THE CONTINUOUS ABSORPTION SPECTRA OF THE HYDROGEN-HALIDES.

PART I—HBr.

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1. INTRODUCTORY.

It is well known that a good deal of controversy exists about the nature of binding of the hydrogen-halides. From chemical notions about binding these had been previously classified as ionic molecules but from spectroscopic evidence Franck [1] declared them to be of the 'atomic' type. In coming to this conclusion he relied on the experimental works of Tinge and Gerke [2] but these gave rather imperfect correlation.

Subsequent workers [3] on the absorption held that the beginning of absorption extended to much longer wave-length with an increase in pressure and from the evidence that the extrapolated long wave-length limit corresponded to dissociation of the molecule into two normal atoms, they considered the molecule to be of the ionic type.

Later on Goodeve and Taylor [4] made a careful determination of the extinction coefficients of HBr and HCl and although the experimentally determined curve appeared to be asymptotic to the wave-length abscissa indicating dissociation into a normal and an excited atom, yet instead of taking that limit they calculated the form of the upper potential curve from the eigen-function of the ground state and the observed values of the extinction coefficients for different wave-lengths and obtained a limit which seemed to indicate that the dissociation products are two normal atoms and concluded the binding to be an ionic one.

Recently, Trivedi [5] by investigating the continuous absorption spectrum of hydrogen chloride and bromide at different temperatures found out the contributions of individual vibrational levels to the total absorption and from a theory previously worked out by him calculated the form of the upper potential curve. From this the energy of dissociation of HBr and HCl were determined and these were found to correspond to an ionic binding.

In view of the discrepancies in the observation of different investigators, it was considered desirable to repeat the experiments on the absorption spectra of hydrogen halides. Further, as the determination of the upper potential curve both by the method of Goodeve and Stein as well as by that of Trivedi rests on hypotheses which are not well established, it was thought better to

determine the long wave-length limit of absorption accurately, as the correlation of this limit with the energy of dissociation according to Franck's theory stands on a very well-confirmed and sound basis.

2. Experimental.

Arrangement was made to transmit light from the usual type of hydrogen discharge tube emitting continuous radiation through a long glass tube (1 metre) provided with quartz windows, on to the slit of a spectrograph. The tube was provided with two side tubes, one of which was connected with a three-way cock to a manometer and an oil pump and the other through a one-way cock to the series of drying tubes leading to the vessel where the desired gas was produced.

The gas was produced by gently heating a fairly concentrated solution of Hydrobromic 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. The gas was then pumped out and the operation was repeated two or three times to remove the last traces of air. The tube was then filled with the gas at the desired pressure, which was noted by the manometer. To avoid errors due to the slightest variation in the width of the slit, both the exposures, one with the tube filled with the gas and the other with air at the same pressure, were taken through the same Hartman diaphragm, the camera 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 spectra, a copper arc spectrum was taken in each case through the second hole of the Hartman diaphragm. This was achieved without disturbing the collimation of the hydrogen tube by interposing a total reflecting quartz prism before the hydrogen tube and the focussing lens so that the light from the arc could be transmitted to the slit from a broadside position.

The experiments were repeated at three different pressures and the blackening of the plate for different wave-lengths was measured with a self-recording microphotometer. By comparing the intensity of the spectrum transmittted 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) in a particular column are the coefficients of a sample of gas in the tube at pressures indicated at the top of each column of Table 1.

TABLE 1.

Wave-length.	5 cm. pressure.	20 cm. pressure.	76 cm. pressure.
	K × 10	K × 100	K × 100
3100	..	0·7	2·0
3071	..	2·3	4·5
3005	1·1	5·5	9·5
2965	4·0	10·1	15·5
2925	4·8	10·8	18·4
2883	4·5	10·6	19·3
2841	4·0	9·7	19·5
2805	2·5	8·8	20·1
2737	1·5	7·9	21·1
2675	2·0	9·2	27·8
2615	5·5	12·8	43·7
2559	8·3	23·2	69·1
2505	14·5	42·5	..

With the above data curves are plotted with the percentage of absorption as ordinate and wave-lengths as abscissae. The curves for different pressures definitely indicate fluctuations of intensity at the long wave-length beginning which can only be explained as arising from two* separate absorption curves as shown by the dotted lines in figs. 1 and 2. By a careful repetition of the experiments the fluctuations recorded here were definitely confirmed and this necessarily delayed the publication of the paper the results of which were announced in the Presidential Address of one of the authors.[6]

The long wave-length beginning of both the feeble secondary absorption and the strong primary continuum cut the abscissa at different points indicating a definite pressure shift in contradiction to the observations of A. K. Datta,[7] who appears to have obtained the cut at one and the same point for different pressures. Extrapolating for zero pressure, fig. 2, the long wave-length beginning of the two absorption continuum are found as given in Table 2 below, which also gives the corresponding energies of dissociation in kilo-calories as well as the energy necessary for thermal dissociation.

TABLE 2.

Primary abs. limit at zero pressure.	Optical Energy.	Thermal Energy.	ΔE.
2750 Å	102·9 k. cal.	86 k. cal.	16·9

It may be remarked here that in spite of so many precautions it has been found extremely difficult to obtain exactly reproducible results, hence no

* The possibility of the HBr absorption curve breaking up into two curves, as in the case of alkali-halides, was previously suggested by Dr. P. K. Sen Gupta (*Zs. fur Phys.*, Vol. 88, p. 659, 1934), although no definite fluctuations were recorded. He, however, interpreted the results quite differently.

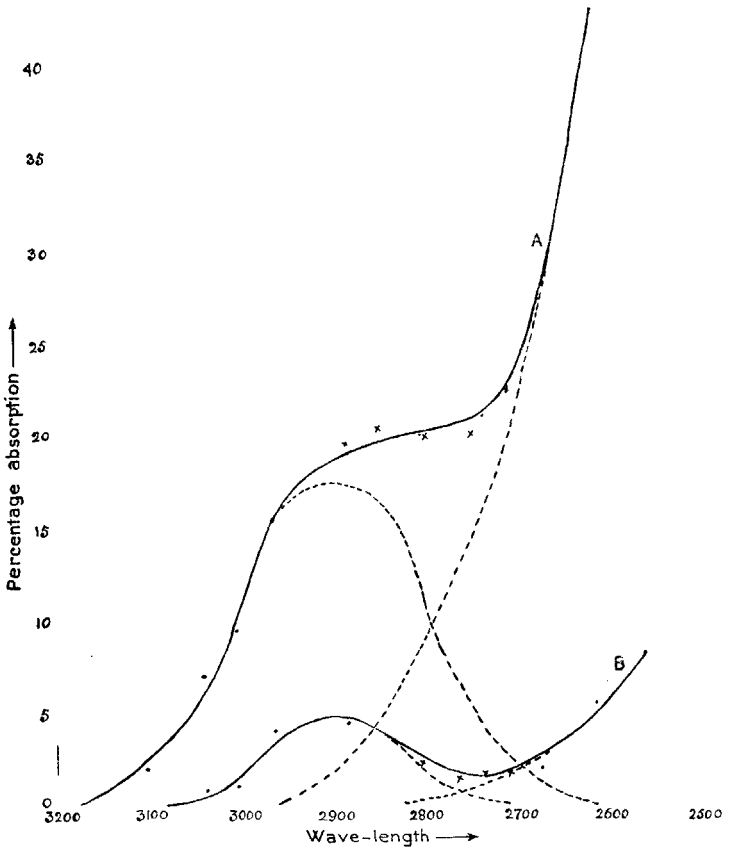

FIG. 1. HBr. A—for 76 cm. pressure.
B— „ 5 „ „

accuracy is claimed beyond the first three figures of the wave-length data expressed in Angstrom units.

4. DISCUSSION OF RESULTS.

In determining the long wave-length limit a departure has been made from the existing practice of determining for what wave-length the absorption coefficient reduces to zero and taking that wave-length as the long-wave limit. Instead, the long-wave limit at various experimental pressures have been plotted and the actual limit found by extrapolating to zero pressure. The justification for such a procedure lies in the fact that an increased pressure enhances the perturbing influences of the neighbouring molecules and may also help the process of dissociation by thermal collision. Besides, with an increase in pressure, the number of molecules in the higher vibrational state would perceptibly increase, particularly in the case of molecules whose vibration frequency is not very high. All these factors will produce a shift towards the

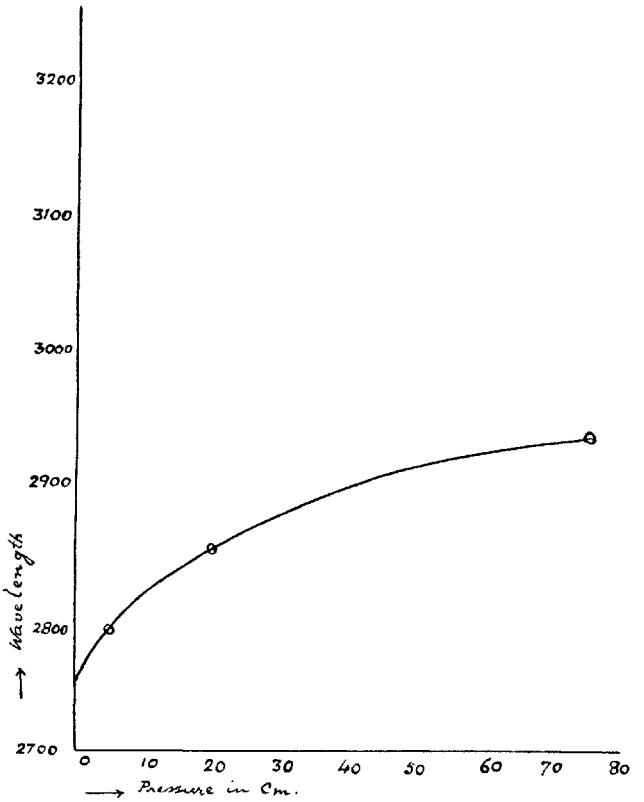

FIG. 2. HBr.

longer wave-length. Hence, in order to get a correct value of the minimum optical energy which will produce dissociation of molecules initially in the fundamental vibrational state, it is clear that the influence of pressure has to be got rid of and this can only be done by extrapolation to zero pressure. The actual plot of wave-length limit and pressure, as given in figure 2, has therefore been extended to zero pressure and the corresponding wave-length taken as the long wave-length limit.

As will be observed from the data in table 2, the observed long wave-length limit does not conform to either atomic or ionic binding of the molecule. Considering, however, the formation of the molecules out of atomic hydrogen and atomic halogen on the lines of Mulliken and as postulated by Datta and Deb, [8] an explanation seems possible.

In the case of the halogens, the atom configuration for a strong field is given by the two possibilities arising from the same normal state. In the case of Br the two states are:—

$$\text{Br } (^2p_0) \ldots \begin{cases} kl & (4s\sigma)^2\ (4p\sigma)^1\ (4p\pi)^4, \quad {}^2\Sigma \\ kl & (4s\sigma)^2\ (4p\sigma)^2\ (4p\pi)^3, \quad {}^2\Pi \end{cases}$$

In combining with the bromine atom, the electron belonging to the H atom is promoted according to the well-established rules of promotion to the lower available σ orbit. Hence for the combined HBr molecule two cases are obtained by combining the two strong field atomic states, as given below:—

$$^2\Sigma + ^2\Sigma = ^1\Sigma,$$
$$^2\Sigma + ^2\Pi = ^1\Pi, ^3\Pi *$$

Hence for the combined HBr molecule two possible configurations arise, viz:—

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

Considering the magnitude of the promotion energies of the hydrogen electron in the two cases, it is found that the promotion energy is small for the formation of the $^1\Sigma$ state than for that of the $^1\Pi$ state. Thus of the two states $^1\Sigma$ is more stable. Further, the stability of the $^1\Sigma$ state is also indicated by the fact that in this configuration the shells are all closed.

As there is a stable $^1\Sigma$ state and an unstable $^1\Pi$ state, higher in level, the appearance of a continuous absorption spectrum by transition from a stable potential energy curve to an unstable repulsive curve is clearly understandable. The reverse process giving rise to a continuous emission spectrum by recombination of the two atoms has also been recorded by Datta and Deb at very nearly the anticipated region.

The amount of energy required to dissociate the molecule in the two processes—thermal and optical—can be best understood if one considers the end products in the two processes. For, in the case of HBr, when the molecule breaks up by thermal agitation, it does so by an increase of its vibrational energy and the end products are those corresponding to the HBr molecule in the ground state and the process may be expressed as:—

$$(4s\sigma)^2 (4p\sigma)^2 (4p\pi)^4 + E_1 \text{ (thermal)} \rightarrow (4s\sigma)^2 (4p\sigma)^1 (4p\pi)^4 \text{ [Br } ^2\Sigma] + 4p\sigma \text{ [H promoted].}$$

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

$$(4s\sigma)^2 (4p\sigma)^2 (4p\pi)^4 + E_2 \text{ (optical)} \rightarrow (4s\sigma)^2 (4p\sigma)^2 (4p\pi)^3 (5s\sigma) \text{ [HBr excited]} \rightarrow (4s\sigma)^2 (4p\sigma)^2 (4p\pi)^3 \text{ [Br } ^2\Pi] + (5s\sigma) \text{ [H promoted].}$$

Consequently, the energy required for the optical dissociation E_2 is in excess of that required for thermal dissociation E_1 by the difference in the energy of the Br and H atom in the respective processes. Now, the difference in the energy of the Br atom corresponds to that between the two different configuration ($^2\Sigma$) and ($^2\Pi$) for a strong electric field and as $^2\Sigma$ state is identified

* $^3\Pi$ state is not considered as it does not combine with $^1\Sigma$ state.

with one P state and $^2\Pi$ state with the other P state, this is practically of the same order of magnitude as the difference in the multiplet levels of the Br atom in the field free state. Further, it has been shown by Hund [9] that the $p\sigma$ electrons lie lower as regards energy than the $p\pi$ electrons, the difference in energy between Br atom in the $p\pi$ and $p\sigma$ state is positive. That due to H atom is also positive and is equal to the difference in energy of H atom between $5S$ and $4P$ state. Thus in the case of HBr molecule the energy for optical dissociation would be equal to:—

$$86 \text{ k. cal. (thermal energy of dissociation.)} + 10{\cdot}5 \text{ k. cal.} \left(^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}\right)_{Br} + 7 \text{ k.cal.} (5S - 4P)_H = 103{\cdot}5 \text{ k. cal.}$$

The observed long wave-length limit of the primary absorption gives a value of nearly 102·9 k.cal.

The discrepancy is not much and it is reasonable to expect a better correlation if the temperature shift could be allowed for, the shift would be towards the shorter wave-length making the observed energy of optical dissociation greater than its present value.

Explanation of the Secondary Absorption.

The appearance of a secondary emission spectrum in very nearly the same position as that recorded here has also been observed by Datta and Deb. This they attempted to interpret as originating from the dissociation and subsequent recombination of the ionised (HBr^+) molecule. The fact that they have been observed in absorption by the cool gas, where there is absolutely no chance of the presence of HBr^+ molecules, compels one to abandon that view.

It is, however, significant that the difference in energy between the long wave-length limits of the primary and secondary absorption, as observed from the plotting of data of Table 1 (see fig. 1), is very nearly of the same order of magnitude as the fundamental vibrational energy of the HBr molecule. For the purposes of comparison these have been collected in Table 3 below:—

Table 3.

Secondary limit at 76 cm. pressure.		Primary limit at 76 cm. pressure.		Diff. in energy in k. cal.	Fundamental vibration energy in k. cal.
Wave-length.	k. cal.	Wave-length.	k. cal.		
3180	89·0	2930	96·6	7·3	7·3

As the secondary absorption band appears on the long wave-length side and is very weak in intensity, it is possible to ascribe it as originating from the next higher vibrational level, that corresponding to the state $v''=1$ of the normal molecule. The fraction of HBr molecules in the state $v''=1$ is of the order of

10^{-6}. But there is evidence on record that with this order of concentration of atoms or molecules feeble absorption is quite possible. The fluctuations in intensity on the long wave-length beginning of continuous absorption of HBr is thus similar to the fluctuations recorded by Sommermayer in the case of the alkali halides, which he explained on similar lines as originating from transitions from the different vibrational states of the normal molecule.

Summary.

1. The continuous absorption of HBr gas has been accurately determined and two absorption continuum—one secondary and the other primary—found on a micro-photometric analysis of the spectrum plate.

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 of the primary band has been determined and the corresponding heat of dissociation, which is in excess of the thermal heat of dissociation has been satisfactorily explained on a theory of the formation of the HBr molecule previously advanced by other authors.

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

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