ON THE ANALYSIS OF THE BAND SPECTRUM OF CADMIUM.

By T. S. Subbaraya, M.Sc., A.Inst.P.,

Department of Physics, University of Mysore, Bangalore.

THE band spectrum of cadmium has been investigated by a number of observers including Mohler and Moore,[1] Winans,[2] Hamada,[3] Kuhn and Arrhenius[4] and Mrozowski.[5] Winans has also discussed the origin of the bands and indicated the molecular states involved; he has also drawn some conclusions regarding the heat of dissociation of the cadmium molecule in the ground state, but Kuhn has shown that there is no basis for these conclusions. Kuhn and Arrhenius have tried to determine the heat of dissociation by studying the absorption of cadmium vapour at different temperatures. All these authors assume that the potential curve for the ground state possesses a very small depression with few vibrational levels and that the structure observed in several of the bands is almost entirely due to the vibrational levels of the upper states involved in their emission. A similar assumption has been made in the case of mercury and zinc. In a recent paper[6] the author has succeeded in arriving at a vibrational analysis of five of the band systems of mercury and in thereby explaining a number of points which appeared obscure. This work, however, revealed a peculiarity in the behaviour of the ΔF^v's of the ground state in that instead of decreasing steadily, they first went on increasing and then began to decrease, $\Delta^2 F$ during the decrease being the same as during the increase. This peculiarity made it difficult to draw definite conclusions regarding the heat of dissociation of the ground state. Since the similarity to be expected between the band spectra of zinc, cadmium and mercury has been experimentally proved to exist, it was thought that further light would be thrown on the question if the bands of cadmium were analysed and their structure compared with the structure of

[1] *Journ. Opt. Soc. America,* 1927, **15,** 74.

[2] *Phil. Mag.,* 1929, **7,** 556.

[3] *Phil. Mag.,* 1931, **12,** 50.

[4] *Zs. f. Phys.,* 1933, **82,** 716.

[5] *Zs. f. Phys.,* 1934, **91,** 600.

[6] *Proc. Ind. Acad. Sci.,* 1934, **1,** 166.

the corresponding bands of mercury. Accordingly the bands measured by Hamada were investigated and a vibrational analysis of these bands was made. It was found that by comparing their structure with that of the previously analysed bands of mercury, the bands corresponding to similar molecular transitions could be picked out without ambiguity. It was also found that the result so obtained was in entire agreement with the expectations of Hamada based on experimental grounds. For the sake of comparison the analysis of the bands attributed by Hamada to transitions from the $^1S_0 + {}^3P_1$ state to the ground state is given in Table I while Table II gives the analysis of the corresponding bands of mercury observed by

TABLE I.

$^1S_0 + {}^1S_0$											
$^1S_0 + {}^3P_1$	26062	*854*	25208	*486*	24722						
	626		*652*		*659*						
	26688	*828*	25860	*479*	25381	*362*	25019	*205*	24814?	*92*	24722*
	597		*595*		*586*		*596*		*567*		*569*
	27285	*830*	26455	*488*	25967	*352*	25615	*234*	25381	*90*	25291
			463		*488*				*479*		*482*
			26918	*463*	26455*				25860	*87*	25773

* Used twice.

Hamada and attributed by him to a similar transition. Table III similarly contains the analysis of the cadmium bands attributed to transitions from the $^1S_0 + {}^3P_0$ state and Table IV gives the results obtained for the similar Volkringer bands of mercury. Of the band systems observed by Mohler and Moore, Walter and Barratt[7] attribute group II to CdO, groups III, IV and V to cadmium chloride and groups VI and VII to thallium chloride. Mrozowski,[8] however, has established that group V belongs to Cd$_2$. On examining the bands of group II it was found that they fitted into the present scheme of vibrational levels (Table V) and their structure showed them to be analogous to the Steubing bands of mercury (given in Table VI). This similarity in their structure lends support to the opinion of Winans that the group II is due to transitions from the ground state to the $^1S_0 + {}^1P_1$ state by absorption, and not due to CdO as Walter and Barratt think. The other groups given by Mohler and Moore do not seem to fit into the present scheme, except group V in which the difference $\simeq 205$ cm.$^{-1}$ characteristic of the ground state occurs twice in a system containing only five bands. This group may therefore belong to Cd$_2$ as has been shown by Mrozowski. From the

[7] *Proc. Roy. Soc. A.*, 1929, **122**, 201.

[8] *Zs. f. Phys.*, 1930, **62**, 314.

TABLE II.

Hamada's Bands of Mercury.

$^1S_0+^1S_0$ $v''=$	8	9		10		11		12		13		14		15
$^1S_0+^3P_1$ $v'=0$														
1	30891													
2		(29961)												
		496?												
3		30457												
		525												
4		30982												
5														
6		31810	*1067*	30743	*735*	30008								
				337		*353*								
7				31080	*719*	30361								
						336								
8						30697	*483*	30214						
						335		*339*						
9				31760	*728*	31032	*479*	30553	*288*	30265	*99*	30166	*55*	30111
								287		*288*		*291*		*302*
10								30840	*287*	30553*	*96*	30457*	*44*	30413
								240		*239*		*240*		*236*
11								31080*	*288*	30792	*95*	30697*	*48*	30649
										190		*194*		*191*
12										30982*	*91*	30891*	*51*	30840
										149		*141*		*142*
13										31131*	*99*	31032*	*50*	30982
												99		*98*
14												31131	*51*	31080*
												51		*51*
15												31182	*51*	31131*

* Used twice.

TABLE III.

$^1S_0+^1S_0$				
$^1S_0+^3P_0$				22401
				122
		23020	*497*	22523
		128		*117*
	23507	*359*	23148	*508*	22640
	122		*124*		*123*
	23629	*357*	23272	*509*	22763
	118		*114*		*120*
	23747	*361*	23386	*503*	22883

present analysis we find that the peculiarity observed in the ΔF^v's of the ground state of mercury is present also in that of cadmium. Since the bands corresponding to the 'wing' bands of mercury have not

TABLE IV.

Volkringer's Bands.

$^1S_0+^3P_0$ $v'=$	$^1S_0+^1S_0$ $v''=$ 3		4		5		6
0	26680						
	230						
1	26910	*746*	26164	*829*	25335		
	219		*228*		*233*		
2	27129	*737*	26392	*824*	25568		
			196		*171*		
3			26588	*849*	25739		
			200 ?		*147*		
4			26788 ?	*902 ?*	25886	*1042*	24844
					142		
5					26028		
					136		
6			27027	*863*	26164*	*1058*	25106
			102		*131*		
7			27129*	*834*	26295		

* Used twice.

TABLE V.

$^1S_0+^1S_0$							
$^1S_0+^1P_1$							35948
							182
							36130
							144
					36673	*399*	36274
					121		*145*
			37012	*218*	36794	*375*	36419
			96		*109*		*120*
			37108	*205*	36903	*364*	36539
			97		*109*		
	37302	*97*	37205	*193*	37012*		
	98		*97*				
	37400	*98*	37302*				
	98		*98*				
	37498	*98*	37400*				
	99		*98*				
	37597	*99*	37498*				
	85						
	37682						

* Used twice.

been measured in cadmium, the vibration quantum numbers could not be fixed. As in the case of mercury it is difficult to determine the heat of dissociation of the ground state. Since the data are not even as extensive as in the case of mercury it is difficult even to determine the relative position of the $v''=0$ level with respect to the $^1S_0+^1S_0$ electronic level as has been possible to do in the case of mercury. If the assumption

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Table VI.

Steubing's Bands.

$^{1}S_{0}+^{1}S_{0}$ $v''=$	1		2		3		4		5
$^{1}S_{0}+^{1}P_{1}$					47373	*801 ?*	46572		
					183		*214*		
			48035	*479*	47556	*770 ?*	46786		
			162		*177*		*213*		
			48197	*464*	47733	*734*	46999	*857*	46142
			161		*148*		*182*		*227 ?*
	48650	*292*	48358	*477*	47881	*700*	47181	*812*	46369
	138		*146*		*154*				
	48788	*284*	48504	*469*	48035*				
	126		*146*						
	48914	*264*	48650						

* Used twice.

is made that the similarity in the structure of the bands of mercury and cadmium extends to all the details, we may estimate the difference between $v''=0$ and the $^{1}S_{0}+^{1}S_{0}$ electronic level as 0·18 volt while it is 0·25 volt in mercury. Because of the difficulty involved in the measurement of these diffuse and weak bands great accuracy is not found. At the present stage, therefore, the attempt to draw potential curves for the various states has been abandoned. Five of the bands recorded by Hamada could not be fitted into the present analysis so that their vibration quantum numbers relative to the rest could not be fixed. The numerical analysis shows, however, that the peculiar behaviour of the ground state in having $\Delta F''$'s which increase at first and then decrease, and in having a large anharmonic term is common to both mercury and cadmium. When this behaviour is explained, the structure of the band spectra of these metals will be better understood.