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The Band Spectra of SbF and BiF

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New band spectra attributed to the molecules SbF and BiF have been excited by active nitrogen. The spectrum of SbF from 2000–5500A is found to have three groups of bands lying in the regions 3600–5200A, 2600–2700A and 2200–2430A. Analysis of the first group shows that sixty-one bands out of sixty-nine can be placed into two systems with the following vibrational constants, in cm^{-1}:—

System	ν_e	ω_e'	$x_e'\omega_e'$	ω_e''	$x_e''\omega_e''$
A_1	21887.5	411.3	1.71	616.9	2.89
A_2	23992.5	420.0	1.75	612.6	2.58

The second group consists of a few isolated bands degraded to shorter wave-lengths and the third of bands in closely spaced sequences and also degraded to shorter wave-lengths. A preliminary analysis indicates that the bands in the latter group can be placed into two systems for which $\omega_e' \sim 700$ cm^{-1}, $\omega_e'' \sim 620$ cm^{-1} and $\Delta\nu_{21} \sim 1850$ cm^{-1}. Three new systems of bands, degraded to shorter wave-lengths and forming a triplet system with wide multiplet separations, (7330 cm^{-1} and 4800 cm^{-1}), are found in the spectrum of BiF at 3050–3250A, 2650–2850A and 2250–2350A. Photographs taken with small dispersion indicate that $\omega_e' \sim 620$ cm^{-1} and $\omega_e'' \sim 520$ cm^{-1}.

INTRODUCTION

THE band spectra of the diatomic halides of related elements, e.g., Ca, Sr and Ba, are, in general, very similar. It is observed that each spectrum contains the same number of band systems, arising from electronic states of the same multiplicity, and that corresponding systems move towards longer wave-lengths with increasing molecular weight.

The recent analysis of the band spectra of the diatomic lead halides has enabled a comparison of the spectra of the related molecules PbCl[1] and SnCl to be made, and has shown that whereas the spectrum of SnCl contains several systems arising from doublet electronic states, only one system occurs in PbCl, due, apparently, to a transition between singlet states. Evidently the ultraviolet systems of PbCl are too weak to appear and the other system which should occur if the ground state of the molecule is a doublet, (by analogy with SnCl), is in the infrared or is also too weak to be observed.

It was therefore thought of interest to search for the band spectra of the halides of other related elements and the two chosen for this purpose were the fluorides of antimony and bismuth (SbF and BiF). A band system of BiF lying in the visible region of the spectrum was already known from the work of Howell,[2, 3] Rochester[2] and Morgan.[4] No previous observations on the spectrum of SbF appear to have been made.

EXPERIMENTAL

Two methods have been used previously to excite the band spectra of BiF and BiCl, namely, the high frequency discharge[2] and active nitrogen.[5] Both methods were therefore tried in the present case to see which was preferable and the second was finally chosen because of the "purity" of the spectrum it produced. Details of the apparatus used and the method of operation were as described by Mulliken[6] in his early work on the band spectra of the copper halides. To excite the spectrum of SbF, the vapor of SbF_3 was introduced into the stream of active nitrogen by gently warming some commercial antimony trifluoride—the "glow" so produced being pale violet in color—but to vaporize

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[1] G. D. Rochester, Proc. Roy. Soc. **A153**, 407 (1936); F. Morgan, Phys. Rev. **49**, 47 (1936).

[2] H. G. Howell and G. D. Rochester, Univ. Durham Phil. Soc. Proc. **9**, 126 (1934).

[3] H. G. Howell, Proc. Roy. Soc. **A155**, 141 (1936).

[4] F. Morgan, Phys. Rev. **49**, 41 (1936).

[5] P. G. Saper, Phys. Rev. **37**, 1710A (1931).

[6] R. S. Mulliken, Phys. Rev. **26**, 1 (1925).

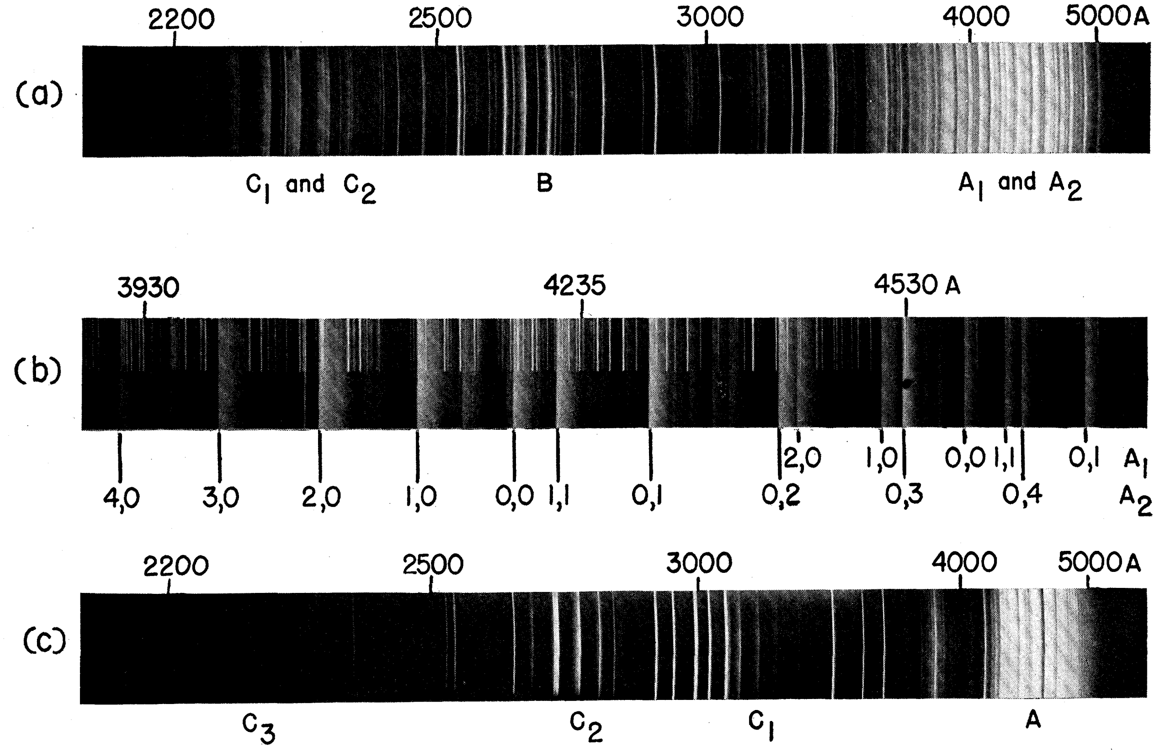

FIG. 1. (a) The band spectrum of SbF between 2200 and 5200A. (b) Systems A_1 and A_2 of SbF. (c) The band spectrum of BiF between 2200 and 5200A.

bismuth trifluoride it was necessary to heat the salt strongly in a quartz tube.

Both spectra when photographed with a Hilger small quartz spectrograph with exposure times varying from three to thirty minutes on fresh Eastman 40 plates revealed groups of bands in the visible and ultraviolet regions of the spectrum. The most intense system in SbF[7] was later photographed on Eastman 33 plates in six hours using a quartz spectrograph with a focal length of three meters and having an average dispersion of 7.5A/mm in the region covered by the bands.

Measurements of these band heads were made on two plates by means of a Société Génevoise Comparator and were reduced to wave-lengths, using iron-arc wave-length standards. Intensities were assigned visually on a 0–10 scale.

DESCRIPTION OF THE SPECTRA

Antimony fluoride (SbF)

Photographs of the spectrum of SbF illustrating its main features are reproduced in Figs. 1a and 1b. Fig. 1a, taken with the small quartz spectrograph, shows clearly that the spectrum of SbF has three groups of bands in the region 2000–5200A, namely, at 3600–5200A, 2200–2430A and 2600–2700A. The first group consists of progression type bands degraded to the red end of the spectrum, as may be seen more easily from Fig. 1b, the second of sequence-type bands degraded to shorter wave-lengths, and the third of a few isolated bands also degraded to shorter wave-lengths. Some of the bands in the "visible" systems resemble those of BiF and PbF in having line-like heads, and well-resolved rotational structure at some distance from the heads.

Bismuth fluoride (BiF)

A photograph of the spectrum of BiF taken with the small quartz spectrograph and repro-

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[7] While this work was in progress Dr. H. G. Howell of University College, Southampton, England, informed the author that he had independently discovered the band spectrum of SbF and was engaged in the analysis of the ultraviolet part of the spectrum; for this reason only preliminary results for this part of the spectrum are reported.

duced in Fig. 1c shows that the spectrum extends from 2200–5200A. In addition to the known system of bands at 4200–5500A, degraded to the red end of the spectrum, three new systems of progression type bands, degraded to shorter wave-lengths, at 2250–2350A, 2650–2850A and 3050–3250A can be recognized.[8]

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[8] System C_3 is clearly visible on the original plate.

Table I. *SbF. System A.* (*Wave numbers of band heads and differences in* cm^{-1}.)

v' \ v''	0	1	2	3	4	5	6	Mean $\Delta G' \begin{cases} A_2 \\ A_1 \end{cases}$
0	23896.0 (10) *2111.5* 21784.5 (6)	23289.0 (10) *2114.5* 21174.5 (7)	22686.5 (10) *2118.0* 20568.5 (3)	22089.0 (9) *2120.5* 19968.5 (1)	21497.5 (6) — —	20910.0 (1) — —		*416.5* *408.3*
1	24313.0 (10) *2119.5* 22193.5 (7)	23705.0 (10) *2123.5* 21581.5 (5)	23103.0 (2) *2125.5* 20977.5 (1)		21913.0 (2) — —	21327.5 (2) — —	20745.5 (0) — —	*412.6* *403.2*
2	24726.0 (10) *2128.0* 22598.0 (7)	24118.5 (2) *2133.5* 21985.0 (1)	23515.0 (2) *2136.0* 21379.0 (0)	22919.0 (3) *2139.0* 20780.0 (0)	22325.0 (1) — —			*410.3* *400.5*
3	25135.0 (8) *2136.5* 22998.5 (3)		23925.5 (3) — —		22736.5 (1) — —	22150.5 (1) — —		*406.5* *397.0*
4	25541.5 (7) *2146.0* 23395.5 (3)	24934.5 (3) *2151.0* 22783.5 (1)	24331.0 (1) — —	23736.0 (1) — —	23144.0 (1) — —			*402.5* *395.0*
5	25944.5 (4) *2154.5* 23790.0 (1)	25337.0 (5) *2158.0* 23179.0 (0)		24138.0 (1) *2166.5* 21971.5 (0)				*398.3* *392.0*
6	26343.0 (2) — —	25736.0 (4) *2166.0* 23579.0 (1)		24535.5 (1) *2171.0* 22364.5 (0)				*395.7* —
7	26739.5 (1) —	26131.0 (2) —	25529.0 (1) —					*394.0* —
8		26525.5 (2) —	25922.5 (2) —					*388.5* —
9			26311.0 (1) —					*383.5* —
10			26694.5 (1) —	26097.5 (1) —				*381.0* —
11				26478.5 (1)	25884.5 (1)			
Mean $\Delta G'' \begin{cases} A_2 \\ A_1 \end{cases}$	*607.5* *611.6*	*602.8* *605.3*	*596.4* *599.5*	*592.9* —	*586.3* —	*582.0* —		

SbF. Progressions (a) and (b). (Intensities in brackets.)

(a) 27202.5 (3) *601.5* 26601.0 (4) *597.0* 26004.0 (4) *591.5* 25412.5 (3) *587.5* 24825.0 (2)
(b) 25233.5 (2) *580.0* 24653.5 (1) *578.5* 24075.0 (1)

TABLE II. *SbF. Classified bands.*

SYSTEM A_1				SYSTEM A_2							
ν (obs. cm^{-1})	I	$0-C$ (cm^{-1})	v', v''	ν (obs. cm^{-1})	I	$0-C$ (cm^{-1})	v', v''	ν (obs. cm^{-1})	I	$0-C$ (cm^{-1})	v', v''
23790.0	1	0	5, 0	26739.5	1	1.0	7, 0	24138.0	1	1.0	5, 3
23570.0	1	0	6, 1	26694.5	1	0.5	10, 2	24118.5	2	0	2, 1
23395.5	3	−0.5	4, 0	26525.5	2	2.5	8, 1	23925.5	3	0	3, 2
23179.0	0	0	5, 1	26478.5	1	0	11, 3	23896.0	10	−0.5	0, 0
22998.5	3	0	3, 0	26343.0	2	0	6, 0	23736.0	1	1.5	4, 3
22783.5	1	−1.5	4, 1	26311.0	1	2.0	9, 2	23705.0	10	−0.5	1, 1
22598.0	7	1.0	2, 0	26131.0	2	0	7, 1	23515.0	2	−1.0	2, 2
22364.5	0	−1.0	6, 3	26097.5	1	0.5	10, 3	23289.0	10	0	0, 1
22193.5	7	0.5	1, 0	25944.5	4	0.5	5, 0	23144.0	1	1.5	4, 4
21985.0	1	−1.0	2, 1	25922.5	2	0	8, 2	23103.0	2	0	1, 2
21971.5	0	−2.5	5, 3	25884.5	1	−2.1	11, 4	22919.0	3	0	2, 3
21784.5	6	−0.5	0, 0	25736.0	4	0.5	6, 1	22736.5	1	0	3, 4
21581.5	5	−0.5	1, 1	25541.5	7	0	4, 0	22686.5	10	0	0, 2
21379.0	0	−2.0	2, 2	25529.0	1	0.5	7, 2	22325.0	1	−2.0	2, 4
21174.5	7	0.5	0, 1	25337.0	5	0.5	5, 1	22150.5	1	0.5	3, 5
20977.5	1	1.0	1, 2	25135.0	8	−0.5	3, 0	22089.0	9	−0.5	0, 3
20780.0	0	−1.5	2, 3	24934.5	3	0.5	4, 1	21913.0	2	−1.0	1, 4
20568.5	3	0	0, 2	24726.0	10	0	2, 0	21497.5	6	0	0, 4
19968.5	1	−0.5	0, 3	24535.5	1	−0.5	6, 3	21327.5	2	0	1, 5
				24331.0	1	−0.5	4, 2	20910.0	1	−1.0	0, 5
				24313.0	10	0	1, 0	20745.5	0	0	1, 6

VIBRATIONAL ANALYSIS

Antimony fluoride (SbF)

The three groups of bands in this system will be designated systems A, B and C, system A referring to the system with the smallest value of "ν_e."

System A.—In the region 3600–5000A there have been observed sixty-nine bands of which sixty-one can be placed into two systems (designated A_1 and A_2, A_1 referring to the system with the smallest value of ν_e), five in one v'' progression, (designated progression (a)), and three in another, (progression (b)). The wave numbers of the band-heads and the Deslandres schemes are given in Table I. The intensity distributions, also given in Table I, are such as would be expected from the Franck-Condon principle for the observed difference in the ω's of the two electronic states and show that the v numerations can be assigned without ambiguity. Since antimony has two isotopes of masses 121 and 123 and abundances 56 and 44, respectively, it might be expected that the antimony isotope effect could be used to confirm the v numerations; however, a careful examination of the band heads shows that the isotopic heads $Sb^{121}F$ and $Sb^{123}F$ are not resolved with the dispersion used. A slight diffuseness of the band heads at some distance from the system origin may be taken as qualitative evidence of an isotope effect and of the correctness of the quantum number allocations. To within the accuracy of measurement the wave numbers of the band heads are given by the formulae:

$$\nu_1 = 21{,}887.5 + 411.3(v'+\tfrac{1}{2}) - 1.71(v'+\tfrac{1}{2})^2 - 616.9(v''+\tfrac{1}{2}) + 2.89(v''+\tfrac{1}{2})^2,$$
$$\nu_2 = 23{,}992.5 + 420.0(v'+\tfrac{1}{2}) - 1.75(v'+\tfrac{1}{2})^2 - 612.6(v''+\tfrac{1}{2}) + 2.58(v''+\tfrac{1}{2})^2.$$

$0-C$ values for all classified bands are listed in Table II.

Systems B and C.—Pending more detailed analyses[7] only preliminary results, from measurements made on plates taken with small dispersion, will be given. Three bands have been found in System B with heads at 2630A, 2672A and 2714A, forming what is probably a v'' progression since the differences are of the same order as the ω''s of Systems A_1 and A_2:

System B
38,010 (5) *600* 37,410 (4) *580* 36,830 (2).

Sixteen bands have been found in the region 2200–2430A, analysis indicating that they can be placed into two systems with the same upper and lower state differences; $\omega_e' \sim 700$ cm^{-1}, $\omega_e'' \sim 620$ cm^{-1} and $\Delta\nu_{21} \sim 1850$ cm^{-1}.

TABLE III. *BiF. System C. (Wave numbers of band heads and differences in* cm^{-1}.)

v' \ v''	0	1	2	3	Mean $\Delta G'$
0	44290 (4) *7330* 36960 (10) *4780* 32180 (7)	43770 (7) *7320* 36450 (7) *4790* 31660 (4)	43260 (4) *7340* 35920 (2) *4780* 31140 (2)	42760 (0) *7340* 35420 (0) —	
					— *620* *620*
1	— 37580 (2) *4780* 32800 (2)		— 36540 (1) *4780* 31760 (1)		
Mean $\Delta G''$	*520*	*520*	*500*		

Discussion

Systems A and C both appear to result from transitions between doublet electronic levels, but, from the present analysis, it is not possible to state in which levels the multiplicity occurs. It is possible, because of the definite, though small, difference between corresponding ω's of systems A_1 and A_2 that the upper and perhaps the lower electronic states of these systems are multiple. The same may be true of systems C_1 and C_2 but the accuracy of measurement of the band heads, (not $>1A$), is not sufficient to allow a definite statement to be made. The occurrence of apparently doublet multiplicity appears to suggest that the emitting molecule is not SbF, for this molecule, having an even number of electrons, should give rise to electronic states of odd multiplicity. The only other possibility is the molecule SbF^+ but it is very unlikely that the spectrum of this molecule could be excited by active nitrogen. Thus it must be concluded that the observed doublets are two levels of a triplet, the other predicted system being too weak to appear or being outside the region investigated. In the case of system A it is possible that one of the progressions (a) or (b) is part of the third system.

Bismuth fluoride (BiF)

Systems A and B.—These two systems, lying in the visible and near ultraviolet regions of the spectrum have been reported previously.[2–4] Howell[3] observed forty-one bands of system A in emission and made an analysis leading to the following vibrational constants, (in cm^{-1}), for the two electronic states involved:

Level	ν_e	ω_e	$x_e\omega_e$	$y_e\omega_e$
A	22959.7	381.0	3.00	0.10
X	0	510.7	2.05	—

Morgan[4] observed twenty-eight bands of the same system in absorption showing that the level X is the ground state of the molecule; his analysis is in good agreement with Howell's.

System B is a weak system observed by Morgan in absorption; no details concerning its position in the spectrum have yet been given. The corresponding systems in the spectra of BiCl, BiBr and BiI have been observed, however, so it is possible to estimate that it should be at about 3700A. By analogy with the other diatomic bismuth halide spectra it is probable that this system results from a transition between the ground state X and a singlet level.

System C.—The analysis of this system has been carried out with measurements made on a plate taken with small dispersion. As Table III clearly shows the system is triplet with wide multiplet separations. It is seen that the values of ω for the upper and lower states are approximately 620 cm^{-1} and 520 cm^{-1}, respectively, showing that the lower state of the system is to be identified with the ground state. The upper state is then a wide triplet with the large separations, 7330 cm^{-1} and 4780 cm^{-1}. The triplet character of the state C is in accordance with the even number of electrons in the neutral molecule BiF.

It is a pleasure to express my appreciation of the generous help given me by Professor F. A. Jenkins.

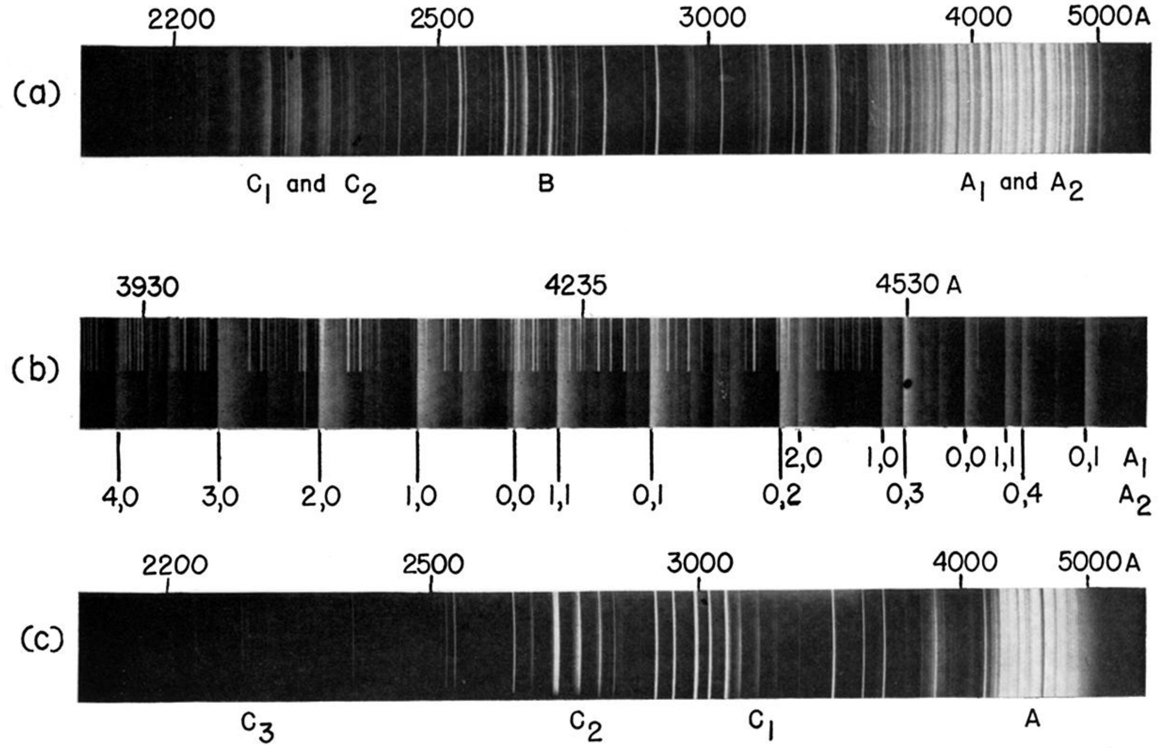

FIG. 1. (a) The band spectrum of SbF between 2200 and 5200A. (b) Systems A_1 and A_2 of SbF. (c) The band spectrum of BiF between 2200 and 5200A.