Optical Absorption Spectra of Pr^{3+} in Maleato Complexes

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It is shown that the absorption spectra of $Pr^{3+}(4f^2)$ can be conveniently analysed in terms of Racah parameters (E^1, E^2, E^3), spin-orbit coupling constant (ζ) and configuration-interaction parameters (α, β, γ) by incorporating relationships based on the matrix elements corresponding to the $^3P_1$, $^3P_0$, $^3F_3$ and $^3H_5$ terms and experimental transition energies. The proposed method leads to more reliable results than those from the usual Taylor series method. The absorption spectra of $Pr(Hmale)_3 \cdot 7H_2O$ (H_2male = maleic acid) and Pr^{3+}-doped maleato complexes of Zn^{2+}, Mg^{2+} and Cd^{2+} have been analysed for the energy parameters. The parameters E^1, E^3 and ζ were invariably found to be significantly less than the free-ion values, while E^2 remains practically unchanged. These variations are accounted for in terms of weak covalency and the nephelauxetic effect. The spectral intensities have been analysed in terms of the Judd–Ofelt parameters and predicted lifetimes have been calculated for the transitions $^3P_2 \longleftarrow {}^3H_4$, $^3P_1 \longleftarrow {}^3H_4$, $^3P_0 \longleftarrow {}^3H_4$ and $^1D_2 \longleftarrow {}^3H_4$.

The optical spectra of lanthanides are of great interest for they exhibit laser fluorescence and the potential laser transitions have been identified in trivalent lanthanides such as Pr^{3+}, Dy^{3+} and Eu^{3+}. Also, the effects of the chemical bonding and weak covalency on the lanthanide spectra continues to attract attention.[1-3] An earlier study of the optical spectra of lanthanides including Pr^{3+}, the ion of interest in the present work, was made by Carnall *et al.*[4] It was shown that the absorption spectra line positions for the lanthanides in general may be analysed in terms of the Hamiltonian (1) where H_e corresponds

$$H = H_e + H_{so} \qquad (1)$$

to interactions between pairs of electrons and H_{so} to the spin–orbit coupling. The electrostatic interaction parameters are represented by Slater radial integrals (F_k) or more commonly in terms of Racah parameters (E^k). In addition, configuration interaction which is also important may be written as[4] in equation (2) where α, β and γ are linear combinations of radial

$$H' = \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \text{three-particle terms} \qquad (2)$$

integrals $L = 0, 1, 2 \ldots$ for the states S, P, D . . ., $G(G_2)$ and $G(R_7)$ are the eigen values of Casimir's operator for the f^N configuration and the last term is not considered significant.[4] Thus, for instance, for Pr^{3+} the analysis in principle can be done by writing down seven matrices corresponding to $J = 0$–6 in the intermediate-coupling scheme where the matrix elements are expressed in terms of the Racah parameters (E^1, E^2, E^3), spin–orbit coupling constant (ζ) and the configuration-interaction parameters (α, β, γ).

In this paper we show that the frequently used Taylor series method for evaluation of the energy parameters may not always lead to reliable results, especially when the number of transitions considered is not large. Further, we show that more reliable values for these parameters can be obtained by incorporating conditions based on the matrix elements of terms corresponding to $J = 0$, 1, 3 and 5 and the differences in the observed spectral transition energies. Such a refinement will be particularly useful in the subsequent calcuation of the eigen vectors used in calculation of line intensities according to Judd–Ofelt theory.[5,6] We apply our procedure to those cases where the optical spectra are fairly well known and also to the new systems of heptaaquatris[maleato(1 –)]praseodymium(III) and Pr^{3+}-doped maleates of Mg^{2+}, Cd^{2+} and Zn^{2+}. These systems have been chosen in view of our interest in organic acid complexes.[7-9] The intensities of the lines in the visible spectra in these cases are analysed by the application of the Judd–Ofelt model as this particular lanthanide is known to show exceptional behaviour.[10] We further derive the radiative lifetimes (τ_R) for the easily observed transitions in view of the interest in this ion as a potential laser.[3]

Experimental

Praseodymium oxide was dissolved in concentrated HCl and the chloride precipitated as the hydroxide by dilute NH_4OH. The excess of NH_4OH was eliminated by slow evaporation and the precipitate treated with a 100% excess of maleic acid (H_2 male). On slow cooling light green crystals of praseodymium maleate heptahydrate, $Pr(Hmale)_3 \cdot 7H_2O$ were formed. They were separated, washed with distilled water and dried in a vacuum. The percentage of Pr^{3+} was estimated as the oxide (observed: 23.0; calc.: 22.99%). The compounds zinc maleate tetrahydrate, $Zn(Hmale)_2 \cdot 4H_2O$, and magnesium maleate tetrahydrate, $Mg(Hmale)_2 \cdot 4H_2O$, doped with Pr^{3+} were prepared as described previously.[7] Cadmium maleate dihydrate, $Cd(male) \cdot 2H_2O$, was prepared as described by earlier workers.[11] In all cases, the Pr^{3+} ion was taken as 1 mol % at the beginning of the preparation.

Absorption spectra were recorded in the visible region on a Perkin-Elmer Lambda 3B spectrophotometer and near-IR spectra on a Hitachi-3310 using 1 cm cells. Accurate peak positions were obtained by recording second-derivative spectra. The absorption intensities were determined experimentally by the area method and the oscillator strength f calculated from the reduced expression[12,13] (3) where η is the refractive index

$$f_{\text{exptl}} = (4.31 \times 10^{-9}) \cdot \frac{9\eta^2}{(\eta^2 + 2)^2} \int \varepsilon(\tilde{\nu})\,d\tilde{\nu} \qquad (3)$$

of the solution and $\varepsilon(\tilde{\nu})$ is the molar absorption coefficient at wavenumber $\tilde{\nu}$ in cm^{-1}. The refractive indices were measured on 0.01 mol dm^{-3} solutions using an Abbe refractometer and water as calibrant.

Table 1 Experimental and calculated energy levels (cm^{-1}) of Pr^{3+}

Energy level from state $^3H_4$	$Pr(Hmale)_3 \cdot 7H_2O$		Pr^{3+}-doped $Mg(Hmale)_2 \cdot 4H_2O$		Pr^{3+}-doped $Cd(male) \cdot 2H_2O$		Pr^{3+}-doped $Zn(Hmale)_2 \cdot 4H_2O$	
	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.
$^3P_2$	22 543	22 500	22 573	22 575	22 563	22 524	22 583	22 527
$^3P_1$	21 390	21 410	21 413	21 408	21 366	21 381	21 372	21 391
$^3P_0$	20 833	20 853	20 799	20 790	20 781	20 795	20 790	20 809
$^1D_2$	16 892	16 903	16 872	16 880	16 906	16 927	16 863	16 870
$^3F_4$	6 270	6 266	6 219	6 242	6 204	6 237	6 211	6 223
$^3F_3$	5 963	5 983	5 970	5 965	5 952	5 975	5 964	5 983
r.m.s.	53		26		62		63	

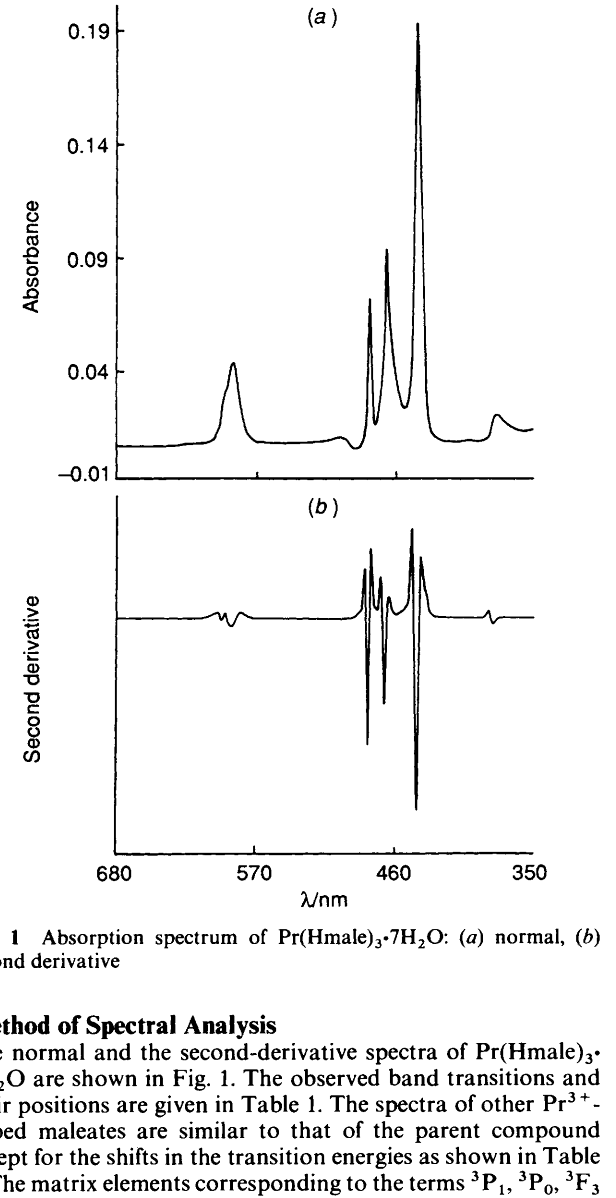

Fig. 1 Absorption spectrum of $Pr(Hmale)_3 \cdot 7H_2O$: (*a*) normal, (*b*) second derivative

Method of Spectral Analysis

The normal and the second-derivative spectra of $Pr(Hmale)_3 \cdot 7H_2O$ are shown in Fig. 1. The observed band transitions and their positions are given in Table 1. The spectra of other Pr^{3+}-doped maleates are similar to that of the parent compound except for the shifts in the transition energies as shown in Table 1. The matrix elements corresponding to the terms $^3P_1$, $^3P_0$, $^3F_3$ and $^3H_5$ lead to the relations (4a)–(4c) where the transition-

$$^3P_1 - {}^3P_0 = \tfrac{1}{2}\{(1 - kR_1)Y + (12 - 10kR_1)\alpha + (1 + kR_1/2)\beta + \gamma + [(1 - kR_1)Y + (12 - 10kR_1)\alpha + (1 + kR_1/2)\beta + \gamma - \zeta + 48\zeta^2]^{\frac{1}{2}}\} \quad (4a)$$

$$^3P_1 - {}^3H_5 = (12Y - 188\alpha - 6\beta)/11 \quad (4b)$$

$$^3F_3 - {}^3H_5 = (3Y - 168\alpha - 7\beta)/11 \quad (4c)$$

energy differences in question can be obtained from the absorption spectra. Here Y is the difference in the transition energies $^3P_1 \longleftarrow {}^3H_4$ and $^3F_3 \longleftarrow {}^3H_4$, R_1 and R_2 are E^1/E^3 and E^2/E^3 respectively, k is a constant equal to 3/11 and α, β, γ and ζ have the same significance as mentioned earlier; R_1, R_2, α, γ and ζ are input parameters, and β can be evaluated from equation (4a). We used free-ion parameters as starting parameters for the full diagonalisation of the matrices, and the parameters were varied systematically with above conditions built in to obtain a good fit between observed and calculated line positions. Incorporation of the above relationships is found to lead to unique values for the parameters. The energy parameters thus obtained for the four maleate complexes are reproduced in Table 2.

The method has been extended to the analysis of the reported optical spectra of Pr^{3+}-doped $LaCl_3$, LaF_3 and Pr^{3+}(aq).[4] The energy parameters thus obtained are found to reproduce the experimental line positions quite satisfactorily. Their values along with the root-mean-square (r.m.s.) values are compared with the earlier reported results in Table 3. The resultant r.m.s. values in our case may be attributed to the uncertainties in the baricentres of the energies, inclusion of which is not warranted unless very well resolved spectral data are available.[4] The r.m.s. values reported for the analysis by the Taylor series method are based on a least-squares fit of the parameters and as such do not truly reflect the deviations. A more appropriate method of checking the results in such cases is a comparison of the r.m.s. deviation between the calculated energies using a full-matrix diagonalisation with the reported energy parameters as input and the experimental positions. The r.m.s. values thus calculated are also given in parentheses in Table 3. From such a comparison (Table 3), it is evident that considerable discrepancies occur in the cases of Pr^{3+}-doped LaF_3 and Pr^{3+}(aq). However, for Pr^{3+}-doped $LaCl_3$ our energy parameters agree closely with those reported.[4] The discrepancies are also revealed by the deviations from the difference in the term energies obtained from line positions which are incorporated in our calculations using equations (4) and those reported by the earlier workers (Table 3).[4]

The following features emerge with respect to the parameters calculated. Non-inclusion of γ is found to lead to $E^1(F_2)$ values larger than the corresponding free-ion values; γ is always found to be positive as suggested.[14,15] The values of β are negative in all cases. The spin–orbit coupling constant, ζ, and $E^1(F_2)$ values are always found to be less than the free-ion value. The values of $E^1(F_2)$ and ζ greater than the free-ion value reported for certain systems[2] may be attributed to non-inclusion of γ. The parameter $E^1(F_2)$ varies by about 5% and ζ varies to a slightly larger extent. Comparison of energy parameters for the earlier reported systems obtained by the above procedure shows that $E^1(F_2)$ and ζ are generally less than the reported values using the Taylor series method and in the cases of Pr^{3+}-doped LaF_3 and Pr^{3+}(aq) ζ is significantly less. The R_1 and R_2 values always lie close to the free-ion values. This is to be expected as they correspond to the ratio of the radial integrals of the electrostatic interactions. In all cases in the present study the corresponding

Table 2 Various energy parameters (cm^{-1}) of prosedymium(III) complexes in solutions

Parameter	$Pr(Hmale)_3 \cdot 7H_2O$	Pr^{3+}-doped $Mg(Hmale)_2 \cdot 4H_2O$	Pr^{3+}-doped $Cd(male) \cdot 2H_2O$	Pr^{3+}-doped $Zn(Hmale)_2 \cdot 4H_2O$
F_2	319.6	316.7	318.3	319.7
F_4	44.4	42.7	43.5	43.9
F_6	4.6	4.3	4.5	4.6
E^1	4646.0	4526.5	4596.4	4631.8
E^2	24.3	24.3	24.4	24.4
E^3	482.4	481.5	480.3	482.0
α	27.9	31.0	28.4	30.6
β	−428.4	−276.3	−319.6	−382.8
γ	690.0	1000.0	700.0	500.0
ζ	686.6	724.7	709.6	709.2
$\bar{\beta}$	0.9795	0.9706	0.9755	0.9798
$b^{\frac{1}{2}}$	0.0857	0.0716	0.0783	0.0711
$T_2(10^9\ cm^2)$	−3.909	−6.54	1.160	14.489
T_4	0.7106	0.785	0.887	1.140
T_6	4.256	3.480	3.716	4.660
$\Omega_2(10^{20}\ cm^2)$	−27.200	−45.200	8.070	100.00
Ω_4	4.940	5.432	6.140	7.880
Ω_6	79.630	24.100	25.700	32.200
η	1.3355	1.3455	1.3440	1.3459

Table 3 Comparison of energy parameters (cm^{-1}) obtained in the present work with those reported earlier[4]

	Free Pr^{3+}		Pr^{3+}-doped $LaCl_3$		Pr^{3+}-doped LaF_3		Pr^{3+}(aq)	
Parameter	Present	Ref. 4	Present	Ref. 4	Present	Ref. 4	Present	Ref. 4
F_2	326.3	322.4	309.9	308.5	315.4	305.1	318.0	305.2
F_4	49.9	49.5	48.2	48.4	51.4	46.9	51.0	46.3
F_6	5.0	4.9	4.8	4.8	4.8	4.4	4.9	4.4
E^1	4924.0	4865.0	4720.0	4714.0	4850.0	4548.0	4868.0	4548.0
E^2	23.5	23.1	22.1	21.9	21.7	21.7	22.3	21.9
E^3	492.0	488.1	466.4	464.2	481.6	470.0	482.0	466.7
α	30.1	23.7	25.6	22.9	30.4	18.6	30.4	21.2
β	−738.8	−585.4	−752.5	−677.0	−1340.0	−754.2	−1602.0	−799.9
γ	690.0	727.8	650.0	599.5	1450.0	1396.0	1446.0	1343.0
ζ	758.9	758.8	742.0	743.0	692.2	743.2	697.0	741.0
r.m.s.	50.0	36.0	45.0	33.0	52.0	47.0	60.0	48.0
		(83.0)*		(82.0)		(88.0)		(108.0)
$^3P_1 - {}^3P_0$	617.5	622.0	606.0	607.0	548.0	629.0	550.0	624.0

* See text.

ratios for the Slater radial integrals F_4/F_2 and F_6/F_2 satisfy the conditions, *viz.* $F_4/F_2 < 0.0206:1$ and $F_6/F_2 < 0.0306:1$.[14,16] The result that $E^1(F_2)$ and ζ are significantly less than the free-ion values is similar to observations made for transition-metal ions and is in accordance with the covalency model proposed which attributes the reduction to the nephelauxetic effect.[1] The nephelauxetic ratio $\bar{\beta}$ is defined as $F^c{}_2/F^f{}_2$ where c and f refer to the complex and free ion respectively. The bonding parameter $b^{\frac{1}{2}}$ given by $[\frac{1}{2}(1 - \bar{\beta})]^{\frac{1}{2}}$ is a measure of the partial covalency in the metal–ligand bond.[15,17] The values of $\bar{\beta}$ and $b^{\frac{1}{2}}$ calculated for the maleato complexes are included in Table 2.

The parameter F_2 is found to be a more reliable covalency parameter in these systems and its values lie in the order Pr^{3+}(free ion, vapour state) > Pr^{3+}-doped LaF_3 > Pr^{3+}(aq) > Pr^{3+}-doped $LaCl_3$. The values for different maleate host lattices are very close to that of the aqua ion, indicating an ionic character intermediate between that of the fluoride and chloride lattices. The spin–orbit coupling constant (ζ) for a given rare-earth-metal ion with different ligands can be complicated in these systems in that, in addition to covalency, configuration interaction is important. This is reflected by the fact that the value for Pr^{3+}-doped $LaCl_3$ is greater than that for Pr^{3+}-doped LaF_3, a result similar to that reported by the earlier workers. For instance, a configuration such as $4d^84f^5$ is known to contribute significantly to Pr^{3+}. The major contribution to γ comes from this configuration and it is found to be quite large and variable in these systems (Tables 2 and 3). This may be the main reason for the observed differences in the ζ values.

Spectral Intensities

The electrostatic model involving a forced electric dipole transition can account for intensities of magnitude 10^{-6}–10^{-5}.[17,18] The oscillator strength f can be calculated theoretically from the relationship (5)[19,20] where $T_\lambda = \tau_\lambda(2J + 1)^{-1}$, σ is the energy of

$$f = \sigma \Sigma T_\lambda \langle f^N \psi_J \| U^\lambda \| f^N \psi_{J'} \rangle^2 \qquad (5)$$

the transition expressed in wavenumbers (cm^{-1}), T_λ (λ = 2, 4 or 6) are the adjustable phenomenological Judd–Ofelt parameters and the matrix element is composed of U^λ, the unit tensor operator connecting the initial and final states ψ_J and $\psi_{J'}$ arising from the electronic configuration fN. Using the matrix elements given in the literature[21] and the experimental oscillator strengths (f_{expt1}), intensity parameters (T_λ) have been calculated by least-squares analysis. The values of the experimental and theoretical oscillator strengths are found to agree within 1% showing that the model satisfactorily accounts for the observed intensities of various bands. The values of the electric dipole line strengths (S_{ed}) are evaluated using the T_λ values thus obtained and the relationship[1] (6) where Ω_λ is defined as in equation (7) where h is Planck's constant, m is the mass of an electron and c is the velocity of light. The values of T_λ and Ω_λ are shown in

$$S_{ed} = e^2 \sum_{2,4,6} \Omega_\lambda \langle \psi_J \| U^\lambda \| \psi_{J'} \rangle^2 \qquad (6)$$

$$\Omega_\lambda(\text{cm}^2) = \frac{3h}{8\pi^2 mc} \cdot \frac{9\eta(2J + 1)T_\lambda}{(\eta^2 + 2)^2} \qquad (7)$$

Table 4 Electric dipole line strengths (S_{ed}) and predicted lifetimes τ_R for the $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ states of Pr^{3+}-doped complexes in solution

Energy level from ground state $^3H_4$	Pr^{3+}-doped Cd(male)·$2H_2O$		Pr^{3+}-doped Zn(Hmale)$_2$·$4H_2O$	
	$10^{22}\ S_{ed}$	$\tau_R/\mu s$	$10^{22}\ S_{ed}$	$\tau_R/\mu s$
$^3P_2$	340.00	28.50	427.00	21.10
$^3P_1$	104.92	43.80	134.63	33.60
$^3P_0$	105.59	52.20	135.50	43.70
$^1D_2$	173.14	381.00	243.59	271.70

Table 2. In the cases of Pr(Hmale)$_3$·$7H_2O$ and Pr^{3+}-doped Mg(Hmale)$_2$·$4H_2O$ T_2 is found to be negative. Negative values of T_2 are not acceptable and may arise due to the non-inclusion of the transition $^3F_2 \longleftarrow {}^3H_4$ which is difficult to observe but has a significant matrix element. On the basis of similar earlier observations, it is concluded that the Judd–Ofelt theory works less well for Pr^{3+} than for other lanthanides.[10,18,22–24] The Ω_2 values for Cd(male)·$2H_2O$ and Zn(Hmale)$_2$·$4H_2O$ are positive and may therefore be considered reliable, that for the latter being significantly larger than that of the former. This is in order with the observed higher intensity for the $^3P_2 \longleftarrow {}^3H_4$ transition for Zn(Hmale)$_2$·$4H_2O$. Both covalency and geometry effects can contribute to Ω_2. As these complexes have similar ionic character as shown by the F_2 values, the enhancement of intensity for the $^3P_2 \longleftarrow {}^3H_4$ transition leading to a higher Ω_2 value is regarding as arising from mixing of the $^3P_2$, $^1D_2$ and $^3F_2$ terms of $J = 2$ matrix due to the geometry effects. The last two terms contribute significantly to Ω_2 as the corresponding U^λ matrix elements in equation (6) for these terms are significant.

We report the electric dipole line strengths (S_{ed}) for the cases of Cd(male)·$2H_2O$ and Zn(Hmale)$_2$·$4H_2O$ only where T_2 has positive values (Table 4). The values of the magnetic dipole line strengths (S_{md}) calculated from the relationship[1] (8) were found to be negligible compared to S_{ed}.

$$S_{md} = \frac{e^2h^2}{16m^2c^2\pi^2}\langle\psi_j|L + 2S|\psi_{j'}\rangle^2 \qquad (8)$$

Radiative Lifetimes.—The radiative transition probability $A(\psi_j, \psi_{j'})$ between the states ψ_j and $\psi_{j'}$ ignoring S_{md}, is given by[1,23] equation (9). The total radiative relaxation A_T is

$$A(\psi_j, \psi_{j'}) = \frac{64\pi^4\nu^3}{3h(2J + 1)}\cdot\frac{[\eta(\eta^2 + 2)^2 S_{ed}]}{9} \qquad (9)$$

obtained from the relationship (10) where the sum runs over all

$$A_T(\Psi_j) = \sum_{\Psi_{j'}} A(\Psi_j, \Psi_{j'}) \qquad (10)$$

$\psi_{j'}$ lower in energy than ψ_j. The radiative lifetime τ_R of a state is then calculated using expression (11). Predicted radiative

$$\tau_R = [A_T(\psi_j)]^{-1} \qquad (11)$$

lifetimes of the four excited states for the Pr^{3+}-doped maleato complexes of Cd^{2+} and Zn^{2+} are given in Table 4.

Conclusion

The absorption spectra of $Pr^{3+}(4f^2)$ can be conveniently analysed in terms of Racah parameters, spin–orbit coupling constant and configuration interaction terms using the matrix elements for $J = 0$–6 terms. Incorporation of conditions obtained using the matrix elements corresponding to $J = 0, 1, 3$ and 5 is found to lead to more reliable results than the commonly used Taylor series method. The merit of the method is shown by analysing the reported spectra of Pr^{3+}-doped $LaCl_3$ and LaF_3 and of Pr^{3+}(aq). The analysis of the optical spectra of the Pr^{3+}-doped maleato complexes shows that the spectral positions are sensitive to the Racah parameters E^1, E^3 and the spin–orbit coupling constant ζ. Their values are invariably found to be less than the free-ion values. This trend, which is similar to that observed for transition-metal ions, has been explained in terms of weak covalency and nephelauxetic effects. It is found that the configuration-interaction parameters α, β and γ are important: α and γ are always positive and β is negative in the above cases. The analysis of the optical spectra shows a variation of 5% for $E^1(F_2)$ and ζ. It is found that F_2 is a more reliable measure of covalency than is ζ. Configuration interaction is important and varies significantly in these systems. This may be the major contributing factor to the observed variations in ζ. The Judd–Ofelt model, although accounting for the intensities, leads to negative values of T_2 for Pr^{3+} in Pr(Hmale)$_3$·$7H_2O$ and Pr^{3+}-doped Mg(Hmale)$_2$·$4H_2O$. This is attributed to non-inclusion of the transition $^3F_2 \longleftarrow {}^3H_4$. In the case of Pr^{3+}-doped Cd(male)·$2H_2O$ and Zn(Hmale)$_2$·$4H_2O$ where the Judd–Ofelt model satisfactorily accounts for the intensities, the predicted lifetimes (τ_R) for the transitions $^3P_2 \longleftarrow {}^3H_4$, $^3P_1 \longleftarrow {}^3H_4$, $^3P_0 \longleftarrow {}^3H_4$ and $^1D_2 \longleftarrow {}^3H_4$ have been found to be of the order of microseconds with the last transition having the largest value.

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