

ON THE EMISSION SPECTRUM OF SiBr_4 .

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Introduction.

MIESCHER¹ has recently studied the spectrum of SiBr_4 and has obtained a number of bands all degraded towards shorter waves. He has given an analysis for these bands, which has been confirmed by Bashford, Briscoe and Jevons.² We have studied the spectrum of SiBr_4 under different conditions of the flowing vapour and with condensed and uncondensed discharge. The results obtained are described below, and it is shown that the nature of the spectrum undergoes certain radical changes under varying conditions of the flowing vapour.

Experimental.

A discharge tube of the H pattern with the usual side bulbs containing P_2O_5 and crushed NaOH and fitted with a quartz window has been used. The substance was contained in another side bulb with a stop-cock for the regulation of the flow of the vapour. The discharge tube was provided with nickel electrodes and was connected to a high vacuum apparatus, operated by a mercury diffusion pump which was backed by a rotary oil pump. The flow of the vapour was adjusted to give the desired pressure by having two stop-cocks on either side of the discharge tube. Pressures were measured on a Macleod gauge. The tubes were run on a quarter K. W. transformer delivering 15,000 volts. For condensed discharge a set of three ordinary Leyden jars arranged in parallel was used with a spark gap of about 2 mm. in series with the tube. Medium Hilger quartz spectrograph has been used to photograph the spectrum in the ultra-violet region. The plates have been measured on an Abbe Comparator, using Cu arc lines as standards. The wave-lengths of the beginning, maximum and end of the continuous emission bands have been determined from microphotometer records, which were obtained on a Zeiss recording microphotometer.

Description of the Spectrum.

With pressures higher than 0.5 mm. of Hg, under both conditions of discharge, the spectrum consists of only a number of continuous emission bands, the details of which are given in Table I. No discrete bands were

TABLE I.

Long wave-length limit A.U.	Maxima A.U.	Short wave-length limit A.U.
5850	4220	3750
3640	3570	3470
3470	3435	3415
3415	3345	3250
3160	3120	3040
3000	2910	2835
2835	2780—2710 (Broad)	2680
2665	2640—2630 „	2600
2425	2420	2400
	2370 ?	

observed. When the pressure of the flowing vapour was reduced to 0.2 mm. of Hg, all the continuous emission bands, except the one at λ 4220 disappeared, giving rise to a system of bands degraded towards shorter waves. These bands have been identified as the bands due to SiBr.^{1,2} At a pressure of 0.05 mm. of Hg, a number of bands degraded towards the longer waves, in addition to those degraded towards shorter waves were observed. At this pressure the continuous emission bands were much reduced in intensity and a set of narrow bands between λ 3700 and λ 3930 in the body of the continuum, similar in structure to the group A bands observed in the experiments with SiCl₄,³ were observed. These, however, were too faint to be measured. In analogy with other molecules SiCl₂ and SnCl₂ discussed elsewhere,³ we tentatively suggest that these narrow bands might be due to a triatomic molecule SiBr₂. Fig. 1 is a reproduction of the plate which shows all the bands but on which these narrow bands are not clearly visible.

The region between λ 3350 and 2700 consists of a large number of bands some of which are degraded towards the shorter waves and the rest towards the longer waves. The wave-lengths of the SiBr bands degraded

towards the shorter waves are given in Table II, together with the measurements of Miescher.* One extra band at λ 3208.2 not observed by Miescher

TABLE II.

Bands degraded towards the Shorter Waves.

Meischer λ in A.U.	Here λ in A.U.	Meischer λ in A.U.	Here λ in A.U.
3233.6	..	3057.6	..
3217.4	..	3047.5	3047.1
..	3208.2	3033.4	3033.2
3192.0	3191.9	3008.8	3008.8
3176.3	3175.2	2995.0	2995.6
3167.5	3166.6	2982.3	..
3151.7	..	2971.2	2971.2
3136.0	3135.3	2958.3	2958.3
3126.6	3126.0	2945.7	..
3111.3	3111.4	2921.8	2922.0
3096.7	..	2910.3	..
3086.9	3086.3	2874.9	..
3072.2	3071.9		

fits into his analysis in the position (0--6). The wave-lengths of the bands degraded towards longer waves are given in Table III. The bands between λ 2862 and 3170 lie in the region covered by Miescher's bands and most of them are confused in the structure of the latter bands.

* These bands have been measured more recently by Jevons and Bashford (*Proc. Phys. Soc. Lond.*, 1937, 49, 554) under higher dispersion. They show that the final level of these bands which is presumably the ground state of SiBr is not a singlet state as previous data indicated but a $^2\Pi$ state with an electronic separation of the expected order of magnitude.

TABLE III.
Bands degraded towards Longer Waves.

λ Air A.U.	Int.	ν in Vac. cm.^{-1}	Classification $v' - v''$
3320	(2)	30112	2-5
3297	(1)	30322	1-4
3274	(0)	30535	0-3
3267	(2)	30600	2-4
3245	(3)	30808	1-3
3222	(5)	31028	0-2
3198 ?			
3170.4	(4)	31533	0-1
3150.6	(6)	31731	
3058 ?	(0) ?	32692	
2990.6	(0)	33428	
2965.9	(8)	33707	
2926.5	(4)	34161	
2872.3	(?)	34805	
2862.5	(3)	34924	0-3
2842.4	(0)	35171	1-3
2822.7	(6)	35417	0-2
2783.3	(6)	35918	0-1
2764.2	(6)	36166	1-1
2745.2	(6)	36417	0-0
2727.7	(2)	36650	1-0
2708.9	(2)	36904	2-0

Group B.

Group A.

(Figures in brackets in Column 2 indicate visually estimated intensities.)

Analysis of the Bands degraded towards Longer Waves.

At first these bands were suspected to be due to the SiO molecule⁴ which shows an extended band system degraded towards longer waves in the region $\lambda\lambda$ 2176—2925. A comparison of the wave-lengths of the bands shows, however, that this is not so. The SiO bands have not been obtained in these investigations either on SiCl₄ or SiBr₄ plates. The bands between $\lambda\lambda$ 2708.9 and 2842.4 (Group A) as well as bands between $\lambda\lambda$ 3198 and 3320 (Group B) are free from the confusion with Miescher's bands of SiBr. On account of the confusion of the intermediate bands it has not been possible to arrive at a satisfactory analysis of all the bands. But a tentative analysis of the two groups of the bands which are free from the confusion is given below in Tables IV and V.

TABLE IV.
Group A Bands.

$v' \backslash v''$	0		1		2		3
0	36417 (233)	499	35918 (248)	501	35417	493	34924 (247)
1	36650 (254)	484	36166				35171
2	36904						

TABLE V.
Group B Bands.

$v' \backslash v''$	1		2		3		4		5
0	31533	505	31028	493	30535 (273)				
1					30808	486	30322 (278)		
2							30600	488	30112

The analysis as it is, does not include the bands at $\lambda\lambda$ 3150.6, 2990.6, 2965.9 and 2926.5, which are among the confused bands. The analysis indicates that the bands belong to two electronic systems, both having the same final state, with a frequency of about 500 cm.^{-1} . The frequency of the excited state of the group A bands is about 250 cm.^{-1} , while that of group B bands is about 275 cm.^{-1} . None of these frequencies corresponds to the two known frequencies of SiBr, *viz.*, $\omega'' = 423.3\text{ cm.}^{-1}$ and $\omega' = 574.0\text{ cm.}^{-1}$. The magnitude of the frequencies, however, are such as could be expected for the SiBr molecule. While considerations of experimental conditions, as well as comparison with known data rule out the possibility of SiO as the emitter of these bands, the absence of a common level between these bands and the already known bands of SiBr renders the attribution of these bands to the emitter SiBr tentative. The only possible emitter other than SiBr which suggests itself to us is SiBr^+ .

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