

## ANALYSIS OF THE BAND SPECTRUM OF ZINC.

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THE band spectrum of zinc has been photographed and measured in absorption by Mohler and Moore,<sup>1</sup> and in emission by Volkringer<sup>2</sup> and Hamada,<sup>3</sup> but no analysis of any of the band systems has been made. Even in the case of mercury and cadmium, a number of papers has been published, but until recently no analysis of the band systems was available. Thus Jevons in his Report (p. 282) remarks under "Metal molecules of group II" that the theoretical interpretation and the molecular constants are not certain. The lack of a definite vibrational analysis of the bands was sought to be remedied by experimental results of a semi-quantitative nature. The long series of bands observed in mercury by Lord Rayleigh and called "core bands" and "wing bands" were each supposed to represent one unbroken  $v'$ -progression due to transitions between the ( $^1S_0 + ^1S_0$ ) ground state and a higher state. The higher state was taken to be ( $^1S_0 + ^3P_1$ ) in the case of the wing bands but in the case of the core bands there was divergence of opinion, some holding the view that the upper state was ( $^1S_0 + ^3P_0$ ) while others inclined to the view that it was ( $^1S_0 + ^3P_1$ ). Some bands observed by Volkringer were assumed to be a continuation of the core bands towards longer wavelengths while a number of bands discovered by Hamada was supposed to form a similar extension of the wing bands. There was no satisfactory explanation of the difficulties arising from these assumptions. With the object of avoiding these difficulties the present author sought for the solution in a new direction and succeeded in arriving at a complete vibrational analysis of all these band systems.<sup>4</sup> This analysis revealed a peculiarity in the behaviour of the common ground state, *viz.*, that the vibration frequencies instead of steadily decreasing, increased at first up to a certain value of  $v''$  and then diminished,  $\kappa_e \omega_e$  having the same magnitude during this decrease as it had during the increase. Such a behaviour has

<sup>1</sup> *Journ. Opt. Soc. Amer.*, 1927, 15, 74.

<sup>2</sup> *Annales de Physique*, 1930, 14, 18.

<sup>3</sup> *Phil. Mag.*, 1931, 12, 50.

<sup>4</sup> *Proc. Ind. Acad. Sci.*, 1934, 1, 166.

also been remarked in LiH,<sup>5</sup> NaH<sup>6</sup> and KH<sup>7</sup> and also in NaD<sup>8</sup> which have all similar spectra. Since the similarity in the band spectra of Hg<sub>2</sub>, Cd<sub>2</sub> and Zn<sub>2</sub> is well known, it was an interesting question whether the same peculiarity of the ground state existed also in Cd<sub>2</sub> and Zn<sub>2</sub>. Accordingly the spectrum of Cd<sub>2</sub> was examined; with the available meagre data, an analysis of the band systems of Cd<sub>2</sub> was successfully carried out. It was then found that the ground state of Cd<sub>2</sub> also presented the same peculiarity.<sup>9</sup> The case of zinc proved to be more complicated. This is due to the fact that whereas in Hg <sup>3</sup>P<sub>0</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>2</sub> are far apart with <sup>3</sup>P<sub>0</sub>—<sup>3</sup>P<sub>1</sub>=1767.3 and <sup>3</sup>P<sub>1</sub>—<sup>3</sup>P<sub>2</sub>=4630.6, they are very close in the case of zinc where <sup>3</sup>P<sub>0</sub>—<sup>3</sup>P<sub>1</sub>=189.8 and <sup>3</sup>P<sub>1</sub>—<sup>3</sup>P<sub>2</sub>=388.9. Hence the systems of Zn<sub>2</sub> corresponding to the "wing" bands, "core" bands and Rayleigh bands (between λ 2341 and 2297) are somewhat mixed up. The various systems were however successfully separated and their analysis was carried out. The result proved that the long series of bands given by Volkringer consist of two band systems corresponding to the "core" bands and Rayleigh's bands, *i.e.*, the two systems arising from the upper and lower potential curves of the <sup>1</sup>S<sub>0</sub>+<sup>3</sup>P<sub>2</sub> state. Some bands observed by Hamada proved to be similar to the "wing" bands while group I of Mohler and Moore was found on analysis to be similar to Steubing's bands. Thus while the upper state of the "wing" bands shows a large ω<sub>e</sub> and x<sub>e</sub>ω<sub>e</sub> is also large, the upper state of the "core" bands shows a small ω<sub>e</sub> and x<sub>e</sub>ω<sub>e</sub> while those of the Steubing's bands and Rayleigh's bands are much smaller. In exactly the same way, the bands observed by Hamada and here ascribed to transitions from (<sup>1</sup>S<sub>0</sub>+<sup>3</sup>P<sub>1</sub>) to (<sup>1</sup>S<sub>0</sub>+<sup>1</sup>S<sub>0</sub>) show a large ω<sub>e</sub> and x<sub>e</sub>ω<sub>e</sub> in the upper state (Table I), while Mohler

TABLE I.

<sup>1</sup> S <sub>0</sub> + <sup>1</sup> S <sub>0</sub> v'' =	1		2		3		4
<sup>1</sup> S <sub>0</sub> + <sup>3</sup> P <sub>1</sub> v'	28944	241	28703	318	28385 753 29138	421 435	27107 857 27964 739 28703 603 29308

<sup>5</sup> Nakamura, *Zs. f. Phys.*, 1930, **59**, 218.

<sup>6</sup> Hori, *Zs. f. Phys.*, 1930, **62**, 352.

<sup>7</sup> Almy and Hause, *Phys. Rev.*, 1932, **39**, 178.

<sup>8</sup> Olsson, *Zs. f. Phys.*, 1935, **93**, 206.

<sup>9</sup> *Proc. Ind. Acad. Sci.*, 1935, **1**, 484.

and Moore's group I here attributed to the transition  $(^1S_0 + ^1P_1) \rightarrow (^1S_0 + ^1S_0)$  shows a small  $\omega_e$  and  $x_e\omega_e$  in the upper state (Table II). The bands mea-

TABLE II.

$^1S_0 + ^1S_0$ $v'' =$	0		1		2		3		4	
$^1S_0 + ^1P_1$ $v'$							33332	407		37925
							207			202
	39188	122	39066	182	38884	345	38539	412		38127
				182			179			
				39066	348		38718			

sured by Volkringer and arising according to the present analysis from transitions from the upper (Table IV) and lower (Table III) potential curves

TABLE III.

$^1S_0 + ^1S_0$ $v'' =$	1	2		3	4		5	6		7			
$^1S_0 + ^3P_2$ $v' = 0$	31929		31747?	31408	428	30980							
	144			129		135							
	1	32073	215	31858	321	31537	422	31115	317	30798	216	30582	
		124		123		130		126		124			
	2	32197	216	31981	314	31667	426	31241	319	30922			
				123		110		108					
	3			32104	327	31777	428	31349					
						112		98					
	4					31889	442	31447					
						92		90					
	5					31981*		31537*				30865	
								89					
	6							31626	336	31290			
								61		59			
	7							31687	338	31349	196	31153	125
									39		39		38
8									31388	196	31192	126	31066

\* Used twice.

of  $(^1S_0 + ^3P_2)$  to the ground state similarly show a small  $\omega_e$  and  $x_e\omega_e$ . In particular the bands given in Table IV are similar to Rayleigh's bands in that  $\omega_e$  of the upper state is very small and almost constant. This similarity suggested that the upper state involved in their emission is the upper potential curve of  $(^1S_0 + ^3P_2)$ . The limit of the upper state comes out at about  $33700 \text{ cm}^{-1}$ . Since  $^1S_0 - ^3P_2 = 32890$ , the distance between the  $v'' = 0$  level and the  $(^1S_0 + ^1S_0)$  limit comes out as  $810 \text{ cm}^{-1} \approx 0.10 \text{ volt}$ . The vibration frequency at this level has that value with which the decrease in the vibration frequencies begins. The same thing occurs in  $\text{Hg}_2$  also. Thus the distance between the  $v'' = 0$  level and the  $(^1S_0 + ^1S_0)$  atomic level is found

TABLE IV.

${}^1S_0 + {}^1S_0$ $v''=$	0		1		2		3		4	
${}^1S_0 + {}^3P_2$ $v'=$					32994?		32628	431	32197	
							85		83	
	33357*	100	33257*	209	33048	335	32713	433	32280	
	67		56				54			
	33424*	111	33313				32767			
	56		44				32			
	33480	123	33357	210	33147	348	32799?	425	32374	
	34		33		33		65?		53?	
	33514	124	33390	210	33180	316	32864	437	32427?	
			34		22					
			33424	222	33202					
			33		33					
		33457	222	33235						
		23		22						
		33480	223	33257						

\* Used twice.

to be 0.25 volt, 0.18 volt and 0.10 volt in  $Hg_2$ ,  $Cd_2$  and  $Zn_2$  respectively. The interpretation of this result is however not clear. What the levels above the ( ${}^1S_0 + {}^1S_0$ ) limit then represent becomes difficult to understand. The levels in the ground state may be favoured positions for the formation of quasi molecules and dissociation may occur at any level. It is thus not certain that the distance between  $v''=0$  and the atomic level really represents the energy of dissociation. For if that is the case, the existence of vibrational levels above the atomic limit is not easy to explain. Until more accurate measurements are made on the several band systems so that the band constants can be more accurately determined, we cannot draw any definite conclusions. The behaviour of the ground state and the above causes of uncertainty require further investigation.

Table V gives a tentative scheme of vibrational levels for Rayleigh's bands. Since  $\omega_e$  is nearly constant the present arrangement is not uniquely determined as the correct one. However, the absence of two bands in the middle, remarked by Lord Rayleigh, seems to find an explanation in the array here given. The absence is to be expected because in one case one  $v'$  progression ends while in the other a larger  $\omega_e$  is required at the beginning of another  $v'$  progression. The array of the bands is also similar to that of the system of  $Zn_2$  here attributed to a similar transition.

The analysis of the  $Hg_2$ ,  $Cd_2$  and  $Zn_2$  bands given by the author removes many of the difficulties inherent in the previous explanation that each one of the band series is a single  $v'$  progression. Quantitative results regarding molecular constants are also made possible. It may be hoped that when

TABLE V.  
Rayleigh's Bands of Mercury.

$^1S_0 + ^1S_0$ $v'' =$	0	1	2	3		
$^1S_0 + ^3P_2$ $v'$		43166	288	42878		
			36	38		
		43202	286	42916		
			28	19		
		(Kuhn) 43230	295	42935		
			22	18		
		43252	299	42953		
			18	21		
		43270	296	42974		
			17	16		
		43287	297	42990		
			16	18		
		43303	295	43008		
			17	19		
		43320	293	43027		
			15	16		
	43427	92	43335	292	43043	
			17	18		
	43444	93	43351	290	43061	
			15	17		
	43459	92	43367	289	43078	
			15	17		
	43474	90	43384	289	43095	
			12			
	43486	88	43398			
			17			
	43503	91	43412	296	43116	
			14			
	43517	90	43427*	294	43133	
				17		
				43150		
				16		
				43166*		
				19		
				43185*	489	42696
				17	17	
				43202*	489	42713
				19	20	
				43221	488	42733
				17	18	
			43238	487	42751	
			14	18		
			43252*	483	42769	
			18	17		
			43270*	484	42786	
			17	16		
			43287*	485	42802	
			16	21		
			43303*	480	42823	
			17	18		
			43320*	479	42841	

\* Used twice.

the behaviour of the ground state is understood, the problem of the constitution of quasi molecules will reach a stage nearer to its solution.