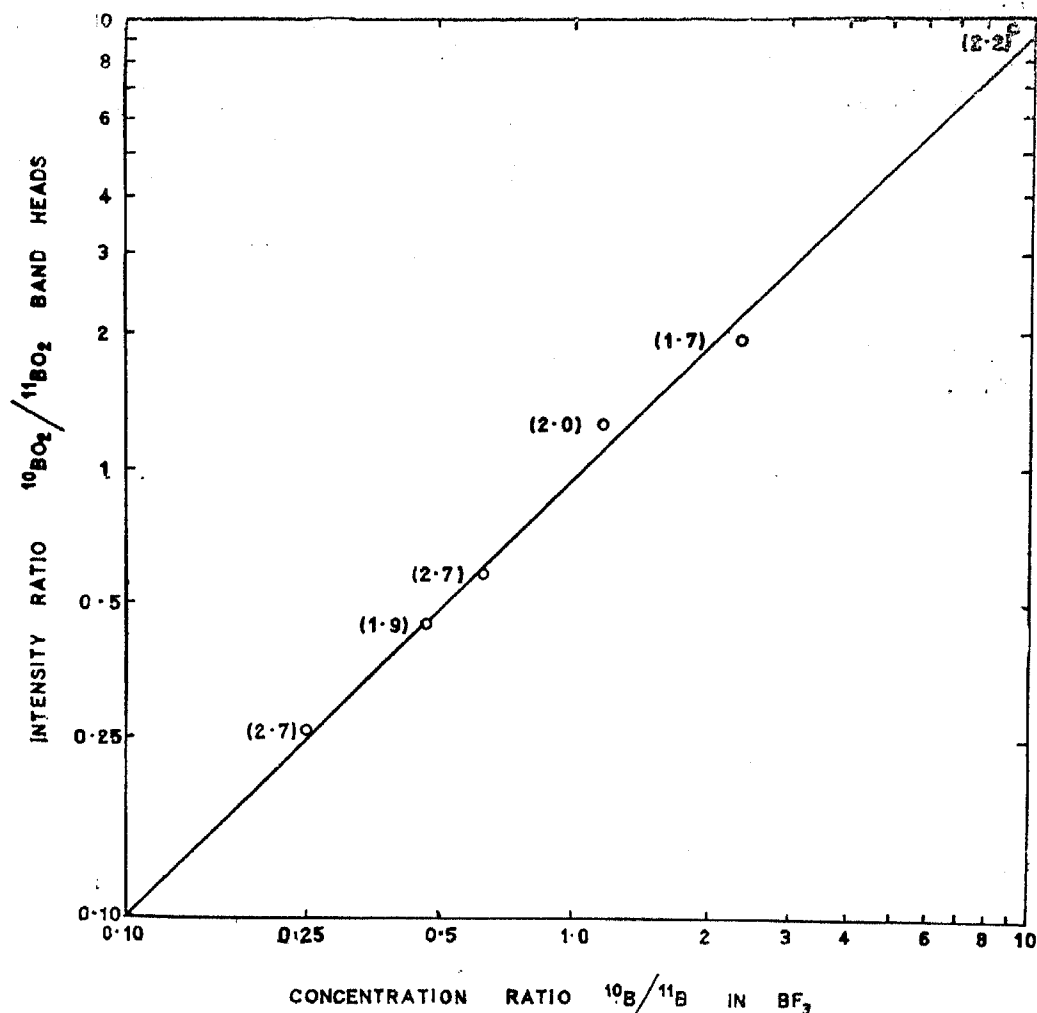


FIG. 1. R_1 heads of $^{10}\text{BO}_2$ and $^{11}\text{BO}_2$ for BF_3 samples of different ^{10}B concentrations,

SUMMARY

A molecular spectroscopic method has been developed to estimate the ^{10}B concentration in BF_3 . This method makes use of the isotopic displacements in the R_1 heads of the BO_2 band at 5457 Å. The emission spectrum of the BO_2 radical was obtained in a microwave oscillator discharge through BF_3 and an excess of argon, having oxygen as trace impurity. The intensities of the R_1 heads were measured for different standards containing 20 to 90 per cent. of ^{10}B in BF_3 . The standard deviation varies from 1.7 to 2.7 in the above concentration range.

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