

EMISSION BANDS OF HALOGENS

Part III. Iodine Bands arising in 1_u (${}^3\Sigma_u^+$) and 1_g (${}^1\Pi_g$) States

By PUTCHA VENKATESWARLU, M.Sc.

(Physics Department, Benares Hindu University)

Received October 28, 1946

(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D. (London), F.A.Sc.)

INTRODUCTION

In previous papers¹ "Emission Bands of Halogens—Parts I and II" which hereinafter will be called Papers I and II we have explained all the emission bands of iodine between 4800–2685 Å including the famous continuum at 3416 Å, except three bands at 4747.2, 4662.1 and 4575.2 Å. In this paper these bands will be explained. Further the emission bands in the region 2685–2400 Å will be discussed.

The three bands (Plate X) at 4747.2 Å (21059 cm.^{-1}), 4662.1 Å (21444 cm.^{-1}) and 4575.2 Å (21849 cm.^{-1}) are very broad and diffuse their overall width being about 332, 239 and 240 cm.^{-1} respectively whereas the width of all other bands in the region 4800–2685 Å is of the order of 115 cm.^{-1} . The wavenumber separation between first and second bands and second and third bands is 389 and 405 cm.^{-1} respectively. These differences being too big to be regarded as vibrational frequencies for I_2 , the bands cannot be explained as forming a single group arising in a single transition.* The bands may probably arise in transitions from a stable state to three different unstable states which will have appreciably steep potential energy curves. In a previous communication,² the P-R, K-M (Pringsheim Rosen—Kimura Miyaniishi) bands have been explained as arising in a transition from the ground state of the I_2 molecule to an excited state $\sigma_g, \pi_u^4, \pi_g^4, \sigma_g^2 \cdot 1_u$ (${}^3\Sigma_u^+$) at 44900 cm.^{-1} which has a frequency of about 90 cm.^{-1} . This state 1_u (${}^3\Sigma_u^+$) is shown in the potential energy diagram (Fig. 1). In Paper I we have discussed five groups of diffuse bands which arise in the state $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u \cdot 0_u^+$

*There is, however, a state $\{[\sigma_g^2, \Pi_u^4, \Pi_g^3, {}^2\Pi_{g3/2}] \sigma_g^x\} \Pi_{2,1g}$ at 56000 cm.^{-1} with $\omega \sim 360\text{ cm.}^{-1}$. If the above three bands are to be explained as a single group arising in the state $\Pi_{2,1g}$, there should be a repulsive state with a nearly flat potential energy curve at about $(56000 - 21059) = 34,941\text{ cm.}^{-1}$. As such a repulsive state is not theoretically possible, and as the mutual wave number separation of these bands, viz., 400 cm.^{-1} is greater than ω of the state $\Pi_{2,1g}$, the three bands cannot be explained as a single group arising in $\Pi_{2,1g}$ state.

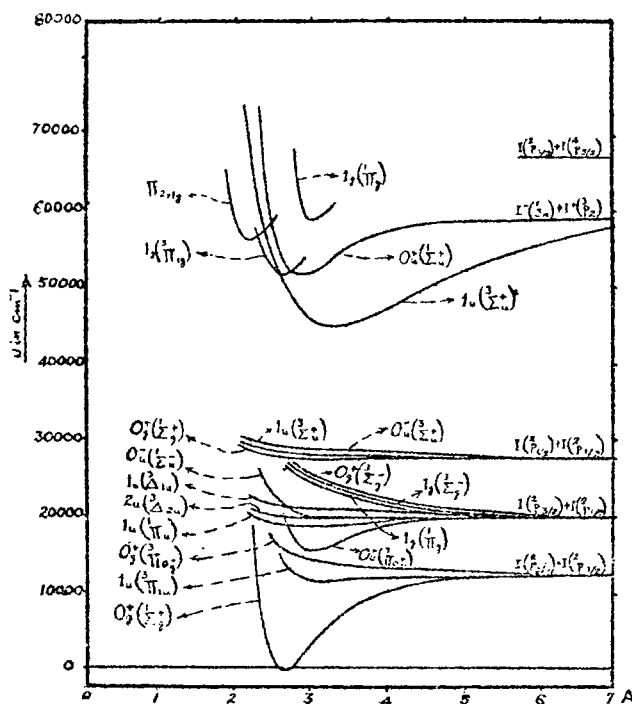
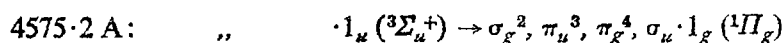
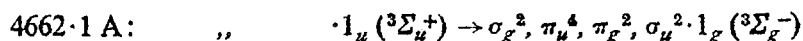
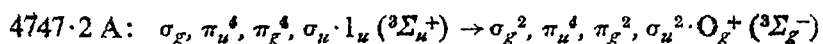


Fig. 1 Potential energy curves for I_2 molecule?

(${}^1\Sigma_u^+$), and which have five different unstable states for their final levels. Second, third and fourth of these five groups, are explained as due to transition from the stable state $O_u^+({}^1\Sigma_u^+)$ at 51683 cm.^{-1} to the unstable states $O_g^+({}^3\Sigma_g^-)$, $1_g({}^3\Sigma_g^+)$ and $1_g({}^1\Pi_g)$ which dissociate in ${}^2P_{3/2} + {}^2P_{1/2}$ iodine atoms at 20037 cm.^{-1} . All these three states, as shown in the potential energy diagram of Paper II as well as in Fig. 1 of this paper, have appreciably steep potential energy curves which run almost parallel except at their meeting point, and are separated from one another by about 400 cm.^{-1} which is of the same order as the mutual wavenumber separation of the broad bands we are discussing. According to selection rules for case (c) type coupling transitions from the state $1_u({}^3\Sigma_u^+)$ at 44900 cm.^{-1} to the three unstable states pointed above are allowed and these transitions will explain satisfactorily the three broad bands. The potential energy curves of the unstable states, being appreciably steep, explain the broad and diffuse nature of the bands. The points on the three potential energy curves vertically below the stable state will be at $(44900-21059) = 23841$, $(44900-21444) = 23456$ and $(44900-21849) = 23051\text{ cm.}^{-1}$. The transitions for the three bands may be written as:



Now we turn to the bands below 2685 A. In the region 2685 to 2400 A we have a number of diffuse bands whose nature seems to be the same as those of the bands in the region 4800–2685 A, except that these bands are weaker and narrower than the others. The experimental details are the same as those described in the previous papers. The wavelengths and wavenumbers of the maxima of the bands between 2685–2448 A are given in Table I. The intensity values correspond to the visually estimated values

TABLE I

Group	Asagoe, Inuzaka $\lambda_{in \text{ air}}$	Present experiments			
		Intensity	$\lambda_{in \text{ air}}$	$\nu_{vac.}$	$\Delta \nu$
I	2672.2	1	2671.1	37427	..
	2662.1	2	2661.1	37567	140
	..	0.5	2652.5	37689	122
	2642.7	2	2642.6	37830	141
	2633.2	2	2633.3	37964	134
	2625.0	0.5	2623.0	38104	140
	2616.8	0.5	2616.6	38206	102
	2608.5	1	2607.5	38339	133
II	2592.7	1	2593.3	38549	..
	2584.0	1	2584.4	38682	133
	2576.1	0.5	2575.9	38810	128
	2569.9	0.5	2569.2	38911	101
	2561.7	1	2562.2	39017	106
		0.5	2555.1	39128	109
		0.5	2548.9	39221	95
		1	2541.6	39333	112
		0.5	2534.1	39450	117
	0.5	2526.7	39565	115	
III		0.5	2522.7	39628	..
		1	2516.0	39734	106
		1	2508.6	39851	117
		?	2501.4	39966	115
		1	2494.1	40083	117
		0.5	2487.2	40194	111
		0.5	2481.0	40294	100
		?	2474.1	40407	113
		0.5	2467.9	40508	101
		0.5	2461.8	40608	100
		0.5	2454.9	40723	115
		0.5	2448.8	40824	101

for the bands obtained on a B-20 process Kodak plate. It may be mentioned that Asagoe and Inuzaki³ have recorded previously the maxima of the

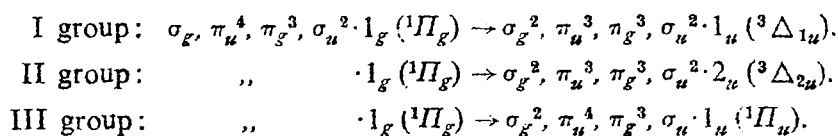
bands only upto 2562 Å. These values are also given in the table besides the values obtained in the present experiments. The wavelengths of the bands below 2562 Å are, however, being recorded here for the first time.

The bands are arranged into three groups by taking the wavenumber separation into consideration. They have an average wavenumber separation of about 120 cm^{-1} among the composite bands. So they can be considered as arising in a common initial level with a frequency of about 120 cm^{-1} and having three different unstable states for their final levels. We have three unstable states $1_u (^3\Delta_{1u})$, $2_u (^3\Delta_{2u})$ and $1_u (^1\Pi_u)$ which have nearly flat potential energy curves and which dissociate into $^2P_{3/2} + ^2P_{1/2}$ iodine atoms at 20037 cm^{-1} (Paper II). These three states form final levels of three groups of bands between 3307 and 2918 Å which arise in $1_g (^3\Pi_{1g})$ state at 51528 cm^{-1} and other three groups between 2903 and 2731 Å arising in a state $\Pi_{3,1g}$ at 56000 cm^{-1} . Transitions from a stable state to these three unstable states will explain satisfactorily all the three groups of bands in Table I. The first bands of these three groups lie at 37427, 38549 and 39628 cm^{-1} . Adding 20037 to each of these and taking the mean we arrive at 58572 cm^{-1} which, therefore, represents the approximate position of the initial level. The points on the three repulsive curves below the stable state, lie at $(58572-37427) = 21145$, $(58572-38549) = 20023$ and $(58572-39628) = 18944 \text{ cm}^{-1}$.

It may be mentioned that there are some bands which are very faint overlapping the third group. Probably these form the extension of the bands of the second group. There are also some bands below 2448 Å upto 2370 Å, *i.e.*, on the short wave side, which are also faint. It appears that these are the extensions of the second and third group of bands, which come from higher vibrational level of the initial state, and which overlap in this region. It is also possible that some of these faint bands (2448–2370 Å) may be due to the transitions [*viz.* From $O_u^+ (^1\Sigma_u^+)$ at 51683 cm^{-1} to $1_g (^3\Pi_{1g})$ dissociating into two $^2P_{3/2}$ atoms and from $1_g (^3\Pi_{1g})$ at 51528 cm^{-1} to $O_u^- (^3\Pi_{0^-})$, $1_u (^3\Pi_{1u})$ dissociating into $^2P_{3/2}$ atoms] which are theoretically possible and which may be expected to give bands in this region.

Now we turn to find the electronic configuration and electronic term of the stable state at 58572 cm^{-1} . The only two terms that can combine with all the three terms $1_u (^3\Delta_{1u})$, $2_u (^3\Delta_{2u})$ and $1_u (^1\Pi_u)$ are according to case (c) type coupling 1_g and 2_g . The state 1_g may be correlated with $^1\Pi_g$ or $^3\Pi_{1g}$ and 2_g may be correlated with $^3\Pi_{2g}$ where $^1\Pi_g$, $^2\Pi_{1g}$ and $^3\Pi_{2g}$ arise from the electronic configuration σ_g , π_u^4 , π_g^3 , σ_u^2 . We have already attributed $1_g (^3\Pi_{1g})$ [*i.e.*, the term 1_g is correlated with $^3\Pi_{1g}$ or case (a) type] to a state at 51528 cm^{-1} .

which has a frequency of about 220 cm.^{-1} . Thus the electronic term of the stable state at 58572 cm.^{-1} , which we are now considering, will be either $1_g (^1\Pi_g)$ or $2_g (^3\Pi_{2g})$. But the state $2_g (^3\Pi_{2g})$ will be expected to lie below $1_g (^3\Pi_{1g})$ state, *i.e.*, below 51528 cm.^{-1} . So the state at 58572 cm.^{-1} which has $\omega \sim 120 \text{ cm.}^{-1}$ will have probably the electronic term $1_g (^1\Pi_g)$. We can now write the transitions for the three groups of bands as:



The potential energy diagram given in Paper II, is also given in Fig. 1 of this paper with the following addition: The curve for the state $1_u (^3\Sigma_u^+)$ at 44900 cm.^{-1} is drawn by using Morse equation with the use of the constants $\omega = 90 \text{ cm.}^{-1}$; $D = (59000 - 44900) = 14100 \text{ cm.}^{-1}$. In calculating r_e value we use Badger's relation $r_e = \left(\frac{C_{ij}}{K_e}\right)^{1/3} + d_{ij}$, where K_e is force constant for the state in megadynes per cm., C_{ij} and d_{ij} are constants whose values for the iodine molecule are given by $(C_{ij})^{1/3} = .49$ and $d_{ij} = 1.765$. r_e value obtained is 3.33 \AA . Similarly r_e for the state $1_g (^1\Pi_g)$ at 58572 cm.^{-1} is calculated as 3.02 \AA . The position of this level is also marked in the figure.

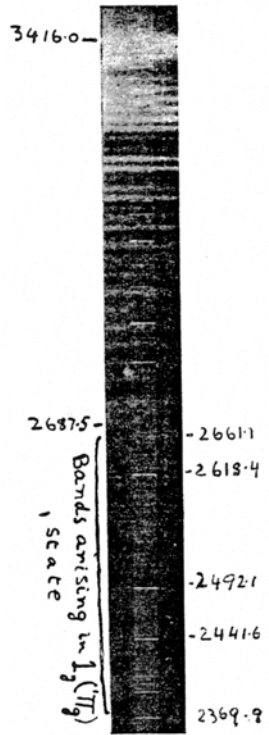
SUMMARY

The three broad bands at 4747.2 , 4662.1 and 4575.2 \AA are explained as due to transitions from a single stable state $1_u (^3\Sigma_u^+)$ at 44900 cm.^{-1} to three unstable states $O_g^+ (^3\Sigma_g^-)$, $1_g (^3\Sigma_g^-)$ and $1_g (^1\Pi_g)$ which dissociate into $^2P_{3/2} + ^2P_{1/2}$ iodine atoms at 20037 cm.^{-1} . The bands in the region 2687 to 2400 \AA form three groups which are explained as arising in a level $1_g (^1\Pi_g)$ at 58572 cm.^{-1} and having for their final level the three unstable states $1_u (^3\Delta_{1u})$, $2_u (^3\Delta_{2u})$ and $1_u (^1\Pi_u)$ which dissociate into $^2P_{3/2} + ^2P_{1/2}$ iodine atoms. The potential energy diagram for iodine molecule is given.

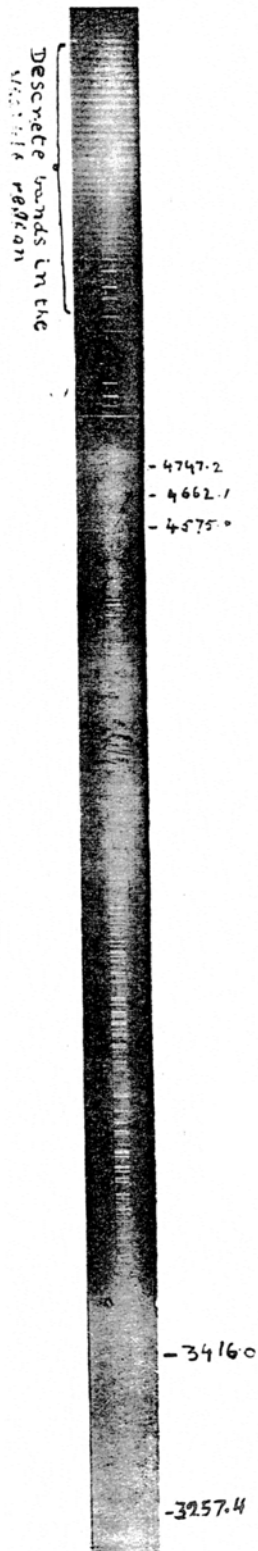
The author wishes to express his sincere thanks to Prof. R. K. Asundi for guidance and to Kamalapat Singhania Trust for the award of a scholarship.

REFERENCES

1. P. Venkateswarlu .. "Emission Bands of Halogens, Part I and II," *Proc. Ind. Acad. Sci.*, 1946, **24 A**, 480 and this number.
2. ————— .. "Absorption Bands of Iodine in Quartz Ultra-violet," *Ind. Journ. Phys.* (in Press).
3. Asagoe and Inuzuka .. *Sc. Rep. Tokyo, Burnika, Daigaku*, 1934, **2 A**, 84.
4. Badger .. *Journ. Chem. Phys.*, 1935, **3**, 710



(b)



(a)