51. ON THE COLOURS OF INORGANIC SALTS

M. N. Saha and S. C. Deb

There have been many diverse opinions regarding the origin of colours shown by inorganic salts in the solid state, and in solution. A short summary is given in the 'Handbuch der Physik', Vol. XXIV, p. 564. According to Hoffmann and his co-workers colour is shown only by compounds of such elements which show a varying valency such as Fe, Co, Ni...Ladenberg made the first attempt to connect colour with atom-structure. He showed from analysis of existing data that colour is almost invariably shown by salts of elements belonging to transitional groups (Sc to Cu) and rare-earths, and very seldom by salts of elements belonging to regular groups. Compounds like NaCl, $MgCl_2$, $AlCl_3$, $SiCl$,...show no colour, while chlorides of all the elements of the transitional groups (Sc to Cu) show colour. Ladenberg tried to define the electron transition responsible for colour in the following way. He pointed out that in elements from Sc to Cu, the 3d-shell is being formed and there are some electrons in the 4s-shell. He points out that there is some sort of competition between the 3d-and 4s-shells for the possession of electrons, and hence light of very small energy (visible) may be able to effect transition of the electron from any one of these two levels to the other, *i.e.*, from 3d→4s.

Meisenheimer showed that the nature of the anion also has some influence on the colour. Fajans attempted to connect colour with deformation of the cation, produced partly by the anion. He points out that CuF_2 and $CuSO_4$ (anhydrous) are colourless, and hence concludes that the Cu^{++}-ion must be colourless, but in aqueous solution as well as in ammoniacal solutions Cu^{++}-ion gives a blue colour. This is ascribed to some deforming action of H_2O or NH_3, molecules on the Cu^{++}-ion.

The question of colour forms part of the larger question of binding of atoms of different types to form aggregates of different orders, e.g.—molecules, crystals, solutions; and light is thrown on the problem from many directions, viz., from consideration of the course of refractive index for solids, magnetic properties, or spectral absorption for solids and gases, etc., etc...., and investigation of the same properties in the case of solutions. Pauli's principle has given us the rule governing the formation of atoms out of nuclei and electrons, but the exact way in which it will have to be modified in formation of molecules and

more complex aggregates is not yet known to the satisfaction of the theoretical physicist.

In a note published in 'Nature,' Vol. 125, page 163, one of the authors tried to show that the colours of the salts of the transitional groups may be ascribed to the electrons of the d-shell, but not in the way imagined by Ladenberg. If we take a compound like $CrCl_3$, we may suppose that the picture of the combination is given by $\left[Cr^{+++} \right] \begin{matrix} Cl^- \\ Cl^- \\ Cl^- \end{matrix}$. Thus there are three chlorine ions surrounding the Cr^{+++} nucleus. That this assumption corresponds to the actual picture is almost guaranteed by magnetic properties of $CrCl_3$. The paramagnetic susceptibility of trivalent chromium compounds is almost entirely due to the Cr^{+++}-ion, the Cl^- ion contributing nothing to the magnetic moment. Hence the colour must be due to the reaction of light either on the electrons or on Cl^-ions. But we know that the absorption of the Cl^-ion in the vapour state is in the ultraviolet below $\lambda 3000$, and hence visible light will be without action on the Cl^-ions. Hence colour arises from the reaction of light on Cr^{+++}-ions. This contains, in the free atomic state, an incomplete d^3-shell, giving rise to ^4F, ^4P, ^2H, ^2G, etc., terms. What will be the nature of these levels in a compound?

Light is thrown on this question from consideration of the magnetic moment of the Cr^{+++}-ion. If, following Hund[1], we suppose that the electrons of the d^3-shell are bound with the usual 'l' and 's' coupling which gives us the fundamental terms of the Cr^{+++}-atom, the magnetic moment cannot be explained. Prof. D. M. Bose[2] showed empirically that the magnetic moment is explained if we suppose that only the 's'-coupling is operative and the 'l'-coupling breaks down in compound formation. Stoner[3] has given theoretical justification for this assumption, and explained many other anomalous cases. The breaking of 'l'-coupling can be inferred also from our present knowledge of molecular spectra, where we find that the 'l' vectors of outer electrons get subdivided along the line of binding of the component nuclei while the 's' vectors take up either the parallel or the anti-parallel directions. We can therefore suppose that the action of light consists in changing the spin of one of the component electrons in the d^3-shell. The

energy required for this process may be inferred. In the gaseous state, Cr+++-ion gives rise to the following terms:—

$$^4(P\ F),\ ^2(P\ D\ F\ G\ H),\ ^2(D)$$

Cr+++-atom is partially analysed by White and some of the term values are known. They are given in Table I.

The difference in value is of the order for the absorption of visible light not only in Cr+++, but as can be seen from the table (Table II), in almost all ions of the elements of the transitional group.

Table I—Terms of d³ elements

Term Elements	⁴F	⁴P	²H_{5,6}	²G_{4,5}	²D_{3,4}	Reference
Sc						
Ti+	0	8965	11769 11867	8190 8210	11721 11851	H. N. Russell, Astro. Journ., 66, 288 (1927)
V++	0	11513	16822	11966	16229	H. E. White, Phy. Rev., 33, 674 (1929)
Cr+++	0	..	21027 21278	15014 15371	..	H. E. White, Phy. Rev., 33, 676 (1929)
Mn+4	0	..	24395 25361	17852 18468	..	H. E. White, Phy. Rev. 33, 679 (1929)

Table II—Difference between the highest and the next term with lesser-multiplicity

Stage of Ionisation Elements	II	III	IV	V
Sc				
Ti	11800	14500		
V		16800	19087	
Cr			21000	23237
Mn				25000

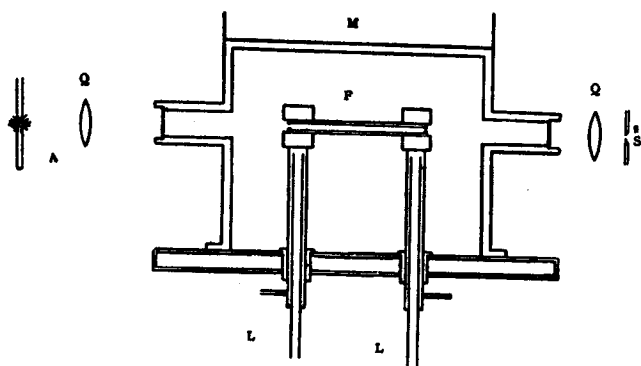[II, III, IV, V denote first, second, third and fourth state of ionisation.]

Fig. 1. F—Furnace, M—Iron mantle, Q—Quartz lens, A—Under water copper spark, L—Leads for heavy current, S—Slit for spectrograph.

A number of experiments can be designed to test this hypothesis. Owing to the limitations of this laboratory we undertook investigation of the absorption spectrum of a few chlorides of the transitional group.

Experimental Procedure

We chose as our first experimental material CrCl₃. This is obtained in pink-coloured scales, and according to information obtained from standard treatises on Chemistry, it forms a stable vapour at 1200°—1350°C, whose vapour density corresponds to the formula CrCl₃. It does not decompose up to a temperature of 1500°C.

F is a vacuum furnace of acheson graphite used in this laboratory for experiments on the thermal ionisation of elements. The CrCl₃ was placed within a silica tube which was placed within the furnace. This was to prevent direct contact of the carbon of the furnace with CrCl₃. The ends of the furnace were plugged with iron rings leaving only narrow opening in the centre for passage of light. These rings prevented quick outflow of hot vapour. The evaporation of CrCl₃ is so rapid that the whole mass disappears before any exposure can be given. When the furnace is filled with N₂ the conditions could be kept steady.

Source of continuous light was an under water-spark between two copper electrodes. The rays from the spark were made parallel with a quartz lens and allowed to pass through the furnace over the hot vapour of CrCl₃ and on emergence again focussed on the slit of an E₁ quartz spectrograph, kindly lent to us by Prof. N. R. Dhar of the Chemistry Department. Copper arc was taken as comparison spectrum. The spectrum was examined between λ5000 to λ2400 Å.

Absorption bands were obtained in the blue-violet region extending slightly into the ultraviolet. They were analysed and are seen to form two distinct systems which we depict below by A and B systems. Following is the analysis of the bands:

Table III—System A

v'' \ v'	0	1	2	3	4
0	22654·5	22241·7	21828		
1	23067	23652	22236	21824	
2	23477	23062	22646	22232	21822
3	23883	23472	23059		
4		23874	23468	23054	
5			23869	23462	

This system of bands can be represented in the following formula:

$$\nu_{head}=22654 \cdot 5+(414 \cdot 07v'-\cdot 87v'^2)+(414 \cdot 2v''-\cdot 60v''^2)$$

The second system of bands which we designate by "System B" is given below:

Table IV—System B

v' \ v''	0	1	2	3
0	22545·1	22117	21689	
1	22958	22525	22093	
2	23352	22926		
3	23741	23318	22907	
4		23699		

The above set of bands is also represented in an empirical formula which we give below:

$$\nu_{head}=22545 \cdot 1+(414 \cdot 0v'-4 \cdot 7v'^2)+(431 \cdot 2v''-3 \cdot 65v''^2)$$

In addition to these band absorptions, continuous absorption was obtained near $\lambda 3000$ Å. U., and the spectrum is completely cut off at $\lambda 2700$ Å. U.

Table V—List of absorbed band heads

| λ	ν (vac)	System	Classification $v''-v'$
4185·8	23883	A	0—3
4187·4	23874	A	1—4
4188·3	23869	A	2—5
4210·7	23742	B	0—3
4219·4	23699	B	1—4
4258·25	23477·2	A	0—2
4259·2	23472	A	1—3
4260·0	23468	A	2—4
4260·9	23462	A	3—5
4280·8	23352	B	0—2
4287·3	23318	B	1—3
4333·88	23067·5	A	0—1
4334·9	23062	A	1—2
4335·5	23059	A	2—3
4336·4	23054	A	3—4
4354·3	22958	B	0—1
4360·6	22926	B	1—2
4364·2	22907	B	2—3
4412·90	22654·5	A	0—0
4413·39	22652·1	A	1—1
4414·5	22646	A	2—2
4434·34	22545·1	B	0—0
4438·2	22525	B	1—1
4494·80	22241·7	A	1—0
4495·9	22236	A	2—1
4496·8	22232	A	3—2
4520·0	22117	B	1—0
4525·0	22093	B	2—1
4580·1	21828	A	2—0
4580·9	21824	A	3—1
4581·3	21822	A	4—2
4609·3	21689	B	2—0

Discussion of the Results

A large amount of work has been published on the absorption spectra of the halides. Two types of absorption have been found. In the case of saturated halides of alkali elements only a continuous absorption is obtained. Franck, Kuhn and Rollefson[4] have shown that the beginning of absorption corresponds to the photodissociation of the halide-molecule into constituent atoms:

$$NaCl+h\nu=Na+Cl$$
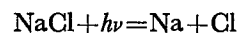
ν corresponds to the atomic heat of dissociation:—

$$Na+Cl=NaCl+R$$
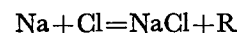
R is calculated from a Born-cycle. We have

$$R=Q+L_{Na}+\tfrac{1}{2}D_{Cl_2}-L_{NaCl} \quad .. \quad .. \quad (1)$$

where Q=heat of formation of solid NaCl out of solid Na and Cl_2 gas, L_{Na} is the latent heat of evaporation of Na, D_{Cl_2} is the heat of dissociation of Cl_2, and L_{NaCl} is the heat of evaporation of NaCl.

Franck has shown that most alkaline halides give the same kind of results as NaCl; he assumes that in these compounds, the valency electron of Na passes over to Cl, thus the binding is electrostatic; due to attraction between Na^+ and Cl^- or polar. When light falls on an NaCl-molecule, the electron in Cl^- passes on to N^+—thus resulting in dissociation of NaCl to neutral Na and neutral Cl.

But there are other cholorides like HCl[5] which show a continuous absorption, but the beginning of absorption does not correspond to the heat of formation of HCl out of H and Cl.

A second class of chlorides like AgCl,[6] ThCl,[7] etc., shows band absorption in addition to the continuous absorption. The band absorption in such cases has not been satisfactorily explained.

Very little work has so far been done on the band-spectra of polyatomic halides, but a few experiments have been carried out in this laboratory (*vide* papers by A. K. Dutt and M. N. Saha, S. C. Deb and H. B. Mohanti). It appears from these works that all saturated halides like $MgCl_2$, $AlCl_3$... show only continuous absorption, and if ν denotes the frequency of the beginning of absorption

$$h\nu=\frac{R}{n}, \quad .. \quad .. \quad .. \quad (2)$$

where R=heat of formation of the gaseous molecule out of constituent atoms, n=valency.

$$R=Q+L_M+\frac{n}{2}D_{Cl_2}-L_{MCl_n} \quad .. \quad .. \quad (3)$$

On the other hand, it appears that non-saturated halides like $CrCl_3$, as well as halides of Ca, Sr, Ba (*vide* forthcoming paper by S. C. Deb and B Mukerji) give, in addition to continuous absorption, well marked band absorption. The continuous absorption seems to be due to the splitting up of a Cl-atom from the molecule. We may try to find out

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

$$R = Q + L_{Cr} + \tfrac{3}{2}D_{Cl_2} - L_{CrCl_3} \qquad \cdots \qquad \cdots \quad (4)$$

Q, the heat of formation of [$CrCl_3$] out of [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 ($X = F, P \ldots$ 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 $\sqrt{4S(S+1)} = \sqrt{4 \cdot \tfrac{3}{2}(\tfrac{3}{2}+1)}$, 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. Bose[8], 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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52. ON THE ABSORPTION SPECTRA OF SATURATED HALIDES OF MULTIVALENT ELEMENTS

A. K. DATTA AND M. N. SAHA

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

$$NaCl + h\nu = Na + Cl$$

$$Nh\nu = D$$
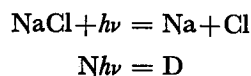
D = heat of dissociation calculated from a Born-cycle.

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

$$Na\,Br + h\nu_1 = Na + Br(^2P_{\tfrac{3}{2}})$$

$$Na\,Br + h\nu_2 = Na + Br(^2P_{\tfrac{1}{2}})$$
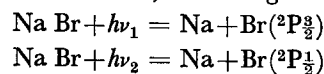
This gives rise to a second absorption-beginning, removed to the short wavelength side by the difference $\triangle\nu = {}^2P_{\tfrac{3}{2}} - {}^2P_{\tfrac{1}{2}}$. This is present also in the case of chlorine, but as $\triangle\nu$ is small in this case, it cannot be distinguished from the first absorption-beginning. But in the case of NaBr and NaI, they obtain two absorption maxima, separated by the distance $\triangle\nu = {}^2P_{\tfrac{3}{2}} - {}^2P_{\tfrac{1}{2}}$, from which they conclude that the molecule NaBr decomposes into Na and Br ($^2P_{\tfrac{3}{2}}$) and Na and Br ($^2P_{\tfrac{1}{2}}$). (*Vide* Fig. 34, p. 230, Photo Processes by Griffiths and Mckeown).

The same consideration would hold also for hydrogen