The Journal of Chemical Physics

RESEARCH ARTICLE | SEPTEMBER 18 2003

Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. II. Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, and Ho^{3+}

W. T. Carnall; P. R. Fields; K. Rajnak

J. Chem. Phys. 49, 4412–4423 (1968)
https://doi.org/10.1063/1.1669892

AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 10 15 NOVEMBER 1968

Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. II. Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, and Ho^{3+}*

W. T. CARNALL, P. R. FIELDS, AND K. RAJNAK†
Chemistry Division, Argonne National Laboratory, Argonne, Illinois

(Received 2 April 1968)

We have correlated the experimentally determined band intensities in the solution absorption spectra of the trivalent lanthanides with a theoretical expression derived by Judd. The spectra were measured in a single medium, dilute acid solution, and, in most cases, in the range ≈6000–50 000 cm^{-1}. In general, the correlation between calculated and observed intensities was very good, even at higher energies. The variation of the intensity parameters over the series is discussed as is the somewhat unexpected degree of correlation obtained in the ultraviolet region.

INTRODUCTION

In the first paper of this series,[1] subsequently referred to as I, we discussed the correlation between calculated and experimentally measured intensities of bands in the solution absorption spectra of Pr^{3+}, Nd^{3+}, Er^{3+}, Tm^{3+}, and Yb^{3+} in three different solvents. The present communication is devoted to a consideration of the same type of correlation with all of the remaining trivalent lanthanides. It considerably extends and revises earlier preliminary results.[2] The calculation of band intensities is based upon the theoretical treatments derived by Judd[3] and by Ofelt.[4]

One of the major obstacles to this investigation was the paucity of information concerning the energy-level structure of those lanthanides which occur near the center of the series. Thus, it was necessary to first obtain sets of electrostatic and spin–orbit coupling parameters from which energy levels could be calculated in agreement with observed transitions before proceeding to the conclusion of the intensity study. The procedure adopted to obtain these parameters is discussed in an accompanying paper[5] and in Ref. 6. For present purposes we assume that the parameters are known and that we can identify the transitions which give rise to lanthanide absorption bands throughout the spectral range ∼6000–50 000 cm^{-1}. We will examine the correlation between calculated intensities and those observed in a single medium, dilute acid solution, i.e., for hydrated lanthanide ions.

Since we have also refined the energy-level parameters for those lanthanide ions considered in I, the resulting modifications of the earlier intensity correlations will also be cited here.

THEORETICAL CONSIDERATIONS

The theoretical aspects of this study were discussed in I; consequently, only the principal relationships will be cited here.

A consideration of the mechanisms by which intra-f-electron transitions may occur shows that the intensities of the observed bands can be adequately accounted for by two processes. In a few cases, the transitions occur wholly or partially by a magnetic-dipole mechanism. Such transitions follow the selection rules

$$\Delta J \leq 1, \qquad \Delta L = 0, \qquad \Delta S = 0, \quad \text{and} \quad \Delta l = 0$$

in the Russell–Saunders coupling scheme which is adopted here. Given the eigenvectors of the states involved, the magnetic-dipole intensities may be readily calculated.[1] The second and principal mechanism treats the transitions as being essentially (forced or induced) electric dipole in character. Both Judd[3] and Ofelt[4] were concerned with developing expressions for the intensity which arises via the latter mechanism.

Judd's result may be written in the form

$$P = \sum_{\lambda} \mathfrak{T}_\lambda \sigma (f^N \psi J \,\|\, U^{(\lambda)} \,\|\, f^N \psi' J')^2,$$

$$\lambda = 2, 4, 6,$$

where P is the oscillator strength corresponding to the induced electric-dipole transition $\psi J \rightarrow \psi' J'$ at energy σ (cm^{-1}) and $\mathbf{U}^{(\lambda)}$ is a tensor operator of rank λ. The matrix elements of $\mathbf{U}^{(\lambda)}$ were calculated from formulas given in I. The three quantities, $\mathfrak{T}_\lambda$, are related to the radial parts of the $4f^N$ wavefunctions, the wavefunctions of perturbing configurations of which the nearest is $4f^{N-1}5d$, the refractive index of the medium, and the ligand-field parameters which characterize the environment of the ion. While in principle values of $\mathfrak{T}_\lambda$ could be calculated, we have treated these quantities as parameters to be determined from experimental oscillator strengths.

The measured intensity of an absorption band is related to the probability (P) for absorption of radiant

---

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

† Present address: Kalamazoo College, Kalamazoo, Mich.

[1] W. T. Carnall, P. R. Fields, and B. G. Wybourne, J. Chem. Phys. **42**, 3797 (1965).

[2] W. T. Carnall and P. R. Fields, Advan. Chem. Ser. **71**, 86 (1967).

[3] B. R. Judd, Phys. Rev. **127**, 750 (1962).

[4] G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

[5] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4424 (1968); see following paper.

[6] W. T. Carnall, P. R. Fields, and K. Rajnak, Argonne Natl. Lab. Rept., ANL-7358, 1967.

TABLE I. Calculated magnetic-dipole oscillator strengths for the 3+ lanthanides.[a]

	$S'L'J'$	E_{calc} (cm^{-1})[b]	$P'\times10^8$ [c]		$S'L'J'$	E_{calc} (cm^{-1})[b]	$P'\times10^8$ [c]
Pr^{3+}	$^3H_5$	2 322	9.76	Tb^{3+}	$^7F_5$	2 112	12.11
	$^3F_3$	6 540	0.02		$^5G_6$	26 425	5.03
	$^3F_4$	6 973	0.49		$^5G_5$	27 795	0.36
	$^1G_4$	9 885	0.25		$^5L_6$	29 550	0.14
Nd^{3+}	$^4I_{11/2}$	2 007	14.11		$^5H_7$	31 537	0.06
	$^2H_{9/2}$	12 738	1.12		$^5H_6$	33 027	0.46
	$^4F_{9/2}$	14 854	0.20		$^5H_5$	33 879	0.03
	$^2G_{7/2}$	17 333	0.02		$^5F_5$	34 927	1.87
	$^2I_{11/2}$	28 624	0.05		$^5G_6$	41 082	0.23
Pm^{3+}	$^5I_5$	1 577	16.36	Dy^{3+}	$^6H_{13/2}$	3 506	22.68
	$^5F_4$	14 562	0.08		$^4I_{15/2}$	22 293	5.95
	$^3H_4$	17 327	1.30		$^4I_{13/2}$	25 919	0.41
	$^5G_4$	20 181	0.26		$^4K_{17/2}$	26 365	0.09
	$^3G_4$	23 897	0.11		$(^4M, {}^4I)_{15/2}$	29 244	0.69
	$^3I_5$	27 916	0.23		$^4M_{17/2}$	30 892	0.03
	$^3H_4$	35 473	0.04		$^4K_{15/2}$	31 795	0.12
Sm^{3+}	$^6H_{7/2}$	1 080	17.51		$^4H_{13/2}$	33 471	0.60
	$^6F_{3/2}$	6 641	0.02		$(^4K, {}^4L)_{13/2}$	33 776	0.37
	$^6F_{5/2}$	7 131	0.08		$(^2K, {}^2L)_{15/2}$	38 811	0.09
	$^4G_{5/2}$	17 924	1.76		$^4I_{15/2}$	41 596	0.03
	$^4F_{3/2}$	18 832	0.03	Ho^{3+}	$^5I_7$	5 116	29.47
	$^4G_{7/2}$	20 014	0.05		$^3K_8$	21 308	6.39
	$^4F_{5/2}$	22 098	0.45		$^3K_7$	26 117	0.28
	$^4H_{7/2}$	28 396	0.67		$^3L_9$	29 020	0.12
	$^4G_{5/2}$	30 232	0.03		$^3L_8$	34 306	0.17
	$^4G_{5/2}$	42 714	0.02		$^3L_7$	38 022	0.04
	$^4G_{7/2}$	42 965	0.06		$^3I_7$	38 470	0.36
	$(^4H, {}^2G)_{7/2}$	44 237	0.04	Er^{3+}	$^4I_{13/2}$	6 610	30.82
Eu^{3+}	$^7F_1$	350	17.73		$^2K_{15/2}$	27 801	3.69
	$^5D_1$	19 026	1.62		$^2K_{13/2}$	33 085	0.11
	$^5F_1$	33 429	2.16		$^2L_{17/2}$	41 686	0.03
Gd^{3+}	$^6P_{7/2}$	32 224	4.13		$^2I_{13/2}$	43 717	0.12
	$^6P_{5/2}$	32 766	2.33	Tm^{3+}	$^3H_5$	8 390	27.25
	$^6D_{9/2}$	39 779	0.03		$^1I_6$	34 886	1.40
	$^6D_{7/2}$	40 712	0.39	Yb^{3+}	$^2F_{3/2}$	10 400	17.76
	$^6D_{5/2}$	40 977	0.20				

[a] Results are recorded only for transitions in which $P'>0.015\times10^{-8}$.

[b] The eigenvectors used in these calculations are those generated by the parameters for solution spectra recorded in Ref. 5 *et seq.*

[c] For dilute acid solutions of the lanthanides, it was assumed that $\eta=1.33$ in the expression $P_{\text{md}}=P'\eta$.

energy (oscillator strength) by the expression[7]

$$P=\frac{2303mc^2}{N\pi e^2}\int\epsilon_i(\sigma)\,d\sigma$$

$$=4.318\times10^{-9}\int\epsilon_i(\sigma)\,d\sigma,$$

where ϵ is the molar absorptivity at the energy σ (cm^{-1}) and the other symbols have their usual meaning. It will be noted that in I a factor involving the index of refraction of the medium was improperly written as part of the experimental P, whereas it should only occur within the expression for $\mathfrak{J}_\lambda$.

At this point we can write

$$P_{\text{exptl}}=P_{\text{md}}+P_{\text{ed}}.$$

For most observed bands, the transitions involved were not magnetic dipole in character, so the experimental oscillator strength (P_{exptl}) could be equated to that calculated for an induced electric dipole transition, P_{ed}. Where there was a significant contribution from P_{md}, the calculated value was subtracted from P_{exptl}, and the residual was equated to P_{ed}. Calculated magnetic-dipole oscillator strengths for all of the 3+ lanthanides considered here were obtained from Table I. The expression for P_{md}, as discussed in I, is of the form

$$P_{\text{md}}=P'\eta,$$

---

[7] J. Hoogschagen, Physica 11, 513 (1946).

TABLE II. Values of $\mathfrak{T}_\lambda$ for the lanthanides in dilute acid.

	$\mathfrak{T}_2\times10^9$ (cm)	$\mathfrak{T}_4\times10^9$ (cm)	$\mathfrak{T}_6\times10^9$ (cm)
Pr^{3+}	42.0±91.8	7.4±3.2	41.2±3.8
Nd^{3+}	1.20±0.41	6.44±0.36	10.2±0.54
Pm^{3+}	3.61±0.31	3.25±0.48	5.42±0.27
Sm^{3+}	1.17±1.12	5.32±0.35	3.47±0.33
Eu^{3+}	1.88	8.59	6.96±0.46
Gd^{3+}	3.30±0.62	6.06±0.53	6.10±0.10
Tb^{3+}	0.005±0.04	9.26±2.96	4.45±0.29
Dy^{3+}	1.93±5.23	4.44±0.21	4.46±0.28
Ho^{3+}	0.47±0.18	4.05±0.21	3.96±0.21
Er^{3+}	2.05±0.16	2.51±0.24	2.45±0.12
Tm^{3+}	1.03±0.82	2.68±0.38	2.40±0.21
Yb^{3+}	···	2.13	2.13

where $P'\times10^8$ is the quantity given in Table I and η is the refractive index of the medium. The calculations of P' were based upon the energy-level parameters for lanthanide aquo ions cited in Ref. 5. For dilute acid solutions, $\eta=1.33$ was used in calculating P_{md}.

Sets of equations in the three $\mathfrak{T}_\lambda$ parameters for a given lanthanide were subjected to a least-squares analysis to select the optimum values for $\mathfrak{T}_\lambda$. These values are recorded in Table II. The root-mean-square deviation (rms) of P_{exptl} and P_{calc} was defined as

$$\text{rms}=\left[\frac{\text{sum of squares of deviations}}{\text{number of levels}-\text{number of parameters}}\right]^{1/2}.$$

ANALISIS OF DATA

The experimental conditions and techniques were identical to those described in I; however, the process by which the data was analyzed has been modified. The spectra were recorded via digital read-out equipment connected directly to the spectrophotometer, and analysis of the data was accomplished on a computer. Originally, we used a Gaussian function as the basis for resolution and curve fitting. Subsequently, it became clear that a function intermediate between a Gaussian, where tailing is not as great as that actually observed experimentally, and a Lorentzian, where tailing is excessive, would be useful.

The modified Gaussian–Lorentzian function which was adopted had the form

$$y=\sum_{i=1}^{m}\frac{a_i}{[(x-b_i)/c_i]^2+1}\exp\left[-\frac{1}{k}\left(\frac{x-b_i}{c_i}\right)^2\right],$$

where m = number of components in the band, a_i = the peak height, b_i = energy at which a_i is observed, c_i is related to the width of the peak, and $k\geq0$ and integral. It was found experimentally that use of the function with $k=24$ usually produced very good agreement with the area obtained independently by integration over the observed data points.

RESULTS

$Pr^{3+}(f^2)$

In an earlier attempt (I) to fit the experimental intensity data for Pr^{3+} using Gaussian curves as a basis for integrating observed absorption bands, we found that $\mathfrak{T}_2$ was particularly poorly determined. Subsequent recalculation of the data, using matrix elements based on a better energy-level fit and resolution of the bands based upon the Gaussian–Lorentzian function, has served to clarify some aspects of the problem.

TABLE III. Oscillator strengths for Pr^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P\times10^6$ HClO$_4$–DClO$_4$ Exptl	Calc[b]	Calc[c]	$PrCl_3$[d] Exptl
5 800– 7 700	$^3F_3$ $^3F_4$	12.79	14.09	41.12	
9 100–11 000	$^1G_4$	0.32	0.67	1.32	0.34
16 000–17 500	$^1D_2$	3.08	2.18	4.45	3.12
20 200–21 000	$^3P_0$	2.54	6.88	2.99	2.52
21 000–22 100	$^3P_1$ $^1I_6$	7.63	4.14	7.27	6.66
22 100–23 500	$^3P_2$	15.06	12.49	14.64	14.6
rms Deviation			3.7×10^{-6}	1.3×10^{-6}	

[a] Range encompassing observed band(s).

[b] This fit included the six indicated bands. $\mathfrak{T}_2=-309.6\pm147.6\times10^{-9}$; $\mathfrak{T}_4=17.28\pm6.66\times10^{-9}$; $\mathfrak{T}_6=32.22\pm9.09\times10^{-9}$.

[c] This fit included data for five bands; the band extending from 5800 to 7700 cm^{-1} was *not* included. $\mathfrak{T}_2=42.0\pm91.8\times10^{-9}$; $\mathfrak{T}_4=7.4\pm3.2\times10^{-9}$; $\mathfrak{T}_6=41.2\pm3.8\times10^{-9}$.

[d] Reference 10.

---

[8] W. F. Krupke, Phys. Rev. **145**, 325 (1966).

Table IV. Oscillator strengths for Nd^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P\times10^6$ $HClO_4$-$DClO_4$ Exptl	 Calc[b]	 $NdCl_3$[c] Exptl	 $Nd(ClO_4)_3$[d] Exptl
5 600– 6 900	$^4I_{15/2}$	0.49	0.28		
11 000–12 000	$^4F_{3/2}$	2.56	2.34	3.02	2.3
12 000–13 000	$^4F_{5/2}$ $^2H_{9/2}$	8.84	8.62	9.22	7.7
13 000–14 200	$^4S_{3/2}$ $^4F_{7/2}$	8.90	9.50	8.88	7.6
14 200–15 200	$^4F_{9/2}$	0.65	0.72	0.83	0.51
15 600–16 200	$^2H_{11/2}$	0.15	0.19	0.39	0.14
16 600–18 200	$^4G_{5/2}$ $^2G_{7/2}$	9.76	9.88	10.5	8.3
18 600–20 200	$^2K_{13/2}$ $^4G_{7/2}$ $^4G_{9/2}$	7.01	5.35	6.58	5.8
20 200–22 400	$^2K_{15/2}$ $^2G_{9/2}$ $(^2D,{}^2F)_{3/2}$ $^4G_{11/2}$	2.33	1.39	2.31	1.9
23 100–23 500	$^2P_{1/2}$	0.41	0.55	0.38	0.30
23 500–24 200	$^2D_{5/2}$	0.09	0.05	0.08	0.06
26 000–26 500	$(^2P,{}^2D)_{3/2}$	0.03	0.04	0.05	0.02
27 600–29 800	$^4D_{3/2}$ $^4D_{5/2}$ $^2I_{11/2}$ $^4D_{1/2}$ $^2L_{15/2}$	9.42	10.29	9.52	9.8
29 800–31 300	$^2I_{13/2}$ $^4D_{7/2}$ $^2L_{17/2}$	2.70	0.15	2.36	1.7
31 300–32 300	$^2H_{9/2}$	0.13	0.17	···	0.76
33 000–34 000	$^2D_{3/2}$ $^2H_{11/2}$	0.33	0.48	···	0.60
34 000–34 900	$^2D_{5/2}$	0.28	0.13	···	0.76
38 200–40 000	$^2F_{5/2}$	0.18	0.09	···	1.9
rms Deviation			5.8×10^{-7}		

[a] Range encompassing observed band(s).

[b] The parameters used to obtain these values are given in Table II.

[c] Reference 10.

[d] D. C. Stewart, Argonne Natl. Lab. Rept. ANL-4812, 1952. These results are quoted in *Nouveau Traité de Chimie Minérale*, P. Pascal, Ed. (Masson & Cie., Paris, 1959), Vol. 7, Pt. 2.

We were not able to resolve the complex band due to transitions to the $^3F_3$ and $^3F_4$ levels near 6700 cm^{-1}, but the ^3P–^1I group was resolved into components due to $^3P_0$, $^3P_2$, and to the combined $^3P_1+{}^1I_6$ transitions. Thus the parameters $\mathfrak{T}_\lambda$ were determined by a fit to a minimum of six bands (Table III).

It was found that large matrix elements of $\mathbf{U}^{(4)}$ and $\mathbf{U}^{(6)}$ for the $^3F_3$ and $^3F_4$ transitions together with values for $\mathfrak{T}_4$ and $\mathfrak{T}_6$ calculated from results in the visible region of the spectrum predicted much more intensity near 6700 cm^{-1} than was actually observed. When data for the 6700-cm^{-1} band was included in the fitting process, a negative value was calculated for $\mathfrak{T}_2$. Within the framework of the problem this is the only mechanism to compensate for the excessively large oscillator strengths computed from $\mathfrak{T}_4$ and $\mathfrak{T}_6$. No additional weighting factors were employed in obtaining the indicated fit.

In fitting the experimental data for Pr^{3+} in LaF_3, Krupke[8] obtained good agreement between observed and calculated intensities for the infrared portion of the spectrum and a poor fit (values of P_{calc} that were too small) to the observed intensities due to $^3P_1+{}^1I_6$ and $^3P_2$. Thus, in effect, the results were similar to those obtained in solution, and we conclude that Judd's theory cannot fully account for the intensity relationships in Pr^{3+}. Since we were able to satisfactorily fit the energy-level scheme, the problem is not one of poorly determined electrostatic and spin–orbit parameters. Clearly it is possible to force a good fit on the bands observed in solution in the visible–near-infrared region and argue that the resulting poor fit to the ^3P–^1I group is related to the proximity of the excited $f^{N-1}d$ configuration.[9] However, the resulting parameters involve a negative value for $\mathfrak{T}_2$, which is inconsistent with Judd's theory.

$Nd^{3+}(f^3)$

Recalculation of the intensity parameters for Nd^{3+} based on more extensive experimental data and on an improved energy-level fit to the bands observed in solution has only slightly modified the values we reported in I. It is characteristic of the spectrum of many of the trivalent lanthanides that the $4f^N \rightarrow 4f^N$ transitions in the ultraviolet region are superimposed upon the tail of a much more intense absorption.[10,11] Thus, any intensity measurements involving $f \rightarrow f$ transitions in the ultraviolet normally require that a backgroup absorption be subtracted. The correction, particularly for weak bands such as are observed in the Nd^{3+} spectrum in the region 30 000–50 000 cm^{-1}, imparts a rather large probable error to the experimental values obtained. Nevertheless, the correlation between observed and calculated oscillator strengths up to 40 000 cm^{-1} (Table IV) is satisfactory in practically every instance. The notable exception is the band near 30 500 cm^{-1}, where for reasons that are not apparent the observed intensity is much greater than that calculated.

$Pm^{3+}(f^4)$

We were only able to obtain reproducible intensity measurements for Pm^{3+} to $\sim$21 000 cm^{-1}, although weaker bands were observed between 21 000 and 25 000 cm^{-1}. Beyond 25 000 cm^{-1}, no bands were observed above the very large background absorption, due primarily to products of radiation decomposition of the solutions.[12]

A comparison of observed and calculated oscillator strengths is given in Table V. Over the limited region in which reproducible measurements could be made, the correlation is very good.

$Sm^{3+}(f^5)$

Aside from the relatively intense bands in the near infrared, most of the transitions in Sm^{3+} give rise to rather weak absorption maxima.[11] The level density is very high in the visible–ultraviolet regions. On the basis of the assignments made, and the resolution of complex groups, it was possible to obtain the intensity correlation shown in Table VI. At energies $>$30 000 cm^{-1}, only very weak bands are observed.

$Eu^{3+}(f^6)$

Europium is the only trivalent lanthanide in which the ground term has $J=0$. This forces special restrictions on the induced-electric-dipole transitions which arise from the ground level. Thus, the Judd–Ofelt theory predicts zero intensity for those transitions which terminate in levels where J' is odd or zero. In addition, for even values of J', no intensity is calculated except for $\lambda = \Delta J$. Thus, the only matrix elements of $\mathbf{U}^{(\lambda)}$ which are nonzero for the transition $^7F_0 \rightarrow {}^7F_2$ are those for $\mathbf{U}^{(2)}$. The spectrum of Eu^{3+} observed at 25° is actually much more complex than the preceding discussion implies,[11] since it includes transitions arising from the $^7F_1$ and $^7F_2$ levels which lie near 350 and 1000 cm^{-1}, respectively. These levels are thermally populated at room temperature.

In aqueous solution we could only measure spectra at $>$6000 cm^{-1}. Thus, transitions from $^7F_{0,1,2}$ to components of the ^5D multiplet give rise to the lowest-energy bands within the experimental range. An extremely weak band was detected near 17 300 cm^{-1} and attributed to $^7F_0 \rightarrow {}^5D_0$.[13,14] Since this transition is forbidden by both electric- and magnetic-dipole selection rules, the slight observed intensity must be the result of a very weak J mixing by the crystal field. A band at 19 028 cm^{-1} was attributed to $^7F_0 \rightarrow {}^7D_1$. In this case, the selection rules forbid an electric-dipole but allow a magnetic-dipole transition. As shown in Table VII, the experimental and calculated results are in good agreement. The magnitude of the band centered

TABLE V. Oscillator strengths for Pm^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P \times 10^6$		
		$HClO_4$–$DClO_4$		$Pm(ClO_4)_3$[c] Exptl
		Exptl	Calc[b]	
12 000–12 600	$^5F_1$	0.77	0.63	2.5
12 600–13 200	$^5F_2$	1.94	1.93	3.2
13 200–14 000	$^5F_3$	3.76	4.00	4.6
14 000–14 400	$^5S_2$	2.38	1.97	3.0
14 400–15 200	$^5F_4$	2.29	2.29	2.8
15 700–16 300	$^5F_5$ $^3K_6$	0.42	0.46	2.5
16 600–18 800	$^3K_7$ $^3H_4$ $^5G_2$ $^5G_3$ $^3K_8$	10.93	10.89	10.4
19 400–21 100	$^3H_5$ $^5G_4$ $^3G_3$	2.57	2.56	5.5
rms Deviation			2.02×10^{-7}	

[a] Range encompassing observed band(s).
[b] The parameters used to obtain these values are given in Table II.
[c] See Table IV, Footnote d.

---

[9] M. H. Crozier, Phys. Rev. **137**, A1781 (1965).

[10] J. Hoogschagen and C. J. Gorter, Physica **14**, 197 (1948).

[11] C. V. Banks and D. W. Klingman, Anal. Chim. Acta **15**, 356 (1956).

[12] W. T. Carnall, P. R. Fields, and G. E. Toogood, J. Phys. Chem. **68**, 2351 (1964).

[13] L. G. DeShazer and G. H. Dieke, J. Chem. Phys. **38**, 2190 (1963).

[14] F. Bayer-Helms, Z. Naturforsch. **13a**, 161 (1958).

TABLE VI. Oscillator strengths for Sm^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P\times10^6$			
		$HClO_4$-$DClO_4$		$Sm(NO_3)_3$[c]	$Sm(ClO_4)_3$[d]
		Exptl	Calc[b]	Exptl	Exptl
5 600– 6 500	$^6F_{1/2}$ $^6H_{15/2}$	0.26	0.26	···	···
6 500– 6 800	$^6F_{3/2}$	0.97	0.99	···	···
6 800– 7 600	$^6F_{5/2}$	1.70	1.84	···	···
7 600– 8 600	$^6F_{7/2}$	2.74	3.00	···	···
8 800– 9 800	$^6F_{9/2}$	1.97	1.98	1.70	1.99
10 200–11 000	$^6F_{11/2}$	0.31	0.32	0.33	0.30
17 600–18 200	$^4G_{5/2}$	0.030	0.023[e] 0.012[f]	0.036	0.057
18 700–19 300	$^4F_{3/2}$	0.009	0.001		
19 800–20 300	$^4G_{7/2}$	0.52	0.62	0.061	0.076
20 300–21 300	$^4I_{9/2}$ $^4M_{15/2}$ $^4I_{11/2}$	1.53	0.54	1.26	1.38
21 300–22 000	$^4I_{13/2}$	0.68	0.34	0.68	0.64
22 000–22 200	$^4F_{5/2}$	0.03	0.006[e] 0.010[f]	0.02	0.08
22 200–23 400	$^4M_{17/2}$ $^4G_{9/2}$ $^4I_{15/2}$	0.39	0.13	0.33	0.40
24 400–24 700	$^4L_{13/2}$	0.43	0.31	4.90	
24 700–25 500	$^4F_{7/2}$ $^6P_{3/2}$ $^4K_{11/2}$ $^4M_{21/2}$	3.84	3.80		4.15
25 500–26 200	$^4L_{15/2}$ $^4G_{11/2}$	0.42	0.11	0.30	0.31
26 400–27 200	$^4D_{1/2}$ $^6P_{7/2}$ $^4L_{17/2}$ $^4K_{13/2}$ $^4F_{9/2}$	1.06	1.26	1.05	1.02
27 200–28 100	$^4D_{3/2}$ $(^4D,{}^6P)_{5/2}$	1.23	1.03	0.90	1.26
28 100–28 600	$^4H_{7/2}$	0.06	0.009[e] 0.020[f]		
28 600–29 800	$^4K_{15/2}$ $^4H_{9/2}$ $^4D_{7/2}$ $(^4K,{}^4L)_{17/2}$ $^4L_{19/2}$ $^4H_{11/2}$	0.80	0.67		1.08
rms Deviation			2.91×10^{-7}		

[a] Range encompassing observed band(s).

[b] The parameters used to obtain these values are given in Table II.

[c] Reference 10.

[d] See Table IV, Footnote d.

[e] Calculated magnetic-dipole oscillator strength (Table I).

[f] Calculated electric-dipole oscillator strength.

at 21 519 cm^{-1}, together with the calculated matrix element of $U^{(2)}$ for $^7F_0\rightarrow{}^5D_2$, determine a value of $\mathfrak{J}_2$ which is consistent with that for other lanthanides. An extremely weak absorption at 24 408 cm^{-1}, identified with the forbidden $^7F_0\rightarrow{}^5D_3$ transition, is attributed to J mixing.

In addition to the foregoing, several bands at higher energies were identified with transitions from $^7F_0$.[6,15] All of the oscillator strengths given in Table VII are for transitions which originate in $^7F_0$ and which were

---

[15] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. 49, 4450 (1968).

Table VII. Oscillator strengths for Eu^{3+} (aq).

Spectral range[a] (cm^{-1})	$S'L'J'$	$P\times10^8$				
		$HClO_4$		$EuCl_3$[c]	$Eu(ClO_4)_3$[d]	$Eu(NO_3)_3$[e]
		Exptl	Calc[b]	Exptl	Exptl	Exptl[f]
17 000–17 400	$^5D_0$	0	0	···	···	~0.01
18 900–19 100	$^5D_1$	1.4	1.4[g] 0[h]	1.5	10	~1.3
21 400–21 600	$^5D_2$	2.1	2.1	0.9	90	~1.3
	$^5D_3$	···	···			
25 100–25 600	$^5L_6$	177	178	158	190	
	$^5G_2$	···	···			
	$^5L_7$	···	···			
	$^5G_3$	···	···			
26 400–27 000	$^5G_4$ $^5G_5$ $^5G_6$	43	56			
	$^5L_8$	···	···			
27 500–27 800	$^5D_4$	17	17			
	$^5L_9$	···	···			
	$^5L_{10}$	···	···			
	$^5H_3$	···	···			
	$^5H_7$	···	···			
	$^5H_4$	···	···			
	$^5H_5$	···	···			
31 400–32 350	$^5H_6$	73	80			
	$^3P_0$	···	···			
	$^5F_2$	···	···			
	$^5F_3$	···	···			
	$^5F_1$	···	···			
	$^5F_4$	···	···			
	$^5I_4$	···	···			
	$^5F_5$	···	···			
	$(^5I,{}^5H)_5$	···	···			
	$^5I_8$	···	···			
	$(^5I,{}^5H)_6$	···	···			
	$^5I_7$	···	···			
	$^5K_5$	···	···			
37 300–37 600	$^5K_6$	22	19			
	$^3P_1$	···	···			
	$^5K_7$	···	···			
	$^5G_2$	···	···			
	$^5K_8$	···	···			
38 900–39 100	$(^3K,{}^3I)_6$	8.2	8.8			
rms Deviation			2.3×10^{-8}			

[a] Range encompassing observed band(s).

[b] The parameters used to obtain these values are a factor of 1.546 smaller than those recorded in Table II.

[c] Reference 10.

[d] See Table IV, Footnote d.

[e] Reference 14.

[f] Corrected to the present experimental conditions (25°).

[g] Calculated magnetic-dipole oscillator strength (Table I), corrected to the experimental conditions $C_0/C_T=0.647$, where C_0/C_T is the fraction of transitions arising from the $^7F_0$ level.

[h] Calculated electric-dipole oscillator strength based upon energy-level parameters given in Refs. 6, 15.

relatively well resolved from identifiable components arising from $^7F_1$ and $^7F_2$. In fitting the data, it should be noted that while $\mathfrak{T}_6$ was well determined, the values of both $\mathfrak{T}_2$ and $\mathfrak{T}_4$ were determined from single transitions.

For purposes of comparison with the results for other lanthanides, it was necessary to correct the values of $\mathfrak{T}_\lambda$ calculated from the experimental data for Eu^{3+}. This correction arises since at 25° the observed oscillator strengths are a function of c_0, the concentration of Eu^{3+} ions in the ground-state $^7F_0$, and this is only a part of the total Eu^{3+} ion concentration, c_T. Thus,

$$c_J/c_0=(g_J/g_0)\exp[-(E_J-E_0)/kT],$$

where $c_T = \sum c_J$, c_J is the concentration of atoms in the initial ^7F_J level with energy E_J, and $g_J = 2J+1$.[14] We neglect terms for $J > 2$.

From the experimental results in solution we obtain $E_1 - E_0 = 360$ cm^{-1}, $E_2 - E_0 = 1020$ cm^{-1}, and we can calculate $c_T/c_0 = (c_0+c_1+c_2)/c_0 = 1.546$. Instead of applying the foregoing to the experimental oscillator strengths in Table VII, an equivalent correction can be made directly to the values of $\mathfrak{T}_\lambda$. Thus the values of $\mathfrak{T}_\lambda$ given in Table II are a factor of 1.546 greater than those used to calculate oscillator strengths for comparison with the experiment in Table VII.

$Gd^{3+}(f^7)$

The $4f^7$ configuration of Gd^{3+} represents a half-filled shell of equivalent electrons. It can be shown that to a first approximation neither the ground state nor the excited states should be split by a crystal field.[16] Indeed, the absorption spectrum as observed in solution is comprised for the most part of extremely sharp bands, all of which occur in the ultraviolet region of the spectrum. Transitions from the ground state to three different multiplet groups ^6P, ^6I, and ^6D are normally observed, but those to ^6P and ^6D result in very weak absorption bands.[2] In addition, we have been able to discern bands arising from transitions to components of the ^6G multiplet near 50 000 cm^{-1}.[6,17]

TABLE VIII. Oscillator strengths for Gd^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P\times10^6$, $HClO_4$ Exptl	$P\times10^6$, $HClO_4$ Calc[b]
32 100–32 300	$^6P_{7/2}$	0.073	0.055[c] 0.013[d]
32 700–32 900	$^6P_{5/2}$	0.041	0.031[c] 0.005[d]
33 300–33 500	$^6P_{3/2}$	0.0014	~0
35 800–36 100	$^6I_{7/2}$	0.121	0.112
36 100–36 450	$^6I_{9/2}$ $^6I_{17/2}$	0.845	0.877
36 450–37 400	$^6I_{11/2}$ $^6I_{13/2}$ $^6I_{15/2}$	1.914	1.918
39 400–40 400	$^6D_{9/2}$	0.078	0.093
40 500–41 200	$^6D_{1/2}$ $^6D_{7/2}$ $^6D_{3/2}$ $^6D_{5/2}$	0.082	0.008[c] 0.130[d]
49 000–49 400	$(^6G, ^6F)_{7/2}$	0.121	0.149
49 400–50 400	$^6G_{9/2}$ $^6G_{11/2}$ $^6G_{5/2}$	0.903	0.765
51 100–51 700	$^6G_{3/2}$ $^6G_{13/2}$	... 0.639	... 0.459
rms Deviation			2.5×10^{-8}

[a] Range encompassing observed band(s).
[b] The parameters used to obtain these values are given in Table II.
[c] Calculated magnetic-dipole oscillator strength (Table I).
[d] Calculated electric-dipole oscillator strength based upon energy-level parameters given in Refs. 6, 17.

TABLE IX. Oscillator strengths for Tb^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P\times10^7$, $HClO_4$ Exptl	$P\times10^7$, $HClO_4$ Calc[b]	$TbCl_3$[c] Exptl
20 000–21 200	$^5D_4$	0.52	0.21	~0.04
25 900–27 600	$^5D_3$ $^5G_6$ $^5L_{10}$	8.46	0.07[d] 7.61[e]	5.7
27 600–28 950	$^5G_5$ $^5D_2$ $^5G_4$ $^5L_9$	7.46	7.61	
28 950–30 200	$^5G_3$ $^5L_8$ $^5L_7$ $^5L_6$ $^5G_2$	3.04	4.03	
30 400–30 900	$^5D_1$	0.37	0.32	
30 950–32 000	$^5D_0$ $^5H_7$	2.02	1.85	
32 500–33 500	$^5H_6$	1.20	1.41	
33 600–34 100	$^5H_5$	0.18	0.47	
34 400–35 800	$^5H_4$ $^5F_5$ $^5H_3$ $^5I_8$ $^5F_4$	5.05	5.32	
rms Deviation			6.4×10^{-8}	

[a] Range encompassing observed band(s).
[b] The parameters used to obtain these values are given in Table II.
[c] Reference 10.
[d] Calculated magnetic-dipole oscillator strength (Table I).
[e] Calculated electric-dipole oscillator strength. Based upon energy-level parameters given in Refs. 6, 18.

For purposes of parameter fitting, the situation in Gd^{3+} is somewhat similar to that in Eu^{3+}. Bands arising from transitions to ^6P and ^6D determine the value of $\mathfrak{T}_2$, whereas $\mathfrak{T}_4$ and $\mathfrak{T}_6$ are independently determined by transitions to ^6G and ^6I, respectively.

The correlation between the observed intensities of the bands arising from transitions to $^6P_{7/2}$ and $^6P_{5/2}$, and their calculated magnetic-dipole oscillator strengths, is of particular interest. As shown in Table VIII, P_{md} accounts for essentially all of the observed intensity. This is consistent with the very weak electric-dipole intensity calculated for these transitions.

---

[16] B. G. Wybourne, Phys. Rev. **148**, 317 (1966).

[17] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4443 (1968).

TABLE X. Oscillator strengths for Dy^{3+} (aq).

Spectral range[a] (cm^{-1})	$S'L'J'$	$P\times10^6$		
		$HClO_4$–$DClO_4$ Exptl	$HClO_4$–$DClO_4$ Calc[b]	$Dy(NO_3)_3$[c] Exptl
5 500–6 400	$^6H_{11/2}$	1.14	1.17	
7 000–8 400	$^6F_{11/2}$ $^6H_{9/2}$	1.10	3.55	
8 400–9 800	$^6F_{9/2}$ $^6H_{7/2}$	2.97	3.38	2.76
9 800–10 400	$^6H_{5/2}$	0.11	2.62	3.04
10 400–11 700	$^6F_{7/2}$	2.74		
11 700–12 900	$^6F_{5/2}$	1.55	1.19	1.61
12 900–13 600	$^6F_{3/2}$	0.33	0.23	0.38
20 400–21 600	$^4F_{9/2}$	0.21	0.20	0.19
21 700–22 600	$^4I_{15/2}$	0.44	0.08[d] 0.42[e]	0.34
23 000–24 000	$^4G_{11/2}$	0.16	0.10	0.11
24 600–26 800	$^4F_{7/2}$ $^4I_{13/2}$ $^4M_{21/2}$ $^4K_{17/2}$	2.38	2.34	2.54
27 000–28 200	$^4M_{19/2}$ $(^4P, ^4D)_{3/2}$ $^6P_{5/2}$ $^4I_{11/2}$	2.85	1.84	2.67
28 200–29 200	$^6P_{7/2}$	4.36	4.24	
29 200–30 100	$(^4M, ^4I)_{15/2}$ $(^4F, ^4D)_{5/2}$ $^4I_{9/2}$	0.39	0.01[d] 0.23[e]	
30 100–32 400	$^4G_{9/2}$ $^6P_{5/2}$ $^4M_{17/2}$ $(^4G, ^2F)_{7/2}$ $^4K_{15/2}$ $(^4D, ^4G)_{5/2}$ $^4D_{1/2}$ $^4L_{19/2}$	2.59	1.36	
32 800–35 200	$^4H_{13/2}$ $^4F_{3/2}$ $(^4K, ^4L)_{13/2}$ $^4D_{7/2}$ $^4H_{11/2}$ $^4G_{9/2}$ $^4F_{5/2}$ $^4G_{11/2}$ $^4L_{17/2}$	1.43	1.23	
35 800–36 200	$(^4G, ^4H)_{7/2}$	0.05	0.04	
rms Deviation			2.05×10^{-7}	

[a] Range encompassing observed band(s).

[b] The parameters used to obtain these values are given in Table II.

[c] Reference 10.

[d] Calculated magnetic-dipole oscillator strength (Table I).

[e] Calculated electric-dipole oscillator strength.

$Tb^{3+}(f^8)$

Intensities in the solution absorption spectrum of Tb^{3+} could only be measured reproducibly at <36 000 cm^{-1} since at higher energies the $4f\rightarrow4f$ transitions are superimposed on more intense absorption bands which arise from $4f\rightarrow4f^{N-1}5d$ transitions.[11,18] It was necessary to treat most of the observed bands as composites involving several transitions, as shown in Table IX. Normally, this procedure would make it possible to calculate all three parameters, $\mathfrak{T}_\lambda$, since a sufficient number of independent groups were resolved. However, in the case of Tb^{3+}, none of the observed transitions were strongly dependent upon the matrix elements of $\mathbf{U}^{(2)}$. As a consequence, $\mathfrak{T}_2$ was poorly defined, but nonetheless was shown to be very small.

$Dy^{3+}(f^9)$

Many of the more intense transitions in Dy^{3+} are well identified, and their intensities could be measured with a high degree of reproducibility. Calculated and experimentally determined oscillator strengths are compared in Table X. There is appreciable general absorption in the ultraviolet region of the Dy^{3+} spectrum.[11] This results in a considerable error in the areas determined for bands at >35 000 cm^{-1}, and no measurements were possible beyond ~43 000 cm^{-1}.

The value of $\mathfrak{T}_2$ given in Table II was determined after excluding the intensity data for $^6F_{9/2}$ and $^6H_{11/2}$ at 7700 cm^{-1} from the averaging process. As can be seen from Table X, the matrix elements of $\mathbf{U}^{(\lambda)}$ for these two transitions, taken with the values of $\mathfrak{T}_4$ and $\mathfrak{T}_6$, which were well determined, gave a calculated oscillator strength that was much larger than observed. By including the results for $^6F_{9/2}$ and $^6F_{11/2}$ in the fit, $\mathfrak{T}_2$ was forced to assume a negative value. The magnitude and sign of $\mathfrak{T}_\lambda$ were effectively determined by the very large value of the matrix element of $\mathbf{U}^{(2)}$ for the transition to $^7F_{11/2}$. The best "fit" resulted from making $\mathfrak{T}_2$ negative to correct for the excess oscillator strength calculated from the matrix elements of $\mathbf{U}^{(4)}$ and $\mathbf{U}^{(6)}$.

$Ho^{3+}(f^{10})$

It was possible to obtain at least a reasonable estimate of band intensities in Ho^{3+} to ~45 000 cm^{-1}, and it was found that in many complex bands the intensity is due almost entirely to one transition. Experimental and calculated oscillator strengths are shown in Table XI. In general the correlation is very good. The discrepancy in the band at 31 000 cm^{-1} may be partly experimental since the subtraction of an arbitrary background in the case of such a broad absorption[11] is subject to considerable error.

$Er^{3+}(f^{11})$

The present intensity data for Er^{3+}, given in Table XII, represents a considerable extension of the results

---

[18] W. T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. **49**, 4447 (1968).

TABLE XI. Oscillator strengths for Ho^{3+} (aq).

Spectral range[a] (cm^{-1})	$S'L'J'$	$P\times10^6$		
		$HClO_4$–$DClO_4$		$HoCl_3$[c] Exptl
		Exptl	Calc[b]	
8 000– 9 000	$^5I_6$	1.07	1.46	···
10 800–11 400	$^5I_5$	0.22	0.27	~0.05
13 000–13 500	$^5I_4$	0.02	0.02	
15 000–16 000	$^5F_5$	3.76	3.62	4.77
18 000–19 200	$^5S_2$ $^5F_4$	5.23	5.07	4.81
20 100–20 900	$^5F_3$	1.78	1.66	3.09
20 900–21 600	$^5F_2$ $^3K_8$	1.43	0.08[d] 1.92[e]	
21 600–23 200	$^5G_6$ $^5F_1$	6.00	6.11	7.66
23 400–24 600	$(^5G, {}^3G)_5$	3.14	3.05	4.0
25 000–26 400	$^5G_4$ $^3K_7$	1.03	0.65	~1.8
27 200–28 500	$(^5G, {}^3H)_5$ $^3H_6$ $(^5F, {}^3F, {}^5G)_2$	3.24	2.53	~2.3
28 500–29 600	$^5G_3$ $^3L_9$	0.83	1.09	
29 600–30 500	$(^3F, {}^3H, {}^3G)_4$ $^3K_6$	0.80	0.95	
30 500–31 600	$^5G_2$	0.13	0.01	
32 900–33 200	$^3D_3$ $^3P_1$	~0.02	0.02	
33 600–34 600	$^3M_{10}$ $^3L_8$	1.01	1.30	
34 600–35 500	$(^5G, {}^5D, {}^3G)_4$ $(^3F, {}^3G)_3$	2.72	3.01	
35 500–37 400	$^3P_0$ $(^3H, {}^5D, {}^1G)_4$ $^3F_2$ $^1L_8$ $(^3H, {}^3G)_5$	2.59	2.41	
37 500–39 700	$(^3P, {}^1D)_2$ $^3L_7$ $^3I_7$ $^3F_4$ $^3I_5$ $^3M_9$	···	···	
39 700–40 500	$^3I_6$ $(^3D, {}^5D, {}^3P)_1$ $^5D_3$	0.54	0.32	
41 100–41 800	$(^3F, {}^5D)_4$	2.54	2.70	
41 800–42 200	$^5D_2$	0.20	0.13	
42 700–43 200	$(^3F, {}^5D)_3$ $^5D_1$	0.10	0.08	
44 400–45 900	$(^1D, {}^3D)_2$ $^3H_4$ $^3M_8$ $(^3H, {}^1I)_6$	0.37	0.21	
rms Deviation			2.87×10^{-7}	

[a] Range encompassing observed band(s).

[b] The parameters used to obtain these values are given in Table II.

[c] Reference 10.

[d] Calculated magnetic-dipole oscillator strength (Table I).

[e] Calculated electric-dipole oscillator strength.

reported in I; however, the re-evaluation of band intensities has modified only a few of those given earlier. The new values for $\mathfrak{T}_\lambda$ are slightly larger than originally computed and are also better determined. In the ultraviolet range, the poor fit to the intense band near 40 000 cm^{-1} [11] may be in part experimental. However, since the whole of the intensity can be unequivocally attributed to one transition ($^4D_{7/2}$) the indication is that the calculated matrix elements of either $\mathbf{U}^{(4)}$ or $\mathbf{U}^{(6)}$ or both are too small. We note that the matrix elements for the corresponding transition in Nd^{3+} were also apparently too small.

$Tm^{3+}(f^{12})$

It was not possible to significantly extend the results reported in I for Tm^{3+}, since accurately reproducible experimental data in the ultraviolet region of the spectrum[11] could not be obtained. An improved energy-level fit, upon which the calculation of the matrix elements of $\mathbf{U}^{(\lambda)}$ was based, and the experimental observation of one additional absorption band, were the principal factors responsible for the differences between the calculated oscillator strengths given in Table XIII and those computed in I.

$Yb^{3+}(f^{13})$

For the single $f\rightarrow f$ transition in Yb^{3+}, Judd's expression can be reduced to the equation

$$P=(\sigma/196)(3\mathfrak{T}_2+10\mathfrak{T}_4+21\mathfrak{T}_6).$$

We note from Table II that for each of the heavy lanthanides the values of $\mathfrak{T}_4$ and $\mathfrak{T}_6$ are nearly identical

Table XII. Oscillator strengths for Er^{3+} (aq).

Spectral range[a] (cm^{-1})	$S'L'J'$	$P\times10^6$ HClO$_4$–DClO$_4$ Exptl	Calc[b]	ErCl$_3$[c] Exptl
6 200– 7 000	$^4I_{13/2}$	2.19	0.41[d] 1.98[e]	...
9 400–10 800	$^4I_{11/2}$	0.84	0.66	0.50
12 000–12 900	$^4I_{9/2}$	0.29	0.35	0.34
14 800–15 800	$^4F_{9/2}$	2.25	2.36	2.37
18 000–18 700	$^4S_{3/2}$	0.66	0.62	0.83
18 700–19 800	$^2H_{11/2}$	2.89	3.26	2.91
20 000–21 100	$^4F_{7/2}$	2.27	2.43	2.22
21 800–23 000	$^4F_{5/2}$ $^4F_{3/2}$	1.25	1.20	1.31
24 100–25 100	$(^2G, ^4F, ^2H)_{9/2}$	0.80	0.92	0.74
25 800–27 100	$^4G_{11/2}$	5.92	5.76	
27 100–27 700	$^4G_{9/2}$	1.75	1.56	
27 700–28 400	$^2K_{15/2}$ $^2G_{7/2}$	0.91	0.05[d] 0.99[e]	
31 300–31 900	$(^2P, ^2D, ^4F)_{3/2}$	0.091	0.083	
32 700–33 600	$^2K_{13/2}$ $^4G_{5/2}$ $^2P_{1/2}$	0.12	0.12	
33 600–34 500	$^4G_{7/2}$	0.21	0.19	
34 500–35 200	$^2D_{5/2}$	0.14	0.12	
36 100–36 900	$(^2H, ^2G)_{9/2}$	0.44	0.29	
38 300–38 700	$^2D_{5/2}$	0.14	0.16	
38 700–40 200	$^4D_{7/2}$	10.2	5.68	
rms Deviation			1.43×10^{-7}	

[a] Range encompassing observed band (s).

[b] The parameters used to obtain these values are given in Table II.

[c] Reference 10.

[d] Calculated magnetic-dipole oscillator strength (Table I).

[e] Calculated electric-dipole oscillator strength.

and $\mathfrak{T}_2<\mathfrak{T}_4$. Thus, neglecting $\mathfrak{T}_2$ under the above circumstances should not lead to a large error since the first term would be expected to contribute $<1/11$ of the total due to $\mathfrak{T}_2$, $\mathfrak{T}_4$, and $\mathfrak{T}_6$. Before calculating $\mathfrak{T}_4(=\mathfrak{T}_6)$, the total observed oscillator strength of the $^2F_{7/2}$ band, as shown in Table XIV, was corrected for the contribution due to magnetic-dipole absorption. Thus we obtain the estimate

$$\mathfrak{T}_4=\mathfrak{T}_6=2.13\times10^{-9}\ (\mathrm{cm}),$$

which is essentially the same as was adopted in I.

CONCLUSIONS

For the tripositive lanthanides the Judd–Ofelt theory has been shown to be applicable even in the near-ultraviolet region of the spectrum. In this range one might have expected it to break down, since the approximation made in the derivation, that the energy difference between configurations is much greater than the transition energy, becomes less valid. Actually, the approximation is probably more valid than it first appears. In the absence of large deviations from *LS* coupling, interaction only occurs between levels of the same spin in two interacting configurations. Since the levels of both f^N and $f^{N-1}d$ tend to be ordered by spin, with the highest spin multiplicity lying lowest, the approximation of a constant energy difference between interacting levels is nearly valid even when considering levels near 40 000 cm^{-1} in the f^N configuration.

The theory appears to be unable to fully account for the observed intensities in the case of Pr^{3+}, and minor discrepancies have been noted for isolated bands in other lanthanides. In the case of Pr^{3+}, perturbing states in the $4f^{N-1}5d$ configuration are only ~50 000 cm^{-1} above the ground level,[9] so the assumption relative to energy differences is admittedly weak at this point. Indeed, one might expect an even more pronounced recurrence of this effect at Tb^{3+}, where the lowest term of $4f^{N-1}5d$ is found near 38 000 cm^{-1}. An examination of the structures of the f^8 and f^7d configurations, however, reveals that this is not the case. In *LS* coupling, the two lowest multiplets of f^7d are expected to be ^9D and ^7D, which result from the coupling of a d electron to the ^8S ground state of f^7. In the case of Gd^{2+} these are spread by approximately 1500 cm^{-1} each, and their centers are 8000–9000 cm^{-1} apart.[19] The structure is

Table XIII. Oscillator strengths for Tm^{3+} (aq).

Spectral region[a] (cm^{-1})	$S'L'J'$	$P\times10^6$ HClO$_4$–DClO$_4$ Exptl	Calc[b]	TmCl$_3$[c] Exptl
5 600– 6 300	$^3F_4$	1.08	1.40	
7 700– 9 200	$^3H_5$	1.67	0.37[d] 1.46[e]	
12 000–13 600	$^3H_4$	2.12	1.92	1.98
13 800–15 500	$^3F_3$ $^3F_2$	3.91	3.97	3.18
20 600–22 100	$^1G_4$	0.71	0.45	~0.45
27 300–29 100	$^1D_2$	2.38	2.30	
34 100–35 900	$^1I_6$ $^3P_0$	0.84	0.89	
35 900–37 400	$^3P_1$	0.56	0.83	
37 400–39 700	$^3P_2$	3.28[f]	2.25	
rms Deviation			2.59×10^{-7}	

[a] Range encompassing observed band (s).

[b] The parameters used to obtain these values are given in Table II.

[c] Reference 10.

[d] Calculated magnetic-dipole oscillator strength (Table I).

[e] Calculated electric-dipole oscillator strength.

[f] This value was not included in the parameter fitting process since a large error was associated with determining background absorption in this region.

---

[19] W. R. Callahan, J. Opt. Soc. Am. **53**, 695 (1963).

expected to be similar for Tb^{3+}. The band at 38 000 cm^{-1} must arise from transitions from $f^8\,{}^7F_6$ to $f^7d\,{}^9D$. One would then expect, by analogy with Gd^{2+}, that the transition to $f^7d\,{}^7D$ would appear at 46 000–47 000 cm^{-1} which agrees well with the band which is observed at 45 800 cm^{-1}.

The crystal-field interaction which mixes f^8 with f^7d is independent of spin. Thus, since there are no nonet states in f^8, it cannot be affected by $f^7d\,{}^9D$. The only septet in f^8 is the ground multiplet, ${}^7F$; consequently, this is the only multiplet which can be affected by $f^7d\,{}^7D$. The higher states of f^7 are ~30 000 cm^{-1} above the ${}^8S$. The next higher states of f^7d are expected to lie at least 25 000 cm^{-1} above ${}^9D$ and ${}^7D$ or about 65 000 cm^{-1}. These are then the first states which could interact with the quintets of f^8. Thus, even though the lowest states of f^7d occur at relatively low energies in Tb^{3+}, they can affect only the ${}^7F$ multiplet. This multiplet lies in the infrared and was not considered in the intensity calculation. We conclude that while the proximity of $f^{N-1}d$ states could contribute to the poor intensity correlation obtained in case of Pr^{3+}, similar arguments would not apply for Tb^{3+}. Consequently, it is not surprising that the theory accounts as well for the Tb^{3+} results as it does for any of the other cases.

In examining the intensity correlations it is useful to recall some of the restrictions that were built into the calculations. In particular, it is possible to derive the selection rule $\Delta J \leq \lambda$, where $\lambda = 2, 4, 6$. For $\lambda = 2$, $\Delta J \leq 2$, i.e., for transitions in which $\Delta J > 2$, the matrix elements of $\mathbf{U}^{(2)}$ will vanish. Clearly, $\mathfrak{T}_2$ will in general be the most poorly determined parameter, since a majority of transitions will involve $\Delta J > 2$. $\mathfrak{T}_4$ will be determined by $\Delta J \leq 4$, and $\mathfrak{T}_6$ by $\Delta J \leq 6$. Thus, the latter will be the best determined parameter. No forced electric dipole intensity is expected for transitions where $\Delta J > 6$.[4]

TABLE XIV. Oscillator strength for Yb^{3+}.

Spectral region[a] (cm^{-1})	$S'L'J'$	$P \times 10^6$ DClO$_4$ Exptl	$P \times 10^6$ DClO$_4$ Calc[b]	$P \times 10^6$ YbCl$_3$[c] Exptl
9400–11 300	${}^2F_{5/2}$	3.74	0.24[d] 3.47[e]	3.86

[a] Range encompassing observed band.

[b] The parameters used to obtain this value are given in Table II.

[c] Reference 10.

[d] Calculated magnetic-dipole oscillator strength (Table I).

[e] Calculated electric-dipole oscillator strength.

Examination of the parameters in Table II, considering the selection rules just cited, indicates that only a limited number of transitions in aqueous solution are at all influenced by the value of $\mathfrak{T}_2$. Most of the data fitting involved only two parameters, $\mathfrak{T}_4$ and $\mathfrak{T}_6$. With the exception of Pr^{3+}, the magnitude of $\mathfrak{T}_\lambda$ does not appear to change appreciably across the series, although there is some decrease with increasing Z. These results for $\mathfrak{T}_4$ and $\mathfrak{T}_6$ are consistent with the trend calculated by Krupke[8] using free-ion radial wavefunctions. The parameters $\mathfrak{T}_2$ and $\mathfrak{T}_6$ for Pr^{3+} are essentially an order of magnitude larger than the average for the series.

The parameters comparable to $\mathfrak{T}_\lambda$, reported by Krupke[8] for spectra observed in crystals at room temperature, appear to be of the same order of magnitude as the present values of $\mathfrak{T}_\lambda$. The intensities for Pr^{3+} and for Nd^{3+} in LaF_3 are approximately $\frac{1}{2}$ to $\frac{1}{3}$ of those observed for the same transitions in solution, but the intensity patterns are quite similar. Comparison of the spectra of lanthanides in a Y_2O_3 matrix with the results in solution is not as straightforward because of the very large crystal-field splitting reported for the oxide crystal. However, the oscillator strengths are comparable in magnitude.

We conclude that the intensity aspects of lanthanide absorption spectra in aqueous solution can be predicted to a good approximation on the basis of two parameters, $\mathfrak{T}_4$ and $\mathfrak{T}_6$. The additional parameter, $\mathfrak{T}_2$, becomes important for only one or two bands in each ion. These bands are, however, identically those that show the hypersensitivity to medium effects that was discussed in I for lanthanides in, for example, molten nitrate salt solutions.

ACKNOWLEDGMENTS

We gratefully acknowledge the large contribution of B. G. Wybourne, University of Canterbury, Christchurch, New Zealand, which made much of this work possible. We would also like to thank F. Clark, C. Chamot, S. Katilavas, and J. Milsted for their assistance in programming and carrying out the computer calculations, and D. Kiple, G. Toogood, S. Neufeldt, A. Walker, and R. McBeth for aid in performing the experimental measurements. We are indebted to J. Conway and T. Clements, Lawrence Radiation Laboratory, University of California, for providing us with a number of the computer programs and tapes used in this work.