filter. In the near infrared powders of quartz, LiF, MgO, and doubtless many other crystals have sharp and conveniently located peaks. In the far infrared the alkali halides form a series, together with the monovalent thallium halides, covering quite a range of wave-lengths. By proper choice of particle size these filters may be made quite opaque in the short wave regions but will still possess a high transmission in the neighborhood of the peak.

(2) The production of comparatively monochromatic beams of light by means of these filters immediately suggests their possible use in the construction of a survey spectrometer for the far infrared, similar to the reststrahlen method introduced by Rubens. Since only a source, two mirrors, and a receiver would be required the apparatus would be simple. Whereas the reststrahlen method requires one or more good sized crystals of each material, which are often difficult or impossible to obtain, only a small amount of the crystal powder is needed to make one of these filters. Using only the substances investigated in the present work, some fifteen or twenty different wave-lengths are available between 6μ and 90μ, and it is very likely that this list will be extended by further work in the field.

(3) Since the very existence of the Christiansen effect depends upon the equality of the refractive indices of particle and medium for some wave-length, we have here a method for determining dispersion curves in the infrared. In case the dispersion of either crystal or medium is known, the measurement of the Christiansen peak gives one point on the dispersion curve of the other. Since it is usually easier to obtain the dispersion curves of crystals in the infrared than of liquids, a series of such crystal powders could be used to establish points on the dispersion curves of liquids. In the inverse case, the dispersions of some liquids are known, and in the previous section were shown curves of the transmissions of MgO, NaCl, and quartz immersed in CS_2 and CCl_4.

(4) It has recently been pointed out to us by Professor E. U. Condon, that since the measurement of the Christiansen peak in air gives one point on the dispersion curve of the crystal, namely, that at which $n=1$, this value may be used in the classical dispersion equation, together with values from the visible and ultraviolet regions of the spectrum to determine the intensity constant characterizing the infrared absorption band of the crystal. This problem will be discussed in a later paper.

The Band Spectrum of Boron Fluoride

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(Received March 16, 1936)

The spectrum of boron fluoride as excited by the electrodeless discharge has been photographed at both high and low dispersion. Sixteen new bands were observed in the region between $\lambda\lambda 3712$ and 2580A. These bands degrade to the violet; have five head-forming branches, and resemble very closely the third positive bands of CO, a result to be anticipated from the fact that CO and BF both possess ten extranuclear electrons and should therefore have similar electronic configurations. Two systems were found with a common lower electronic level: an A system $(\nu^{(0,0)}=32,020.5$ cm$^{-1})$ of 12 bands and one isotope band, and a B system $(\nu^{(0,0)}=37,991$ cm$^{-1})$ of three bands. The constants obtained from the vibrational analysis are: ω_e', 1631.40 cm^{-1}; ω_e'', 1323.64 cm^{-1}; $x_e'\omega_e'$, 23.10 cm^{-1}; $x_e''\omega_e''$, 9.40 cm^{-1}.

INTRODUCTION

THE BF molecule is isoelectronic with N_2 and CO, hence considerable interest attaches to its band spectrum. Largely because of difficulties in exciting and isolating the band

spectrum of BF, it has been inadequately investigated. The chemically stable compound of boron and fluorine, BF_3, is a gas at room temperature, and a Geissler discharge in BF_3 has been used by several investigators in searching for BF

bands. Johnson and Jenkins[1] attempted to excite the BF spectrum in BF_3 gas but were troubled with the appearance of SiF bands. Under better conditions of purity, Tawde and Johnson[2] obtained bands in the visible region of the spectrum which they ascribed to BF. However, the bands did not show the expected resemblance to CO bands.

Experience with the electrodeless discharge in this laboratory[3] showed that the band spectrum of a diatomic fragment of a polyatomic molecule is brought out strongly in this source, hence the project was undertaken of subjecting BF_3 to this type of discharge for the purpose of obtaining BF bands. This technique also offered to simplify the problem of eliminating impurities.

While this investigation was in progress, Dull[4] reported obtaining three bands of BF in the ultraviolet, showing a marked similarity in structure to bands of the third positive group of CO. We have observed the same bands, and sixteen others of the same type. This report deals with the vibrational analysis of the observed bands.

EXPERIMENTAL

Preliminary experiments were made with gas generated by the method of Germann and Booth.[5] The generator was sealed to an electrodeless discharge tube and a pumping system. A Féry type quartz spectrograph was used to photograph the spectrum, and many bands were obtained, including those of CO, BO, SiF, OH, N_2, and some which could not be fitted into any known band system. Visual observation with a spectroscope showed the presence of the bands of Tawde and Johnson.[2] Upon seeking conditions for the maximum intensity of the latter, it was found that the presence of a liquid-air trap in the pumping system weakened the intensity of these bands very rapidly. Lowering the liquid-air bath on the trap resulted in releasing BF_3 back into the discharge tube. In a very short time, how-

ever, the bands of Tawde and Johnson again disappeared, and CO bands became very intense. This always occurred with a tube that was not baked out, suggesting that the CO was released from the walls of the tube, while the BF or BF_3 apparently was "cleaned up" under the influence of the discharge.

Through the kindness of Professor H. S. Booth, and Mr. Karl Willson at Western Reserve University, we obtained some samples of BF_3 gas which they had dried and purified very carefully. The technique adopted in transporting and exciting the gas was as follows. A discharge tube of about 30 cm length and 5 cm diameter was fitted with a window transparent to the ultraviolet, either of quartz attached by a quartz-to-Pyrex graded seal, or of glass blown into a very thin re-entrant bubble. The other end of the discharge tube was provided with a side arm, and an exhaust tube. A short section of the exhaust tube was constricted, and contained a pellet of Wood's metal. The tube was baked for several hours at 500°C while exhausting, and then sealed off from the pumps. The Wood's metal was melted into the constriction in the exhaust tube, closing the latter so that it could be attached to the BF_3 generator without readmitting air to the discharge tube. The Wood's metal was then melted out of the constriction, and pure BF_3 gas was admitted at a pressure of about half an atmosphere. Thereupon the tube was sealed off once more, and was ready to be transported to this laboratory. The precautions described were found to be essential in order to eliminate impurities, of which the most persistent was CO. With the technique described, the only remaining bands appearing besides those of BF were the SiF bands. Undoubtedly, some SiF_4 is formed by reaction of BF_3 with the hot glass when sealing off, as well as with the walls of the tube during the discharge.

The discharge tube was placed within the helix of a high-frequency oscillator, and the pressure of the gas within the tube was brought down to a suitable value by refrigerating the side arm with liquid air. It was found that with a Dewar flask placed to bring the liquid-air level about one cm below the tip of the arm, the pressure could be maintained indefinitely by occasional adjustments as the liquid air evaporated. In this way,

[1] R. C. Johnson and H. G. Jenkins, Proc. Roy. Soc. A116, 327 (1927).

[2] N. R. Tawde and R. C. Johnson, Phil. Mag. 13, 501 (1932).

[3] H. M. Strong, Thesis (M. S., Ohio State University, 1933).

[4] R. B. Dull, Phys. Rev. 47, 458 (1935).

[5] A. F. O. Germann and H. S. Booth, J. Phys. Chem. 30, 369 (1926).

the vapor pressure in the discharge was substantially constant in spite of "clean-up" produced by the discharge.[6]

The 100-watt oscillator previously described[7] was used for some of the preliminary work. The three-meter oscillator of the Central Scientific Company was also used at moderate dispersion. For exposures at higher dispersion, a more powerful oscillator was constructed. This consisted of an 852 triode in a Hartley circuit, the output of which was condenser coupled to a tuned circuit using an 849 triode biased for class C amplification. The plates of the tubes were supplied with direct current at 1200 volts by means of a motor-generator. A frequency of approximately 3000 kilocycles per second was obtained with the circuit elements employed.

A Hilger E_1 Littrow mounted quartz spectrograph was used to photograph the region from 4000 to 2300A. This instrument has a dispersion of 14A/mm at 4200A, and 5A/mm at 2300A. Suitable exposures were obtained in $1\frac{1}{2}$ hours. Longer exposures brought out more general blackening, rather than more band features.

A 21-foot grating was also used, the region 6000 to 2500A being covered in the first order.

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[6] H. M. Strong and H. P. Knauss, Phys. Rev. **47**, 642A (1935).

[7] H. P. Knauss and J. C. Cotton, Phys. Rev. **38**, 1190 (1931).

The grating has 30,000 lines to the inch, giving a dispersion of 1.2A/mm, and is mounted on a Paschen-Runge mounting. The maximum exposure time attempted was 36 hours.

The spectrum of the iron arc was superimposed on the band spectrum for comparison. A Geneva Society comparator was used to make wavelength measurements.

RESULTS

Nineteen bands, degraded to the ultraviolet, which were observed in the region 4000 to 2300A on plates taken with the Hilger E_1 spectrograph have been ascribed to BF. Of these, six were sufficiently intense to appear on the 21-foot grating plates in the first order, including three bands reported by Dull.[4]

The probable error of measurements made on the 21-foot grating plates is 0.05 cm^{-1}. The other measurements, on Hilger E_1 plates, have a probable error varying from 1 to 6 cm^{-1} in going from higher to lower frequencies in the region occupied by the observed bands.

In Fig. 1 the band at 3122A is reproduced together with a comparable band of CO at 2833A. The scale of enlargement for the latter is only about 0.6 as large as that for the former, chosen in order to match similar features of the
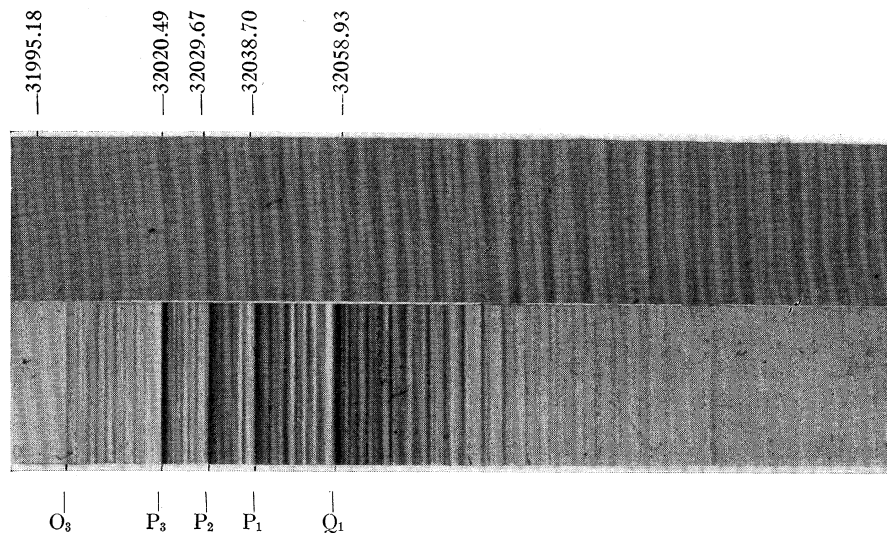

FIG. 1. *Above.* (0,0) Band of the A system of BF at 3122A, with frequencies of heads shown in cm^{-1}. *Below.* (0,0) Band of the third positive system of CO at 2833A. Designation of heads from rotational analysis of Dieke and Mauchly.[8] The lower strip is enlarged about 0.6 as much as the upper one in order to illustrate similarities of band structure.

two bands. The designations for the sub-heads of the CO band are taken from the rotational analysis of Dieke and Mauchly.[8] The features of the BF band are not sufficiently clear-cut for purposes of rotational analysis. Three strong subheads could be distinguished in most of the bands, corresponding to the P_3, P_2 and P_1 heads of CO. Weaker heads, observable in some of the bands, appear to correspond to O and Q branch heads of the CO bands, and have been designated accordingly. The edge of the Q branch, while not strictly a head, is listed wherever it appears as a distinct feature of the band.

Twelve of the observed bands belong to the same system, designated as the A system. One band at 3560A is the isotope band of $B^{10}F^{19}$, corresponding with the (0,3) band of $B^{11}F^{19}$ at 3548A. The intensities and frequencies of the heads of the A system bands are listed in Table I. Three other bands have final levels in common with the A system, but an initial level which is different; these are designated as members of a B system, and are tabulated in Table II. In Table III are listed three bands not assigned to either system.

The vibrational spacing of bands of the A system is represented by the equation:

$$\nu_h = 31{,}869.98 + 1631.40(v' + \tfrac{1}{2}) - 23.10(v' + \tfrac{1}{2})^2$$
$$- 1323.64(v'' + \tfrac{1}{2}) + 9.40(v'' + \tfrac{1}{2})^2$$

where ν_h represents the frequency in cm^{-1} of the sub-head assumed to be nearest the band origin, the one corresponding to the P_3 sub-head of the CO band, Fig. 1. The frequency separation of the sub-heads varies from one band to the next, and in the absence of a rotational analysis of the bands, no attempt is made to show this in the equation. The B system bands are represented by:

$$\nu_h = 38{,}651.4 - 1323.64(v'' + \tfrac{1}{2}) + 9.40(v'' + \tfrac{1}{2})^2$$

where ν_h again refers to the P_3 head.

The constants in the above equations are based on the high dispersion plates. The residuals (obs.-calc.) thus obtained for the heads measured at low dispersion are preponderantly positive, which may indicate a slight displacement of the iron comparison lines relative to the bands.

[8] G. H. Dieke and J. W. Mauchly, Phys. Rev. **43**, 12 (1933).

TABLE I. *A system bands of BF.*

v' v''	INT.	ν OBS. (cm⁻¹)	OBS.-CALC. (cm⁻¹)
	9	32058.93 Q_1	
	9	*32038.70 P_1	
0 0	9	*32029.67 P_2	
	7	*32020.49 P_3	+0.06
	2	*31995.18 O	
	5	30751.6 Q_1	
	7	*30734.70 P_1	
0 1	5	*30724.80 P_2	
	5	*30715.41 P_3	−0.18
	4	30696.82 O	
	5	29467.5 Q_1	
	6	*29449.30 P_1	
0 2	5	*29438.67 P_2	
	3	*29429.70 P_3	+0.15
	4	29413.2 O	
	4	28199.2 Q_1	
	5	*28182.66 P_1	
0 3	5	*28172.23 P_2	
	4	*28162.20 P_3	−0.11
	3	*28144.07 O	
0 3** 0	0	28087.5 Q_1	
	0	28072.1 P_1	
	1	28057.4 P_2	
	0	28039.3 P_3	−4.3
	0	26952.4 Q_1	
	0	26938.4 P_1	
0 4 0	0	26922.3 P_3	+8.4
	0	26898.4 O	
	3	33640.7 Q_1	
	4	*33623.59 P_1	
1 0 4	4	*33613.86 P_2	
	4	*33605.69 P_3	+0.06
	2	33580.0 O	
	0	32334.6 P_1	
	0	32320.1 P_2	
1 1 0	0	32301.7 P_3	+0.9
	1	32287.2 O	
	1	31052.1 P_1	
1 2 1	1	31029.6 P_2	
	1	31019.5 P_3	+4.7
	3	29782.1 P_1	
1 3 2	4	29765.4 P_2	
	2	29756.2 P_3	+8.7
	2	28534.8 Q_1	
	1	*28518.60 P_1	
1 4 0	0	*28509.07 P_2	
	0	*28499.36 P_3	+0.29
	1	28482.3 O	
	0	27305.6 P_1	
	0	27290.4 P_2	
1 5 0	0	27278.0 P_3	+8.6
	0	27255.9 O	
	0	35181.7 Q_1	
	2	35162.6 P_1	
2 0 0	3	35153.8 P_2	
	2	35145.2 P_3	+0.6
	1	35124.8 O	

* Frequencies computed from wave-length measurements made on 21-foot grating plates are marked by an asterisk. Other wave-length measurements and all intensity estimates are based on E_1 plates.
** Isotope band, $B^{10}F^{19}$.

Since the residuals are not large in comparison with the probable error, no adjustment of the data seemed necessary.

DISCUSSION

With the aid of constants of the A system of the $B^{11}F^{19}$ molecule, positions were calculated for possible bands of what we may call the A^i system of the less abundant molecule $B^{10}F^{19}$. Only one measured band could be assigned to the A^i system. In all other cases, the failure to observe the A^i bands could be accounted for either by the low intensity to be expected or by confusion with an A band. The excellent agree-

TABLE II. *B system bands of BF.*

v'	v''	INT.	ν OBS.	OBS.–CALC.
		6	38028.3 Q_1	
		7	38009.7 P_1	
0	0	8	37999.1 P_2	
		7	37991.4 P_3	−0.5
		6	36722.1 Q_1	
		4	36704.7 P_1	
0	1	6	36700.5 P_2	
		4	36687.9 P_3	+0.8
		2	36660.3 O	
		4	35435.8 Q	
		3	35418.4 P_1	
0	2	4	35409.4 P_2	
		3	35400.8 P_3	−0.3
		2	35390.7 O	

TABLE III. *Unassigned bands.*

INT.	ν OBS.	INT	ν OBS.	INT.	ν OBS.
0	38833.1	0	38544.5	0	37224.8
1	38801.4	0	38518.3	0	37207.1
2	38787.3	1	38505.4	1	37196.0
1	38775.1	0	38493.7	0	37187.1
				0	37118.6

TABLE IV. *Comparison of lower level of BF bands with a $^3\Pi$ level of CO.*

	$\omega_e(H)$ (cm^{-1})	$x_e\omega_e(H)$ (cm^{-1})	D (volts)	r_e (A)	B_e (cm^{-1})
CO	1739.3	14.5	4.0	1.204	1.686
BF	1323.64	9.40	?	1.33*	1.36*

* Computed from empirical relationship of Allen and Longair.[9]

ment between the observed and calculated position of the isotope band removes any doubt which otherwise might attach to the identification of the emitter of the bands.

An estimate of the interatomic distance, r_e, can be made with the aid of the relationship proposed by Allen and Longair:[9]

$$r_e{}^3\omega_e\mu^{\frac{1}{2}} = 10.6 \times 10^{-33},$$

where μ is the reduced mass, and ω_e is the frequency (in wave numbers) for vibrations of small amplitude about the equilibrium position, obtained from the spectrum. On this basis, the value of r_e for the common (lower) state of the A and B systems of BF is 1.33A; that for the upper state of the A system is 1.24A.

On the basis of the predicted similarity between BF and CO spectra, and the observed resemblance illustrated in Fig. 1, it is natural to

[9] H. S. Allen and A. K. Longair, Phil. Mag. **19**, 1032 (1935).

suppose that the A system bands correspond to the third positive bands of CO, and the B system to the $3A$ bands of CO. If this is correct, the lower level of the bands is itself an excited state, and the molecular constants obtained for it do not apply to the unexcited state of the molecule. As suggested by Dull,[4] the lower state may be either $^3\Pi$ or $^3\Sigma$ depending on whether the transition is $^3\Pi - {}^3\Sigma$ or $^3\Sigma - {}^3\Pi$. In Table IV a comparison is made with the a $^3\Pi$ level of CO, on the basis of the assumed correspondence.
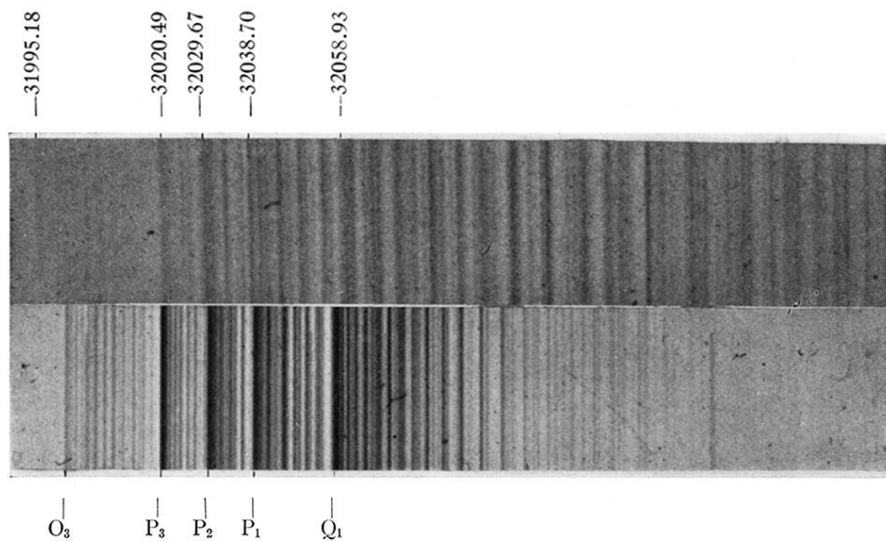
ACKNOWLEDGMENTS

FIG. 1. *Above.* (0,0) Band of the *A* system of BF at 3122A, with frequencies of heads shown in cm^{-1}. *Below.* (0,0) Band of the third positive system of CO at 2833Å. Designation of heads from rotational analysis of Dieke and Mauchly.[8] The lower strip is enlarged about 0.6 as much as the upper one in order to illustrate similarities of band structure.