ON THE BAND SPECTRUM OF CADMIUM IODIDE.

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1. *Introduction.*

In the foregoing paper we presented the results obtained during an investigation of the group III bands of mercury iodide. The present paper deals with the similar results obtained with cadmium iodide. As in the case of mercury iodide, Wieland[1] obtained bands of group III in emission, but was not able to determine their wave-lengths. He observed, however, that the bands followed at intervals of about 18 to 20 Å and that after groups of five or six bands there occurred places where the band structure was almost washed out. Oeser[2] has obtained the bands in fluorescence, but the small dispersion employed by him did not allow of sufficient accuracy being attained in the wave-length measurements. In view of the importance of bands of group III for the problem of the heats of dissociation, we have taken up a study of them. Their regular succession at almost equal intervals and their diffuseness suggested a close resemblance to the bands of Hg_2 observed by Lord Rayleigh[3] and also to the spectra of Se_2 and Te_2. One of us[4] has analysed the bands of Hg_2, Cd_2 and Zn_2 and found a peculiarity in the lowest state, *viz.*, that the vibration quanta first increase and then decrease. The result of the present investigation shows that the external similarity between the spectra of these molecules and the group III bands of the Hg, Cd and Zn halides is reflected also in the behaviour of the lower level of the latter bands as compared with the ground level of Hg_2, Cd_2 and Zn_2.

2. *Experimental.*

We have used different sources for getting the bands with sufficient intensity. A vacuum arc with three limbs, the two outer having electrodes and containing cadmium, and the middle containing CdI_2, gave a bright spectrum of the bands when the CdI_2 was heated and a good photograph was obtained with Hilger's E_1 spectrograph. The cadmium, however, soon affected the pyrex glass and when the arc once went out (which was usually in about 20 minutes), the tube cracked and no further exposure was possible. On account of the diffuse nature of the bands we could not get accurate wave-lengths with a spectrum obtained by means of the E_1 spectrograph. We later on used the type of tube figured in the previous paper, having electrodes cooled by a stream of water and energised by a $\frac{1}{2}$ KW, 10,000 volt transformer. With this source and a 10 ft. concave grating in a Rowland mounting, having a dispersion of 5·5 Å. per mm. in the first order, we obtained good photographs in about half an hour, but longer exposures were not practicable since the substance got exhausted very rapidly. The bands were most intense when the discharge had a whitish yellow colour. An iron arc was juxtaposed without using a condensing lens so that second order lines have appeared and made up for paucity of lines in the red region of the iron spectrum. Although we could see the bands very well as is seen from the reproduction, they could not be measured under the microscope when the usual magnification was employed. Accordingly the magnification was reduced by removing the eye-piece and putting the cross wires farther down the microscope tube. Measurements were also taken on a microphotometer tracing of the bands. In both cases different measurements agreed with one another to within 1 Å and the final wave-lengths must be correct to within 0·5 Å or better. No heads however can be recognised and so readings have been taken for the centre of each band. The wave-numbers are also correct to within 1 cm.$^{-1}$ but common differences differ somewhat more than 2 cm.$^{-1}$ on account of the difficulty of locating the corresponding points in different bands.

3. *Results.*

The final wave-lengths are given in Table I. The degree of accuracy reached is sufficient to arrive at definite conclusions regarding some assumptions made by previous workers. The bands of group III have been assumed to have the same lower level as those of group I analysed by Wieland. An attempt at analysis on this basis was found to be futile, and the final analysis presented here was suggested by the wash-out of the bands at intervals of five or six. According to this analysis presented in Table II, the lower level shows the peculiarity of vibration quanta which first increase and then decrease, just as in the case of HgI, but the actual value of the vibration frequency in the lower state, is far smaller than that of the upper state, whereas in HgI the lower state has the higher frequency. This difference accounts for the difference in the appearance of the bands. No doublet structure has been found in CdI whereas HgI exhibits such a doublet structure. The reason might be that the doublet interval is too small, as is to be expected.

TABLE I.

Int.	Wave-length	Wave-number	Int.	Wave-length	Wave-number
1	6340·57	15767·1	1	5988·13	16695·1
1	21·17	15815·5	1	71·07	16742·8
2	01·84	15864·0	1	52·58	16794·8
2	6283·22	15911·0	2	5936·64	16839·9
2	64·33	15959·0	2	19·90	16887·5
1	44·40	16009·9	2	02·67	16936·8
?	22·06	16067·4	2	5885·37	16986·6
?	01·38	16121·0	2	68·85	17034·4
1	6187·10	16158·2	1	51·91	17083·7
3	68·28	16207·5	1	35·79	17130·9
3	49·65	16256·6	2	20·16	17176·9
2	31·96	16303·5	2	04·11	17224·4
2	13·10	16353·8	3	5787·41	17274·1
?	6096·99	16397·0	2	70·61	17324·4
1	76·83	16451·4	1	54·86	17371·8
2	58·46	16501·3	1	39·07	17419·6
2	41·28	16548·2	?	24·48	17464·0
2	23·16	16598·0	1	09·44	17510·0
1	05·75	16646·1	1	5693·35	17559·5

TABLE II.

v'	$v''=0$		1		2		3		4		5		6
0	..		..		..		..		..		..		..
1	..		..		..		..		..		..		..
2	(16067·4)		(16009·9)		15959·0	*48·0*	15911·0	*47·0*	15864·0	*48·5*	15815·5	*48·4*	15767·1
			343·9		*344·5*		*345·6*		*343·5*		*342·7*		
3	(16397·0)		16353·8	*50·3*	16303·5	*46·9*	16256·6	*49·1*	16207·5	*49·3*	16158·2		(16121·0)
			341·3		*342·6*		*341·4*		*340·7*		*343·1*		
4	16742·8	*47·7*	16695·1	*49·0*	16646·1	*48·1*	16598·0	*49·8*	16548·2	*46·9*	16501·3		(16451·4)
	340·9		*339·3*		*340·5*		*338·8*		*339·3*		*338·6*		
5	17083·7	*49·3*	17034·4	*47·8*	16986·6	*49·8*	16936·8	*49·3*	16887·5	*47·6*	16839·9	*45·1*	16794·8
	335·9		*337·4*		*337·8*		*337·3*		*336·9*		*337·0*		*336·1*
6	17419·6	*47·8*	17371·8	*47·4*	17324·4	*50·3*	17274·1	*49·7*	17224·4	*47·5*	17176·9	*46·0*	17130·9
									335·1		*333·1*		*333·1*
7									17559·5	*49·5*	17510·0	*46·0*	17464·0

Note.—The bands with $v' = 0$ and $v' = 1$ could not be measured since the continuum masked them. In the photograph taken with the E_1 spectrograph the last measured band was 15118 cm.$^{-1}$ corresponding to $v' = 0$, $v'' = 5$. There exist no bands beyond $v'' = 6$ for any value of v'. This termination of the bands at a particular value of v'' is characteristic of the peculiar lower state.

As explained in the previous paper, we have refrained here also from attempting to represent our results by a formula since the peculiar ground state does not allow this to be done. An interpretation of Oeser's fluorescence data is left for future consideration.

Finally, the important point brought out by these investigations is that the lower level of system B in CdI and HgI shows the peculiarity previously observed by one of the authors[4] in Hg_2, Cd_2 and Zn_2, *viz.*, that the vibration frequencies first increase and then decrease, and the vibration levels terminate when the vibration frequency becomes equal to what it was between the 0th and 1st vibration levels.

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