THE CONTINUOUS ABSORPTION SPECTRA OF THE HYDROGEN-HALIDES.

PART II—HCl.

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1. INTRODUCTORY.

In the previous paper it has been shown that the controversy about the atomic or the ionic binding of the hydrogen-halides can be satisfactorily solved by assuming a new type of binding, which is neither atomic nor ionic in the ordinary sense of the words but in which the formation is essentially atomic with the difference that one of the atoms, namely the hydrogen atom, is in a promoted state.

It has been shown in that paper 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 case of HBr, it was considered worth while to repeat the experiments with HCl in the first instance.

2. EXPERIMENTAL.

As before, arrangement was made to transmit the light from a hydrogen discharge tube emitting continuous radiation through a similar one metre long tube provided with quartz windows on to the slit of a spectrograph. Hydrochloric acid gas was prepared by gently heating a fairly concentrated solution of extra pure Hydrochloric acid in water and was led into the absorption tube through a series of drying tubes so as to remove all traces of water vapour. 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 absorption spectrum studied in the usual way. The experiments were repeated at three different pressures and the blackening of the plate for different wave-lengths was measured as before with the self-recording microphotometer of the University College of Science. By comparing the intensity of the spectrum transmitted through the gas with that through air, the percentage of absorption for different wave-lengths was computed in the usual way.

3. Results.

The absorption coefficients (K) given in columns 2–4 of Table 1 are the averages of a large number of plates and indicate the coefficients of a sample of gas in the tube at pressures given at the top of the column.

Table 1.

Wave-length.	5 cm. pressure.	20 cm. pressure.	76 cm. pressure.
	K × 100	K × 100	K × 100
3011	..	..	0·3
2997	..	..	0·6
2961	..	0·01	2·0
2883	0·2	1·2	4·1
2825	0·9	4·1	8·0
2767	1·0	4·5	8·1
2705	0·1	2·1	6·0
2661	..	1·0	3·7
2618	..	1·0	3·0
2551	0·3	2·0	4·2
2492	1·0	4·5	10·5
2442	3·0	7·2	20·9
2407	4·3	11·7	31·5
2370	8·1	16·5	43·0

With the above data curves are plotted with the percentage of absorption as ordinate and wave-lengths as abscissae. As in the case of HBr there is a secondary maximum which is more pronounced as it has very little overlapping with the primary absorption continuum. The long wave-length beginning of both the feeble secondary absorption and the strong primary absorption continuum show definite pressure shifts.

Both the exposures for the tube filled with the gas at the desired pressure and the empty tube were taken through the same hole in the Hartman diaphragm attached to the slit, the camera holder being raised for the successive exposures. To allow for the measurement of the density of the plate at exactly the corresponding wave-length of the two strips of the spectrogram a copper arc was photographed along with each spectrum from a broadside position. The exposures were timed by means of a stop-clock and were correct to within 0·25 secs. in an exposure time of ten minutes. Before giving the exposures the discharge tube was run continuously for over an hour until a steady state was reached as indicated by the constancy of the discharge current.

The development and washing of the plates were done with the utmost care with distilled water so that no dust particles could accumulate on them.

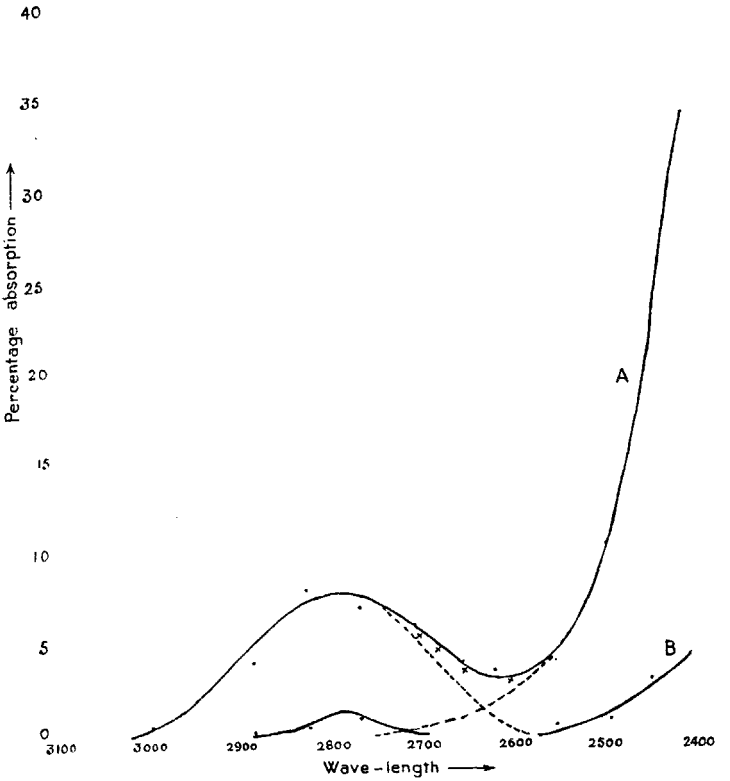

FIG. 1. Absorption of HCl. A—for 76 cm. pressure.
,, ,, B— ,, 5 ,, ,,

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

TABLE 2.

Primary abs. limit at zero pressure.	Thermal energy.	ΔE
2480 .. 114·2 k. cal.	101 k. cal.	13·2

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

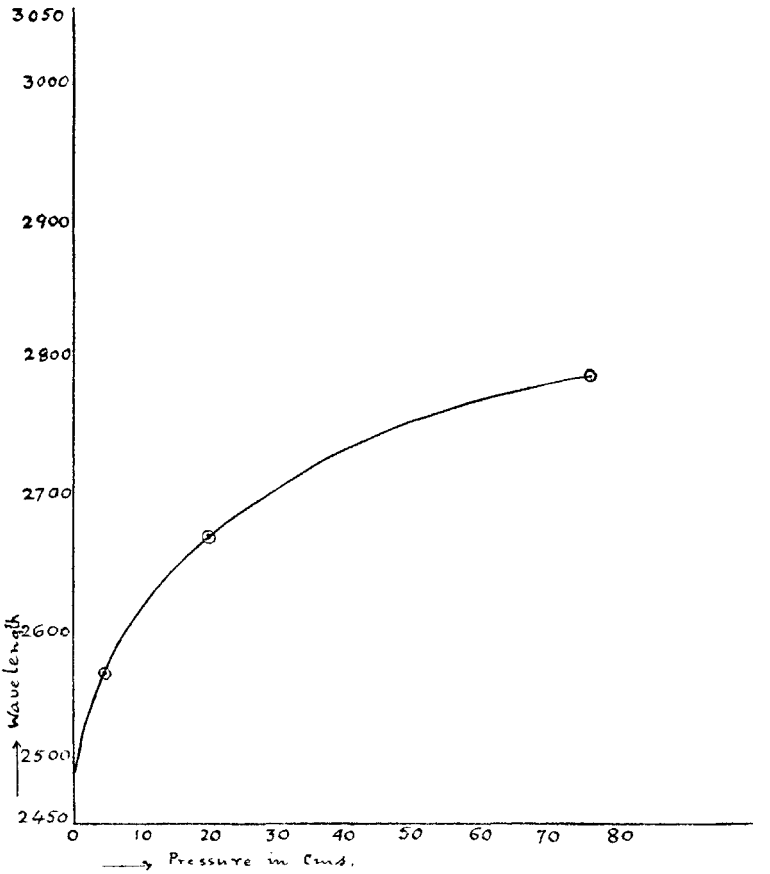

FIG. 2. HCl.

As before accuracy is claimed up to the first three figures of the wavelength data expressed in Angstrom units.

4. DISCUSSION OF RESULTS.

Considering the formation of the HCl molecule in the same way as that of the HBr molecule, there are two possible configurations of the HCl molecule, viz.:—

$$kl \ldots . \ (3s\sigma)^2 \ (3p\sigma)^2 \ (3p\pi)^4, \ ^1\Sigma$$
$$kl \ldots . \ (3s\sigma)^2 \ (3p\sigma)^2 \ (3p\pi)^3 \ (4s\sigma), \ ^1\Pi$$

of which $^1\Sigma$ state is stable and $^1\Pi$ state is unstable. The absorption continuum is to be explained as arising from a transition from the stable $^1\Sigma$ state 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 HBr molecule in the ground state and the process may be expressed as:—

$$(3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^4 + E_1\ (\text{thermal}) \rightarrow (3s\sigma)^2\,(3p\sigma)\,(3p\pi)^4\,[\text{Cl}\ ^2\Sigma] + 3p\sigma$$
[H promoted].

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

$$(3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^4 + E_2\ (\text{optical}) \rightarrow (3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^3\,(4s\sigma)\ [\text{HCl excited}]$$
$$\rightarrow (3s\sigma)^2\,(3p\sigma)^2\,(3p\pi)^3\,[\text{Cl}\ ^2\Pi] + 4s\sigma$$
[H promoted].

Consequently, the energy required for the optical dissociation is in excess of that required for thermal dissociation by the difference in the energy of the Cl and H atoms in the respective processes. The difference in the energy of the Cl atom is as in the case of Br of the same order of magnitude as the difference in the multiplet levels of the Cl atom in the field free state, and is positive. That due to H atom is also positive and is equal to the difference of the energy of H atom between $4s$ and $3p$ state. Thus in the case of HCl molecule, the energy required for optical dissociation would be equal to:—

$$101\ \text{k. cal. (thermal)} + 2{\cdot}5\ \text{k. cal.}\left[{}^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}\right]\text{Cl} + 15\ \text{k. cal.}\ [(4s-3p)\ \text{H}]$$
$$= 118{\cdot}5\ \text{k. cal.}$$

The observed long wave-length limit of the primary absorption gives a value of nearly 114·2 k. cal.

Explanation of Secondary Absorption.

As in the case of HBr the primary absorption continuum is accompanied with a secondary patch, which is more prominent as it practically stands detached from the main patch. Here also the difference in energy between the long wave-length limits of the primary and secondary absorption, as given in Table 3 below, is very nearly of the same order of magnitude as the funda-

Table 3.

Secondary limit at 76 cm.	Corresponding dissociation energy.	Primary limit at 76 cm.	Corresponding dissociation energy.	Difference in energy in k. cal.	Fundamental vibrational energy in k. cal.
λ3040	93·1	λ2780	101·8	8·7	8·5

mental vibrational energy of the HCl molecule, which thereby gives support to the hypothesis originally made to explain the corresponding spectrum of

HBr, namely that the secondary absorption band is due to jumps from the next higher vibrational level ($v'' = 1$) of the normal molecule. As the fundamental vibrational frequency of HCl is a little higher than that of HBr, the fraction of molecule of HCl in the state $v'' = 1$ is comparatively lower. This probably accounts for the lower intensity of the secondary continuum of HCl gas.

Summary.

1. The continuous absorption of HCl gas has been accurately determined and two absorption continuum, one secondary and the other primary found.

2. Both these continuous bands show a shift of the long wave-length limit on the red side with an increase in pressure.

3. Extrapolating for 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 the HCl molecule.

4. The secondary absorption continuum has been explained as due to a jump from the next higher vibrational state ($v'' = 1$) of the normal molecule.