ON THE BAND SPECTRUM OF MERCUROUS IODIDE.

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1. *Introduction.*

THE band spectra of the halogenides of zinc, cadmium and mercury have been investigated by a large number of observers. K. Wieland[1] who has observed the various spectra in emission, and has also succeeded in analysing a number of them, gives references to previous observations. According to him, the spectrum emitted by each salt can be divided into three groups denoted by the numerals I, II and III. Group I consists of bands in the ultra-violet with recognizable heads, which can be ascribed to diatomic halogenide molecules. Bands of this group have been analysed by Wieland in the case of HgCl, HgBr and HgI, CdBr and CdI and ZnI. Group II is made up of bands which show little regularity and are ascribed to triatomic molecules. Bands of Group III, which are the subject of this and the following paper, are very faint, diffuse and without sharp heads. In the case of HgI these bands have been observed in fluorescence and measured under low dispersion by A. Terenin[2] and K. Wieland.[3] The values given by them are however discordant. Sponer[4] has attempted to determine the heats of formation of the diatomic and triatomic halogenides on the basis of Wieland's measurements and analysis. Since the bands of Group III play an important part in this determination and yet have not been measured accurately nor properly analysed, we have taken them up for study, and have been able to measure them under high dispersion and also succeeded in arriving at an analysis in the case of HgI and CdI. Our results for HgI are presented in this paper while the next deals with CdI.

2. *Experimental.*

We have tried various methods of exciting the spectra such as the arc and various types of discharge. The arc spectrum develops the lines in greater intensity to the detriment of the bands, while the electrodeless discharge is too feeble. We obtained successful photographs with a discharge tube energised by a 10,000 volt, ½KW transformer, but the intensity was not

365

sufficient for the bands to be seen under the microscope. Preliminary measurements correct to 0·02 to 0·05 mm. were obtained by placing a scale reading 0·1 mm. directly on the spectrogram and taking readings by means of a reading lens. Such a scale was prepared by photographing a good half-metre scale so that the size of its image was 5 cm. The dispersion was produced by a 10 ft. concave grating in a Rowland mounting, the dispersion being 5·5 Å per mm. in the first order. The exposure was about an hour. Later on, we used the type of tube represented in the figure, with electrodes cooled by a stream of
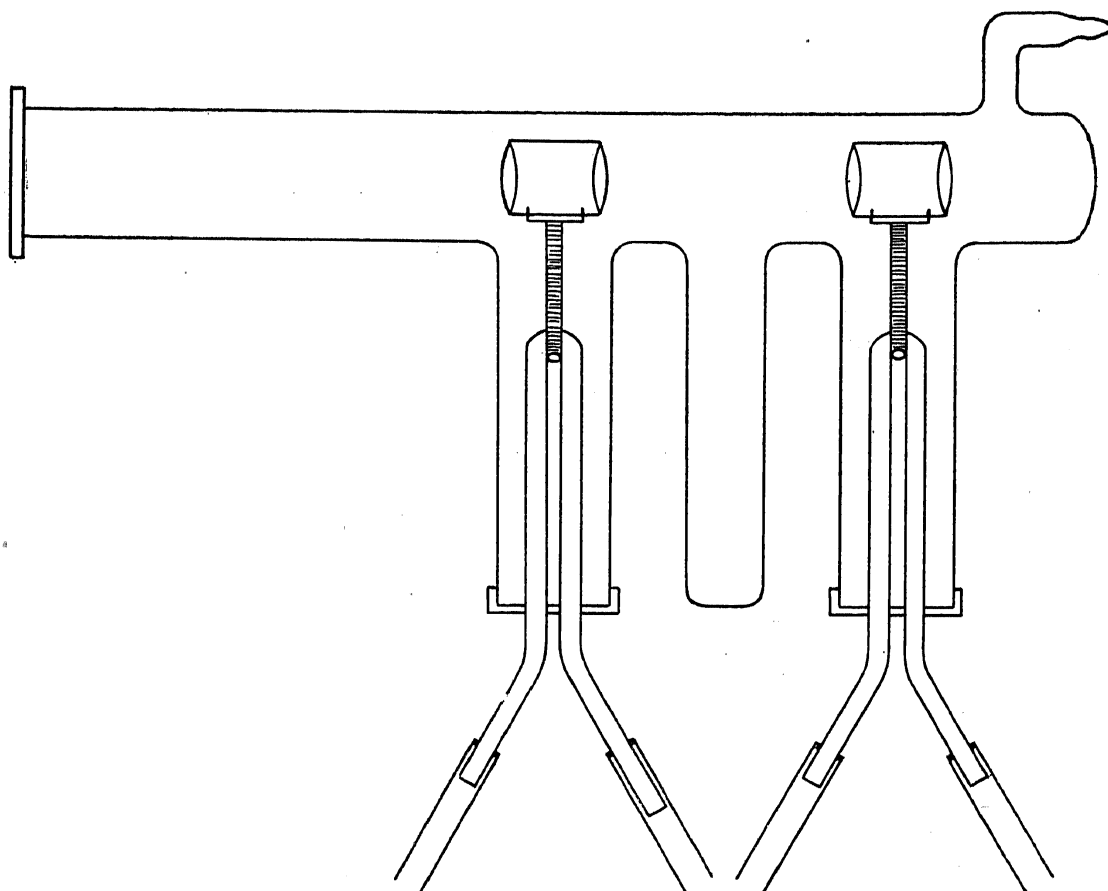
water, and a 3KVA transformer giving 2000 volts. We were now able to reduce the slit width to 0·05 mm. and obtained good photographs with exposures ranging between 30 min. and 1 hour. An iron-arc spectrum was always juxtaposed for comparison, by using a Hartmann diaphragm. Ilford hyper-sensitive panchromatic films were used throughout. The bands could now be measured under the microscope. On account of their diffuse nature and the absence of sharp heads, measurements by different observers agreed only to 0·2 Å. The mean wave-lengths given are believed to be correct to within 0·1 Å. With the finer slit each head appears double, and the

measurements refer to the more intense components which are believed to be due to Q-branches, on account of the absence of intense heads and the degradation of the bands to the red. The R-heads do not belong to that Q-head which forms a pair with them but to the preceding Q-head. With this interpretation and the analysis given below, the distance between Q- and R-heads increases with increasing v'' and diminishes with increasing v', as required by the theory developed by Jevons. The measurements for the R-heads are not however given here since their intensity is very low and consequently the values not quite accurate. Another point which requires to be mentioned is that the measurements have been taken at the most intense part of the Q-branches since the heads could not be made out under the microscope.

3. Results.

The wave-lengths obtained are given in the table below and they are accurate to about 0·1 Å. They are in agreement with Terenin's measurements within the limits of his accuracy, but Wieland's values do not harmonise with either. The wave-numbers have been obtained from Kayser's *Tabelle der Schwingungszahlen*.

TABLE I.

Intensity	Wave-length	Wave-number	Terenin's Wave-length
3	4488·27	22274·1	··
3	4476·27	22333·8	··
diff. 3	4466·55	22382·4	··
4	4456·05	22435·1	4458
2	4449·44	22468·4	4451
diff. 2 ?	4442·35	22504·3	4444
v. diff. 2	4437·31	22529·9	4433
4	4430·20	22566·0	··
4	4423·64	22599·5	4425
4	4413·14	22653·3	4414

TABLE I—(*Contd.*)

Intensity	Wave-length	Wave-number	Terenin's Wave-length
diff. 3	4402·86	22706·1	4403
2	4392·55	22759·4	..
4	4381·56	22816·5	4382
v. diff. 2	4331·94	23077·9	4333
5	4320·84	23137·2	4322
4	4309·89	23195·9	4313
3	4299·14	23254·0	4301
2	4291·16	23297·2	4290
diff. 3	4282·17	23346·1	4283
diff. 4	4271·28	23405·6	4271
v. diff. 3 ?	4262·60	23453·3	..
3	4260·36	23465·6	4262
3	4251·50	23514·5	4251
2	4241·59	23569·5	4243
1	4225·78	23657·6	4224
3	4213·83	23724·7	4217
2	4204·18	23779·2	4205
2	4193·95	23837·2	4187
1	4169·60	23976·4	4165
3	4159·46	24034·8	..
diff. 2	4148·48	24098·4	4147
3	4139·11	24153·0	..
2	4134·31	24181·0	..
3	4129·28	24210·5	4127

The vibrational analysis of these bands is given in Table II. The analysis shows that these bands have not got any level in common with the systems analysed by Wieland. All attempts at an analysis based on the assumption of a common ground level for these bands and those analysed by Wieland proved to be entirely fruitless. Our analysis shows that one of the levels is a doublet level. Whether the doublet separation is due to the upper level or the lower level cannot be determined indubitably, but it is probable that the lower state is the $^2\Pi$ level to be expected from a combination of the $^1S_0$ state of Hg with the ^2P state of I. The lower level shows a peculiarity which has been previously observed in the hydrides and deuterides of the alkalies and in Hg_2, Cd_2 and Zn_2, namely, that the vibration quanta first increase and then decrease. Another peculiarity observed in Hg_2, Cd_2 and Zn_2, *viz.*, that the vibration levels of the lower term terminate when the vibration quantum attains its initial value (*i.e.*, $\omega_{\frac{1}{2}}$) seems to be present here also. The diffuse and weak nature of the bands seems to be due to these peculiarities.

TABLE II.

| v'	$v''= 0$	1		2		3		4		5
0		(23514·5)		(23137·2)		(22759·4)		(22382·4)		
		55·0		*58·7*		*57·1*		*52·7*		
		23569·5	*373·6*	23195·9	*379·4*	22816·5	*381·4*	22435·1		
		267·7		*269·7*				*271·0*		
1	(24153·0)	(23779·2)		(23405·6)				(22653·3)		(22274·1)
	57·5	*58·0*		*60·0*				*52·8*		*59·7*
	24210·5 *373·3*	23837·2	*371·6*	23465·6		23077·9?		22706·1	*372·3*	22333·8
		261·2		*259·1*						*265·7*
2		(24034·8)		(23657·6)						(22529·9)
		63·6		*67·1*						*69·6*
		24098·4	*373·7*	23724·7	*378·6*	23346·1				22599·5
				251·7						
3				23976·4						

4. *Discussion.*

Our analysis of the bands shows that this system (system B in the nomenclature adopted by Wieland) has not got the same lower level as systems C and D analysed by Wieland. He has interpreted the results of his fluorescence experiments on the basis of a common lower level for all these systems. The present analysis, however, is not in contradiction with the fluorescence

A5   Γ

data. Thus while systems C and D with ν_{00} at 4·05 and 4·5 volts respectively are excited by light of energy 6·4 and 7·1 volts, giving for the energy available for the dissociation of HgI_2 into HgI and I the values 2·3 and 2·6 volts, Wieland's assumption that system B has the same lower level and that its ν_{00} is at 3·4 volts leaves only 2·1 volts for the dissociation of HgI_2. On the basis of our analysis ν_{00} of system B is at 2·95 volts. We may also assume that the lower state of B splits into $Hg\ {}^1S_0$ and $I\ {}^2P$ just as the common lower level of systems C and D is supposed to do. If on the analogy of Hg_2 we also assume that the position of the electronic level corresponds to the point where the vibration quantum is a maximum, the $v'' = 0$ level of system B will be 0·19 volt below the $({}^1S_0 + {}^2P)$ level. According to Wieland's analysis of system C, its $v'' = 0$ level is 0·5 volts below $({}^1S_0 + {}^2P)$. Hence $v'' = 0$ of system B is 0·31 volt above the $v'' = 0$ level of system C. Taking this lower level of the system C to be the ground-level, ν_{00} of system B is at 2·95 + 0·31 or 3·26 volts above the ground-level, so that when system B is excited by light of 5·5 volts, the energy available for the dissociation of HgI_2 into $HgI + I$ is 2·24 volts. This value accords better with those obtained from the other systems. The present analysis also removes another difficulty that was associated with the older point of view. Thus in order to explain the appearance of successive differences of about 120 cm.$^{-1}$ between consecutive bands, Wieland assumes that 120 cm.$^{-1}$ represents the vibration frequency of the ground-level and that the difference 180 cm.$^{-1}$ appearing later is the vibration frequency of the upper state, and yet he assumes that the upper potential curve is shifted to longer wave-lengths as compared with the lower curve. This assumption is therefore in direct contradiction with Morse's rule. In the case of the analysis presented here, ω'' is larger than ω' and the intensity distribution gives a Condon parabola which corresponds to the case of ω'' being larger than ω'. The difficulty that was experienced in interpreting the system B is due to the peculiar behaviour of the lower level. Mulliken[5] has recently discussed the type of potential curve which will represent such a level. But his results are qualitative and their application to the present case is not quite clear. So we have refrained from drawing potential curves or representing our results by formulæ. Our analysis of the system B of CdI, to be presented in the following paper, shows that the peculiar behaviour of the lower state is common to HgI and CdI. The connection between this behaviour and the difficulties met with in the discussion of the type of binding into which an atom in a ${}^1S_0$ state can enter requires further investigation for its elucidation.

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and others.

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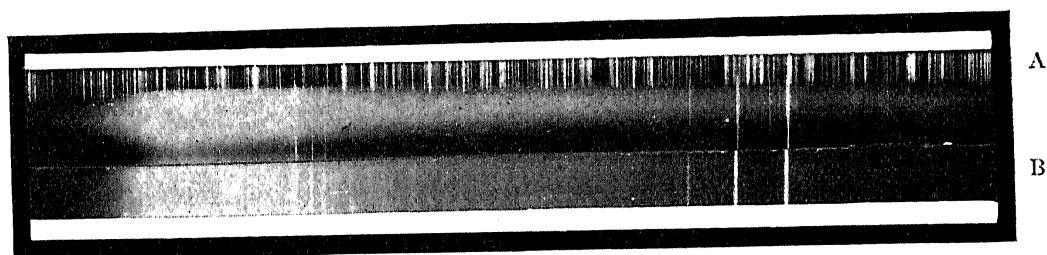
A 2000 volt 3 KVA Transformer Discharge; Slit width 0·05 mm.
B 10000 volt ½ KW Transformer Discharge; Slit width 0·08 mm.

The doubling of some of the bands can be made out in A.