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An Absorption Spectral Study of *4f*-*4f* Transitions for the Interaction of Pr(III) with Different Amino Acids in Aqueous and Aquated Organic Solvents

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By employing absorption difference and comparative absorption spectrophotometry, the interactions of Pr(III) with DL-valine, L-leucine, L(–)-hydroxyproline, DL-alanine, L(+)-arginine and β-alanine in aqueous and different aquated organic solvents have been discussed. The magnitude of various electronic spectral parameters like Slater-Condon (F_k), Racah (E^k), Lande factor (ξ_{4f}), nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ) and intensity parameters like oscillator strength (P) and Judd-Ofelt electric dipole intensity (T_λ) parameters have been evaluated using partial and multiple regression analysis following linear curve analysis and Gaussian curve analysis. The changes in the oscillator strengths of the different *4f*-*4f* transitions and experimentally determined Judd-Ofelt parameters (T_λ) are going to explain nature of binding of lanthanide with different ligands in aqueous and different aquated organic solvents.

Key Words: Spectral studies, Pr(III), Amino acids, Aquated organic solvents.

INTRODUCTION

The study of the chemical bonding between trivalent lanthanide ions (Ln^{3+}) and amino acids or peptides has its origin in the interest in using these ions as structural probes in biological systems, particularly in those systems which contain Ca^{2+} in their structure[1,2]. Lanthanides coordinate with the unprotonated carboxyl groups of amino acids. Sherry *et al.*[3] suggested that alanine participates in monodentate coordination with lanthanides from Pr^{3+} to Tb^{3+}, and in bidentate coordination from Dy^{3+} to Yb^{3+}. The study of the substances doped with certain impurities has been found to be very useful in the field of science and technology[4]. Katzin[5] applied the ability of lanthanide ions as absorption difference probe in studies of sugar acids and amino acids as ligands. In this paper, Pr(III) ion has been doped with ligands namely DL-valine, L-leucine, L(+)-hydroxyproline, DL-alanine, L(+)-arginine and β-alanine in different 50% (v/v) solvents—water,

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CH_3OH, CH_3CN, dioxane, DMF and their equimolar mixtures. Pr(III) absorption spectra yield four bands in the visible region. Various electronic spectral parameters, *viz.*, Slater-Condon (F_k), Racah (E^k), Lande spin orbit coupling constant (ξ_{4f}), Nephelauxetic ratio (β), bonding ($b^{1/2}$), percentage covalency (δ), oscillator strength (P) and Judd-Ofelt Intensity (T_λ) parameters for the different ligands have been evaluated.

EXPERIMENTAL

Pr(III) nitrate of 99.9% purity was purchased from CDH Analytical Reagent and amino acids from Loba-Chemie Indo-Australian Co. The solvents used are CH_3OH, CH_3CN, DMF and dioxane, they are of AR grade from Qualigens. The saturated solutions of ligands and Pr(III) nitrate of 10^{-2} M were prepared in different solvents (50% v/v). The solution spectrum of each solution at pH 4 and at temperature 298 K were recorded on a Perkin-Elmer Lambda-35 upgraded with high resolution and expansion of scale having water jacket cell holder in the range 350 nm–900 nm.

For Pr(III) complexes, the values of interelectronic parameters, *i.e.*, F_2, F_4, F_6 and ξ_{4f} were determined by using the technique developed by Misra *et al.*[6]

$$E_{obs} = E_{oj} + \frac{\delta E_j}{\delta F_2}\Delta F_2 + \frac{\delta E_j}{\delta \xi_{4f}}\Delta \xi_{4f} \qquad (1)$$

Then, we get approximate values of F_2 and ξ_{4f} by using the partial regression method. Approximate values of F_4 and F_6 are obtained from the following relation:

$$\frac{F_4}{F_2} = 0.13805 \quad \text{and} \quad \frac{F_6}{F_2} = 0.0151 \qquad (2)$$

Nephelauxetic ratio 'β' measures the change in F_k with respect to free ion, which is defined as:

$$\beta_1 = \frac{F_k^c}{F_k^f}; \quad \beta_2 = \frac{\xi_{4f}^c}{\xi_{4f}^f} \quad \text{and} \quad \beta = \left[\frac{\beta_1 + \beta_2}{2}\right] \qquad (3)$$

where, F_k^c and F_k^f refer to parameters in complex and free ion respectively.

The amount of mixing of 4*f*-orbital and ligand orbital can be given by another bonding parameter $b^{1/2}$, which is related to nephelauxetic effect and is defined as:

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2} \qquad (4)$$

Sinha[7] introduced another parameter known as the percentage covalency parameter (δ%) which is defined as:

$$\delta\% = \left[\frac{1-\beta}{\beta}\right] \times 100 \qquad (5)$$

The oscillator strength (P) is directly proportional to the area under the absorption curve. This is given by

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + \eta)^2} \right] \int \varepsilon_{max} \bar{\nu} \, d\bar{\nu} \quad (6)$$

where ε_{max} = molar extinction coefficient
$\bar{\nu}$ = energy of transition in wave number
η = refractive index of the medium

The experimental value of oscillator strength (P_{obs}) of absorption band given by Gaussian Curve Analysis[8] is

$$P_{obs} = 4.6 \times 10^{-9} \times \varepsilon_{max} \times \bar{\nu}_{1/2} \quad (7)$$

where, $\bar{\nu}_{1/2}$ = half-band width
ε_{max} = molar extinction coefficient

The observed oscillator strengths (P_{obs}) of the transition energies were expressed in terms of parameters defined by Judd[9] and Ofelt[10] known as the T_2, T_4 and T_6 parameters which are given by the following equation:

$$\frac{P_{obs}}{\nu} = [(U^2)]^2 T_2 + [(U^4)]^2 T_4 + [(U^6)]^2 T_6 \quad (8)$$

where U^λ is the matrix element given by Carnall *et al.*[11] and ν is the energy of transition.

RESULTS AND DISCUSSION

The sensitivity of hypersensitive bands in lanthanides towards coordination environment has been recognized since long. A few, however, are very sensitive to the environment and are usually more intense when a lanthanide ion gets complexed than it is in the corresponding aquo ion. Such transitions are called hypersensitive transitions[12]. The transitions $^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ of Pr(III) do not obey the selection rules for hypersensitive transition, but have been found to exhibit substantial sensitivity in the complexes[13]. The comparative absorption spectra of Pr(III) : DL-valine, Pr(III) : L-leucine, Pr(III) : L(–)-hydroxyproline, Pr(III) : DL-alanine, Pr(III) : L(+)-arginine and Pr(III) : β-alanine in aquated DMF (50%) are given in Fig. 1. The addition of ligands (*i.e.*, DL-valine, L-leucine, L(–)-hydroxyproline, DL-alanine, L(+)-arginine and β-alanine) in Pr(III) ion results in the red shift in all the energy bands but the changes in the intensity data are substantial. The changes in the intensity data are seen from the intensification of intensities of 4*f*-4*f* transition bands when the ligands are added. The intensification of the bands was interpreted in terms of increased interaction of 4*f*-orbitals with ligand orbitals. The intensification of bands, especially of $^3H_4 \rightarrow {}^3P_2$ transition can be correlated with lowering of the coordination number and shortening of the metal-ligand distance. From Tables 1 and 2, one can clearly see that in all the systems there is decrease in Slater-Condon (F_k), Racah (E^k) and spin-orbit interaction (ξ_{4f}) which indicates lowering of both columbic (F_k) and spin-orbit interaction (ξ_{4f}) parameters thus leading to expansion of the central

metal-ion orbital when the ligands are added to Pr(III) ion. The values of nephelauxetic effect (β) in all the systems range from 0.9446 to 0.9471, *i.e.*, its values is less than unity and the values of bonding parameter ($b^{1/2}$) are positive which indicates covalent bonding. It is in accordance with the theory of $f \leftrightarrow f$ transitions reported earlier[14, 15].

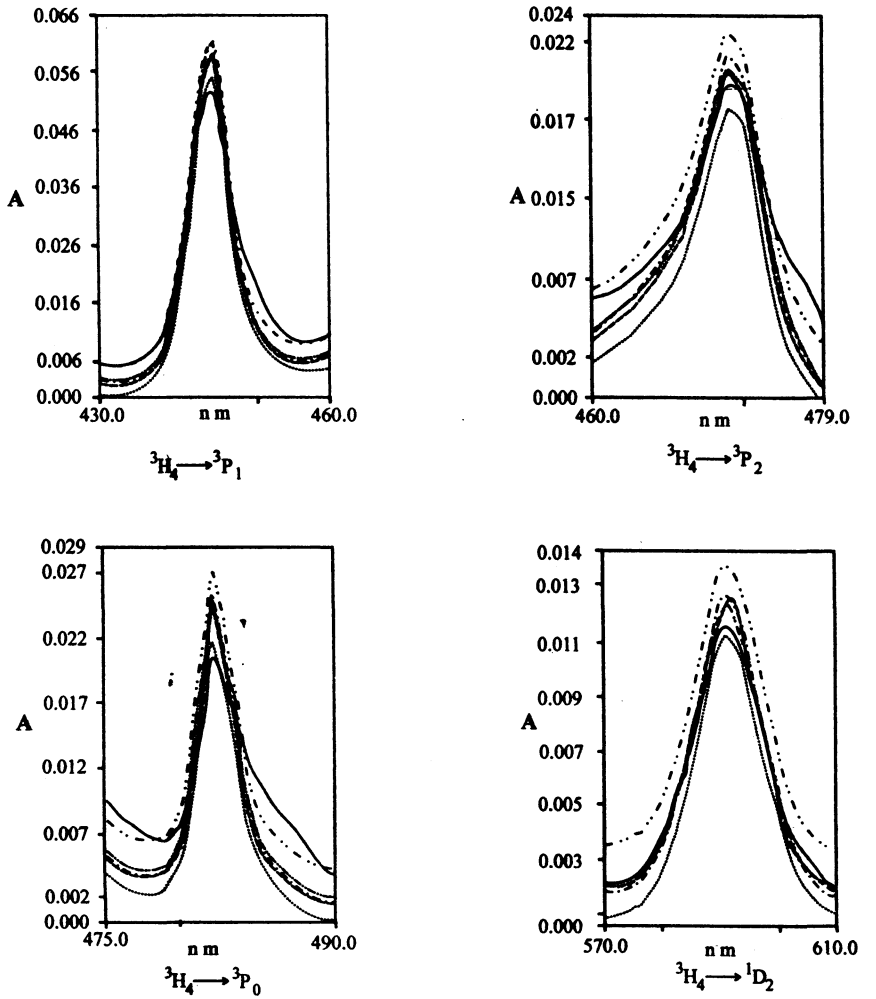

Fig.1. Comparative absorption spectra of (a) Pr(III):β-Alanine ····· (b) Pr(III):L(+)-Arginine ———
(c) Pr(III):DL-Alanine - · - · - (d) Pr(III):Hydroxyproline ——— (e) Pr(III):L-Leucine - · - · - ·
(f) Pr(III):DL-Valine – – – – in DMF(50%)

From Table-3, we can see that the variation of solvent has significant effect on the oscillator strengths of *4f-4f* bands and this leads to variation in the magnitudes of Judd-Ofelt (T_λ) parameters. When L-leucine, L(–)-hydroxyproline,

TABLE-1

COMPUTED VALUE OF ENERGY INTERACTION SLATER CONDON F_k (cm^{-1}), SPIN ORBIT INTERACTION ξ_{4f} (cm^{-1}), RACAH ENERGY E^K (cm^{-1}), NEPHELAUXETIC RATIO (β) BONDING ($b^{1/2}$) AND COVALENCY (δ) PARAMETERS OF Pr(III) : AMINO ACID (1 : 1) IN AQUEOUS AND DIFFERENT AQUATED ORGANIC SOLVENTS (50 : 50)

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. Solvent-Water										
Pr(III) : DL-Valine	309.3324	42.7033	4.7033	722.5336	3512.3610	23.7688	586.9479	0.9471	0.1627	5.5886
Pr(III) : L-Leucine	309.3451	42.7051	4.6711	722.6096	3512.5050	23.7697	586.9719	0.9471	0.1626	5.5807
Pr(III) : L(–)Hydroxyproline	309.2893	42.6974	4.6703	721.3613	3511.8720	23.7654	586.8661	0.9462	0.1640	5.6851
Pr(III) : DL-Alanine	309.3391	42.7043	4.6710	722.5234	3512.4370	23.7693	586.9606	0.9471	0.1627	5.5883
Pr(III) : L(+)-Arginine	309.3233	42.7021	4.6708	722.3987	3512.2580	23.7681	586.9307	0.9470	0.1628	5.6003
Pr(III) : β-Alanine	309.2659	42.6942	4.6699	722.4860	3511.6060	23.7636	586.8217	0.9469	0.1629	5.6031
2. Solvent-Methanol										
Pr(III) : DL-Valine	309.2198	42.6878	4.6692	722.3394	3511.0830	23.7601	586.7343	0.9468	0.1631	5.6218
Pr(III) : L-Leucine	309.2073	42.6861	4.6690	722.1571	3510.9410	23.7591	586.7106	0.9466	0.1634	5.6377
Pr(III) : L(–)Hydroxyproline	309.2010	42.6852	4.6689	721.9832	3510.8690	23.7587	586.6985	0.9465	0.1635	5.6520
Pr(III) : DL-Alanine	309.2317	42.6894	4.6694	722.4058	3511.2180	23.7610	586.7569	0.9468	0.1630	5.6148
Pr(III) : L(+)-Arginine	309.1917	42.6839	4.6688	722.2939	3510.7630	23.7579	586.6808	0.9467	0.1632	5.6298
Pr(III) : β-Alanine	309.1760	42.6817	4.6686	721.9172	3510.5850	23.7567	586.6511	0.9464	0.1637	5.6612

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
3. Solvent-MeCN										
Pr(III) : DL-Valine	309.3033	42.6993	4.6705	722.0497	3512.0310	23.7665	586.8928	0.9467	0.1633	5.6302
Pr(III) : L-Leucine	309.3145	42.7009	4.6706	722.1209	3512.1580	23.7674	586.9139	0.9468	0.1632	5.6230
Pr(III) : L(–)Hydroxyproline	309.3346	42.7036	4.6710	722.1544	3512.3860	23.7689	586.9521	0.9468	0.1631	5.6171
Pr(III) : DL-Alanine	309.3073	42.6999	4.6705	722.0103	3512.0760	23.7668	586.9003	0.9467	0.1633	5.6326
Pr(III) : L(+)-Arginine	309.2689	42.6946	4.6700	721.9420	3511.6400	23.7639	586.8274	0.9466	0.1634	5.6441
Pr(III) : β-Alanine	309.2468	42.6915	4.6696	721.8895	3511.3900	23.7622	586.7855	0.9468	0.1635	5.6517
4. Solvent-DMF										
Pr(III) : DL-Valine	308.9533	42.6510	4.6652	719.8364	3508.0570	23.7396	586.2286	0.9447	0.1663	5.8569
Pr(III) : L-Leucine	308.9481	42.6503	4.6651	719.7700	3507.9980	23.7692	586.2187	0.9446	0.1664	5.8628
Pr(III) : L(–)Hydroxyproline	308.9498	42.6505	4.6651	719.8001	3508.0170	23.7394	586.2220	0.9446	0.1664	5.8603
Pr(III) : DL-Alanine	308.9562	42.6514	4.6652	719.8796	3508.0900	23.7399	586.2342	0.9447	0.1663	5.8531
Pr(III) : L(+)-Arginine	308.9110	42.6452	4.6646	719.8782	3507.5770	23.7364	586.1484	0.9446	0.1664	5.8606
Pr(III) : β-Alanine	308.9507	42.6506	4.6652	719.8978	3508.0270	23.7394	586.2237	0.9447	0.1663	5.8526
5. Solvent-Dioxane										
Pr(III) : DL-Valine	309.1796	42.6822	4.6686	721.7896	3510.6260	23.7570	586.6580	0.9463	0.1638	5.6703
Pr(III) : L-Leucine	309.1130	42.6731	4.6676	720.8343	3510.8700	23.7519	586.5316	0.9456	0.1649	5.7543
Pr(III) : L(–)Hydroxyproline	309.1969	42.6846	4.6689	721.9437	3510.8220	23.7583	586.6907	0.9465	0.1636	5.6557
Pr(III) : DL-Alanine	309.1206	42.6741	4.6677	720.9547	3509.9570	23.7525	586.5461	0.9457	0.1648	5.7438
Pr(III) : L(+)-Arginine	309.0844	42.6691	4.6672	721.0401	3509.5450	23.7497	586.4773	0.9457	0.1648	5.7432
Pr(III) : β-Alanine	309.0852	42.6692	4.6672	720.8510	3509.5540	23.7498	586.4788	0.9456	0.1650	5.7576

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
6. Solvent-MeOH : MeCN										
Pr(III) : DL-Valine	309.2752	42.6954	4.6701	722.5105	3511.7120	23.7644	586.8394	0.9470	0.1628	5.5997
Pr(III) : L-Leucine	309.2833	42.6966	4.6702	722.4545	3511.8040	23.7650	586.8547	0.9469	0.1629	5.6026
Pr(III) : L(–)Hydroxyproline	309.2603	42.6934	4.6698	722.1597	3511.5430	23.7632	586.8112	0.9467	0.1632	5.6289
Pr(III) : DL-Alanine	309.2401	42.6906	4.6695	722.0233	3511.3130	23.7617	586.7727	0.9466	0.1634	5.6426
Pr(III) : L(+)-Arginine	309.2366	42.6901	4.6695	722.3225	3511.2730	23.7614	586.7662	0.9468	0.1631	5.6203
Pr(III) : β-Alanine	309.2616	42.6936	4.6698	722.5638	3511.5570	23.7633	586.8135	0.9470	0.1628	5.5978
7. Solvent-MeOH : DMF										
Pr(III) : DL-Valine	309.0714	42.6673	4.6670	720.8227	3509.3980	23.7487	586.4527	0.9455	0.1650	5.7620
Pr(III) : L-Leucine	309.0743	42.6677	4.6670	720.8658	3509.4300	23.7489	586.4581	0.9456	0.1650	5.7582
Pr(III) : L(–)Hydroxyproline	309.0684	42.6669	4.6669	720.7870	3509.3640	23.7485	586.4470	0.9455	0.1651	5.7652
Pr(III) : DL-Alanine	309.0716	42.6673	4.6670	720.8411	3509.4000	23.7487	586.4530	0.9455	0.1650	5.7605
Pr(III) : L(+)-Arginine	309.0540	42.6649	4.6667	720.9182	3509.2000	23.7474	586.4196	0.9456	0.1650	5.7575
Pr(III) : β-Alanine	309.0194	42.6601	4.6662	720.3329	3508.8070	23.7447	586.3540	0.9451	0.1657	5.8080
8. Solvent MeOH : Dioxane										
Pr(III) : DL-Valine	309.1339	42.6759	4.6679	721.5486	3510.1070	23.7535	586.5712	0.9461	0.1642	5.6962
Pr(III) : L-Leucine	309.1362	42.6763	4.6680	721.5021	3510.1340	23.7537	586.5757	0.9461	0.1642	5.6994
Pr(III) : L(–)Hydroxyproline	309.0873	42.6695	4.6672	721.0231	3509.5780	23.7499	586.4828	0.9457	0.1648	5.7440
Pr(III) : DL-Alanine	309.1373	42.6764	4.6680	721.5247	3510.1460	23.7538	586.5778	0.9461	0.1642	5.6975
Pr(III) : L(+)-Arginine	309.1042	42.6718	4.6675	721.4284	3509.7700	23.7512	586.5149	0.9460	0.1643	5.7103
Pr(III) : β-Alanine	309.1123	42.6730	4.6676	721.4282	3509.8620	23.7518	586.5303	0.9460	0.1643	5.7090

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
9. Solvent-MeCN : DMF										
Pr(III) : DL-Valine	309.0386	42.6628	4.6665	720.4760	3509.0250	23.7462	586.3904	0.9452	0.1655	5.7939
Pr(III) : L-Leucine	309.0287	42.6614	4.6663	720.4250	3508.9120	23.7454	586.3716	0.9452	0.1656	5.7994
Pr(III) : L(–)Hydroxyproline	309.0440	42.6635	4.6666	720.5419	3509.0870	23.7466	586.4008	0.9453	0.1654	5.7880
Pr(III) : DL-Alanine	309.0529	42.6648	4.6667	720.6632	3509.1880	23.7473	586.4177	0.9454	0.1653	5.7772
Pr(III) : L(+)-Arginine	309.0089	42.6587	4.6660	720.4039	3508.6880	23.7439	586.3342	0.9451	0.1656	5.8043
Pr(III) : β-Alanine	309.1116	42.6729	4.6676	720.8787	3509.8540	23.7518	586.5189	0.9456	0.1649	5.7511
10. Solvent-MeCN : Dioxane										
Pr(III) : DL-Valine	309.2274	42.6888	4.6693	722.1229	3511.1690	23.7607	586.7487	0.9466	0.1633	5.6371
Pr(III) : L-Leucine	309.2235	42.6883	4.6693	722.1483	3511.1250	23.7604	586.7413	0.9466	0.1633	5.6358
Pr(III) : L(–)Hydroxyproline	309.2290	42.6891	4.6694	722.2192	3511.1870	23.7608	586.7516	0.9167	0.1632	5.6294
Pr(III) : DL-Alanine	309.2078	42.6861	4.6690	722.0058	3510.9470	23.7592	586.7115	0.9465	0.1635	5.6492
Pr(III) : L(+)-Arginine	309.1703	42.6810	4.6685	721.9800	3510.5210	23.7563	586.6404	0.9465	0.1636	5.6573
Pr(III) : β-Alanine	309.1116	42.6729	4.6676	720.8787	3509.8540	23.7518	586.5289	0.9456	0.1649	5.7511
11. Solvent-DMF : Dioxane										
Pr(III) : DL-Valine	309.0827	42.6689	4.6671	721.0613	3509.5260	23.7496	586.4742	0.9457	0.1648	5.7419
Pr(III) : L-Leucine	309.0736	42.6676	4.6670	720.9472	3509.4230	23.7489	586.4569	0.9456	0.1649	5.7521
Pr(III) : L(–)Hydroxyproline	309.0868	42.6694	4.6672	721.0380	3509.5720	23.7499	586.4818	0.9457	0.1648	5.7430
Pr(III) : DL-Alanine	309.0809	42.6686	4.6671	720.9591	3509.5050	23.7494	586.4706	0.9456	0.1649	5.7500
Pr(III) : L(+)-Arginine	309.0595	42.6657	4.6668	721.1085	3509.2620	23.7478	586.4301	0.9457	0.1648	5.7421
Pr(III) : β-Alanine	309.0376	42.6626	4.6665	720.5654	3509.0140	23.7461	586.3885	0.9453	0.1654	5.7872

TABLE-2

COMPUTED AND OBSERVED VALUES OF ENERGIES (cm^{-1}) AND R.M.S. VALUES FOR Pr(III) : AMINO ACID (1 : 1) IN AQUEOUS AND DIFFERENT AQUATED ORGANIC SOLVENTS (50 : 50)

System	$^3H_4 \rightarrow$ E_{obs}	$^3P_2$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_1$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_0$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^1D_2$ E_{cal}	R.M.S.
1. Solvent-Water									
Pr(III) : DL-Valine	22523.03	22472.63	21341.98	21261.91	20756.36	20700.83	16975.62	17148.01	102.17
Pr(III) : L-Leucine	22523.03	22473.87	21343.35	21263.10	20756.79	20701.86	16977.93	17148.81	101.34
Pr(III) : L(–)Hydroxyproline	22473.43	22463.83	21345.63	21254.23	20757.22	20695.57	16976.20	17142.62	99.93
Pr(III) : DL-Alanine	22523.54	22473.04	21344.72	21262.34	20756.79	20701.28	16974.18	17148.29	103.36
Pr(III) : L(+)-Arginine	22529.63	22471.34	21340.16	21260.74	20756.79	20699.94	16968.71	17147.20	105.83
Pr(III) : β-Alanine	22519.48	22467.90	21335.61	21257.06	20752.05	20.696.07	16972.17	17144.81	102.19
2. Solvent-Methanol									
Pr(III) : DL-Valine	22511.37	22464.05	21330.15	21253.25	20749.47	20692.56	16971.88	17142.27	100.53
Pr(III) : L-Leucine	22509.85	22462.29	21330.60	21251.65	20749.47	20691.34	16967.27	17141.17	102.61
Pr(III) : L(–)Hydroxyproline	22509.85	22460.99	21331.51	21250.52	20749.90	20690.56	16962.38	17140.37	105.06
Pr(III) : DL-Alanine	22511.37	22465.19	21331.51	21254.35	20749.90	20693.52	16973.89	17143.01	99.83
Pr(III) : L(+)-Arginine	22510.36	22461.92	21328.78	21251.10	20747.75	20690.49	16968.71	17140.84	101.60
Pr(III) : β-Alanine	22509.85	22458.97	21328.78	21248.50	26748.61	20688.68	16959.50	17139.03	105.90

System	$^3H_4 \rightarrow$ E_{obs}	$^3P_2$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_1$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_0$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^1D_2$ E_{cal}	R.M.S.
3. Solvent-MeCN									
Pr(III) : DL-Valine	22523.03	22468.24	21343.81	21257.95	20756.79	20697.87	16960.94	17145.27	109.34
Pr(III) : L-Leucine	22523.54	22469.35	21343.81	21259.02	20757.22	20698.79	16963.53	17145.99	108.20
Pr(III) : L(–)Hydroxyproline	22523.54	22470.88	21342.44	21260.56	20758.52	20700.26	16967.85	17147.01	106.03
Pr(III) : DL-Alanine	22523.03	22468.31	21345.17	21258.07	20757 .22	20698.07	16959.79	17145.34	110.12
Pr(III) : L(+)-Arginine	22528.10	22465.37	21335.61	21255.11	20755.50	20695.24	16956.34	17143.37	110.71
Pr(III) : β-Alanine	22522.02	22463.61	21340.16	21253.36	20753.78	20693.60	16953.18	17142.21	112.14
4. Solvent-DMF									
Pr(III) : DL-Valine	22480.50	22433.46	21310.15	21224.63	20743.45	20689.09	16919.61	17122.75	118.66
Pr(III) : L-Leucine	22480.50	22432.77	21309.69	21224.00	20743.45	20668.60	16917.90	17122.31	119.38
Pr(III) : L(–)Hydroxyproline	22480.50	22433.04	21308.79	21224.24	20743.45	20668.78	16919.33	17122.48	118.58
Pr(III) : DL-Alanine	22481.51	22433.87	21310.60	21225.01	20743.45	20669.38	16919.90	17123.01	118.67
Pr(III) : L(+)-Arginine	22484.54	22430.81	21299.71	21221.84	20740.86	20666.20	16919.04	17120.92	117.56
Pr(III) : β-Alanine	22481.00	22433.59	21308.79	21224.69	20743.02	20669.03	16921.05	17122.80	117.79
5. Solvent-Dioxane									
Pr(III) : DL-Valine	22511.88	22458.57	21332.42	21248.25	20749.47	20688.69	16953.75	17138.82	109.40
Pr(III) : L-Leucine	22512.38	22449.27	21331.06	21239.79	20749.90	20682.20	16926.49	17132.99	122.00
Pr(III) : L(–)Hydroxyproline	22513.90	22460.51	21333.79	21250.07	20749.90	20690.19	16956.91	17140.06	108.36
Pr(III) : DL-Alanine	22512.89	22450.39	21329.24	21240.80	20749.90	20682.96	16930.79	17133.69	119.77
Pr(III) : L(+)-Arginine	22509.34	22448.37	21326.05	21238.60	20746.89	20680.58	16931.93	17132.27	118.21
Pr(III) : β-Alanine	22508.84	22447.47	21330.15	21237.90	20747.75	20680.28	16925.92	17131.76	121.65

System	$^3H_4 \rightarrow$ E_{obs}	$^3P_2$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_1$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_0$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^1D_2$ E_{cal}	R.M.S.
6. Solvent-MeOH : MeCN									
Pr(III) : DL-Valine	22518.97	22468.65	21337.43	21257.81	29752.48	20696.77	16973.03	17145.31	102.05
Pr(III) : L-Leucine	22518.97	22468.92	21337.43	21258.16	20753.35	20697.23	16973.03	17145.52	102.09
Pr(III) : L(–)Hydroxyproline	22519.48	22465.88	21336.52	21255.38	20753.35	20695.06	16964.39	17143.61	106.03
Pr(III) : DL-Alanine	22518.47	22463.83	21339.25	21253.41	20752.48	20693.38	16957.78	17142.28	109.42
Pr(III) : L(+)-Arginine	22524.55	2246510	21332.88	21254.36	20751.19	20693.71	16963.53	17142.99	106.32
Pr(III) : β-Alanine	22516.44	22468.00	21336.06	21257.07	20751.19	20695.91	16974.76	17144.84	100.71
7. Solvent-MeOH : DMF									
Pr(III) : DL-Valine	22489.09	22446.40	21321.05	21236.82	20746.46	20679.25	16942.26	17131.04	110.76
Pr(III) : L-Leucine	22490.10	22446.81	21321.51	21237.20	20746.46	20679.54	16942.55	17131.30	110.78
Pr(III) : L(–)Hydroxyproline	22489.60	22446.02	21321.05	21236.47	20746.46	20678.98	16940.83	17130.80	111.46
Pr(III) : DL-Alanine	22490.61	22446.50	21320.60	21.236.91	20746.46	20679.30	16941.97	17131.10	110.94
Pr(III) : L(+)-Arginine	22495.67	22445.70	21317.42	21235.98	20745.17	20678.21	16939.96	17130.52	111.71
Pr(III) : β-Alanine	22490.10	22440.42	21316.96	21231.23	20745.60	20674.67	16927.63	17127.23	116.92
8. Solvent-MeOH : Dioxane									
Pr(III) : DL-Valine	22504.78	22454.27	21330.15	21244.09	20747.32	20685.02	16948.87	17136.02	110.53
Pr(III) : L-Leucine	22504.78	22454.19	21329.69	21244.07	20747.75	20685.10	16948.58	17135.99	110.61
Pr(III) : L(–)Hydroxyproline	22513.40	22448.48	21326.96	21238.74	20747.32	20680.75	16928.78	17132.35	120.28
Pr(III) : DL-Alanine	22505.29	22454.38	21329.24	21244.24	20747.75	20685.22	16949.15	17136.11	110.32
Pr(III) : L(+)-Arginine	22502.76	22451.66	21324.23	21241.53	20746.03	20682.71	16947.72	17134.31	109.86
Pr(III) : β-Alanine	22501.24	22452.21	21326.05	21242.10	20746.46	20683.28	16948.58	17134.68	109.63

System	$^3H_4 \rightarrow$ E_{obs}	$^3P_2$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_1$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^3P_0$ E_{cal}	$^3H_4 \rightarrow$ E_{obs}	$^1D_2$ E_{cal}	R.M.S.
9. Solvent-MeCN : DMF									
Pr(III) : DL-Valine	22491.12	22442.44	21321.96	21233.15	20746.03	20676.29	16929.07	17128.52	117.16
Pr(III) : L-Leucine	22490.61	22441.51	21321.51	21232.25	20745.60	20675.50	16927.35	17127.92	117.81
Pr(III) : L(–)Hydroxyproline	22491.12	22443.14	21322.87	21233.79	20746.03	20676.80	16930.50	17128.97	116.64
Pr(III) : DL-Alanine	22490.10	22444.35	21321.51	21234.90	20746.03	20677.66	16935.66	17129.73	113.94
Pr(III) : L(+)-Arginine	22496.86	22440.07	21317.87	21230.79	20744.74	20674.07	16922.77	17126.95	119.87
Pr(III) : β-Alanine	22492.63	22446.13	21321.96	21236.36	20744.74	20678.48	16940.25	17130.78	112.00
10. Solvent-MeCN : Dioxane									
Pr(III) : DL-Valine	22516.44	22463.48	21334.24	21252.93	20751.19	20692.68	16962.66	17141.99	106.06
Pr(III) : L-Leucine	22515.93	22463.34	21334.24	21252.75	20750.76	20692.45	16962.95	17141.88	105.86
Pr(III) : L(–)Hydroxyproline	22516.95	22464.07	21335.61	212 53.42	20750.76	20692.97	16963.53	17142.34	105.91
Pr(III) : DL-Alanine	22514.92	22461.56	21335.15	21251.09	20750.33	20691.08	16958.06	17140.75	108.17
Pr(III) : L(+)-Arginine	22524.55	22458.90	21326.51	21248.36	20748.61	20688.40	16952.03	17138.95	110.66
Pr(III) : β-Alanine	22514.92	22449.39	21336.06	21239.86	20749.47	20682.18	16922.10	17133.05	125.04
11. Solvent-DMF : Dioxane									
Pr(III) : DL-Valine	22499.12	22448.36	21322.42	21238.57	20746.03	20680.50	16946.28	17132.25	109.24
Pr(III) : L-Leucine	22491.12	22447.17	21321.51	21237.48	20746.03	20679.65	16943.41	17131.50	110.43
Pr(III) : L(–)Hydroxyproline	22492.13	22448.52	21322.87	21238.76	20746.46	20680.74	16945.42	17132.37	109.84
Pr(III) : DL-Alanine	22491.62	22447.72	21322.42	21238.03	20746.46	20680.18	16943.70	17131.87	110.51
Pr(III) : L(+)-Arginine	22498.71	22447.03	21316.05	21237.13	20744.74	20678.96	16943.41	17131.32	110.16
Pr(III) : β-Alanine	22493.64	22442.87	21321.96	21233.44	20745.60	20676.39	16929.07	17128.74	117.34

TABLE-3

OBSERVED AND COMPUTED VALUES OF OSCILLATOR STRENGTHS ($P \times 10^6$) AND JUDD-OFELT ($T_\lambda \times 10^{10}$) PARAMETERS FOR Pr(III) : AMINO ACID (1 : 1) IN AQUEOUS AND DIFFERENT AQUATED ORGANIC SOLVENTS (50 : 50)

System	$^3H_4 \rightarrow {}^1D_2$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. Solvent-Water											
Pr(III) : DL-Valine	1.4481	1.4481	0.7907	1.1976	1.6297	1.2164	6.0775	6.0775	–74.1843	3.3390	19.0220
Pr(III) : L-Leucine	1.4538	1.4538	0.7830	1.1612	1.5637	1.1795	5.0863	5.0863	–7.8534	3.2375	15.8013
Pr(III) : L(–)Hydroxyproline	1.4896	1.4896	0.8594	1.0553	1.2711	1.0721	5.3992	5.3992	–19.8405	2.9422	16.9046
Pr(III) : DL-Alanine	1.5063	1.5063	0.8028	1.2008	1.6242	1.2199	5.3405	5.3405	–12.6549	3.3479	16.6039
Pr(III) : L(+)-Arginine	1.3581	1.3581	1.0471	1.1448	1.2619	1.1627	4.1016	4.1016	35.2994	3.1917	12.5828
Pr(III) : β-Alanine	1.5670	1.5670	0.7985	1.2033	1.6332	1.2221	5.3188	5.3188	0.9216	3.3555	16.6124
2. Solvent-Methanol											
Pr(III) : DL-Valine	1.6740	1.6740	0.8832	3.3120	1.7678	3.3634	5.7977	5.7977	–11.8306	9.2374	16.5395
Pr(III) : L-Leucine	1.5096	1.5096	0.8537	1.2603	1.6928	1.2799	5.6059	5.6059	–29.5861	3.5150	17.4403
Pr(III) : L(–)Hydroxyproline	1.5033	1.5133	0.8337	1.2266	1.6446	1.2456	6.1886	6.1886	–66.7421	3.4208	19.3759
Pr(III) : DL-Alanine	1.6410	1.6410	0.8532	1.2717	1.7165	1.2915	5.6121	5.6121	–0.3812	3.5467	17.4513
Pr(III) : L(+)-Arginine	1.3323	1.3323	0.7056	0.9753	1.2643	0.9904	5.3914	5.3914	–54.7978	2.7203	16.9494
Pr(III) : β-Alanine	1.5074	1.5074	0.8037	1.1570	1.5336	1.1749	5.2908	5.2908	–8.9378	3.2269	16.4842

System	$^3H_4 \rightarrow {}^1D_2$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
3. Solvent-Acetonitrile											
Pr(III) : DL-Valine	1.5389	1.5389	0.7758	1.1949	1.6394	1.2137	5.1842	5.1842	5.2466	3.3313	16.0970
Pr(III) : L-Leucine	1.3260	1.3260	0.7365	1.1425	1.5455	1.1605	5.2453	5.2453	–46.8992	3.1853	16.3355
Pr(III) : L(–)Hydroxyproline	1.4075	1.4075	0.7775	1.1601	1.5667	1.1782	5.3316	5.3316	–34.2099	3.2340	16.6052
Pr(III) : DL-Alanine	1.5527	1.5527	0.8054	1.1010	1.4187	1.1184	5.3306	5.3306	–0.8847	3.0696	16.6466
Pr(III) : L(+)-Arginine	1.4243	1.4243	0.9645	1.0880	1.2342	1.1048	4.9333	4.9333	–3.7753	3.0334	15.3509
Pr(III) : β-Alanine	1.4441	1.4441	0.7471	1.0748	1.4246	1.0917	5.0020	5.0020	–3.7710	2.9970	15.5900
4. Solvent-DMF											
Pr(III) : DL-Valine	1.8830	1.8830	0.5228	1.1816	1.8678	1.1992	6.6879	6.6879	–15.0290	3.2966	21.0753
Pr(III) : L-Leucine	1.8224	1.8224	1.0434	1.4176	1.8185	1.4387	6.6638	6.6638	–27.9599	3.9551	20.8203
Pr(III) : L(–)Hydroxyproline	1.8832	1.8832	1.0820	1.5373	1.9162	1.4784	6.9117	6.9117	–285.7668	4.1752	29.0334
Pr(III) : DL-Alanine	1.7939	1.7939	1.0277	1.3937	1.7860	1.4145	6.7045	6.7045	–87.0408	3.8884	20.9698
Pr(III) : L(+)-Arginine	1.6940	1.6940	1.0823	1.2950	1.5295	1.3137	6.3794	6.3794	–37.9981	3.6132	19.9733
Pr(III) : β-Alanine	1.8911	1.8911	1.0192	1.3911	1.7890	1.4116	6.4549	6.4549	1.4059	3.8809	20.1534
5. Solvent-Dioxane											
Pr(III) : DL-Valine	1.5866	1.5866	0.7971	1.1493	1.5250	1.1673	5.2228	5.2228	13.6651	3.2056	16.2654
Pr(III) : L-Leucine	1.5568	1.5568	0.8123	1.1606	1.5322	1.1785	5.2025	5.2025	8.7828	3.2367	16.1906
Pr(III) : L(–)Hydroxyproline	1.5373	1.5373	0.7886	1.1412	1.5172	1.5191	5.2250	5.2250	2.3328	3.1828	16.2772
Pr(III) : DL-Alanine	1.4623	1.4623	0.7860	1.1323	1.5013	1.1497	5.2711	5.2711	–14.8442	3.1578	16.3191
Pr(III) : L(+)-Arginine	1.4646	1.4646	0.7277	1.0049	1.3018	1.0204	4.9707	4.9707	3.3871	2.8029	15.5487
Pr(III) : β-Alanine	1.6832	1.6832	0.8001	1.1257	1.4739	1.1432	5.0812	5.0812	45.5296	3.1398	15.8210

System	$^3H_4 \rightarrow {}^1D_2$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
6. Solvent-CH_3OH : CH_3CN											
Pr(III) : DL-Valine	1.5611	1.5611	0.8363	1.2553	1.7005	1.2750	5.6772	5.6772	–22.5460	3.5005	17.6705
Pr(III) : L-Leucine	1.8973	1.8973	0.9419	1.4947	1.9672	1.4361	6.1685	6.1685	–217.2083	4.0539	25.7384
Pr(III) : L(–)Hydroxyproline	1.5504	1.5504	0.8418	1.2607	1.7058	1.2804	5.6092	5.6092	–20.3223	3.5154	17.4437
Pr(III) : DL-Alanine	1.6180	1.6180	0.8401	1.2453	1.6766	1.2650	5.5456	5.5456	–0.6852	3.4728	17.2474
Pr(III) : L(+)-Arginine	1.3510	1.3510	1.0468	1.1564	1.2856	1.1743	5.2669	5.2669	–42.6785	3.2248	16.3949
Pr(III) : β-Alanine	1.5441	1.5641	0.8074	1.1775	1.5719	1.1960	5.3992	5.3992	–3.4745	3.2838	16.8197
7. Solvent-CH_3OH : Dioxane											
Pr(III) : DL-Valine	1.4493	1.4493	0.8196	1.1529	1.5093	1.1708	5.5192	5.5192	–36.9438	3.2157	17.2400
Pr(III) : L-Leucine	1.4148	1.4148	0.8110	1.1383	1.4884	1.1560	5.4311	5.4311	–38.9459	3.9749	16.9620
Pr(III) : L(–)Hydroxyproline	0.0471	0.0471	0.0264	0.0384	0.0511	0.0390	0.2002	0.2002	–2.5528	0.1070	0.6277
Pr(III) : DL-Alanine	1.4847	1.4847	0.8234	1.1669	1.5339	1.1850	5.5296	5.5296	–29.6396	3.2548	17.2637
Pr(III) : L(+)-Arginine	1.4002	1.4002	0.7097	0.9559	1.2206	0.9706	5.6712	506712	–57.4128	2.6665	17.8869
Pr(III) : β-Alanine	1.4778	1.4778	0.7968	1.0968	1.4185	1.1138	5.4038	5.4038	–22.7843	3.0596	16.9064
8. Solvent-CH_3OH : DMF											
Pr(III) : DL-Valine	1.7070	1.7070	1.0031	1.3547	1.7323	1.3753	6.2657	6.2657	–28.2307	3.7789	19.5522
Pr(III) : L-Leucine	1.7150	1.7150	0.9955	1.3753	1.7820	1.3964	6.1722	6.1722	–20.3518	3.8365	19.2291
Pr(III) : L(–)Hydroxyproline	1.7891	1.7891	1.0338	1.3786	1.7497	1.3996	6.2598	6.2598	–9.248	3.8456	19.5141
Pr(III) : DL-Alanine	1.8273	1.8273	1.0071	1.3624	1.7439	1.3832	6.2497	6.2497	0.1405	3.8004	19.4921
Pr(III) : L(+)-Arginine	1.5222	1.5222	0.8036	1.1117	1.4409	1.1282	6.1739	6.1739	–63.1809	3.1004	19.4259
Pr(III) : β-Alanine	1.7637	1.7637	0.9775	1.3403	1.7288	1.3605	6.0982	6.0982	–3.9685	3.7389	19.0123

System	$^3H_4 \rightarrow {}^1D_2$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
9. Solvent-CH_3CN : DMF											
Pr(III) : DL-Valine	1.7425	1.7425	0.9865	1.3845	1.8097	1.4056	6.1970	6.1970	–15.4220	3.8620	19.3027
Pr(III) : L-Leucine	1.8205	1.8205	1.0005	1.4111	1.8496	1.4327	6.2900	6.2900	–3.8442	3.9363	19.5880
Pr(III) : L(–)Hydroxyproline	1.7839	1.7839	0.9869	1.3714	1.7829	1.3925	6.3565	6.3565	–16.4881	3.8256	19.8358
Pr(III) : DL-Alanine	1.8454	1.8454	0.9937	1.3976	1.8291	1.4190	6.3654	6.3654	–3.3311	3.8987	19.8464
Pr(III) : L(+)-Arginine	1.6120	1.6120	1.1029	1.2511	1.4205	1.2700	6.0078	6.0078	–29.3120	3.4901	18.6429
Pr(III) : β-Alanine	1.7523	1.7523	0.9707	1.3319	1.7190	1.3523	5.9934	5.9934	0.1178	3.7154	18.6721
10. Solvent-CH_3CN : Dioxane											
Pr(III) : DL-Valine	1.6145	1.6145	0.7785	1.1546	1.5546	1.1726	5.4148	5.4148	7.2574	3.2200	16.8879
Pr(III) : L-Leucine	1.4766	1.4766	0.7758	1.1620	1.5723	1.1801	5.4136	5.4136	–23.9556	3.2405	16.8784
Pr(III) : L(–)Hydroxyproline	2.5954	2.5954	0.8202	1.2040	1.6096	1.2206	5.5145	5.5145	222.9533	3.3513	1701788
Pr(III) : DL-Alanine	1.5837	1.5837	0.4201	1.0142	1.6336	1.0301	25.6639	25.6639	–1326.637	2.8286	83.3667
Pr(III) : L(+)-Arginine	1.2586	1.2586	0.8955	0.9700	1.0605	0.9849	4.7778	4.7778	–30.7552	2.7053	14.9312
Pr(III) : β-Alanine	1.4575	1.4575	0.7600	1.1195	1.5022	1.1371	5.4063	5.4063	–24.9387	3.1221	16.7673
11. Solvent-DMF : Dioxane											
Pr(III) : DL-Valine	1.7213	1.7213	1.1674	1.4568	1.7728	1.4790	6.3479	6.7439	–30.7749	4.0636	19.7440
Pr(III) : L-Leucine	1.7775	1.7775	0.9812	1.3829	1.8119	1.4040	6.2910	6.2910	–13.9676	3.8576	19.6123
Pr(III) : L(–)Hydroxyproline	1.7344	1.7344	1.0081	1.3642	1.7467	1.3851	6.2996	6.2996	–2402817	3.8055	19.6536
Pr(III) : DL-Alanine	1.7795	1.7795	0.9844	1.3767	1.7961	1.3978	6.2129	6.2129	–8.3732	3.8404	19.3598
Pr(III) : L(+)-Arginine	1.5239	1.5239	1.1356	1.2464	1.3777	1.2652	6.2294	6.2294	–66.8934	3.4771	19.5046
Pr(III) : β-Alanine	1.6405	1.6405	0.9700	1.3088	1.6727	1.3288	6.1855	6.1855	–37.5344	3.6508	19.3187

L(+)-arginine and β-alanine are added to Pr(III) in different solvents, in general, we find maximum intensities observed in cases where dimethylformamide (DMF) is the organic solvent or DMF is one of the organic solvents. It is also seen that when DL-alanine is added to Pr(III) in different solvents, we find maximum intensity in cases where the solvent mixture is CH_3CN and dioxane and the minimum intensity is observed when L(–)-hydroxyproline is added to Pr(III) in the solvent mixture CH_3OH : Dioxane.

From Table-3 one can clearly see that T_2 occasionally showed negative values which become meaningless. This is because only the $^3H_4 \rightarrow {}^3F_2$ transition occurring around 5200 cm^{-1} has a significant $U^{(2)}$ matrix element. Here, the T_6 parameter is most significant followed by T_4 and T_2.

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