

chemical decomposition, as the compounds remain perfectly white after heating. However, there is distinct evidence of instability, indicated by the fact that heated radium bromide becomes almost black in time, while the unheated specimens show only a slight change in color.

Seitz<sup>7</sup> explains the luminescence of heat-treated pure ZnS as due to Zn atoms diffusing into the interstices of the crystal lattice and acting in the same way as impurity atoms. A similar displacement may be taking place in the case of barium compounds. This would explain the brightness-temperature curves if it be assumed that the number of displaced atoms depends on

<sup>7</sup> F. Seitz, *J. App. Phys.* **10**, 479 (1939).

the temperature of heat treatment. It is still necessary, however, to explain why these give a much broader emission band than other impurity activators as shown in Fig. 6. A more thorough examination of the emission bands and their dependence on the temperature of heat treatment seems desirable.

The author wishes to acknowledge his indebtedness to Dr. G. P. Harnwell and Dr. F. Seitz for many valuable suggestions and criticisms. This research was aided by a grant from the Faculty Research Committee of the University of Pennsylvania and also by a grant from the American Philosophical Society which are hereby gratefully acknowledged.

APRIL 15, 1940

PHYSICAL REVIEW

VOLUME 57

## The Band Spectrum of Antimony Chloride

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(Received February 9, 1940)

A band spectrum attributed to the molecule SbCl<sub>3</sub> in the region  $\lambda\lambda 4200-5600$ , has been excited by introducing SbCl<sub>3</sub> into active nitrogen. No other bands appeared in the range  $\lambda 2000$  to  $\lambda 7000$ . The spectrum consists of bands showing pronounced progressions and degraded towards the red. They can be placed in two sub-systems of bands, designated as *A*<sub>1</sub> and *A*<sub>2</sub>. Vibrational analysis shows that within experimental error the wave numbers of the heads of forty-one bands of SbCl<sub>3</sub><sup>36</sup> are represented by the formulas:

$$A_1 : \nu_1 = 22395 + 244.4u' - 2.28u'^2 - 368.0u'' + 0.84u''^2,$$

$$A_2 : \nu_2 = 25855 + 240.2u' - 2.19u'^2 - 370.0u'' + 1.00u''^2.$$

The chlorine isotope effect appears in 13 bands and is used to confirm the *v'*, *v''* designations. The analysis of the spectrum given here is somewhat different from that originally presented two years ago. Many more bands are here accounted for and identified. An attempt failed to produce a spectrum of AsCl<sub>3</sub> by introducing AsCl<sub>3</sub> vapor into active nitrogen.

THE electron configurations of the lighter diatomic molecules have already been determined with a fair degree of certainty. Comparatively few measurements have thus far been made of the spectra of the heavy diatomic molecules. Spectra have been produced, however, for many of the diatomic halides of the elements in group IVb of the periodic table. For group Vb there are only the spectra due to SbF<sup>1</sup> and the four bismuth halides.<sup>2</sup> This experiment was

undertaken to find out whether the same regularities exist for the halides of group Vb as have been shown to exist for group IVb.<sup>3</sup>

The arrangement of the apparatus and the methods employed for the excitation of the bands of antimony chloride are essentially the same as those originated by Strutt and Fowler<sup>4</sup> in their work with active nitrogen, and as further de-

<sup>1</sup> G. D. Rochester, *Phys. Rev.* **51**, 486 (1937).

<sup>2</sup> F. Morgan, *Phys. Rev.* **49**, 41 (1936).

<sup>3</sup> W. Jevons, L. A. Bashford and H. V. A. Briscoe, *Proc. Phys. Soc.* **49**, 532 and 537 (1937); W. Jevons and L. A. Bashford, *Proc. Phys. Soc.* **49**, 554 (1937).

<sup>4</sup> R. J. Strutt and A. Fowler, *Proc. Roy. Soc.* **A86**, 105 (1911).

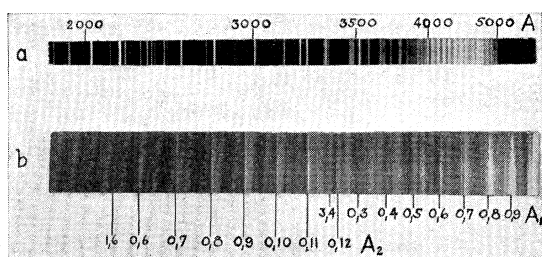


FIG. 1. The spectrum of  $\text{SbCl}$ ; (a) low dispersion, (b) higher dispersion,  $\lambda 4200\text{--}\lambda 5600$ , with vibrational quantum numbers for systems  $A_1$  and  $A_2$ .

veloped by Mulliken<sup>5</sup> in his early work on the band spectra of the copper halides. By introducing the vapor of pure antimony trichloride into a stream of active nitrogen, the spectrum attributed to the molecule  $\text{SbCl}$  was excited. The wave-length region  $\lambda 2000$  to  $\lambda 7000$  was photographed and examined.

A Hilger quartz spectrograph of low dispersion (200  $A$ /mm at  $\lambda 5000$ ) was used in the preliminary stages with Eastman 40 plates. With exposures varying up to 70 minutes only one group of bands, between the wave-lengths  $\lambda 4200\text{--}\lambda 5600$ , was disclosed. Using a glass spectrograph with lenses of 492-mm focal length, dispersion 42  $A$ /mm at  $\lambda 5000$ , this system of bands was photographed on Ilford S. G. panchromatic backed plates in ten hours. Intensities were visually assigned. The iron arc was used for wave-length standards.

The bands shade towards the red. Enlarge-

<sup>5</sup> R. S. Mulliken, *Phys. Rev.* **26**, 1 (1925).

ments of the photographs, Fig. 1, illustrate their main features. Fig. 1a was taken with the small quartz spectrograph and shows clearly the existence of the group of bands in the region  $\lambda 4200\text{--}5600$ . Taken with the glass instrument of greater dispersion, the general characteristics of the bands are more easily recognized from Fig. 1b. This figure contains the assignments of some of the vibrational quantum numbers in the two systems,  $A_1$  and  $A_2$  (see below).

The heads of forty-one bands which have been observed can be arranged in two sub-systems, designated  $A_1$  and  $A_2$ , where  $A_1$  identifies the less refrangible system (smaller value of  $\nu_e$ ). The wave numbers of the band heads are shown in a  $\nu' - \nu''$  array in Table I, in which are indicated the intensities in parentheses.  $A_1$  bands are placed above  $A_2$  bands with  $\delta\nu_e$  between. Several band heads which were impossible of identification, with their estimated intensities, follow: 23970(2); 20141(3); 19789(3); 19490(3); 18838(3); 18114(4); 18088(3); 17726(5)  $\text{cm}^{-1}$ .

Within experimental error the heads of these two sub-systems of bands of  $\text{SbCl}^{35}$  are represented by the formulas:

$$\begin{aligned} \nu_1 &= 22395 + 244.4u' - 2.28u'^2 - 368.0u'' + 0.84u''^2, \\ \nu_2 &= 25855 + 240.2u' - 2.19u'^2 - 370.0u'' + 1.00u''^2, \end{aligned}$$

where  $u = v + \frac{1}{2}$ .

The average of the differences between observed values of the band heads of  $\text{SbCl}^{35}$  and values calculated by the formulas is  $\pm 3.1 \text{ cm}^{-1}$ . The constants are different from those originally

TABLE I. Wave numbers of  $\text{SbCl}^{35}$  band heads, in  $\text{cm}^{-1}$ ;  $A_1$  above  $A_2$ .

$\nu'$	$\nu''=3$	4	5	6	7	8	9	10	11	12	13	14	MEANS $\Delta G''(A_1)$ $(A_2)$
0	21248(1)	20880(2)	20516(3)	20157(4)	19802(4)	19446(4)	19093(4)	18743(5)					236.5 236.3
				3460	3456	3455	3454	3455					
				23617(3)	23258(4)	22901(4)	22547(4)	22198(4)	21852(4)	21503(2)	21161(2)	20823(0)	
1	21485(2)	21119(2)	20758(3)	20394(4)	20038(1)	19694(0)		18980(2)					235.5 232.3
				3457	3458	3447		3454					
				23851(2)	23496(0)	23141(0)		22434(0)	22087(2)	21743(2)	21397(1)	21054(2)	
2	21717(1)	21358(3)				23375(0)	23021(0)	22664(0)	22319(1)			21287(0)	234.5 —
3	21943(0)	21591(2)											
Means $\Delta G''(A_1)$ $(A_2)$		361.0	362.5	361.0	355.5	353.0	350.0	350.0	350.0	346.0	346.5	344.0	340.5

given in a note on the spectrum of SbCl.<sup>6</sup> Whereas only 28 band heads were identified in the earlier note, 54 band heads (including isotope heads) are taken into account here and identified.

It was to be expected that the band heads due to the individual antimony isotopes would not be resolved with the instrument here employed. Weaker heads of SbCl<sup>37</sup> are displaced toward the system origin from stronger SbCl<sup>35</sup> heads; the displacement coefficient,  $\rho - 1$ , is  $-0.0210$ . The origins of the  $A_1$  and  $A_2$  systems are found by extrapolation to zero displacement. The displacements of 13 bands due to the SbCl<sup>37</sup> isotope shift are given in Table II.

The agreement of observed and calculated values of the isotope displacements confirms the locations of the system origins ( $A_1$  and  $A_2$ ). Also, the relative intensities of the isotope bands appear satisfactory for chlorine isotopes.

Evidence for the identity of the emitter of this spectrum was weighed. Vapor of SbBr<sub>3</sub> introduced into active nitrogen produced only the NBr spectrum.<sup>7</sup> Vapor of Sb metal produced no spectrum in active nitrogen. The presence of SbN seemed therefore to be eliminated. If, nevertheless, SbN (or SbO) were the emitter, no isotope displacement would be observed. So an alternative classification of the band heads was speculated upon, by considering the above band heads of the isotopic molecule SbCl<sup>37</sup> as  $R$  heads of SbCl<sup>35</sup> displaced from more intense  $Q$  heads of SbCl<sup>35</sup>. This appeared reasonable but was precluded, however, because  $\omega_e' - \omega_e''$  is large. Each band would then be characterized by a small interval between  $Q$  and  $R$  head.<sup>8</sup> This was not the case here.

From the similarity of vibrational constants of these two band systems it is probable that they comprise a doublet system. It is not possible from the present analysis to determine in which state the multiplicity occurs. The existence of a third system, making a triplet, is not impossible; because an odd multiplicity of electronic states is expected for a molecule possessing an even number of electrons. The above statements have likewise been made in reference to SbF.<sup>1</sup>

TABLE II. Displacements of bands due to SbCl<sup>37</sup> isotope shift.  $\Delta\nu_{\text{CALC.}}$  is  $[(\rho - 1)(\nu - \nu_e)]$ .

BAND $A_1$	$\Delta\nu_{\text{OBS.}}$ ( $\text{CM}^{-1}$ )	$\Delta\nu_{\text{CALC.}}$ ( $\text{CM}^{-1}$ )	BAND $A_2$	$\Delta\nu_{\text{OBS.}}$ ( $\text{CM}^{-1}$ )	$\Delta\nu_{\text{CALC.}}$ ( $\text{CM}^{-1}$ )
0,5	41.	40.	0,6	45.	47.
0,6	49.	47.	0,7	52.	54.
0,7	50.	54.	0,8	64.	62.
0,8	57.	62.	0,9	68.	69.
0,9	60.	69.	0,10	76.	76.
1,5	36.	34.	1,8	56.	57.
1,6	36.	42.			

For group Vb halides a comparison between the constants of the antimony halides and the bismuth halides was made. The constants of the bismuth halides were plotted against the number of electrons in the molecule and were then compared to similar plots for the antimony halides. The expected trends were found in both cases, namely, with increasing number of electrons and mass of a molecule there is a decrease in the values of  $\omega_e$  and  $X_e\omega_e$  in both the upper and lower states, a decrease in  $\nu_e$ , and an increase in the value of  $\delta\nu_e$ . Similar trends were found also in the values of the constants of any one halide of the two metals.

The introduction of AsCl<sub>3</sub> into streaming active nitrogen produced no characteristic band spectrum in the region  $\lambda\lambda 2000-7000$ .

Appreciation is expressed to Thomas J. W. O'Neil for his assistance with this experiment.

<sup>6</sup> I. Hudes, Phys. Rev. **52**, 1256 (1937).

<sup>7</sup> A. Elliott, Proc. Roy. Soc. **A169**, 469 (1939).

<sup>8</sup> W. Jevons, Report on Band Spectra of Diatomic Molecules, p. 63.

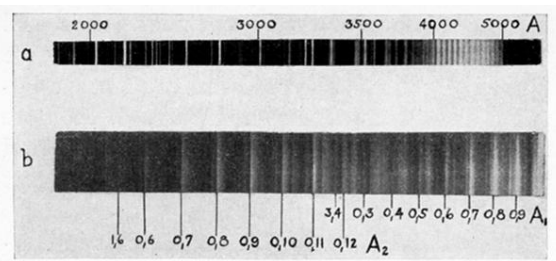


FIG. 1. The spectrum of SbCl; (a) low dispersion, (b) higher dispersion,  $\lambda 4200 - \lambda 5600$ , with vibrational quantum numbers for systems  $A_1$  and  $A_2$ .