THE CONTINUOUS ABSORPTION SPECTRA OF THE HYDROGEN-HALIDES.

PART III—HI.

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1. INTRODUCTORY.

It was shown in the two previous papers how the controversy regarding the nature of binding of the hydrogen-halides can be satisfactorily solved by assuming a new type of binding which is neither atomic nor ionic in the true sense of the terms. According to it, these molecules may be regarded as having been formed out of promoted hydrogen in the atomic state and atomic halogen. It was found that the supposition of such a type of binding gives a satisfactory correlation between the thermal heat of dissociation and that obtained from the optical method by a study of the long wave-length limit of the primary absorption continuum. In view of the success attained in the cases of HCl and HBr, it was considered worth while to test the validity of these ideas in the case of HI as well.

2. EXPERIMENTAL.

Light from a hydrogen discharge tube emitting continuous radiation was transmitted through a long tube provided with quartz windows on to the slit of a quartz spectrograph. Hydrogen-iodide gas was prepared by slowly dropping distilled water on Phosphorus tri- and penta-iodide formed on gently warming a mixture of iodine and red phosphorus in the ratio 4:1 by weight. The gas was freed from iodine and part of its moisture by passing it through a tower containing pumice stone and red phosphorus. The bulk of the moisture was condensed by passing the gas first through a long water-cooled tube, then through a U-tube immersed in a freezing mixture and finally dried by passing through a tower containing calcium-fluoride. The pressure gauge was filled with a few centimetres of pump oil so as to prevent direct contact of HI with mercury with which it reacts strongly making the gauge unworkable. After washing the tube several times so as to remove the last traces of air, the tube was filled with the gas at the desired pressure and its absoprtion spectrum studied in the usual way by taking all the precautions regarding the maintenance of the discharge tube and the development and washing of the photographic plates which have been described in detail in the previous papers. The exposures were given for different pressures of the gas and the blackening of the plate for different wave-lengths was measured as before with

the self-recording micro-photometer of the University College of Science. By comparing the intensity of the spectrum transmitted through the gas with that when the tube was empty, the percentage absorption coefficient for different wave-lengths was calculated.

3. Results.

In the following table are given the percentage absorption coefficients ($K \times 100$) of a sample of HI gas in the tube at the pressure indicated at the top of the column. The asterisks (*) signify negligible values.

Table 1.

Percentage absorption coefficient of HI *at different pressures.*

Wave-lengths λ Å	60 cm. K×100	30 cm. K×100	15 cm. K×100	10 cm. K×100	5 cm. K×100	2 cm. K×100
3073	..	..	..	..	..	12·15
3194	..	..	..	..	..	2·45
3248	35·47	30·07	16·86	10·43	5·26	0·36
3274	34·84	25·06	12·72	8·62	3·68	*
3307	29·83	16·33	8·62	3·68	2·18	*
3335	22·87	11·25	5·59	2·31	1·86	*
3380	11·78	5·82	3·10	1·22	0·92	*
3402	8·10	4·03	3·50	1·08	0·68	*
3450	3·99	1·26	0·52	0·41	*	*
3484	2·89	0·68	0·16	0·08	*	*
3512	1·06	0·40	0·46	0·38	*	*
3546	1·13	0·40	0·46	0·38	*	*
3602	0·36	0·10	0·28	0·08	*	*
3622	0·06	*	*	*	*	*
3659	0·60	0·68	0·28	*	*	*
3698	0·30	0·38	*	*	*	*
3745	*	*	*	*	*	*
3886	*	*	*	*	*	*
3934	*	*	*	*	*	*
4022	0·17	0·21	0·13	*	*	*
4063	0·07	0·09	0·29	*	*	*
4128	0·57	0·58	*	*	*	*
4178	0·55	0·35	*	*	*	*
4275	0·88	0·66	*	*	*	*

With the above data curves are plotted with the percentage of absorption as ordinate and wave-lengths as abscissae (fig. 1). To avoid crowding of the figure, curves at four pressures only are shown. As in the cases of HCl and HBr there is the indication of a secondary maximum which has no overlapping with the primary absorption continuum. The long wave-length beginnings of these absorptions show definite pressure shifts as shown in Table 2.

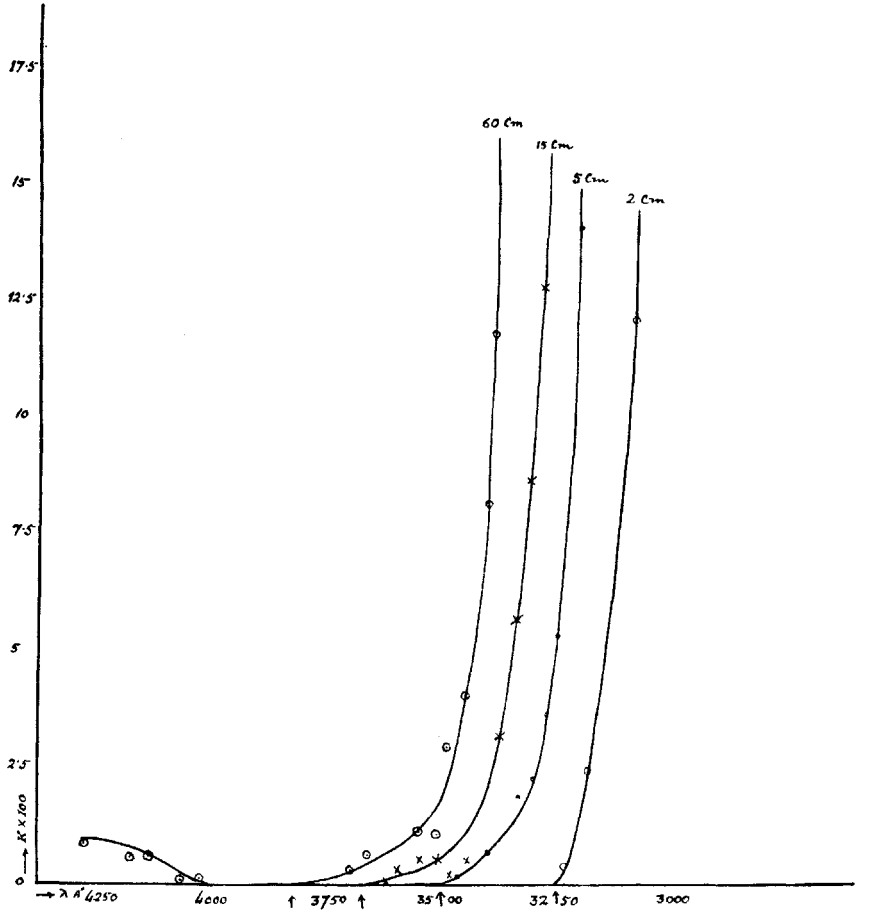

FIG. 1. Absorption of HI at different pressures.

TABLE 2.

Long wave-length beginning of primary absorption at different pressures.

Pressure in cm.	Wave-lengths λ Å
60	3850
30	3750
15	3675
10	3625
5	3500
2	3245

Extrapolating to zero pressure, fig. 2, the long wave-length beginning of the absorption continuum is found as given in Table 3, which also gives the

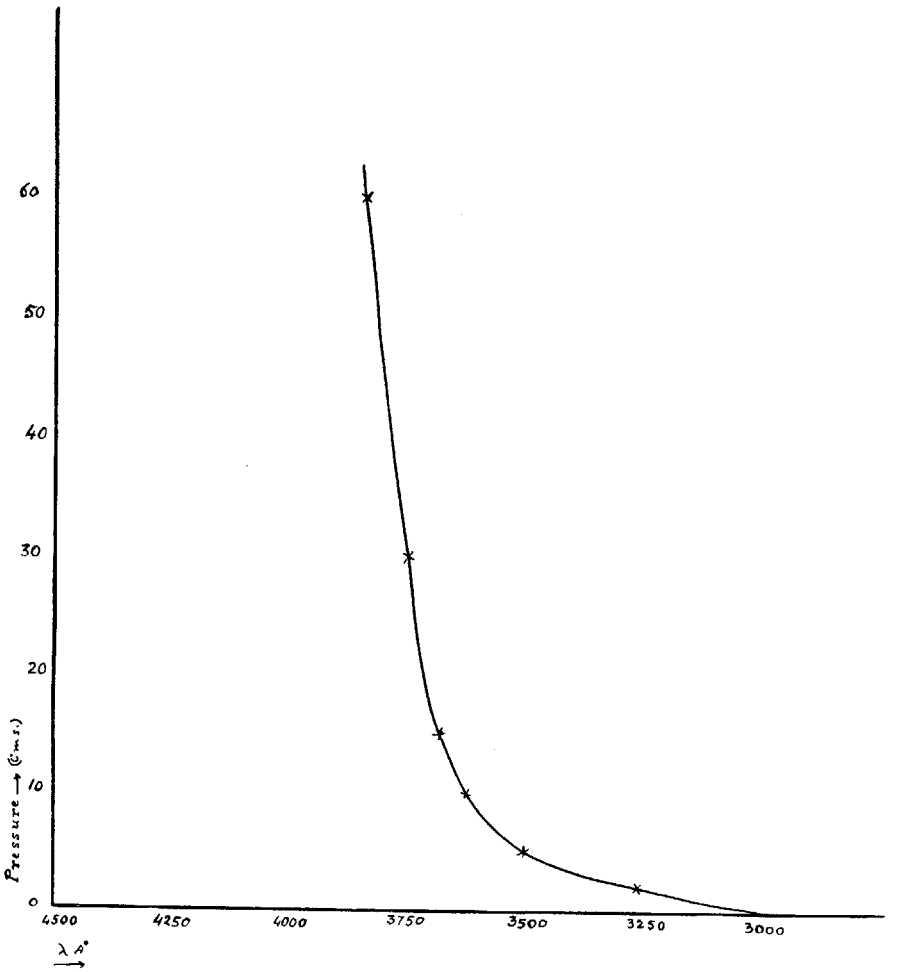

FIG. 2.

corresponding energies of dissociation in kilo-calories as well as the energy for thermal dissociation.

TABLE 3.

Primary absorption extrapolated to zero pressure.		Thermal energy k. cal.	ΔE Experimental k. cal.
λ Å	k. cal.		
3000	94·8	70	24·8

As before, accuracy is claimed up to the first three figures of the wave-length data expressed in Angstrom units.

4. Discussion of Results.

If we consider the formation of HI molecule in the same way as that of HCl and HBr, there are two possible configurations of the HI molecule, viz:—

$$kl \ldots . \ (5s\sigma)^2 \ (5p\sigma)^2 \ (5p\pi)^4, \qquad {}^1\Sigma$$
$$kl \ldots . \ (5s\sigma)^2 \ (5p\sigma)^2 \ (5p\pi)^3 \ (6s\sigma), \ {}^1\Pi$$

of which $^1\Sigma$ state is stable and $^1\Pi$ state unstable. The primary absorption continuum is to be explained as arising from a transition from the stable $^1\Sigma$ to the unstable $^1\Pi$ state.

Hence when the molecule breaks up by thermal agitation by an increase of its vibrational energy, the end products are those corresponding to the HI molecule in the ground state and the process may be expressed as:—

$$(5s\sigma)^2 \ (5p\sigma)^2 \ (5p\pi)^4 + E_1 \ (\text{thermal}) \rightarrow (5s\sigma)^2 \ (5p\sigma) \ (5p\pi)^4 \ [\text{I} \ {}^2\Sigma]$$
$$+ 5p\sigma \qquad [\text{H}-\text{promoted}].$$

When decomposition takes place optically, the HI molecule is first excited to the repulsive upper state, where it breaks up automatically as shown below:

$$(5s\sigma)^2 \ (5p\sigma)^2 \ (5p\pi)^4 \ (\text{optical}) \rightarrow (5s\sigma)^2 \ (5p\sigma)^2 \ (5p\pi)^3 \ (6s\sigma) \ [\text{HI}-\text{excited}]$$
$$\rightarrow (5s\sigma)^2 \ (5p\sigma)^2 \ (5p\pi)^3 \ [\text{I} \ {}^2\Pi] + 6s\sigma \ [\text{H}-\text{promoted}].$$

Consequently, the energy required for optical dissociation is in excess of that required for thermal dissociation by the difference in the energy of the I and H atoms in the respective processes. The difference in the energy of the I atom is, as in the case of Br and Cl, of the same order of magnitude as the difference in the multiplet levels of the I atom in the field-free state, and is positive. That due to the H atom is also positive and is equal to the difference of the energy of the H atom between $6s$ and $5p$ states. Thus in the case of the HI molecule, the energy required for optical dissociation would be equal to:—

$$70 \ (\text{thermal}) + 21{\cdot}6\left[\left({}^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}\right)\text{I}\right] + 3{\cdot}8[6s-5p)\text{H}] = 95{\cdot}4 \text{ k. cal.}$$

The observed long wave-length limit of the primary absorption gives a value of nearly 94·8 k. cal.

Regarding the presence of a secondary absorption on the long wave-length side of the primary absorption continuum, which was observed in the case of HCl and HBr and which could be correlated with the fundamental vibrational frequency of the corresponding molecule, it may be observed that there are definite indications of its presence in the case of HI also, as is evident from the second rising of the curves towards the longer wave-length side. But as the Hydrogen discharge tube has a very feeble intensity in the region where the secondary absorption continuum appears to be situated, the computation of absorption coefficient from the darkening of the photographic plate is likely

to give misleading results. No attempt was therefore made to fix the long wave-length limit of the secondary absorption continuum.

SUMMARY.

1. The continuous absorption of HI gas has been determined accurately.

2. The continuous primary band shows a shift of the long wave-length beginning, the limit increasing in wave-length with an increase in pressure.

3. Extrapolating to zero-pressure, the long wave-length limit has been determined and the corresponding heat of dissociation which is in excess of thermal heat of dissociation has been satisfactorily explained on a previously existing theory of the formation of HI molecule.

4. The presence of a secondary absorption band has been indicated.