

## ULTRAVIOLET BANDS OF CADMIUM IODIDE

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(Plate IV)

**ABSTRACT.** The emission bands of cadmium iodide as excited in a transformer and in a high frequency oscillatory discharge, are photographed with a Hilger quartz Litrow spectrograph. A doublet system due to the electronic transition  ${}^2\Pi - {}^2\Sigma$ , analogous to the halide bands of related molecules is established. The far ultraviolet system, partially recorded by Wieland is extended and the vibrational formula

$$\gamma = 41912.4 + [108.5(v' + \frac{1}{2}) - 1.0(v' + \frac{1}{2})^2] \\ - [179.1(v'' + \frac{1}{2}) - 0.8(v'' + \frac{1}{2})^2]$$

is calculated. The common final  ${}^2\Sigma$  state is probably the ground state of the molecule.

## INTRODUCTION

The first extensive work on the band spectrum of cadmium iodide was done by Wieland (1929) who recorded the following characteristic systems and divided them into three classes. The last column in the Table I is the new designation suggested by us in conformity with that of the iodide bands of zinc and mercury.

TABLE I

Region	Class	New Designation
$\lambda$ 6600- $\lambda$ 3600	III	B
A group of three bands at about $\lambda$ 3560	--	C
$\lambda$ 3500-3250	I	D
$\lambda$ 2550- $\lambda$ 2350	II	E

The wave-lengths of the group of three violet degraded bands of system C are 3586.3(0), 3563.2(3), 3541.1(4). The method of excitation was a high frequency discharge through the vapour of cadmium iodide and the largest dispersion used was about 10 Å per millimeter at  $\lambda$  2500. A complete vibrational analysis was given only of one of these system (Class I) and regularities were shown among the bands of the Class II system. The visible system (Class III) was at first ascribed to the triatomic molecule  $\text{CdI}_2$  but later work by the same author indicated that this system too was due to the diatomic molecule  $\text{CdI}$ .

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In recent work on the structure of the band spectra of the halides of Group II-b elements of the Periodical Table by Howell (1943) and by Rao and others (1944a, 1944b, 1946) the view was established that these molecules give rise to band systems corresponding to the electronic transition  ${}^2\Pi-{}^2\Sigma$ , in which the electronic width of the  ${}^2\Pi$  term is related to the corresponding atomic interval of the metal atom and that the transition is between the non-banding or atomic orbitals.

Examining the cadmium iodide bands in the light of this view, Howell suggested that the system analysed by Wieland between  $\lambda$  3500-32250 is one of the components of the predicted  ${}^2\Pi-{}^2\Sigma$  systems, the other missing component is to be sought among the fragmentary group in the vicinity of  $\lambda$  3550 mentioned by Wieland. The system, further to the ultraviolet lying, at  $\lambda$  2400, is interpreted as probably due to the transition  ${}^2\Sigma-{}^2\Sigma$  the lower  ${}^2\Sigma$  state being the ground state of the molecule. The present work is carried out in order to establish, if possible, the missing component of  ${}^2\Pi-{}^2\Sigma$  system and to study the vibrational analysis of the far ultraviolet system (system E).

#### EXPERIMENTAL

As in the previous work on the bands of the iodides of zinc and mercury, two different sources of excitation have been employed for the excitation of cadmium iodide bands—a transformer discharge and a high frequency valve oscillatory discharge through the vapour. The h. f. oscillator set was specially constructed by one of the authors for the purpose. A much higher temperature of the vapour was found necessary with cadmium iodide than with either zinc or mercury iodides. A discharge tube of quartz or of special ignition pyrex had to be employed and heating was done continuously by a set of etna burners along the length of the tube.

#### RESULTS

About 90 bands were measured between  $\lambda$  3516.8 to 3288.2 in system D by Wieland comprising of the sequences from (0,8), to (4,0). In addition to these bands, the authors obtained on their plates a number of new bands towards the violet end of the system as seen in the reproduction (Plate IV A). The wave-length data of these additional bands is given in Table II.

Two possibilities of assignment of these bands are considered, one being to regard them as the extension of the system D, the bands forming higher members of the sequence (3,0) and (4,0) obtained by Wieland. But a somewhat abrupt increase in the intensity of the bands is observed at  $\gamma$  30434.8 and 30257.1, leading to the possibility of regarding these bands as forming a different system altogether. The vibrational scheme given in Table III was then examined giving  $\Delta G(v'')$  values agreeing with those of the final  ${}^2\Sigma$  state. If this were correct, it would seem that this may be the missing component system with the interval between the (0,0) bands equal to  $30434.8 - 29532.9 = 901.9$  cm. This is much too different from the

predicted separation of 1140 cm. Further, the missing system more probably lies towards the longer wave-length side of the main component, as observed by Howell. On this account, the new bands are believed to form part of system D itself. A search further to the violet did not reveal any bands ascribable to CdI molecule.

TABLE II

Wavelength	Wave number	Int.
3340.06	30257.1	2
3300.41	30290.6	1
3297.23	30319.8	1
3293.97	30340.8	0
3291.17	30375.6	0
3287.83	30406.5	0
3284.87	30434.8	4
3282.08	30459.7	1
3279.17	30487.8	2
3276.06	50515.7	2
3273.26	30541.8	0

TABLE III

	0 (177.7)	1 (169.1)	2 (167.9)	3 (165.8)	4 (166.2)	5	6
0	30434.8	30257.1					
1		30459.7	30290.6				
2			30487.8	30319.9			
3				30615.7	30349.9		
4					30541.8	80376.6	
5							30406.5

The three bands, (designated by us as system C) mentioned by Wieland, are distinctly observed on our plates (Plate IV A) and their wave lengths obtained from a quartz Littrow plate are given in Table IV.

TABLE IV

$\lambda$	$\nu$ (int)	$\delta\nu$	( $\nu'$ , $\nu''$ )
3541.04	28232.9 (6)		(0,0)
3563.52	28054.5 (4)	178.4	(0,1)
3585.84	27880.2 (2)	174.3	(0,2)

If, on the analogy of the remaining halide bands, both the components of the doublet system,  $^2\Pi-^3\Sigma$  are observable on the spectrogram, one of the components being feebly developed, then these three bands are the only hands which must be regarded as constituting the missing system.

TABLE V  
CdI—Ultraviolet System.  $\lambda$  2550—2350

Wieland		Authors		Classification
$\nu$ cm. <sup>-1</sup>	Int.	$\nu$ cm. <sup>-1</sup>	Int.	( $\nu'$ , $\nu''$ )
		39349.7	0	(0,15)
		477.8	1	(1,15)
		526.6	1	(0,14)
		673.7	0	(0,13)
		726.8	1	(2,14)
		82.1	0	(3,14)
		891.7	1	(2,13)
		954.0	1	(1,12)
		980.1	0	(3,13)
		40053.7	1	(2,12)
		113.5	1	(1,11)
		156.1	0	(3,12)
		177.5	0	(0,10)
		226.5	2	
		270.2	4	(1,1)
40435.0	2	440.7	3	(1,9)
443.5	1			
		483.4	1	(3,10)
		510.4	0	(0,8)
		553.1	1	(2,9)
600.0	2	608.3	4	(1,8)
607.5	1			
648.0	0	646.4	1	(3,9)
		679.6	1	(0,7)
		717.4	1	(2,8)
768.0	2	775.8	4	(1,7)
775.5	1			
812.5	0	810.4	1	(3,8)
		40839.5	0	(0,6)
4087.5	1	878.2	3	(2,7)
939.5	3	934.1	2	(1,6)
943.5	1			
		999.3	1	(0,5)
41046.0		41050.1	4	(2,6)
112.3	1	112.9	3	(1,5)
		163.5	0	(0,4)
211.0	3	220.7	3	(2,5)
217.0	3			
		243.2	0	(4,6)
281.5	1	279.9	1	(1,4)
315.0	1	325.9	3	(3,5)
385.0	3	389.9	4	(2,4)
		456.2	0	(1,3)
488.0	2	489.1	3	(3,4)
		525.0	0	(5,5)
567.5	2	561.6	3	(2,3)
		585.7	0	(4,4)
		626.4	0	(1,2)
661.0	3	664.0	3	(3,3)
732.0	1	737.3	1	(2,2)
763.5	2	768.5	1	(4,3)
		804.8	1	(1,1)
834.5	3	840.1	3	(3,2)
		857.5	1	(5,3)
		874.8	1	(0,0)
		907.1	5	(2,1)
937.0	2	936.7	0	(4,2)
		954.0	1	(6,3)
		41979.6	1	(1,3)
42009.5	1	42017.1	1	(3,1)
112.0	1	113.3	1	(4,1)

TABLE VI

Vibrational analysis and Intensity distribution in CdI bands (E System)

$v''/v'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	$\Delta G'$
0	1				0	1	3	1	0		0			0	1	0	
1	1	1	0	0	1	3	2	4	4	3	4	1	1		1	1	103.7
2		3	1	3	4	3	4	3	1	1			1	1	1		107.1
3		1	3	3	3	3				1	1		0	0	0		102.6
4		1	0	1	0		0										18.5
5				1		0											89.0
6				1													96.5
$\Delta G''$	174.8	175.4	172.5	176.4	165.9	169.7	163.4	165.8	165.3	162.2	165.7	159.5	169.0	156.0			

On this basis, the ( $v'$ ,  $v''$ ) numbering in the last column is suggested. The wave number intervals support the assignment. The electronic doublet width, 1300, is much less than the predicted value, 1140, although of the right order of magnitude.

## SYSTEM E

28 heads were measured in this far ultraviolet system by Wieland from  $\lambda$  2473 to  $\lambda$  2364 and regularities were shown among them. These same regularities were presented in a Deslandre scheme by Howell, indicating  $\Delta G$  ( $v''$ ) values, in agreement with those of the lower state of the D system. Since the bands lie in the vicinity of  $^1S-^1P$  line of cadmium, they are ascribed to the electronic transition  $^2\Sigma-^2\Sigma$ . In the present work, about 60 bands are altogether measured in this system as shown in Table V, in which Wieland's data are also given for the purpose of comparison. The vibrational analysis of these bands is presented in Table VI. The  $v''$  values in this scheme are identical with those given by Howell but the  $v'$  values are increased by one, several band heads being thereby included in the analysis. The following vibrational formula is calculated:--

$$\lambda = 41912.4 + [108.5(v' + \frac{1}{2}) - 1.0(v' + \frac{1}{2})^2] \\ - [179.1(v'' + \frac{1}{2}) - 0.8(v'' + \frac{1}{2})^2]$$

The final state values distinctly indicate a common ground level with the D system of bands.

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