Diffuse Reflectance Spectrum of Some Pr$^{3+}$ Complexes

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Diffuse reflectance spectra of eight Pr$^{3+}$ complexes in the visible region have been recorded for the first time. From them, values of Slater-Condon ($F_2$, $F_4$, $F_6$), Racah ($E^2$, $E^3$, $E^4$) interelectronic repulsion, and Landé ($\xi_l$) parameters have been computed. The decrease in $F_2$ values of the complexes as compared to the free ion is greatest among all the parameters. The bonding parameter $b_k$ has been computed from the observed nephelauxetic ratio. The relative variation of covalent bonding in the complexes has been discussed.

Introduction

The diffuse reflectance spectra of some 3d complexes$^{1-7}$ and other compounds$^{8-11}$ has been studied recently. But in the case of 4f complexes no such studies have been reported. The absorption spectra of these complexes have been widely studied$^{12-19}$ either in solutions or in rare earth doped crystals. In the former, the effect of the solvent, and in the later the crystal forces affect the spectrum of the complex. The diffuse reflectance is expected to give an unmodified spectrum which is analogous to the absorption spectrum due to the complex alone. Consequently, the present investigations on Pr$^{3+}$ complexes were carried out. This article reports the values of Slater-Condon ($F_2$), Racah ($E^2$), Landé ($\xi_l$) and bonding ($b_k$) parameters and electronic states computed from these parameters in the case of eight Pr$^{3+}$ complexes.

I. Experimental and Results

Diffuse reflectance from the samples has been measured with a Hilger's UVISPEK spectrophotometer fitted with an annular ring type of diffuse reflectance attachment. Lithium fluoride has been used as reference standard for the reasons described in earlier communications. The praseodymium oxide, chloride and sulphate under study were of spectrograde. The Pr$^{3+}$ complexes of acetylacetonate (A), benzoylacetonate (BA), thenonylfluoroacetate (TFA), ethyl-1-methylacetoacetate (E-1-MA) and ethylacetoacetate (EA) were synthesised using the method described by WHAN and coworkers$^{20,21}$ starting with PrCl$_3$ of spectrograde. The reagents used were of A.R. grade. The observed and calculated energy levels have been given in Table 1.

II. Parameters

The forbidden transitions within the ground 4$^2$ configuration give rise$^{19}$ to the visible and near

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7 S. P. TANDON and J. P. GUPTA, Spect. Letters, in press.
infrared spectrum of Pr$^{3+}$. The energy level structure of 4f$^2$ configuration to a first approximation may be considered to arise from electrostatic and magnetic interactions between the 4f electrons. The electrostatic interaction ($E_e$) and Slater-Condon ($F_{kk}$) parameters are related by

$$ E_e = \sum_{k=0}^{6} j^k F_{kk} = \sum_{k=0}^{6} j^k F_{kk} \tag{1} $$

where $j^k$ is the angular coefficient and $F_{kk}$ is given by

$$ F_{kk} = D_{kk} \int_0^\infty \int_0^\infty r_< r_<^k r_>^{k+1} R^2(r_1) R_2(r_2) dr_1 dr_2 \tag{2} $$

where the subscripts 1 and 2 refer to electron 1 and 2, respectively, $R$ is the 4f radial function, $r_<$ denotes the radius of the electron near the nucleus, $r_>$ denotes the radius of more distant electrons, $D_{kk}$'s denote the denominators whose values are given in CONDON and SHORTLEY’S book. In Eq. (1) $k$ is even and the $j^k$'s are coefficients of the linear combination and represent the angular part of the interaction. The Racah parameters, $F_{kk}$s, as shown below, are linear combinations of the $F_{kk}$'s.

$$ E^3 = (70 F_2 + 231 F_4 + 2002 F_6)/9, $$
$$ E^2 = (F_2 - 3 F_4 + 7 F_6)/9, $$
$$ E^1 = (5 F_2 + 6 F_4 - 91 F_6)/3. \tag{3} $$

The spin orbit interaction is an important magnetic interaction. Its energy $E_{so}$ is given by

$$ E_{so} = A_{so} \zeta_{4t} \tag{4} $$

where $A_{so}$ represents the angular part and $\zeta_{4t}$ the radial integral, known as Landé parameter. The nephelauxetic ratio $\beta$ is given by

$$ \beta = F_k^S / F_k^F \tag{5} $$

where $F_k^S$ and $F_k^F$ refer to the complex and free ion respectively. The bonding parameter $b^{1/2}$ is given by

$$ b^{1/2} = [\frac{1}{2} (1 - \beta)]^{1/2}. \tag{6} $$

III. Evaluation of Parameters and Energy Levels

Since the transitions to all the expected levels have not been observed in the present case, it is not possible to evaluate all the $F_k$ and $\zeta_{4t}$ parameters simultaneously by the method of least squares fit to energy levels. It has been shown earlier that in this case the radial eigenfunctions may be reasonably assumed to be hydrogenic. Under this assumption the ratios of the $F_k$'s for 4f electrons are

$$ F_4/F_2 = 0.13805, \quad F_6/F_4 = 0.01511. \tag{7} $$

The parameters $F_2$ and $\zeta_{4t}$ can be evaluated by expressing the energy of the levels as a Taylor series expansion

$$ E_j(F_2, \zeta_{4t}) = E_{0j}(F_2, \zeta_{4t}) + (\partial E_j/\partial F_2) \Delta F_2 $$
$$ + (\partial E_j/\partial \zeta_{4t}) \Delta \zeta_{4t}. \tag{8} $$

The $\beta$ and $b^{1/2}$ values have been calculated using Eqs. (5) and (6) respectively. The computed values of various parameters have been collected in Table 2.

The energy levels have been computed from the refined set of $F_k$ and $\zeta_{4t}$ parameters.

IV. Discussion

Energy Levels

A comparison of the observed and calculated values of energy levels (Table 1) show that the average deviation is 36 to 97. The r.m.s. deviation 46 to 126 indicates good results even though the radial eigenfunctions have been assumed to be hydrogenic.

Interelectronic Repulsion and Magnetic Interaction Parameters

The interelectronic repulsion, $F_k$ and $E_k$, and Landé $\zeta_{4t}$ parameters exhibit a decrease from the values of the corresponding parameters of Pr$^{3+}$ "free" ion (Table 2). This is due to the decrease in interelectronic repulsion and spin-orbit interaction due to expansion of the central metal ion orbital on complexation.

Table 1. Energy level assignments of Pr\(^{3+}\) complexes.

<table>
<thead>
<tr>
<th>Levels</th>
<th>PrCl(_3)</th>
<th>Pr(_2)(SO(_4))(_3)</th>
<th>Tris-E-1-MA</th>
<th>Tris-BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{1}\text{D}_2)</td>
<td>16 949 215</td>
<td>17 035 75</td>
<td>16 806 230</td>
<td>16 750 122</td>
</tr>
<tr>
<td>(^{3}\text{P}_0)</td>
<td>20 746 0</td>
<td>20 618 61</td>
<td>20 068 0</td>
<td>20 408 66</td>
</tr>
<tr>
<td>(^{3}\text{P}_1)</td>
<td>21 276 14</td>
<td>21 276 -66</td>
<td>21 052 55</td>
<td>20 920 -44</td>
</tr>
<tr>
<td>(^{3}\text{P}_2)</td>
<td>22 472 18</td>
<td>22 472 -66</td>
<td>22 371 -89</td>
<td>22 123 -114</td>
</tr>
</tbody>
</table>

Average deviation: 62, 67, 94, 87
rms deviation: 108, 67, 126, 92

<table>
<thead>
<tr>
<th>Levels</th>
<th>Pr(_2)O(_3)</th>
<th>Tris-EA</th>
<th>Tris-A</th>
<th>Tris-TFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{1}\text{D}_2)</td>
<td>16 949 121</td>
<td>16 806 235</td>
<td>16 806 -3</td>
<td>16 750 10</td>
</tr>
<tr>
<td>(^{3}\text{P}_0)</td>
<td>20 618 -17</td>
<td>20 576 -6</td>
<td>20 424 -1</td>
<td>20 120 65</td>
</tr>
<tr>
<td>(^{3}\text{P}_1)</td>
<td>21 186 -81</td>
<td>21 033 -86</td>
<td>20 833 -178</td>
<td>21 881 -1</td>
</tr>
<tr>
<td>(^{3}\text{P}_2)</td>
<td>22 321 -15</td>
<td>22 123 -178</td>
<td>21 223 -180</td>
<td>21 881 -1</td>
</tr>
</tbody>
</table>

Average deviation: 97, 84, 67, 36
rms deviation: 107, 124, 99, 46

Table 2. Computed values of various parameters of Pr\(^{3+}\) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(F_2) Cm(^{-1})</th>
<th>(F_4) Cm(^{-1})</th>
<th>(F_6) Cm(^{-1})</th>
<th>(\zeta_{4f}) Cm(^{-1})</th>
<th>(E^1) Cm(^{-1})</th>
<th>(E^2) Cm(^{-1})</th>
<th>(E^3) Cm(^{-1})</th>
<th>(\beta)</th>
<th>(b^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free ion</td>
<td>322.1(^{27})</td>
<td>44.46</td>
<td>4.867</td>
<td>741.0</td>
<td>4729</td>
<td>24.75</td>
<td>478.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PrCl(_3)</td>
<td>310.2</td>
<td>42.82</td>
<td>4.887</td>
<td>714.4</td>
<td>4464</td>
<td>23.84</td>
<td>460.47</td>
<td>0.9635</td>
<td>0.135</td>
</tr>
<tr>
<td>Pr(_2)(SO(_4))(_3)</td>
<td>308.4</td>
<td>42.71</td>
<td>4.875</td>
<td>708.4</td>
<td>4433</td>
<td>23.77</td>
<td>459.28</td>
<td>0.9606</td>
<td>0.140</td>
</tr>
<tr>
<td>Tris-ethyl-1-methyl acetooacetate</td>
<td>309.1</td>
<td>42.67</td>
<td>4.671</td>
<td>687.7</td>
<td>4448</td>
<td>23.75</td>
<td>458.82</td>
<td>0.9596</td>
<td>0.142</td>
</tr>
<tr>
<td>Tris-benzoylacetonate</td>
<td>308.2</td>
<td>42.55</td>
<td>4.657</td>
<td>645.5</td>
<td>4436</td>
<td>23.68</td>
<td>457.50</td>
<td>0.9568</td>
<td>0.147</td>
</tr>
<tr>
<td>Pr(_2)O(_3)</td>
<td>308.1</td>
<td>42.53</td>
<td>4.655</td>
<td>715.3</td>
<td>4434</td>
<td>23.66</td>
<td>457.36</td>
<td>0.9565</td>
<td>0.147</td>
</tr>
<tr>
<td>Tris-ethylacetooacetate</td>
<td>307.8</td>
<td>42.49</td>
<td>4.651</td>
<td>710.1</td>
<td>4430</td>
<td>23.65</td>
<td>456.90</td>
<td>0.9556</td>
<td>0.149</td>
</tr>
<tr>
<td>Tris-acetylacetonate</td>
<td>303.5</td>
<td>41.90</td>
<td>4.586</td>
<td>695.9</td>
<td>4366</td>
<td>23.32</td>
<td>450.52</td>
<td>0.9423</td>
<td>0.170</td>
</tr>
<tr>
<td>Tris-thienoyltrifluoroacetate</td>
<td>302.8</td>
<td>41.80</td>
<td>4.575</td>
<td>692.4</td>
<td>4358</td>
<td>23.27</td>
<td>449.49</td>
<td>0.9408</td>
<td>0.172</td>
</tr>
</tbody>
</table>

\(^{27}\) J. Sugar, Phys. Rev. Letters 14, 731 [1965].

Nephelauxetic Ratio and Bonding

In Table 2 the Pr\(^{3+}\) complexes have been arranged in decreasing order of nephelauxetic ratio and increasing order of bonding parameter \(b^{1/2}\). The \(b^{1/2}\) values are positive indicating covalent bonding. Among the complexes the covalent bonding is least in chloride and maximum in TFA complex.

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