IDENTIFICATION OF THE 1-0 AND 1-2 BANDS OF THE $c\ ^3\Sigma^+ \rightarrow a\ ^3\Pi$ SYSTEM OF BF

S. L. N. G. KRISHNAMACHARI AND MAHAVIR SINGH

Spectroscopy Division, Atomic Energy Establishment, Trombay, 414 A, Cadell Road, Bombay-28

TWO triplet band systems, $b\ ^3\Sigma^+ \rightarrow a\ ^3\Pi$ and $c\ ^3\Sigma^+ \rightarrow a\ ^3\Pi$, are known for the BF molecule.[1,2] The vibrational frequencies for the $a\ ^3\Pi$ and $b\ ^3\Sigma^+$ states were known while that for the $c\ ^3\Sigma^+$ state was unknown so far as no bands involving $v' \geqslant 1$ of this state were observed earlier, and the failure to observe these bands was presumed to be due to predissociation.[3]

During the course of our investigations on the discharges through BF_3 gas, while using a radio-frequency oscillator (3-11 Mc./sec. frequency and 100 watts power) two new bands were observed at 2525 Å and 2707 Å (for ^{10}BF molecule) along with the other known bands of the $c \rightarrow a$ and $b \rightarrow a$ systems. The new bands could be obtained with good intensity at very low pressures (few microns) of BF_3. These are violet degraded and contain five prominent heads, four of which are strong. They resemble closely the bands of the $c \rightarrow a$ system. Further, the bands could be fitted into the $c \rightarrow a$ system as the 1–0 and 1–2 bands.

In order to confirm the vibrational assignment of these new bands, spectra were obtained using BF_3 samples enriched to 20, 54 and 90% ^{10}B. The resulting spectra are shown in Fig. 1 for the $c \rightarrow a$ system. The intensity of the band heads due to ^{10}BF increases approximately with increasing ^{10}B content while that of ^{11}BF decreases in the same proportion. Table I represents the vibrational scheme for all the observed band heads of the $c \rightarrow a$ system of ^{10}BF along with the isotope shifts (average value for the four heads) for the 1–0, 0–0, 0–1, 1–2, 0–2 bands immediately below their respective wave-number values. Calculated shifts are given in parenthesis. The agreement between the calculated and observed shifts confirms the proposed vibrational assignment for the bands.

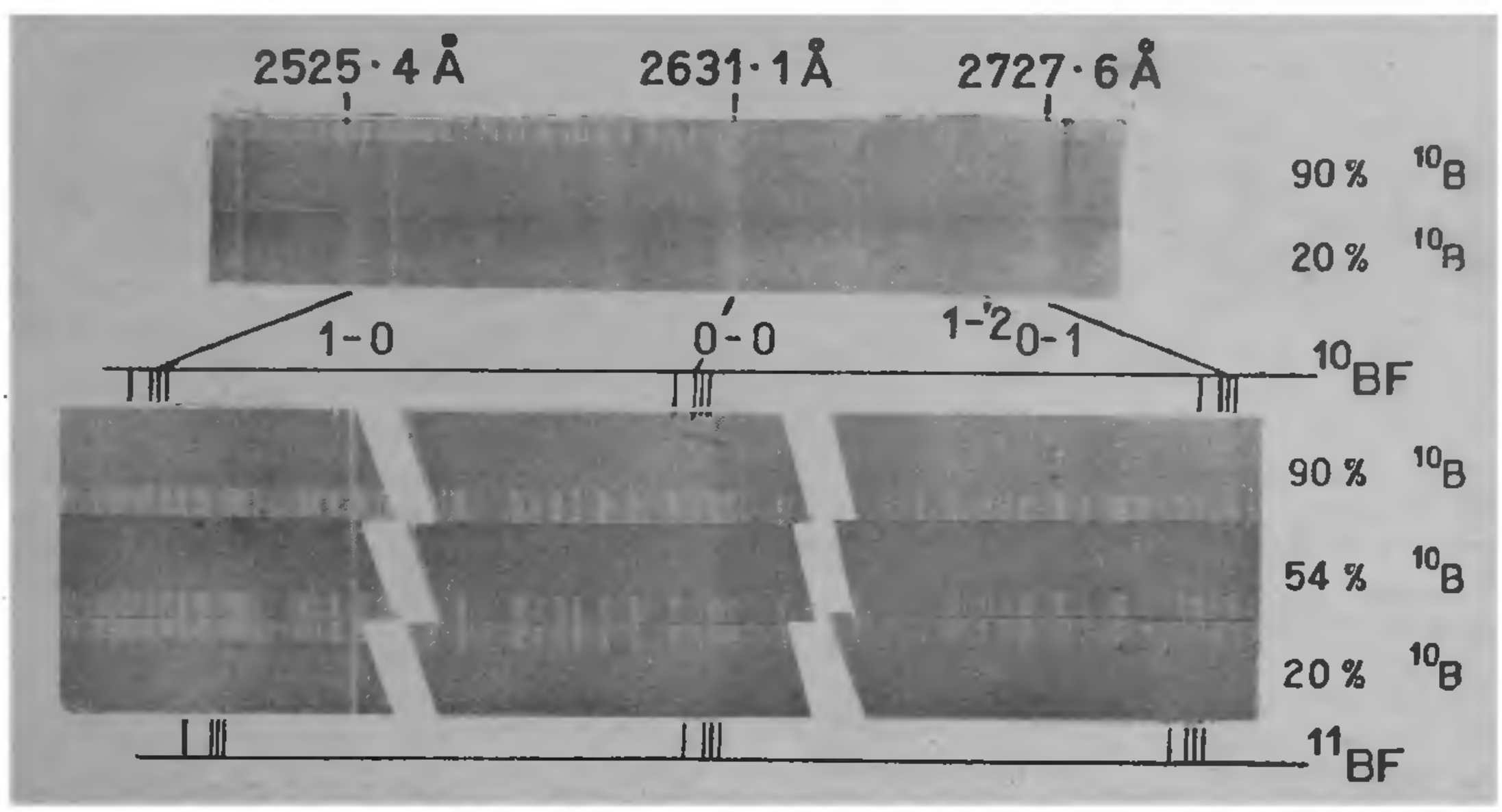

FIG. 1. Part of the $c\ ^3\Sigma^+ \rightarrow a\ ^3\Pi$ system of the BF molecule recorded on Hilger large quartz spectrograph at a dispersion of 2·8 Å/mm. at 2500 Å. The upper and lower sets of spectra are prints from the same negative with different enlargements.

In the present studies, though the $v' = 1$ level of the upper $c\ ^3\Sigma^+$ state is located, it has not been possible to observe further levels of $v' \geqslant 2$. It is noticed that even the bands arising from $v' = 1$ level are comparatively weak and occur at very low pressure of BF_3 in the RF discharge. Predissociation of the upper vibrational levels is believed to be responsible for the above effects.

TABLE I

Deslandres scheme for band heads of c $^3\Sigma^+ \rightarrow$ a $^3\Pi$ system of ^{10}BF

v' \ v''	0		1		2		3	
0	37996·2	P_3	1344·9	36651·3	P_3	1324·5	35326·8	P_3	1304·3	34022·5	P_3
	38003·5	P_2	1344·6	58·9	P_2	1323·6	35·3	P_2	1304·8	30·5	P_2
	12·2	P_1	1344·0	68·2	P_1	1324·3	43·9	P_1	1303·4	40·5	P_1
	33·6	Q	1346·5	87·1	Q	1324·3	62·8	Q	1304·6	58·2	Q
(*i.s.*)	*4·2*	(*3·6*)		*36·4*	(*36·4*)		*73·9*	(*75·3*)			
	1589·4						1588·9				
	1589·0						1588·6				
	1587·7						1591·0				
	1588·6						1590·1				
1	39585·6	P_3					36915·7	P_3			
	92·5	P_2					23·9	P_2			
	99·9	P_1					34·9	P_1			
	622·2	Q					52·9	Q			
(*i.s.*)	*51·9*	(*51·0*)					*27·0*	(*28·0*)			

For calculating the isotope shift, value of $\omega_e \chi_e$ for $c\ ^3\Sigma^+$ state has been taken as that of $a\ ^3\Pi$ state.

Bands observed for the $b \rightarrow a$ system of the ^{10}BF molecule are arranged in a Deslandres vibrational scheme shown in Table II. The

TABLE II

Deslandres scheme for band heads of b $^3\Sigma^+ \rightarrow$ a $^3\Pi$ system of ^{10}BF

v' \ v''	0		1	
0	32025·2	P_3	1345·0	30680·2	P_3
	33·4	P_2	1344·7	88·7	P_2
	42·6	P_1	1344·8	97·8	P_1
	63·4	Q	1347·0	30716·4	Q
(*i.s.*)	*4·2*	(*4·6*)		*35·8*	(*35·5*)
	1632·5				
	1632·1				
	1631·0				
	1630·8				
1	33657·7	P_3			
	65·5	P_2			
	73·6	P_1			
	94·2	Q			
(*i.s.*)	*51·8*	(*52·5*)			
	1584·8				
	1583·6				
	1582·8				
2	35242·5	P_3			
	49·1	P_2			
	56·4	P_1			
(*i.s.*)	*95·5*	(*97·6*)			

isotope shifts from the corresponding ones of ^{11}BF, observed and calculated, are given below the wave-number values of the band heads. Thus the present data give confirmatory evidence of the vibrational analysis of the $b \rightarrow a$ system as well.

The vibrational constants derived for the $a\ ^3\Pi$, $b\ ^3\Sigma^+$ and $c\ ^3\Sigma^+$ states for the ^{10}BF molecule are given in Table III and compared against the calculated values.

TABLE III

Vibrational constants for ^{10}BF (in cm.$^{-1}$)

State	Derived from present data		Calculated from data of ^{11}BF	
	ω_e	$\omega_e\chi_e$	ω_e	$\omega_e\chi_e$
$c\ ^3\Sigma^+$	[1588·7]		[1588·7*]	
$b\ ^3\Sigma^+$	1679·5	24·0	1680·0†	23·7
$a\ ^3\Pi$	1365·4	10·2	1365·1†	9·8

Values given in [ ] are $\Delta G_{\frac{1}{2}}$.

* The ^{11}BF data used here are obtained in the present investigation.

† The ^{11}BF data used here are taken from ref. 3.

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1. Strong, H. M. and Knauss, H. P., *Phys. Rev.*, 1936, **49**, 740.
2. Paul, F. W. and Knauss, H. P., *Ibid.*, 1938, **54**, 1072.
3. Barrow, R. F., Premaswarup, D., Winternitz, J. and Zeeman, P. B., *Proc. Phys. Soc.*, 1958, **71**, 81.