

OPTICAL ABSORPTION SPECTRUM OF THULIUM ACETATE IN SOLUTION

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The partial derivatives for Tm^{3+} ion have been calculated in terms of Racah (E^k) parameters. Radiative transition probabilities for fluorescence levels 3P_0 , 1I_6 , 1D_2 and 1G_4 of Tm^{3+} in Thulium Acetate are estimated.

Keywords : Absorption Spectrum; Thulium Acetate; Second Derivative Spectrum; Rare Earths

INTRODUCTION

CONSIDERABLE progress has been made in interpreting the optical spectra of Tm^{3+} ion embedded in crystalline solids (Bethe & Spedding, 1937; Wong & Richman, 1961; Ibuki & Langer, 1964; and Krupke & Gruber, 1965), in different solution media (Carnall *et al.*, 1965) and in glasses (Reisfeld, 1975).

Since no detailed investigation of the optical absorption spectrum of Thulium acetate has so far been reported in literature, the authors took up the present investigation. For the first time, derivative spectrum of this sample has been studied by the authors.

EXPERIMENTAL

Thulium acetate solution of 0.1 mole per cent was prepared. Spectra in the wavelength region 8400Å-2400Å was recorded on a Perkin-Elmer 551 Recording Spectrophotometer. Using a derivative accessory, second derivative spectrum was also recorded in this wavelength region.

The near infrared spectrum in the wavenumber region of 7000 cm^{-1} -9000 cm^{-1} was recorded on a Carl-Zeiss Specord 61 Recording Spectrophotometer. Second derivative spectrum in this region was not recorded as there is no derivative accessory for this NIR instrument.

The refractive index of the solution was measured on a PZO WARSZAWA 3275 refractometer.

RESULTS AND ANALYSIS

Under the influence of the electric field of the solution matrix, the changes in the parameters E^k and ξ_4 are very small. To a first order approximation, therefore the

energy E_J of the level J may be expressed in terms of the changes in the parameter E^k by a Taylor-Series expansion as follows :

$$E_J = E_{0J} + \frac{dE_J}{dE^1} \Delta E^1 + \frac{dE_J}{dE^2} \Delta E^2 + \frac{dE_J}{dE^3} \Delta E^3 \\ + \frac{dE_J}{d\xi_{4f}} \Delta \xi_{4f} + \frac{dE_J}{d\alpha} \Delta \alpha + \frac{dE_J}{d\beta} \Delta \beta \quad \dots(1)$$

E_{0J} is the zero order energy of the level J and $\frac{dE_J}{dE^k}$, $\frac{dE_J}{d\xi_{4f}}$, $\frac{dE_J}{d\alpha}$ and $\frac{dE_J}{d\beta}$ are the partial derivatives. Further

$$\left. \begin{aligned} \Delta E^k &= E^k - E^{k^0}, \\ \Delta \xi_{4f} &= \xi_{4f} - \xi_{4f}^0, \\ \Delta \alpha &= \alpha - \alpha^0, \\ \Delta \beta &= \beta - \beta^0 \end{aligned} \right\} \quad \dots(2)$$

and

where E^{k^0} , ξ_{4f}^0 , α^0 and β^0 are the free ion parameters and E^k , ξ_{4f} , α and β are the parameters of the ion in the crystal or solution matrix. Since these partial derivatives for Tm^{3+} are not available in literature, they have been evaluated following the procedure outlined by Wong (1961). These are presented in Table I.

TABLE I

The zero-order energies and partial derivatives of the energies with respect to E^1 , E^2 , E^3 , ξ_{4f} , α and β for Tm^{3+}

Level	E_{0J}	$\frac{dE_J}{dE^1}$	$\frac{dE_J}{dE^2}$	$\frac{dE_J}{dE^3}$	$\frac{dE_J}{d\xi_{4f}}$	$\frac{dE_J}{d\alpha}$	$\frac{dE_J}{d\beta}$
3H_6	0	0	0	0	0	0	0
3H_4	5610	0.5682	-77.8512	6.9637	-0.1939	-14.3162	-0.2660
3H_5	8188	-0.0174	-0.6072	-0.1390	3.2057	-0.1043	-0.0014
3F_4	12518	0.2426	-34.6147	2.9756	3.7893	-6.3326	-0.1167
3F_3	14308	-0.0174	-0.6072	8.8610	3.2057	-18.1043	-0.5014
3F_2	14914	0.3980	57.9768	7.1938	2.0145	-19.5385	-0.3536
1G_4	21172	1.1371	-149.3557	3.6437	6.0216	-7.6640	0.0450
1D_2	27830	0.8055	116.3405	17.5800	2.5047	-24.5991	-0.0258
1I_6	34684	1.9652	68.7856	15.7220	2.9113	11.7915	0.1638
3P_0	35435	0.3870	-0.6072	40.3770	2.2252	-28.1941	-0.0464
3P_1	36096	-0.0174	-0.6072	41.8610	3.2057	-28.1043	-0.0014
3P_2	37991	0.7444	109.8612	23.8093	5.0979	-26.1751	0.0418
1S_0	79390	8.5783	-0.6072	10.3450	4.1862	-30.0144	-0.9565

Free ion values : $E^1 = 7142.4$, $E^2 = 33.795$, $E^3 = 674.27$, $\xi_{4f} = 2628.7$, $\alpha = 14.677$, $\beta = -631.79$

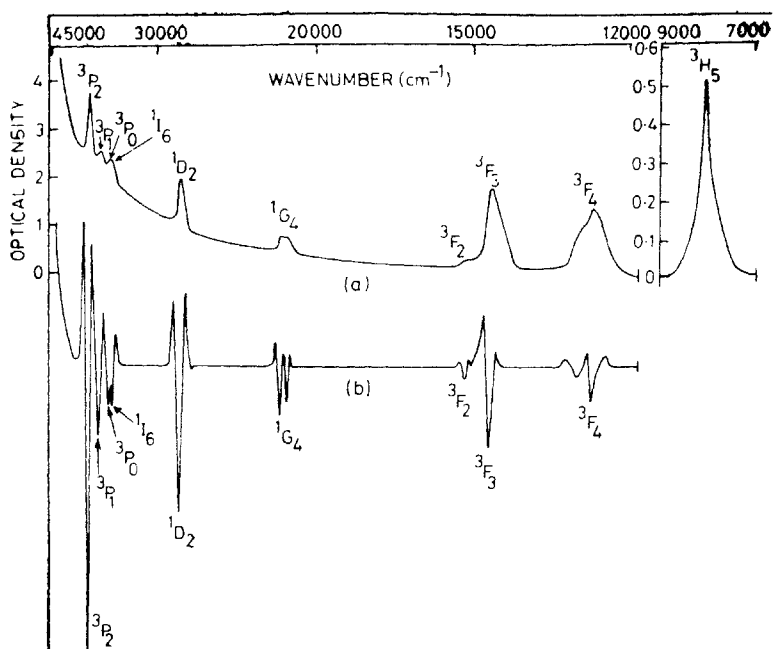


FIG. 1.

Fig. 1 shows the normal and second derivative spectra of Thulium acetate. The assignments of electronic transitions to the observed bands was straight forward.

For the numerical evaluation of the E^k , ξ_{4f} , α and β parameters, the observed energy levels were substituted for E_j in eqn. (1). Using the numerical values of the zero order energies and partial derivatives given in Table I, a number of linear equations equal to the number of observed levels were formed. By employing the method of least square fit, the values of ΔE^k , $\Delta \xi_{4f}$, $\Delta \alpha$ and $\Delta \beta$ were calculated. From these delta values, the parameters E^k , ξ_{4f} , α and β for Tm^{3+} in Thulium acetate were evaluated using the formula given in eqn. (2) and are presented in Table II. The energy levels calculated using the above parameters are presented in Table II along with the observed band positions.

It is interesting to note that the calculated energy levels obtained by diagonalizing the energy matrices using the parameters obtained from the least square fit are almost the same. As is seen from this Table II, the RMS deviation is reduced from 264cm^{-1} to 202cm^{-1} when correction factors α and β were employed.

DISCUSSION

The nephelauxetic ratio β is defined as (Tandon & Mehta, 1969)

$$\beta = \frac{\nu_c}{\nu_a} \quad \dots(3)$$

TABLE II

Experimental and calculated energy levels without and with configuration interaction parameters and bonding parameter for $\text{Tm}^{3+} : \text{Tm}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 4\text{H}_2\text{O}$

Energy level	Aquo-ion ^a Cm ⁻¹	E_{exp} cm ⁻¹	E_{cal}^b without α, β		$E_{\text{exp}}E_{\text{cal}}$ cm ⁻¹	E_{cal} with α, β		$E_{\text{exp}} - E_{\text{cal}}$ cm ⁻¹	
			Least-square	Diag.		Least-square	Diag.		
3H_4	5900	...	5558	5558	...	5797	5795 ^c
3H_5	8400	7830	8231	8231	-401	8180	8180	-350	0.93214
3F_4	12700	12647	12549	12549	98	12592	12594	53	0.99583
3F_3	14500	14637	14222	14222	415	14598	14598	39	1.00945
3F_2	15100	15182	14960	14955	227	15170	15170	12	1.00543
1G_4	21350	21226	21301	21302	-76	21191	21191	35	0.99419
1D_2	28000	27925	28082	28087	-162	27963	27963	-38	0.99732
1I_6	34900	34712	34526	34526	186	34675	34675	37	0.99461
3P_0	35500	35139	35502	35497	-358	35542	35541	-402	0.98983
3P_1	36400	36486	36188	36188	298	36156	36156	330	1.00236
3P_2	38250	38157	38299	38300	-143	38083	38083	74	0.99757
1S_0	79126	79126	...	80389	80390 ^c
RMS	Deviation	264	202	...
$\bar{\beta}$		0.99187
δ		0.81966

$$E^1 = 7194.9, E^2 = 33.966, E^3 = 674.03, \xi_{4f} = 2626.4, \alpha = 11.907, \beta = -1131.1$$

a : Carnall *et al.* (1968); b : Lakshman *et al.* (1980); c : The theoretical value for 1S_0 and 3H_4 energy levels were used for further calculations.

where ν_c and ν_a refer to the energies of the corresponding transitions in the complex (Thulium acetate) and the aquo-ion (Carnall *et al.*, 1968) respectively. The β values for all the observed transitions are computed and their average value $\bar{\beta}$ is used to estimate (Sinha, 1966) the parameter of bonding δ (in per cent) using the relation

$$\delta = \left(\frac{1 - \bar{\beta}}{\bar{\beta}} \right) \times 100 \quad \dots(4)$$

Depending on the ligands, the value of δ may be positive or negative indicating covalent or ionic bonding. As is seen from Table II the nature of the bonding is Covalent in Thulium acetate.

SPECTRAL INTENSITIES

The intensity of an absorption band is measured by its oscillator strength which is directly proportional to the area under the absorption curve. The oscillator strength f can be expressed in terms of the molar absorptivity ϵ , the energy of the transition in wavenumber σ by the relation

$$f = 4.32 \times 10^{-9} \int \epsilon(\sigma) d\sigma \quad \dots(5)$$

Here f is a dimensionless quantity. The molar absorptivity at a given energy is computed from the Beer-Lambert law

$$\epsilon = \frac{1}{cl} \log \frac{I_0}{I}, \quad \dots(6)$$

where c is the concentration of the substance in moles/litre, l is the light path in the solution (cm) and $\log \frac{I_0}{I}$ is the absorptivity or optical density. Experimentally measured intensities are given in Table III.

TABLE III

Experimental and calculated oscillator strengths and squared reduced matrix elements [$f^{12} {}^3H_6 \| U^\lambda \| f^{12} S'L'J' \|^2$ for $Tm^{3+} : Tm(C_2H_3O_2)_3 \cdot 4H_2O$]

S'L'J'	$f_{exp} \times 10^6$	$f_{cal} \times 10^6$	$[U^2]^2$	$[U^4]^2$	$[U^6]^2$
3H_5	3.2314	1.9827	0.10739	0.23142	0.63835
3F_4	3.1960	4.2368	0.24889	0.11822	0.60704
3F_3	2.3452	3.1087	0	0.31639	0.84112
3F_2	0.0674	0.4697	0	0	0.25669
1G_4	0.8792	1.5799	0.05115	0.07820	0.01411
1D_2	2.5588	3.4364	0	0.31816	0.09470
1I_6	1.7221	0.8543	0.01059	0.03881	0.01340
3P_0	1.0463	0.3200	0	0	0.07558
3P_1	0.6299	0.5447	0	0	0.12391
3P_2	3.7428	3.6082	0	0.26200	0.02178
RMS deviation	...	0.772×10^{-6}			

Refractive index (n) = 1.3358

$$T_2 = 0.88541 \times 10^{-9}$$

$$\tau_2 = 11.51033 \times 10^{-9}$$

$$\Omega_2 = 8.90543 \times 10^{-20}$$

$$T_4 = 0.35091 \times 10^{-9}$$

$$\tau_4 = 4.56183 \times 10^{-9}$$

$$\Omega_4 = 3.52944 \times 10^{-20}$$

$$T_6 = 0.12051 \times 10^{-9}$$

$$\tau_6 = 1.56663 \times 10^{-9}$$

$$\Omega_6 = 1.21209 \times 10^{-20}$$

$$\text{where } \tau_\lambda = (2J + 1) T_\lambda$$

There is some magnetic dipole character in a few transitions (f_{md}) but an induced electric dipole mechanism (f_{ed}) must be invoked to account for the intensities of most lanthanide absorption bands. Neglecting higher multipole mechanisms such as electric quadrupole etc., we have

$$f = f_{ed} + f_{md}. \quad \dots(7)$$

JUDD-OFELT THEORY

The actual calculation of intensities has been made feasible by the work of Judd (1962) and Ofelt (1962). They have independently shown that the oscillator strength

of an induced electric-dipole transition may be related to the energy of the transition $\sigma(\text{cm}^{-1})$ and the square of the matrix elements of the Unit Tensor Operator U^λ connecting the initial and final state ($\psi^J \rightarrow \psi'^{J'}$) via three phenomenological parameters $T_\lambda (\lambda = 2, 4, 6)$. These three parameters are complex expressions relating the radial wavefunctions of the states, the refractive index of the medium and the ligand field parameter which characterize the environmental field. In principle, they can be calculated but in practice they are treated as parameters to be determined from the experimental data.

According to the Judd-Ofelt theory

$$f_{ed} = \sum_{\lambda=2,4,6} T_\lambda \sigma (f^N \psi^J \| U^\lambda \| f^N \psi'^{J'})^2, \quad \dots(8)$$

where $\sigma(\text{cm}^{-1})$ is the mean energy of the transition $\psi^J \rightarrow \psi'^{J'}$, U^λ is a unit tensor operator of rank λ and the sum running over the three values $\lambda = 2, 4, 6$.

EVALUATION OF REDUCED MATRIX ELEMENTS U^λ

The matrix elements U^λ were calculated in the LS basis using the eqn. of Judd (1963)

$$(f^N \alpha SLJ \| U^\lambda \| f^N \alpha' SL'J') = (-1)^{S+L'+J+\lambda} [(2J+1)(2J'+1)]^{1/2} \\ \times \left\{ \begin{matrix} JJ'\lambda \\ L'LS \end{matrix} \right\} (f^N \alpha SL \| U^\lambda \| f^N \alpha' SL') \quad \dots(9)$$

The reduced matrix elements on the right hand side were taken from the Tables of Nielson *et al.* (1964). The values of 6- J symbols were taken from the Tables of Rotenberg *et al.* (1959). From the equation, we note that the sign of the numerical value depends on the S, L', J and λ values. The sign of the value does not play any significant role in the LS base because we are always using squared value of U^λ . But in the intermediate coupling case, the sign plays a dominant role because the states of f^N electronic configuration are taken as linear combinations

$$|f^N \psi^J \rangle = \sum_{\alpha, S, L} C(\alpha, S, L) |f^N \alpha SLJ \rangle, \quad \dots(10)$$

where $C(\alpha, S, L)$ are the numerical coefficients resulting from the diagonalization of the matrices. The eigenvectors of eqn. (10) are calculated by diagonalizing complete energy matrices using the evaluated parameters E^k, ξ_4, α and β . The wavefunctions in the intermediate scheme are given in Table IV.

These reduced matrix elements (U^λ) in the LS basis are presented in Table V. They have been transformed from the LS basis states to the physical coupling scheme prior to being squared and substituted in eqn. (8). The squares of U^2, U^4 and U^6 thus calculated and tabulated in Table VI, were substituted in eqn. (8) and using f_{exp} for f_{ed} (neglecting for the moment f_{md} as it is very small compared to f_{ed}), the values of T_λ parameters were evaluated by the least square fit method and are presented in Table III.

TABLE IV
The free ion wavefunctions for Tm^{3+} : $Tm(C_2H_3O_2)_3 \cdot 4H_2O$

${}^3H'_6 >$	$= 0.09317$	$ {}^1I >$	$+ 0.99565$	$ {}^3H >$
${}^3H'_4 >$	$= -0.29516$	$ {}^3H >$	$+ 0.55099$	$ {}^1G >$
${}^3H'_6 >$	$= 1.00000$	$ {}^3H >$		
${}^3F'_4 >$	$= -0.77045$	$ {}^3H >$	$+ 0.34590$	$ {}^1G >$
${}^3F'_8 >$	$= 1.00000$	$ {}^3F >$		
${}^3F'_2 >$	$= -0.87729$	$ {}^3F >$	$+ 0.45928$	$ {}^1D >$
${}^1G'_4 >$	$= 0.56506$	$ {}^3H >$	$+ 0.75945$	$ {}^1G >$
${}^1D'_2 >$	$= 0.43448$	$ {}^3F >$	$+ 0.63658$	$ {}^1D >$
${}^1I'_6 >$	$= -0.99565$	$ {}^1I >$	$+ 0.09317$	$ {}^3H >$
${}^3P'_0 >$	$= -0.97826$	$ {}^3P >$	$+ 0.20737$	$ {}^1S >$
${}^3P'_1 >$	$= 1.00000$	$ {}^3P >$		
${}^3P'_2 >$	$= 0.20392$	$ {}^3F >$	$+ 0.61954$	$ {}^1D >$
${}^1S'_0 >$	$= 0.20737$	$ {}^3P >$	$+ 0.97826$	$ {}^1S >$

TABLE V
The LS coupling values of $(f^N \alpha SLJ \| U^\lambda \| f^N \alpha S' L' J')$ for f^2 or f^{12} configurations

SLJ	S'L'J'	[U ²]	[U ⁴]	[U ⁶]	
3H_6	3H_6	1.10953	-0.84945	-0.89133	
	3H_5	-0.32914	0.48316	0.80246	
	3H_4	0.04331	-0.14305	-0.39510	
	3F_4	0.90851	0.93773	-0.82878	
	3F_3	0	-0.56495	0.92113	
	3F_2	0	0.14437	-0.55048	
	3P_0	0	0	-0.26726	
	3P_1	0	0	0.35355	
	3P_2	0	0.75018	-0.23837	
3H_6	3H_5	0.95879	-0.60568	-0.34847	
	3H_4	-0.32757	0.47446	0.76409	
	3F_4	0.76427	0.62202	-0.94281	
	3F_3	0.79282	0.58888	0	
	3F_2	0	-0.54595	0.81650	
	3P_0	0	0	0	
	3P_1	0	0.53452	0.29881	
	3P_2	0	0.43644	-0.35355	
	3H_4	3H_4	0.90520	-0.65555	-0.60328
3F_4		0.05216	0.24555	-0.65134	
3F_3		0.26427	0.60481	-0.84087	
3F_2		0.70630	0.64657	-0.37605	
3P_0		0	0.39841	0	
3P_1		0	0.43644	0	
3P_2		0	0.20101	-0.41872	
3F_4		3F_4	-0.34194	-0.25754	-0.12199
		3F_3	0.15749	0.24398	0.22048
	3F_2	-0.03367	-0.13041	-0.28172	
	3P_0	0	-0.41786	0	
	3P_1	0	0.57217	0	
	3P_2	1.04978	-0.41411	0	

TABLE V—(Contd.)

SLJ	$S'L'J'$	$[U^2]$	$[U^4]$	$[U^6]$
3F_3	3F_3	-0.25000	-0.05556	0.25000
	3F_2	0.15430	0.22023	0
	3P_0	0	0	0
	3P_1	0.75593	0.44320	0
	3P_2	0.53452	-0.57217	0
3F_2	3F_2	-0.23328	-0.11772	0
	3P_0	0.53452	0	0
	3P_1	0.53452	0	0
	3P_2	0.20203	-0.61168	0
3P_0	3P_0	0	0	0
	3P_1	0	0	0
	3P_2	-0.46291	0	0
3P_1	3P_1	0.40089	0	0
	3P_2	-0.69437	0	0
3P_2	3P_2	-0.61237	0	0
1I_6	1I_6	2.21906	1.27417	0.35653
	1G_4	0.58109	1.43945	1.06017
	1D_2	0	0.43312	1.37620
	1S_0	0	0	0.75593
1G_4	1G_4	0.22381	-1.07698	1.19770
	1D_2	0.94761	0.16682	0.36037
	1I_6	0.58109	1.43945	1.06017
	1S_0	0	0.75593	0
1D_2	1D_2	-0.64153	0.70630	0
	1S_0	0.75593	0	0
1S_0	1S_0	0	0	0

TABLE VI

Values of $[SLJ||U^\lambda||S'L'J']^2$ for $Tm^{3+} : Tm(C_2H_3O_2)_8 \cdot 4H_2O$

SLJ	$S'L'J'$	$[U^2]^2$	$[U^4]^2$	$[U^6]^2$
3H_4	3H_4	0.00732	0.42790	0.28821
	3H_5	0.09179	0.11936	0.92440
	3F_4	0.13565	0.12642	1.56386
	3F_3	0.00202	0.00014	0.17664
	3F_2	0.31355	0.06033	0.04160
	1G_4	0.00322	0.02098	0.08022
	1D_2	0.56625	0.09759	0.02491
	1I_6	0.06446	0.51487	0.39818
	3P_0	0	0.27090	0
	3P_1	0	0.10100	0
	3P_2	0.11939	0.08252	0.00005
	1S_0	0	0.09950	0

(Contd. Table VI)

TABLE VI—(contd.)

SLJ	$S'LJ'$	$[U^2]^2$	$[U^1]^2$	$[U^0]^2$	
3H_5	3H_5	0.91929	0.36684	0.12143	
	3F_4	0.01229	0.48809	0.00703	
	3F_3	0.62857	0.34678	0	
	3F_2	0	0.29136	0.58611	
	1G_4	0.07306	0.00456	0.54130	
	1D_2	0	0.00167	0.01677	
	1I_6	0.00094	0.00203	0.00559	
	3P_0	0	0	0	
	3P_1	0	0.28571	0.08929	
	3P_2	0	0.19550	0.18879	
	1S_0	0	0	0	
	3F_4	3F_4	0.25917	0.15150	0.61974
3F_3		0.08291	0.35596	0.28067	
3F_2		0.28491	0.16940	0.08083	
1G_4		0.15773	0.00306	0.34987	
1D_2		0.14298	0.01139	0.22689	
1I_6		0.06178	0.28330	0.08727	
3P_0		0	0.01839	0	
3P_1		0	0.41300	0	
3P_2		0.27239	0.01046	0.00600	
1S_0		0	0.05690	0	
3F_3		3F_3	0.06250	0.00309	0.06250
		3F_2	0.00371	0.07450	0
	1G_4	0.00971	0.06922	0.29837	
	1D_2	0.16616	0.07230	0	
	1I_6	0	0.00277	0.00737	
	3P_0	0	0	0	
	3P_1	0.57143	0.19643	0	
	3P_2	0.13966	0.22908	0	
	1S_0	0	0	0	
	3F_2	3F_2	0.14150	0.04325	0
		1G_4	0.00582	0.07011	0.03978
		1D_2	0.06437	0.30941	0
1I_6		0	0.04005	0.34505	
3P_0		0.35265	0	0	
3P_1		0.13850	0	0	
3P_2		0.00409	0.04085	0	
1S_0		0.05245	0	0	
1G_4		1G_4	0.13217	0.89627	0.52245
		1D_2	0.17689	0.17231	0.00086
		1I_6	0.21566	1.26367	0.63608
		3P_0	0	0.05428	0
	3P_1	0	0.00386	0	
	3P_2	0.61782	0.00066	0.10504	
	1S_0	0	0.40479	0	

TABLE VI—(contd.)

SLJ	$S'L'J'$	$[U^4]^a$	$[U^4]^b$	$[U^4]^c$
1D_2	1D_2	0.19427	0.00558	0
	1I_6	0	0.05024	0.82572
	3P_0	0.02596	0	0
	3P_1	0.45518	0	0
	3P_2	0.00033	0.15218	0
	1S_0	0.20953	0	0
1I_6	1I_6	4.88159	1.57687	0.11951
	3P_0	0	0	0.01735
	3P_1	0	0	0.00109
	3P_2	0	0.10075	0.70985
	1S_0	0	0	0.54974
3P_0	3P_0	0	0	0
	3P_1	0	0	0
	3P_2	0.12445	0	0
	1S_0	0	0	0
3P_1	3P_1	0.16071	0	0
	3P_2	0.17417	0	0
	1S_0	0	0	0
3P_2	3P_2	0.44925	0.20730	0
	1S_0	0.30638	0	0
1S_0	1S_0	0	0	0

The Ω_λ values were calculated from the equation

$$\Omega_\lambda = \left[1.085 \times 10^{14} \frac{n(n^2 + 2)}{9} \right]^{-1} (2J + 1) T_\lambda, \quad \dots(11)$$

where n is the refractive index of the substance.

The electric dipole linestrengths for all transitions were calculated from the formula.

$$S_{ed} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda (\psi J \| U^\lambda \| \psi' J')^2. \quad \dots(12)$$

The same eigenvectors are used in calculating the magnetic dipole linestrength S_{md} , Carnall *et al.* (1965).

$$S_{md} = \frac{e^2 h^2}{16\pi^2 m^2 c^2} (\psi J \| L + 2S \| \psi' J')^2 \quad \dots(13)$$

TRANSITION PROBABILITIES

The total oscillator strength f of a band with energy $\sigma(\text{cm}^{-1})$ is given by

$$f(\psi J : \psi' J') = \frac{8\pi^2 mc \sigma}{3he^2(2J + 1)} \left[\frac{(n^2 + 2)^2}{9n} S_{ed} + nS_{md} \right] \quad \dots(14)$$

The total radiative transition probability is given by

$$A(\psi J : \psi' J') = \frac{64\pi^4 \sigma^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right] \quad \dots(15)$$

Since the excited state relaxation usually involves transition to a number of states, we define a total radiative relaxation rate

$$A_T(\psi J) = \sum_{\psi' J'} A(\psi J : \psi' J'), \quad \dots(16)$$

where the sum runs over all $\psi' J'$ lower in energy than ψJ . The radiative lifetime of a state is

$$\tau_R(\psi J) = [A_T(\psi J)]^{-1}. \quad \dots(17)$$

All these calculated values are tabulated in Table VII.

TABLE VII

Electric dipole linestrength (S_{ed}), magnetic dipole linestrength (S_{md}) total transition probability (A) and total oscillator strength (f) and the radiative lifetime (τ_R) for $Tm^{3+} : Tm(C_2H_3O_2)_3 \cdot 4H_2O$

SLJ	$S'L'J'$	$\frac{S_{ed}}{e^2} \times 10^{22}$	$\frac{S_{md}}{e^2} \times 10^{22}$	$f \times 10^6$	A	A_T	$\tau_R(\mu\text{Sec.})$	
3P_0	1I_6	2.103	0	0.012	0			
	1D_2	23.118	0	2.155	132			
	1G_4	19.158	0	3.443	785			
	3F_2	314.050	0	80.970	37991			
	3F_3	0	0	0	0			
	3F_4	6.491	0	1.886	1124			
	3H_5	0	0	0	0			
	3H_4	95.613	0	36.247	36768			
	3H_6	9.161	0	4.159	6049	82849	12.07	
	1I_6	1D_2	117.817	0	0.795	43		
1G_4		715.158	0	9.585	2054			
3F_2		55.959	0	1.086	488			
3F_3		1.871	0	0.037	18			
3F_4		165.585	0	3.631	2082			
3H_6		2.231	0	0.060	51			
3H_4		287.388	0	8.259	8135			
3H_6		24.753	0.4865	0.873	1239	14110	70.87	
1D_2		1G_4	218.448	0	3.781	200		
		3F_2	166.529	3.2876	5.604	1072		
	3F_3	173.490	0	5.957	1239			
	3F_4	158.851	0	6.271	1724			
	3H_5	2.622	0	0.136	65			
	3H_4	541.733	0	30.976	17871			
	3H_6	123.771	0	8.930	8204	30374	32.92	
	3G_4	3F_2	34.750	0	0.301	13		
3F_3		69.243	0	0.655	34			
3F_4		183.953	11.3798	2.422	210			
3H_5		132.283	0	2.544	538			
3H_4		19.996	0.5865	0.457	128			
3H_6		74.862	0	2.281	1211	2134	468.60	

The radiative lifetime for Tm^{3+} in Thulium acetate is highest in 1G_4 while it is least in 3P_0 level. Similar results have been reported in glasses also (Nisson Spector *et al.*, 1977). Second derivative spectra exhibit (Fig. 1) splittings in 3H_4 , 1G_4 levels. Since the crystal symmetry for Tm^{3+} in Thulium acetate is not clearly known, no attempt to calculate the approximate crystal field parameters could be made. It is interesting to note that the closely lying 3P_0 and 1I_6 levels are found separated in the second derivative spectrum (See Fig. 1).

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