

THE ULTRA-VIOLET ABSORPTION SPECTRA OF Pr^{+++}
AND Nd^{+++} IONS IN SOLUTION.*

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ABSTRACT.—The ultra-violet absorption spectra of Pr^{+++} and Nd^{+++} ions in solution have been investigated using chlorides and sulphates. In $\text{Pr}_2(\text{SO}_4)_3$ solution, a broad and diffuse band has been observed which is resolved into three components at 2730Å, 2605Å, and 2560Å at a suitable concentration. This band has been investigated also with a Hilsch double monochromator and its origin discussed. In Nd^{+++} ion only four new lines have been observed at 2775 Å, 2730 Å, 2600 Å and 2505 Å. Working with $(\text{NdCl}_3, 6\text{H}_2\text{O})$ crystal Freed has reported the existence of a broad and diffuse band which extends from 2280Å to 2100Å; but here no such band has been observed in either of the solutions investigated. In chloride solution continuous absorption occurs in the near ultra-violet and this partly masks the absorption effect.

It is generally assumed that in the elements of the rare earth group the '4f' shell inside the (5s, p) octet is gradually filled up. In these ions the different orientations of the spin 's' and orbital moment 'l' vectors of the 4f-electrons in the incomplete shell give rise to several quantum states, transitions amongst which result in fairly sharp absorption lines, due to the 4f-electrons being shielded from external perturbations by the screening action of the (5s, p) octet shell. Such absorption lines have been observed in solutions of all rare earth ions with the exception of the Ce^{+++} ion, the first member of the series. The single electron in 4f-shell of Ce^{+++} gives rise to two terms ${}^2F_{5/2}$, ${}^2F_{7/2}$ transition between which can give rise to an absorption line in the infra-red; this line has so far not been observed. On the other hand, due to absorption a second type of electronic excitation is possible, in which the 4f electron may skip over the octet shell and find its place in some outer virtual orbit like 5d, 6s, etc. The energy required for such transition is much higher and therefore the corresponding absorption is to be expected in the ultra-violet region. Further, the electron in the outer orbit will be subject to the perturbing action of the neighbouring molecules, and hence transition to the outer level will result in broad bands sensitive to external conditions, such

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as is known to be the case in the compounds of the iron group. This latter type of absorption of the Ce^{+++} ion in solution was first investigated by Bose and Datta,¹ who observed two bands at 2970\AA , 2525\AA , and later three more bands at 2380\AA , 2225\AA and 2105\AA . The first two bands were ascribed to the transitions $4^2F_{3/2} - 5^2D_{3/2, 5/2}$ and this explained all their peculiarities. Freed² studied these bands over a wide range of temperature from room temperature to that of liquid hydrogen, using cerium chloride and cerium-ethyl sulphate, both diluted and undiluted with the corresponding isomorphous lanthanum salts. There is a considerable shift in the position of the bands with the change of temperature as also with the change of the anions, and from these Freed was led to the conclusion that the bands have their origin in transitions to some virtual outer orbit, such as $5d$, which is split up in the inhomogeneous crystalline electric field.

In the ions of the next higher elements, viz., Pr^{+++} and Nd^{+++} , the line absorption is known from a long time and it seemed worth-while to investigate whether this second type of absorption, giving rise to broad and diffuse band, also exists. It is well known that with the increasing atomic number, the position of the bands, if there be any, will shift gradually to the farther ultra-violet side. The present work was undertaken with the object of investigating the presence of similar absorption bands, if any, in the ions of the second and third members of the rare earth series. The salts of Pr^{+++} and Nd^{+++} of very high purity both as chloride and sulphate, were kindly supplied by Dr. P. B. Sarkar, of the Chemistry Department.

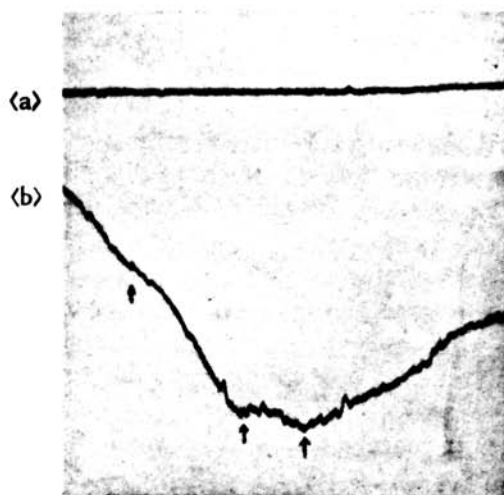
The investigation was carried out by two different methods, viz., (1) with a spectrograph and (2) with a Hilsch double monochromator, which are described below.

1. In the qualitative investigation of absorption a quartz Hilger spectrograph and a hydrogen discharge tube were used. The latter was run from a small 3 K. V. transformer with a current not exceeding 100 M. A.

RESULTS.

(a) It was found using $Pr_2(SO_4)_3$ solution that at a certain concentration a broad and diffuse band made its appearance, extending from 2750\AA to 2530\AA . On increasing the dilution still more, the broad band began to show some structure and at a suitable concentration three separate component bands were distinctly visible, all of them being weak and diffuse. The mean positions of the centres of the bands are given in table I together with the dilution at which they appear most distinct. A microphotometric record of the absorption spectra is reproduced in figure 1, along with that of the continuous source used. The absorption spectra are shown in figure 2.

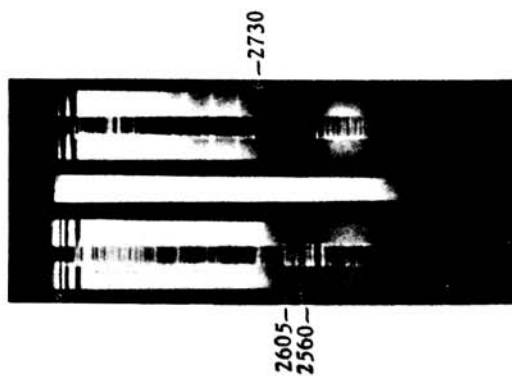
Fig. 1



(a) Microphotometric record of the continuous source.

(b) do do of the absorption spectra of $\text{Pr}_2(\text{SO}_4)_3$ soln. in water. Bands at 2730, 2605 and 2560 Å (from the left).

Fig. 2



The result with the chloride solution, however, was not so satisfactory, there being a continuous absorption in the ultra-violet which could not be got over even by repeated treatment with HCl and re-crystallisation.

TABLE I.

Dilution.	Thickness.	Centre of absorption bands.
1/10 mol.	5 cms ₄	(One band) 2750 Å—2530 Å
1/40 mol.	..	(Three bands) 2730Å, 2605Å and 2560Å.

(b) $\text{Nd}_2(\text{SO}_4)_3$ solution was similarly investigated, but no such broad or diffuse absorption band was noticed. Some lines both of sharp and diffuse nature, which have not been previously noted, appeared in the ultra-violet extending upto 2500Å, but no band of the type discussed above could be discerned even upto 2250Å, which marked the long wave-length edge of the continuous absorption. On increasing dilution, gradually the position of the absorption edge shifted to the ultra-violet side, till finally the whole of the ultra-violet region upto 2100Å, was transmitted. The position and nature of these new lines obtained are given in table II.

In repeating the experiment with NdCl_3 solution, difficulties, similar to those met with in PrCl_3 solution, were experienced—continuous absorption commencing at much longer wave-length. In consequence of this, the last two of the new lines were not observed when using the chloride solution.

TABLE II.

Number.	Nature.	Wave-length.
1	Very sharp ; weak	2775 Å
2	do. do.	2730 Å
3	Diffuse ; weak	2600 Å
4	do. do.	2505 Å

2. The absorption was next studied with a Hilsch double monochromator, in order to estimate the intensity of absorption as also to determine precisely the position of the bands. The details of the working of the instrument is given in a joint paper by Hilsch and Pohl³ and the actual experimental arrangement here adopted was the same as that used by Datta and Deb⁴ in their recent investigations on Ce^{+++} ion.

In order to measure the absorption, two identical quartz cells were filled respectively with the solution of suitable strength and distilled water, and were placed successively in the path of the monochromatic beam, the photoelectric current being recorded in each case. The ratio of the currents gave the ratio of the intensities of the transmitted light in either case from which the percentage of absorption was calculated. This was repeated at close intervals on the monochromator scale and a curve drawn with the percentage of absorption and wave-length as ordinate and abscissa.

The curve for $\text{Pr}_2(\text{SO}_4)_3$ solution is given in figure 3 in which using very dilute solution the first band is isolated, but the following two closer bands coalesce into one on account of the relatively small dispersion of the monochromator. The wave-lengths corresponding to the absorption peaks observed here are given in table III. This whole process was repeated with $\text{Nd}_2(\text{SO}_4)_3$ solution and observation continued up to 2350 \AA , the short wave-length limit of the intense portion of the spectrum emitted by tungsten-steel spark, but no selective absorption band could be detected.

FIG. 3.

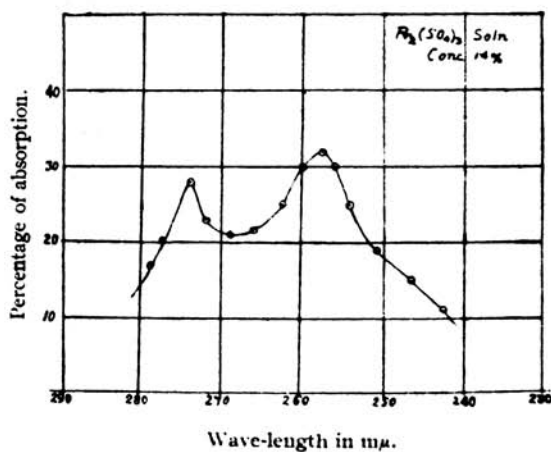


TABLE III.

Concentration	Thickness	Absorption maxima
1.4 %	1 cm.	2735 \AA .
		2573 \AA .

DISCUSSION OF RESULTS.

In Pr^{++} ion, with the sulphate solution a broad diffuse band is observed which shows a distinct structure on dilution, being resolved into three components at 2730 \AA , 2605 \AA and 2560 \AA . This is in contradistinction to the behaviour of the other lines and bands in the visible region, where no amount of dilution brings in any change in structure, there being only a gradual fading of the absorption lines and bands with the reduced concentration of the ion. Further, it is well-known that the $(\text{SO}_4)^{--}$ ion has no absorption in the ultra-violet region before $200m\mu$, so that the band observed here must be associated with the cation, Pr^{++} . The origin of this diffuse band, so sensitive to the influence of the neighbouring ions and molecules, from which the inner states are completely free, is to be attributed to a transition from an inner to a virtual outer orbit of the cation, as has been done successfully for the Ce^{++} ion. Again, in the latter case the first band appears at 3000 \AA , which is decidedly on the longer wave-length side of the band in question in accordance with expectations.

The outer electronic configuration of the Pr^{++} ion in the unexcited state is given by

$4f$	$5s$	$5p$	$5d$	$6s$	$6p$
2	2	6	—	—	—

and on account of the complication arising from the presence of two electrons in the $4f$ -shell, it is difficult to ascertain the particular quantum transition giving rise to the bands. The equivalent electrons in any shell have generally their l -moments strongly coupled with each other as also their s -moments, and accordingly the states allowed for the two $4f$ -electrons are given by ${}^3(H, F, P)$ and ${}^1(I, G, D, S)$, of which 3H evidently represents the ground or normal state. When in the process of absorption one of these two electrons is excited to the next outer virtual orbit, *viz.*, $5d$, the state of lowest energy of the new configuration ($4f, 5d$) is again given by 3H ; and this transition is forbidden by the usual selection rules. On the other hand, if the electron proceeds to $6s$ or $6p$ orbits, the final states are 3F or 3G , of which the former is again forbidden as the l -value differs by 2 from that of the normal state. The latter transition, though not impossible would be infrequent on account of the increase of the principal quantum number by two units and hence would result in a very faint band, which would be located in the far ultra-violet. If, on the contrary, it be assumed that the strong coupling between the l - and s -vectors of the two $4f$ -electrons no longer exists when the ion is in the excited state, as they are separated by a closed octet shell, the other type of coupling, *viz.*, the j - j coupling is possible. According to this second type of coupling, it is easy to see that the transition of one of the electrons from $4f$ to $5d$ orbit is quite possible, and it may be concluded, therefore, that the band is due to similar transition as in the Ce^{++} ion. The higher bands due

to excitation to still higher orbits will naturally be much weaker and lie on the far ultra-violet side and so have not been observed.

The result obtained with Nd^{+++} -ion is not so conspicuous. New lines have been observed in addition to those obtained previously by Baxter and his co-worker⁵, which are more or less sharp and their appearance is not influenced by change in concentration. Freed⁶ has reported to have observed a very weak and broad band of diffuse nature, extending from 2280 to 2100 Å, using undiluted crystal of $NdCl_3 \cdot 6H_2O$. The nature and position of the band is in close conformity with the above view, remembering that Nd is the third member in the rare earth series; but in the present investigation no trace of such a band was perceptible.

As noted above the absorption bands in solutions of the rare earth chlorides are not so prominent as those in the case of sulphate solutions, as their effect in the former case is masked by the presence of continuous absorption on the ultra-violet side. In order to test whether the continuous absorption in the chloride solution was due to formation of any complex ions on aging, a portion of the sulphate solution was converted into chloride solution of the same strength and the fresh solution examined spectroscopically. It was found that the continuous absorption still persisted and masked the appearance of the selective bands. This shows that the continuous absorption was not due to any effect of aging of the solution but is to be attributed to the presence of the halogen anion. The presence of such continuous absorption in the near ultra-violet region has been noticed in other halide solutions, when the halogen atom is attached by covalent bond to the metal atom. It is, therefore, to be presumed that in the chloride solutions of Pr^{+++} - and Nd^{+++} -ions investigated, there is some sort of covalent binding, resulting in the near ultra-violet continuous absorption, which is not the case with the more stable sulphate solutions.

In conclusion, the writer desires to express his grateful thanks to Prof. D. M. Bose, for his kind interest and advice during the progress of the work.

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REFERENCES.

- 1 D. M. Bose and S. Datta, *Nature.*, **138**, 270 (1931).
Zett. f. Phys., **80**, 378 (1933).
- 2 S. Freed, *Phys. Rev.*, **38**, 2123 (1931).
- 3 R. W. Pohl, *Nachr. d. Gotting. Akad. d. Wissensch.*,
Math-Phys. Klasse, 185 (1936).
R. Hilsch Zeits. f. Phys., **84**, 421 (1927).
- 4 S. Datta and M. Deb, *Ind. J. Phys.*, **10**, 163 (1936).
- 5 Baxter and Woodward, *J.A.C.S.*, **33**, 270 (1911).
- 6 S. Freed, *loc. cit.*