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THE EFFECT OF COLLISIONS ON THE CONTINUOUS ABSORPTION SPECTRA

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ABSTRACT Continuous absorption spectra of polar molecules have been found to shift towards longer wavelength by collisions with both polar and non-polar gases. The change in absorption co-efficient is found to depend on the number of collisions suffered by a molecule with the foreign gas and reaches a maximum value with a definite proportion of the absorbing gas and foreign gas, irrespective of the polarity of the foreign gas. With inert foreign gas it appears that there is a sort of screening giving rise to a decrease in the absorption co-efficient value after the maximum is reached.

INTRODUCTION

It is accepted now, that molecules with atomic binding, break up on dissociation into two neutral atoms—one normal and the other excited, whereas those with ionic binding into two neutral atoms both of which are normal. The energies of dissociation in the two cases are thus, different and consequently the beginning of absorption also (Frank, 1927) Some work on the absorption limit of the hydrogen halides has been done to decide its type of binding. Some decision was in favour of the atomic type. Dutta (1934) concluded on his investigations, that they corresponded to ionic binding.

In these works the effect on the absorption spectra due to collisions and intermolecular fields could not be detected As it was observed by Goodey and Taylor, the Beer's law holds for these gases This tends to indicate that the pressure or the collisions have not got any effect on the probability of transition of the molecules. The hydrogen-halide molecules being polar, exert strong intermolecular electric influences on one another and it is probable that the energy levels in the molecules are, in some way, modified from absolutely free molecules. The spectra which we generally observe, are thus, not expected to be those of pure unaffected gaseous molecules, but should be due to molecules under various amount of intermolecular forces ranging from zero to a maximum. To know the absorption limit of unaffected gas molecules accurately and thereby to predict the type of binding we must know the quality and the quantity of this modification. It is with this point in view that the experiment had been undertaken.

EXPERIMENTAL

The absorption spectrum studied was that of HI and CCl_4 molecules. The total number of collisions suffered by a molecule was increased by adding a foreign gas. This, however, keeps the total number of collisions with similar molecules the same. But each molecule has suffered, besides, a number of collisions with the foreign gas introduced, according to its quantity. If the foreign gas has no absorption in the region studied, we can study only the effect of increased collisions on a molecule, some of which are with foreign polar and some with non-polar gases. These experiments have been

carried out both with a polar (HI) and a non-polar (CCl_4) gaseous substance, which primarily show a continuous absorption spectrum. The foreign gases selected were HCl gas as polar and argon as non-polar—none of which has any absorption in the regions where those of HI and CCl_4 begin.

HI gas was prepared by the action of distilled water on a mixture of 4 gms. of red phosphorus and 20 gms. of iodine crystals. The gas was purified by passing through glass beads with moist red phosphorus and a U-tube containing fused calcium chloride.

The vapour pressure of CCl_4 was sufficient for the purpose. HCl gas was prepared by the ordinary method of adding conc. H_2SO_4 on pure sodium chloride. Argon was taken from a storage cylinder. Different initial pressures of 1 cm., 2 cm. and 4 cm. of the absorbing gases were taken and increasing amounts of foreign gas added from time to time. After each addition photographs were taken of the absorption spectrum. The spectrograph used was an E_1 spectrograph with high dispersion.

Intensity measurements were carried out by means of a Zeiss photoelectric recording photometer and absorption co-efficients calculated. The spot of light of the photometer was allowed to run along the breadth of the different spectra along a particular wavelength. The absorption co-efficients at that particular wavelength were determined for the various spectra, each of which was modified to a different amount due to the presence of various amounts of foreign gases.

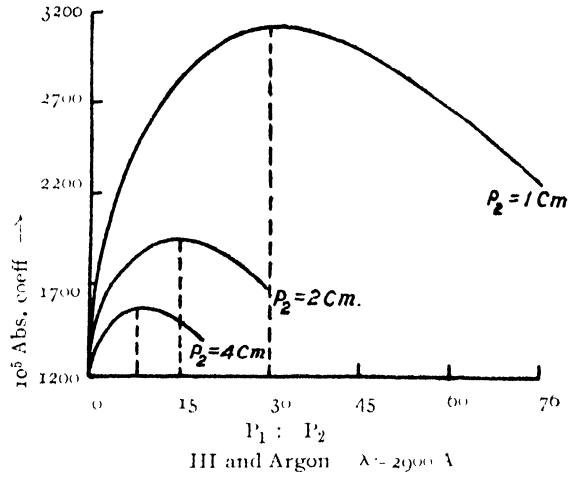

FIG. 1

RESULTS AND DISCUSSION

In the figure P_2 is the pressure of the absorbing gas and P_1 that of the foreign gas, so that P_1/P_2 denotes the ratio of the foreign gas quantity to the absorbing gas quantity.

It would be observed from the graph that in the case of mixtures of both HI and argon, and HI and HCl, the absorption co-efficient α increases

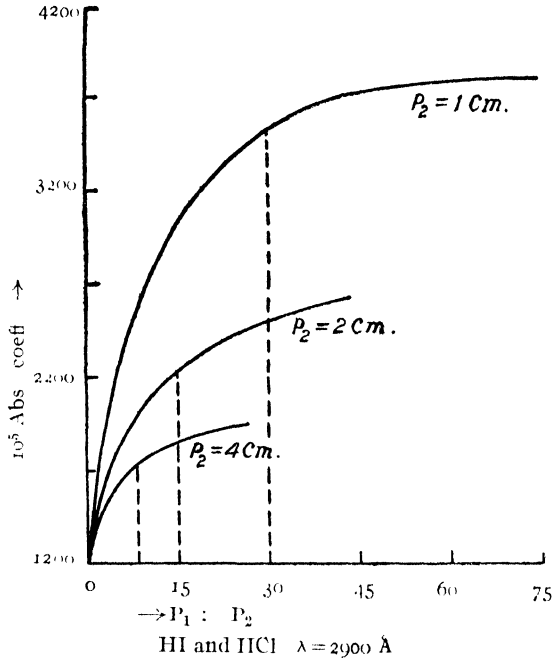

FIG. 2

with $P_1 : P_2$ value *i.e.*, as the amount of the foreign gas is increased. One must remember here that the quantity of the absorbing gas is always the same along any one graph. To say that the absorption co-efficient increases at a particular wavelength is the same as saying that the absorption limit shifts towards the longer wavelength side. So the experimental results show (*vide* introduction that collisions or electric field help in dissociation and give the amount of change suffered.

We find that with HI, the maximum with argon mixture or the saturation point with HCl mixture occurs at values of P_1/P_2 equal to 30, 15 and 7 when P_1 is equal to 1, 2 and 4 cms. This means that the maximum or the saturation point occurs at the partial pressure of the foreign gas equal to 30 cms. without any regard to the quantity of the initial gas present. It means that the number of collisions suffered by one absorbing gas molecule with the foreign gas molecules is a fixed quantity to give the maximum or the saturation point, no matter what the initial absorbing gas or the nature of the colliding partners may be. The total change in the absorption spectra which is determined by the perturbation suffered in the energy levels of a molecule is a quantity which is thus mainly determined by the number of collisions per sec. of each molecule with the foreign molecules. The maximum change in the absorption co-efficient in the case of the mixture HI and HCl is, however, greater than that in the case of the mixture of HI and argon. This is due to the fact that HCl is polar and argon is non-polar. One HCl molecule can, at the time of collision, disturb to a greater extent, the molecular equilibrium, due to its extra facility of possessing an electric

moment. We have further, observed that the P_1/P_2 curve becomes more and more steep as the pressure of the absorbing gas is decreased. For example, we have obtained for HI + HCl mixture that with $P_1/P_2=1$, the change in α-value (from that when P_1 $P_2=0$) becomes equal to 800×10^{-5} units for $P_2=1$ cm., 300×10^{-5} units for $P_2=2$ cms. and 100×10^{-5} units for $P_2=4$ cms. Thus the observed change in the absorption co-efficient for 1 cm. gas pressure is about double the change in absorption co-efficient for 2 cms. gas pressure (Figs. 1 and 2) Considering the fact that the absorption co-efficient or their changes have been obtained from the relation $\log I-\log I_0=\alpha.P_2$, we see that the change in α has also been obtained under the implied condition of division by P_2. Hence the total change introduced in the absorption co-efficient due to molecule tend to remain of the same value It means that the molecular effect on the change of absorption co efficient is not very widely variable with initial gas pressure. We have also to note here the peculiar characteristic of a maximum for 'α' with argon as foreign gas on HI. An HI molecule under collision with another HI molecule will be more influenced as compared to the case when under a collision with an argon molecule (due to polar nature of HI). The result indicates that due to large number of HI-argon collisions, some of the HI-HI collisions tend to become somehow ineffective and thus to decrease the absorption co-efficient value. The exact mechanism, however, cannot be clearly seen at present, for it goes against the principle of the kinetic theory. Lastly, considering the case of HI-argon with the hypothetical case of HI-HI, we note that if argon and HCl, by their collision, change the absorption co-efficient value, HI-HI collisions would also tend to change the α value. Let us consider that in 2 cms. of HI gas, 1 cm. acts as the absorbing material and the remaining 1 cm only as colliding molecule, as with the cases considered in the present set of investigations. Since with 1 cm. HI and 1 cm. of any colliding gas like argon or HCl, the α value suffers a change from, say, 1200×10^{-5} units to about 1800×10^{-5} units, we should expect a value of the same order with HI colliding molecules also But due to Beer's law, the total change in α-value must be from 1200×10^{-5} to 2400×10^{-5} units, so that we get that in the case of the pure gas like HI, a fairly large percentage of the absorption is due to collisional processes. Perhaps on a more detailed study, one can analyse the different contributing causes of Beer's law more quantitatively.

Results indicated that HCl has no effect on the absorption spectrum of CCl_4. Such results have also been observed by Harding (1936) and Schneider (1937) in the case of I_2 and O_2 which are also non-polar as CCl_4.

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