

ULTRA VIOLET BANDS OF ZINC IODIDE--PART I

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(Plate III)

ABSTRACT. A brief system (designated as D) consisting of about ten diffuse bands, is detected among the bands of the zinc iodide molecule, in the region λ 3277-3193 and found to have the same final state as the system (here designated as C) previously established by Wieland. The view is advanced that the two systems are components of an electronic transition ${}^2\Pi-{}^2\Sigma$ with the ${}^2\Pi$ interval 370 cm^{-1} , agreeing closely with the value 386 cm^{-1} , predicted by Howell for the zinc halide bands. The occurrence of a third system E is also reported.

INTRODUCTION

In a recent paper, Howell (1943) photographed the emission spectrum of HgI^{\dagger} in a high frequency discharge and analysed the ultra violet bands into two systems which he considered as components of a single doublet system arising from the electronic transition ${}^2\Pi-{}^2\Sigma$. The separation of ${}^2\Pi$ level was 3940 cm^{-1} which agrees very closely with the atomic coupling constant 4205 cm^{-1} for the mercury atom corresponding to the $6s\ 6p^3P$ state. Further as Cornell (1938) has pointed out in the case of HgCl , the two systems in HgI^{\dagger} occur near the mercury resonance line $\lambda 2537$. From these two features, Howell concluded that the electronic transition involved in the emission spectrum of HgI^{\dagger} should essentially be between non-bonding or atomic orbitals. If this view is correct, the same feature must present itself in the band systems of all the halides of mercury, cadmium and zinc, as pointed out by Howell.

Extending the study of the emission bands of the HgCl molecule, Rao and Ramachandra Rao (1944) confirmed the existence of a similar ${}^2\Pi-{}^2\Sigma$ transition band system with the ${}^2\Pi$ separation equal to 3890 cm^{-1} . A doublet separation of the same order (3538 cm^{-1}) was found by Rao, Sastry and Krishnamurty, (1944) also in the Hg I molecule between the C and D systems.

Howell, applying this argument to the known band systems of CdF , CdCl , ZnF and ZnCl , found in each case the occurrence band systems ascribable to ${}^2\Pi-{}^2\Sigma$ electronic transition with ${}^2\Pi$ interval agreeing with the corresponding atomic interval. A systematisation from this point of view is not clear with respect to the band systems of ZnBr and ZnI . Even the origin of the absorption bands ascribed by Walter and Barratt to the zinc bromide molecule, was considered doubtful by Howell when he compared them with the known band systems of zinc iodide. In view of this, an investigation of the band systems of the zinc halides has been undertaken by the authors. The results obtained for the zinc iodide molecule are presented in this paper (a brief report of which was published in *Curr. Sci.*, 15, p. 122, 1946).

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EXPERIMENTAL

The usual H type discharge tube containing zinc iodide, excited by an one-fourth kilowatt transformer, is employed for producing the emission bands. In a second series of experiments the zinc iodide is contained in a quartz tube with an end-on sealed in window of quartz. The tube is excited by a high frequency oscillator of low power, with external electrodes and continuously evacuated by a Cenco High-Vac pump. Photographs of the emission spectrum are taken when the discharge takes place predominantly through the zinc iodide vapour. Constant heating by an etna burner is found necessary to maintain this discharge. Hilger quartz spectrographs of medium and E₁ types are employed.

RESULTS

Only one system has till now been definitely established for the ZnI molecule. Wieland (1929) has given the analysis identifying the head at λ 3318 as the (0, 0) band, and has just mentioned the occurrence of a weak group of three bands at λ 3236.

The experimental work described above, carried out with a pure specimen of ZnI (supplied by B.D.H.) in the discharge tube, has led the authors to establish definitely the existence of the three following different systems in the ultra violet, which, on the analogy of the HgI bands, are designated as the C, D and E systems respectively.

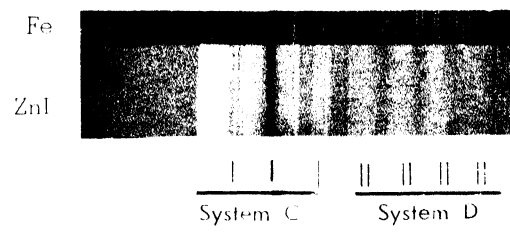
TABLE I

System	Region	Electronic transition
C*	λ 3393-3257	$^2\Pi - ^2\Sigma$
D	λ 3278-3193	
E	λ 2392-2300	Probably $a^2\Sigma - ^2\Sigma$

* Due to Wieland.

In the system C, analysed by Wieland no more sequences could be obtained than were reported by Wieland. But under the higher dispersion used in this work, the (0, 0) band is distinctly seen to be accompanied by a subsidiary head on the longer wavelength side, which, from its intensity and separation from the main head, cannot be regarded as due to an isotope of zinc. The two components, 3317.9 and 3317.6 may be the P and Q heads of the (0, 0) band. No such well separated components are seen in the case of the (1,0) and (2,0) bands but they appear to be broadened out slightly.

A close examination of the violet end of this C system has revealed the existence of a brief and new system (D). The first evidence of this is the observation of three or perhaps four well marked and prominent doublets (Plate III) which are diffuse, slightly broad and headless. Attempts to include



Zinc Iodide Bands (Fig. A)

them as higher members of the C (Wieland) system, seemed to be unjustified from a consideration of the much higher intensity of these pairs as compared to the fading intensity of the system at this end. A further clue to regard these pairs as forming another system is afforded by a measurement of the wave-lengths. An interval of about 220 cm^{-1} is found to repeat itself in some of these members, this interval being of the order of magnitude of the vibrational constant ω'' of the C system. The wave-lengths, wave numbers and intensity data of the bands of this system are given in Table II. Two of the bands $\lambda 3265.7$ and $\lambda 3262.5$ which are included in this table consist perhaps of overlapping faint band heads belonging to both the systems. Their classification is hence not shown. The vibrational analysis of the bands is given in a diagonal array in Table III. The line $\nu 30715$ occurs at two places. The (0, 0) band is suggested at $\nu 30499$.

Exact vibrational constants cannot justifiably be determined. From the order of the $\Delta G'(\nu)$ values, the vibrational constants of the final state are regarded as identical with those of the C system. On this basis, the vibrational constants of the upper state for this C system have been calculated as.

$$\omega' = 2117 \text{ cm}^{-1}$$

$$x'\omega' = 2.5 \text{ ,,}$$

$$\nu = 30506.3 \text{ ,,}$$

TABLE II
ZnI Bands (system D)

TABLE III
Vibrational analysis of system D

Wavelength	Wave number	Intensity	Classification			
				0	1	2
3277.7	30499	0	(0,0)	0 30499(0)		
3265.7	30612	2	()	216		
3262.5	30642	3	()	1 30715(2)*		
3257.2	30692	2	(3,2)	212		
3254.8	30715	2	(1,0)	2 30927(3)	212 30715(2)*	
3235.7	30806	4	(3,1)	192	181	
3232.5	30927	3	(2,0)	3 31119(3)	223 30896(4)	204 30692(2)†
3215.0	31095	3	(4,1)	186	199	
3212.5	31119	3	(3,0)	4 31305(2)	210 31095(3)	
3196.5	31275	2	(5,1)		180	
3193.5	31305	3	(4,0)	5	31275(2)	

* Occurs at two places.

† Too diffuse to be measured accurately.

The correctness of the identification of system D for ZnI is further strengthened when it is seen that the difference between the (0, 0) bands ($\nu_{30129.5}$) of system C and ($\nu_{30499.4}$) of system D is equal to 370 cms.^{-1} , which is in excellent agreement with the predicted value 386 cms.^{-1} for zinc halides. The systems C and D may therefore be regarded as the two components of a ${}^2\Pi - {}^2\Sigma$ transition analogous to those found previously in zinc fluoride and zinc chloride.

System E

In addition to systems C and D, a third system (designated as E, *cf.* Table I) is also obtained in the region λ_{2392} to λ_{2300} . The bands of this system are not so diffuse as those of the D system but they are faint even when photographed, after long exposures of about five hours, with a medium Hilger quartz spectrograph. They are degraded probably to the red but the direction could not be definitely seen. A preliminary examination of the wave numbers of the band heads indicated a recurring interval of the order of 216, equal approximately to the vibrational constant $\omega'' = 223$, of the common ground state of systems C and D. It is considered that the system may correspond to the transition $a^2\Sigma - {}^2\Sigma$. Further work on this system as well as on the absorption bands of zinc halides is still in progress and a complete account will be presented in a subsequent communication.

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