

## The Absorption of Praseodymium Ion in Solutions and in the Solid State

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Following the methods outlined in Condon and Shortley's *Theory of Atomic Spectra*, the energy states of praseodymium IV were calculated. It was assumed in the solid and liquid phases that the sharp absorption spectrum would arise from transitions within the incomplete  $4f$  shell, in other words from states arising from the  $f^2$  configuration. Excellent agreement was found with the experimentally observed values of Pr IV.

THE absorption spectrum of praseodymium ion in solutions and in the solid state has been studied by a great many investigators during the past forty years. The spectrum always consists of three narrow bands in the blue-green region and an additional band in the red. These bands show some structure at room temperatures and resolve into many extremely sharp lines at low temperatures. While the positions of these bands in the spectrum remain approximately constant regardless of the praseodymium compound and are therefore to be attributed to electronic transitions involving the Pr ion, they do shift slightly, and the fine structure of the bands may vary considerably.

On account of the weak intensity and extreme sharpness of these bands Van Vleck<sup>1</sup> concluded on theoretical grounds that they must be due to transitions between electronic states arising from rearrangement of the  $4f$  electrons of the rare earth ion. In other words they are transitions entirely within the incomplete  $4f$  shell. If this is true and if Russell-Saunders coupling is assumed, it can readily be shown by the application of Pauli's principle that the only states allowed for  $\text{Pr}^{+++}$  are  $^3H$ ,  $^3F$ ,  $^3P$ ,  $^1I$ ,  $^1G$ ,  $^1D$  and  $^1S$  and that the absorption bands must arise from transitions between these states. Hund's<sup>2</sup> work on magnetic susceptibilities shows that at least for the lowest state Russell-Saunders coupling is closely approximated.

From analogy with the La II spectrum Ellis<sup>3</sup> concluded that the blue bands of praseodymium arose from a  $^3H_4 - ^3P_{0,1,2}$  and that the red band

arose from the  $^3H_4 - ^1I_6$  transition. Bethe and Spedding<sup>4</sup> next showed that the spectrum of Tm IV could be completely accounted for on theoretical grounds. This is the companion rare earth to Pr IV and has the same energy states except that they are inverted due to the incomplete  $4f$  shell being more than half completed. They assumed that the bands were due to transitions between states arising from the  $4f^{12} = 4f^2$  configuration. Following the methods outlined in the book by Condon and Shortley,<sup>5</sup> they calculated the separation of the levels due to electrostatic interaction and then took into account the spin-orbital interactions including *perturbations*. It was found for the upper states that Russell-Saunders coupling was far from being obeyed, since in some cases the perturbations amounted to as much as  $10,000 \text{ cm}^{-1}$ . The theoretically predicted bands, however, are in excellent agreement with the experimentally observed ones, the discrepancies in all cases being much smaller than might reasonably be expected when one considers the very simple assumptions which were made in the theoretical calculations. This holds also for the four new bands<sup>6</sup> which now have been observed, but which were not reported at the time the predictions were made.

<sup>4</sup> H. Bethe and F. H. Spedding, *Phys. Rev.* **52**, 454 (1937).

<sup>5</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge 1935), p. 207.

<sup>6</sup> Selection rules state that the  $^3H_6 - ^3P_1$   $^3H_6 - ^3P_0$  should be absent or at least very faint. Gobrecht, *Ann. d. Physik* **31**, 600 (1935), finds bands between  $34,000 \text{ cm}^{-1}$  and  $38,000 \text{ cm}^{-1}$  which he attributes to Tm IV but states his salts contained Gd as an impurity. Meehan and Nutting, *J. Chem. Phys.* **7**, 1001 (1939), fail to report any bands in this region. Spedding and Gladrow in work now in progress have photographed  $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  crystals 2.5 mm in thickness and find no trace of these bands. They are planning to photograph much thicker crystals in the near future to see if any trace of them exists.

<sup>1</sup> J. H. Van Vleck, *J. Phys. Chem.* **41**, 67 (1937).

<sup>2</sup> F. Hund, *Zeits. f. Physik* **33**, 855 (1925).

<sup>3</sup> C. B. Ellis, *Phys. Rev.* **49**, 875 (1936).

Lueg,<sup>7</sup> Freyman and S. Takavorian,<sup>8</sup> Gobrecht<sup>9</sup> and Rosenthal,<sup>10</sup> have investigated the infra-red spectrum of praseodymium and have reported bands at about 5200, 6500 and 9800  $\text{cm}^{-1}$ . Lange<sup>11</sup> by arbitrarily evaluating the  $F$  constants in the formulae for the  $f^2$  configuration given by Condon and Shortley<sup>12</sup> in their electrostatic-interaction calculations, forces a rough fit with experimentally obtained levels. It is tacitly assumed that good Russell-Saunders coupling is

TABLE I. *Electrostatic interaction.*

	LaII $\text{cm}^{-1}$	PrIV $\text{cm}^{-1}$	TmIV $\text{cm}^{-1}$
<sup>3</sup> H	0	0	0
<sup>3</sup> F	1,718	4,120	5,670
<sup>1</sup> G	2,750	6,600	9,080
<sup>1</sup> D	3,260	7,820	10,750
<sup>1</sup> I	5,964	14,330	19,700
<sup>3</sup> P	8,015	19,230	26,450
<sup>1</sup> S	13,756	33,000	45,400

obeyed by all levels, and that the perturbations can be neglected. Gobrecht<sup>13</sup> extending Lange's work does the same thing for Tm and also obtains a forced agreement. He objects to the spectroscopic designations given the bands by Bethe and Spedding<sup>4</sup> on the grounds that they used the wrong screening constant. This objection is groundless, since Bethe and Spedding calculated the spacing of the levels for various values of Condon and Shortley's<sup>12</sup>  $\zeta$  which is directly related to the screening constant  $\sigma$  and chose the best value of  $\zeta$  to fit with experiment. This value is in excellent agreement with the  $\sigma$  determined from x-ray measurements. Further the designations given by Gobrecht must obviously be wrong since he has levels with the same  $J$  quantum number crossing each other which arose from the same electronic configuration. Therefore, the perturbations which he neglected must be extremely large and in fact do amount to as much as 10,000 wave numbers. It also follows that most of the conclusions in these papers regarding screening constants of the rare earths

<sup>7</sup> P. Lueg, *Zeits. f. Physik* **39**, 391 (1926).

<sup>8</sup> R. Freyman and S. Takavorian, *Comptes rendus* **194**, 963 (1932).

<sup>9</sup> H. Gobrecht, *Ann. d. Physik* **28**, 673 (1937).

<sup>10</sup> Gottfried Rosenthal, *Physik. Zeits.* **40**, 508 (1939).

<sup>11</sup> H. Lange, *Ann. d. Physik* **31**, 609 (1938).

<sup>12</sup> E. U. Condon and G. H. Shortley, reference 5, p. 207.

<sup>13</sup> H. Gobrecht, *Ann. d. Physik* **31**, 600 (1938).

are invalid on account of the neglected perturbations.

Mukherji<sup>14</sup> also gives a designation to the transitions of Pr IV and has done this by extrapolating the spacings of the observed levels of La II to the larger spacings which they would occupy in the stronger fields of Pr IV. He has therefore taken into account the perturbations as they exist for La II, but has neglected the greatly increased perturbations which would occur for some levels in Pr IV, and therefore gives the wrong designation for them.

In this paper the levels for the free ion of Pr IV were calculated as follows. For the electrostatic interaction, between the electrons, the calculated value of La II which is analogous to Pr IV was taken as a basis. It was assumed that the spacing between the energy levels without spin orbital interaction is simply multiplied by a constant factor on going from La II to Pr IV. This arises from (a) the higher degree of ionization (b) the greater internal nuclear charge. Assuming Ellis's designation to be correct this turns out to be about 2.4 (Table I).

The constant  $\zeta$ <sup>12</sup> characteristic of the spin-orbit interaction was calculated for La II from the splitting of the  $H$  level which has most nearly Russell-Saunders coupling and was found to be about 170  $\text{cm}^{-1}$ . It is assumed that  $\zeta$  increased again by a factor of 2.4 from La II to Pr IV and should therefore be about 400  $\text{cm}^{-1}$  for Pr IV. In column 2 of Table II the positions of the Pr levels are given for this value of  $\zeta$  when the perturbations are omitted, in other words, pure Russell-Saunders coupling is assumed to exist. In column 3, the positions of the levels are given

TABLE II. *Spin orbital interaction with and without perturbations.*

	$\zeta = 400 \text{ cm}^{-1}$			$\zeta = -1,400 \text{ cm}^{-1}$			
	PrIV WITHOUT	PrIV WITH	$\Delta$	TmIV WITHOUT	TmIV WITH	$\Delta$	
<sup>3</sup> H <sub>4</sub>	-2,400	-2,639	+239	<sup>3</sup> H <sub>6</sub>	-7,000	-7,490	+490
<sup>3</sup> H <sub>5</sub>	-400	-400	0	<sup>3</sup> H <sub>5</sub>	1,400	1,400	0
<sup>3</sup> H <sub>6</sub>	2,000	+1,923	+77	<sup>3</sup> H <sub>4</sub>	8,400	-1,925	+10,325
<sup>3</sup> F <sub>2</sub>	2,520	1,857	+663	<sup>3</sup> F <sub>4</sub>	1,470	5,780	-4,310
<sup>3</sup> F <sub>3</sub>	3,720	3,720	0	<sup>3</sup> F <sub>3</sub>	7,070	7,070	0
<sup>3</sup> F <sub>4</sub>	5,320	4,391	+929	<sup>3</sup> F <sub>2</sub>	11,270	3,250	+8,020
<sup>1</sup> G <sub>4</sub>	6,600	7,767	-1,167	<sup>1</sup> G <sub>4</sub>	9,080	15,090	-6,010
<sup>1</sup> D <sub>2</sub>	7,820	8,239	-419	<sup>1</sup> D <sub>2</sub>	10,750	16,240	-5,490
<sup>1</sup> I <sub>6</sub>	14,330	14,407	-77	<sup>1</sup> I <sub>6</sub>	19,700	20,190	-490
<sup>3</sup> P <sub>0</sub>	18,430	17,921	+509	<sup>3</sup> P <sub>2</sub>	25,000	27,530	-2,530
<sup>1</sup> P <sub>1</sub>	18,830	18,830	0	<sup>3</sup> P <sub>1</sub>	27,800	27,800	0
<sup>3</sup> P <sub>1</sub>	19,630	19,873	-243	<sup>3</sup> P <sub>0</sub>	29,200	24,665	+4,535
<sup>1</sup> S <sub>0</sub>	33,000	33,509	-509	<sup>1</sup> S <sub>0</sub>	45,400	49,935	-4,535

<sup>14</sup> P. C. Mukherji, *Ind. J. Phys.*, January, 1938, p. 399.

after perturbations are taken into account. This was done according to the methods outlined by Condon and Shortley<sup>15</sup> or M. H. Johnson, Jr.<sup>16</sup> The secular equations for the  $f^2$  configuration are given below.

$$\begin{array}{l}
 J=6 \quad \begin{array}{cc} {}^1I_6 & {}^3H_6 \\ \begin{array}{|c|} \hline I & 6\frac{1}{2}\zeta \\ \hline \end{array} & \begin{array}{|c|} \hline 6\frac{1}{2}\zeta & H+5\zeta \\ \hline \end{array} \end{array} \\
 \\
 J=5 \quad \begin{array}{c} {}^3H_5 \\ \begin{array}{|c|} \hline H-\zeta \\ \hline \end{array} \end{array} \\
 \\
 J=4 \quad \begin{array}{ccc} {}^3H_4 & {}^1G_4 & {}^3F_4 \\ \begin{array}{|c|} \hline H-6\zeta & -2(10/3)\frac{1}{2}\zeta & 0 \\ \hline \end{array} & \begin{array}{|c|} \hline -2(10/3)\frac{1}{2}\zeta & G & 2(11/3)\frac{1}{2}\zeta \\ \hline \end{array} & \begin{array}{|c|} \hline 0 & 2(11/3)\frac{1}{2}\zeta & F+3\zeta \\ \hline \end{array} \end{array} \\
 \\
 J=3 \quad \begin{array}{c} {}^3F_3 \\ \begin{array}{|c|} \hline F-\zeta \\ \hline \end{array} \end{array} \\
 \\
 J=2 \quad \begin{array}{ccc} {}^3F_2 & {}^1D_2 & {}^3P_2 \\ \begin{array}{|c|} \hline F-4\zeta & -2(6)\frac{1}{2}\zeta & 0 \\ \hline \end{array} & \begin{array}{|c|} \hline -2(6)\frac{1}{2}\zeta & D & 3(2)\frac{1}{2}\zeta \\ \hline \end{array} & \begin{array}{|c|} \hline 0 & 3(2)\frac{1}{2}\zeta & P+\zeta \\ \hline \end{array} \end{array} \\
 \\
 J=1 \quad \begin{array}{c} {}^3P_1 \\ \begin{array}{|c|} \hline P-\zeta \\ \hline \end{array} \end{array} \\
 \\
 J=0 \quad \begin{array}{cc} {}^3P_0 & {}^1S_0 \\ \begin{array}{|c|} \hline P-2\zeta & -4(3)\frac{1}{2}\zeta \\ \hline \end{array} & \begin{array}{|c|} \hline -4(3)\frac{1}{2}\zeta & S \\ \hline \end{array} \end{array}
 \end{array}$$

These equations were solved for  $\zeta$  equals 350  $\text{cm}^{-1}$ , 400  $\text{cm}^{-1}$  and 450  $\text{cm}^{-1}$ , and the results compared with experiment. The best agreement was found for a value of  $\zeta=400$  in good agreement with our preliminary assumption. The agreement with experiment was exceptionally

TABLE III. Comparison of calculated and observed terms.

	PrIV CALC. CM <sup>-1</sup>	PrIV OB. CM <sup>-1</sup>	TmIV CALC.	TmIV OB.
<sup>3</sup> H <sub>4</sub>	0	0	<sup>3</sup> H <sub>6</sub>	0
<sup>3</sup> H <sub>5</sub>	2,239		<sup>3</sup> H <sub>4</sub>	5,565
<sup>3</sup> F <sub>2</sub>	4,496	4,750 *	<sup>3</sup> H <sub>5</sub>	8,490
<sup>3</sup> H <sub>6</sub>	4,562	5,650 }	<sup>3</sup> F <sub>2</sub>	10,740
<sup>3</sup> F <sub>3</sub>	6,359	5,950 **	<sup>3</sup> F <sub>4</sub>	13,270
<sup>3</sup> F <sub>4</sub>	7,030	7,250 }	<sup>3</sup> F <sub>3</sub>	14,560
<sup>1</sup> G <sub>4</sub>	10,406	9,469 }	<sup>1</sup> G <sub>4</sub>	22,580
<sup>1</sup> D <sub>2</sub>	10,878	10,200 }	<sup>1</sup> D <sub>2</sub>	23,730
<sup>1</sup> I <sub>6</sub>	17,046	16,630 }	<sup>1</sup> I <sub>6</sub>	27,680
		17,480 }		
<sup>3</sup> P <sub>0</sub>	20,560	20,660 }	<sup>3</sup> P <sub>0</sub>	32,155
		20,910 }		
<sup>3</sup> P <sub>1</sub>	21,469	21,150 }	<sup>3</sup> P <sub>2</sub>	35,020
		22,305 }		
<sup>3</sup> P <sub>2</sub>	22,512	22,810 }	<sup>3</sup> P <sub>1</sub>	35,290
		24,050 }		
<sup>1</sup> S <sub>0</sub>	36,144		<sup>1</sup> S <sub>0</sub>	57,425

\*Maximum at 5180  $\text{cm}^{-1}$ .

\*\*Maximum at 6557  $\text{cm}^{-1}$  shows a distinct indentation on short wave side.

† These bands were not observed when levels were first calculated. See reference 6.

good (see Table III), the deviations in every case being much smaller than one might expect considering the simple assumptions used. Further in every case where a band was predicted one was found except for the <sup>3</sup>H<sub>4</sub>–<sup>3</sup>H<sub>5</sub> transition which occurs so far in the infra-red that that region of the spectrum has not yet been investigated. In no case was a band found where none was predicted. Also the interpretation of the spectrum of praseodymium is completely consistent with the interpretations of the spectrum of La II and Tm IV. By shifting the arbitrary constants slightly (2.4 for the electrostatic interaction and 400  $\text{cm}^{-1}$  for  $\zeta$ ) an apparently better fit with experiment might have been obtained. It would not, however, have had any real meaning unless the fine structure of the multiplets due to crystal splitting had been investigated and other possible perturbations taken into account.<sup>17</sup>

<sup>17</sup> The multiplets due to crystal splitting are always associated with superimposed crystal and molecular frequencies. This causes the multiplets to be composed of many lines. As the sharp absorption spectra are obtained at low temperatures, the observed associated lines are usually due to vibrations superimposed on the excited or upper state and therefore the lines usually occur on the violet side of the multiplets.

<sup>15</sup> E. U. Condon and G. H. Shortley, reference 5, p. 267.

<sup>16</sup> M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).