The Absorption Spectrum of Tm$_2$ (SO$_4$)$_3$:8H$_2$O

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THE absorption spectra of the salts of the rare earths have been attributed by some authors[1] exclusively to transitions within the 4f shell; others, including one of the present authors,[2] considered transitions of a 4f electron to one of the outer shells, e.g., 5d, as an alternative possibility. This note is to present evidence for the first assumption and to show that at least semiquantitative agreement may be obtained for Tm salts.

Two theoretical arguments may be given *a priori* for the transitions within the 4f shell: First, the sharpness of the absorption lines would be immediately evident in the case of a transition within an inner shell and second, the intensity of the absorption lines is extremely small (about $10^{-8} - 10^{-7}$ dispersion electrons for the stronger lines). This indicates that they are due to a "forbidden" transition which would be true for a rearrangement within the 4f shell.

Thulium was selected as the rare earth most favorable for a comparison between theory and experiment. Tm IV has its 4f shell filled except for two "holes" so that the energy levels are comparatively simple. It is preferable to Pr IV which contains two *electrons* in the 4f shell because the spectra of Pr salts (and salts of other "light" rare earths) possess a large number of lines many of which are probably due to coupling with crystal vibrations. The smaller 4f shell in Tm will have smaller coupling with vibrations so that we obtain a simpler spectrum representing, probably, only transitions between electronic states. Yb would have an even simpler spectrum than Tm because it has only one hole in the 4f shell: But this reduces the spectrum to a single line $^2F_{7/2} - {}^2F_{5/2}$ which lies in the infrared.

The levels of the free ion Tm IV were calculated as follows: For the electrostatic interaction between the electrons, the empirical spectrum of La II (which is analogous to Tm IV) was taken as

basis. It was assumed that the spacing between the energy levels without spin-orbit interaction is simply multiplied by a constant factor when we go over from La II to Tm IV which arises (a) from the higher degree of ionization and (b) from the greater "internal" nuclear charge. The effect (a) was estimated from a comparison of the spectra of La II and Pr IV,[4] to introduce a factor of about 2.4. Because of (b), the electrostatic interaction is directly proportional to the effective nuclear charge; taking a screening constant of 34 for the 4f shell of all rare earths, this gives for the ratio Tm IV/Pr IV $= (69-34)/(59-34) = 1.4$, and therefore Tm IV/La II $= 3.3$.

The constant ζ (cf. Condon and Shortley) characteristic of the spin-orbit interaction was found to be about 170 cm^{-1} for La II, from the splitting of the H levels which have most nearly Russell-Saunders coupling. We assume that ζ increases again by a factor of 2.4 from La II to Pr IV (probably underestimated) and is proportional to Z_{eff}^3 for ions of the same degree of ionization. This gives another factor $1.4^4 = 3.8$ from Pr IV to Tm IV, giving $\zeta = 1500$ cm^{-1} for Tm IV. In order to get a better value, we calculated the levels of Tm IV including spin-orbit interaction, assuming for ζ values in the neighborhood of 1500 cm^{-1}. Very satisfactory agreement with the position of the line groups in the absorption spectrum of thulium sulfate[4] was obtained for $\zeta = 1400$ cm^{-1}. With this value for ζ, the coupling is very far from the Russell-Saunders case. Table I gives the calculated and observed positions of the levels in cm^{-1} above the ground state. For each level, we give the spectroscopic designation of the Russell-Saunders level to which it is connected by an adiabatic change of ζ.

The splitting of the levels in the crystalline field was calculated by using essentially the

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[1] S. Freed, J. Chem. Phys. 5, 22 (1937); J. H. Van Vleck, J. Phys. Chem. Jan. (1937).

[2] F. H. Spedding, J. Chem. Phys. 5, 416 (1937).

[3] C. B. Ellis, Phys. Rev. to be published.

[4] Brandtl and Scheiner, Zeits. f. anorg. allgem. Chemie 220, 107 (1934). Nutting and Meehan, unpublished work. Spedding and Keller, unpublished work.

TABLE I. *Absorption multiplets of $Tm_2(SO_4)_3 \cdot 8H_2O$.*

TERM	CALCULATED 1400 cm⁻¹	OBSERVED cm⁻¹
$^3H_6$	0	0
$^3H_4$	5565	infrared
$^3H_5$	8490	"
$^3F_2$	10740	"
$^3F_4$	13270	14600
$^3F_3$	14560	15150
$^1G_4$	22580	21500
$^1D_2$	23730	21100
$^1I_6$	27680	28000
$^3P_0$	32155	—
$^3P_2$	35020	
$^3P_1$	35290	—
$^1S_0$	57425	—

TABLE II. *Crystalline states of Tm IV in a cubic field.*

	$^3H_6$	$^1I_6$ (cm⁻¹)
Γ_1	0	183
Γ_4	14	162
$\Gamma_{5\alpha}$	31	137
Γ_2	97	37
$\Gamma_{5\beta}$	116	9
Γ_3	122	0

	$^3H_4$	$^3F_4$	$^1G_4$
Γ_5	0	0	0
Γ_3	64	47	120
Γ_4	85	62.5	160
Γ_1	115	84	216

	$^3F_3$	$^1D_2$	
Γ_2	0	Γ_3	0
Γ_5	7	Γ_5	25
Γ_4	13		

method of Penney and Schlapp[5] but taking into account the large deviation from Russell-Saunders coupling. The field was assumed to be cubic on the strength of the experimental evidence obtained with erbium.[6] From the experimental data on erbium we also deduced the strength of the cubic field. Table II gives the crystalline states of Tm IV calculated in this way.

The intensity of the absorption lines was calculated on the basis of the following considerations: Direct dipole transitions within the 4f shell are forbidden as long as the 4f electrons are subject to an electric field symmetrical with respect to inversion at the atomic nucleus. There are therefore three possible types of transitions:

(a) Ordinary quadrupole transitions. Selection rule $\Delta J = 0$, ± 1 or ± 2.

(b) Dipole transitions caused by a *natural* lack of symmetry of the crystalline field. This symmetry may correspond to a term in the potential energy which is either linear or cubic (or of higher order) in the coordinates with respect to the nucleus. The linear term will in general be absent because of the equilibrium condition; moreover, it will give the same selection rules which hold for the ordinary quadrupole radiation. The cubic

[5] Penney and Schlapp, Phys. Rev. **41**, 194 (1932).
[6] F. H. Spedding, J. Chem. Phys. **5**, 316 (1937).

term will therefore be the most important, and was considered in our calculations. J may change by any amount up to 4.

(c) Dipole transitions caused by coupling with crystal vibrations. In general, only the term of first order in the vibrational amplitude will be important. In this case, the selection rule will be the same as in (a).

The J selection rules should hold rather strictly since the crystal splitting is small compared to the spacing between levels of different J. A simple estimate shows that the quadrupole transitions should, for Tm, be about 10 times as strong as the dipole transitions (b), (c). Since the ground state is $^3H_6$, we expect therefore particularly strong transitions to states with $J=6$ ($^1I_6$), $J=5$ ($^3H_5$, in the infrared) and $J=4$ ($^3H_4$, $^1G_4$, $^3F_4$) which agrees with experiment.

The intensities of the individual lines were calculated, assuming quadrupole transitions in all cases where J changes by 2 or less, and type (b) dipole transitions for larger changes of J. Good agreement was obtained for the transition $^3H_6 - {}^3F_4$, and reasonable agreement for the other line groups. A more extensive account of this work will appear in the *Journal of Chemical Physics*.