

when (3) holds in the case of CrCl_3 in absorption. We have

$$R = Q + L_{\text{Cr}} + \frac{3}{2}D_{\text{Cl}_2} - L_{\text{CrCl}_3} \quad \dots \quad (4)$$

Q , the heat of formation of $[\text{CrCl}_3]$ out of $[\text{Cr}]$ and Cl_2 , is about 145 kcal, but neither L_{Cr} nor L_{CrCl_3} is known. Hence (4) cannot be tested.

Band Absorption

The band absorption of CrCl_3 is certainly due to the reaction of light on the d^3 -shell of the Cr^{+++} -ion. As is known from theories of complex spectra, the spin moments of all the electrons in the normal state for the d^4 -shell are parallel giving rise to a 2X -term ($X = F, P$, . . . when Pauli's principle is operative). The action of light would be to turn the spin of one of the electrons in the opposite direction giving us a 2Y -term. Thus the magnetic moment of the Cr^{+++} -ion on light absorption will be changed from $\sqrt{4S(S+1)} = \sqrt{4 \cdot \frac{3}{2}(\frac{3}{2}+1)}$, *i.e.*, from $\sqrt{15}$ to $\sqrt{3}$, *i.e.*, will get changed by about 2.5 times per quantum absorbed. The effect has been qualitatively found by Prof. D. M. Bose⁸, but contrary to expectation, the magnetic moment of CrCl_3 solutions is found to increase on illuminations by light which can be absorbed. Prof. D. M. Bose is of opinion that the increase is

due to the supposed fact that the coupling of the d -electrons of the paramagnetic ions with the associated water molecules, known as l -coupling is broken down by the act of light absorption.

The suggestion is rather vague. An alternative suggestion may be made. It is known from the works of Herzberg that in molecule formation, atoms are not always in their lowest state. Thus in SiN as well as in CN , the silicon and carbon atoms are in the 4D_2 -state, and not in the 3P -states which are deeper. Probably in CrCl_3 the d^4 -shell of Cr^{+++} -ion is in the 2Y -state, *i.e.*, the spins of two electrons oppose each other. When light falls, the molecule breaks up, and the Cr^{+++} -ion takes up the more stable condition in which the electrons have their spins in the same direction.

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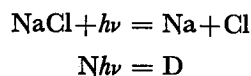
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52. ON THE ABSORPTION SPECTRA OF SATURATED HALIDES OF MULTIVALENT ELEMENTS

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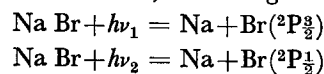
(*Bull. Acad. Sci., U.P.*, **1**, 19, 1931)

The absorption spectra of alkali halides in the vapour state have received a good deal of attention in recent years from Angerer and Müller,¹ Müller,² Franck, Kuhn and Rollefson.³ They found that the absorption spectra were strictly continuous, *i.e.*, started from a rather ill-defined long wavelength limit and stretched towards the ultraviolet. In the case of bromides and iodides, two absorption maxima were noted. In some cases there was re-transmission of the spectrum in the shorter wavelength side. Franck showed that the long wavelength limit of the continuous spectrum marks the photo-dissociation of the molecule into neutral atoms according to the scheme



D = heat of dissociation calculated from a Born-cycle.

In the case of bromides and iodides the molecule, in addition may decompose into an excited halogen atom and a metallic atom, according to the scheme



This gives rise to a second absorption-beginning, removed to the short wavelength side by the difference $\Delta\nu = {}^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$. This is present also in the case of chlorine, but as $\Delta\nu$ is small in this case, it cannot be distinguished from the first absorption-beginning. But in the case of NaBr and NaI , they obtain two absorption maxima, separated by the distance $\Delta\nu = {}^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$, from which they conclude that the molecule NaBr decomposes into Na and $\text{Br}({}^2P_{\frac{3}{2}})$ and Na and $\text{Br}({}^2P_{\frac{1}{2}})$. (*Vide* Fig. 34, p. 230, Photo Processes by Griffiths and Mckeown).

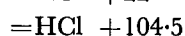
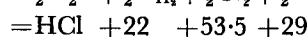
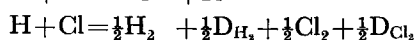
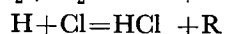
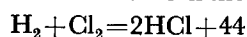
The same consideration would hold also for hydrogen

halides⁴, but here the agreement is not good, as can be seen from the following table:—

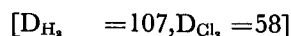
TABLE 1

Substances	Q (Heat of Formation)	R _{calc} (Atomic Heat of Formation)	λ Observed long wave-length limit of absorption	R _{obs}
HCl	22.0	105	2350	122
HBr	8.6	84	2640	108
HI	2.89	76	3320	86

The calculation of R in the third column is as follows:—



Hence R = 105 kcal.



The discrepancy between R calculated from photo-dissociation according to Franck's idea and R experimentally obtained is too large and is beyond experimental error. Hence Franck's rule does not seem to apply to the hydrogen halides. Franck is of opinion that the binding in HCl is non-ionic. A difficulty appears in the interpretation of the dipole moment of HCl molecule. The distance between the nuclei is found to be 1.28×10^{-8} cm. from an analysis of the rotation spectrum of HCl, but the dipole moment is found to be 2×10^{-18} units. If we suppose that HCl consists of H⁺ and Cl⁻ ions forming a closed shell, then μ , the dipole-moment, ought to be 3 times larger, being $1.28 \times 10^{-8} \times 4.70 \times 10^{-10} = 6 \times 10^{-18}$. Hence the presumption is that in HCl, the electron does not completely leave H and attach to Cl, giving rise to an ionic compound. But it is not completely atomic as in that case μ should be nil.

Another class of halides, like AgCl³ and ThCl⁴ give band absorption in addition to continuous absorption. These facts have not yet been satisfactorily explained.

No systematic investigation of the absorption spectra of the poly-atomic saturated halides has been undertaken so far, excepting some previous work of Evans⁷ and Leifson⁴. The present work was taken up to see the implications of the above ideas in the case of the poly-atomic compounds. The halides so far investigated by us are CCl₄, SiCl₄, SnCl₄, TiCl₄. These were chosen because they are usually volatile liquids and a large vapour pressure can be easily obtained.

For carrying out the experiment, an absorption tube of ordinary glass was used; to this was attached a bulb which

contained the liquid under investigation. At first the quartz plates were fitted with sealing wax, but as it was attacked by chlorides, soluble silicate of soda was used to fix up the plates. For this the ends of the tube must be well ground. The spectrographs used were a Hilger E₃ and a bigger Zeiss apparatus corresponding to E₂ of Hilger but with greater light gathering power. The source of continuous light was underwater spark of copper. Good continuous spectrum reaching up to λ 2000 was obtained after an exposure of 3 minutes in the E₃ and 5 to 7 minutes in the Zeiss apparatus.

All the spectra showed continuous absorption and no trace of bands. In the case of SnCl₄ re-transmission was obtained for a short region after the first absorption beginning. The nature of re-transmission varies with vapour pressure and the points need further careful investigation. The preliminary results are shown in the following table:—

TABLE 2

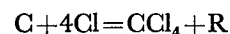
Results of experiment with tetra-halides

Substance	λ Long-wave limit	Q _m in kcal	L _m of the element	2.DCl ₂	Q heat of formation	R	R/4
CCl ₄	240 μμ	118	282	58 × 2	68.5	466.5	117
SiCl ₄	280 „	102	—	„	121.8
TiCl ₄	328 „	87	—	„	—
SnCl ₄	386 „	74	73.9	„	118	308	77

The second column gives the experimentally obtained values of λ and the third column gives the corresponding values of Q_m obtained from the quantum relation

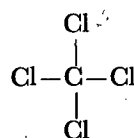
$$Q_m = N h \nu_m / J$$

In column 7, we have given the value of R, the atomic heat of formation of the molecule. R may be defined by the reaction



where all the substances are supposed to be in the gaseous state and C and Cl are atomic. It is seen from comparison of columns 3 and 7 of the Table 2 that R is nearly 4Q_m in the cases where the data are available, and this is the main result obtained from the present investigation. The explanation seems to be quite simple.

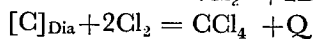
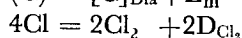
In a CCl₄ molecule, the structure may be imagined to be given by



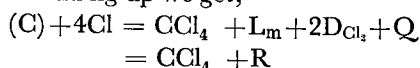
If in continuation of Franck's argument we assume that

the effect of light, producing continuous absorption in vapour, is to drive out one Cl atom from the molecule, then $h\nu_m = \frac{1}{4}R$ as the total R can be supposed to be equally distributed amongst all the 4 C-Cl bondages. The investigation seems to confirm this view.

R in the seventh column of the Table 2 has been calculated from the following reaction—



Hence adding up we get,

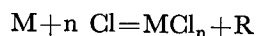


L_m in the case of carbon has been taken from a calculation by Fajans from the vapour pressure of carbon as determined by Lummer. For the heat of dissociation of Cl_2 the latest accepted value by Franck has been taken. The value of Q has been taken from Landolt and Börnstein's tables [p. 1500, (1923)]. They are due to Thomsen.

For $SiCl_4$, the value of L_m is still lacking. If the present ideas hold the value of L_m comes up as 178.2 kcal—a fairly probable value.

For $SnCl_4$ the value of L_m is 73.9 kcal and is due to Greenwood and $Q = 118$ kcal (L and B tables).

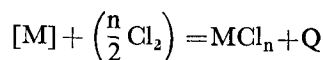
It cannot be said, however, on account of the uncertainty in some of the data* used, that the relation $R = 4Q$ has been established. If it is true, we should expect that generally $R = nQ$ where we are treating a saturated poly-atomic halide with n chlorine atoms. R is the heat of reaction in the process.



and is equal to $L_m + \frac{n}{2}D + Q - L_{com}$, where L_m is the heat of evaporation from the solid state to the monatomic gas state.

D = heat of dissociation of Cl_2

Q = heat of reaction in the process



We can test the possibilities in some of the poly-atomic halides. The available data are given in the following table.

In the case of di-valent halides the latent heat of the compound is not known excepting in the case of $HgCl_2$ for which it has been calculated from vapour pressure data. The absorption spectrum of $HgCl_2$ was studied by Evans and has again been studied recently in this laboratory by Deb and Mohanty. Without entering into details, it may be said that the results of the experiments do not agree with our theory. We should get continuous absorption at $\lambda = 5280$, while Evans finds the beginning at $\lambda = 3500$ while

* The uncertainty mostly refers to the latent heat of the element. Thus L_m for C is given for all values from 146 kcal to 280 kcal.

TABLE 3

Element	L_m Heat of Sublimation	$\frac{n}{2} = D_{Cl_2}$	Q Heat of Formation	L_{com} Heat of Sublimation of the chloride	R	$\lambda = \frac{R}{n}$
Be	..	57	112
Mg	47	..	151	..	255 — L_{com}	..
Ca	44.2	..	190.3	..	291.5 — L_{com}	..
Sr	195.6
Ba	197
Zn	31.3	..	97.2	..	185.5 — L_{com}	..
Cd	27	..	93.2	10.5?
Hg	15.5	..	53.5	16.9?
B	..	84	(90)
Al	48	84	161	28?
In	128
Tl	38.2	..	80	..	202.2 — L_{com}	..
Pb	46	114

Deb and Mohanty find that the absorption begins at $\lambda = 2500$. The data are therefore contradictory. But no trace of absorption has been found at the expected point. Fresh light has been thrown on the question of binding from the study of Raman effect of the chlorides. It has been found that the chlorides can be divided into two groups. Firstly, those which do not show Raman scattering and to this group belong most of the ionic compounds, NaCl for example.* Secondly, those which show Raman scattering. To this group belong most of the atom compounds including $HgCl_2$. But it must be remembered that Raman effect has been studied only in the solid state and hence it may not be safe to deduce any conclusion from it regarding the nature of binding. Anyway, there may be expected some discrepancies in the case of some molecules, just as HCl does not fall in line with NaCl and other compounds. The subject is receiving further consideration.

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