

The Electronic Absorption Spectra of Lanthanum (III), Cerium (III) and Thorium (IV) Ions in Different Solvents

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Résumé

Nous avons étudié les spectres électroniques d'absorption des ions La^{3+} , Ce^{3+} et Th^{4+} dans différents solvants. Les spectres observés montrent un nombre de bandes superposées qui ont été étudiées par analyse Gaussienne pour leur assigner leurs transitions électroniques correspondantes. Les bandes d'absorption observées correspondent aussi bien à des transitions permises qu'interdites. Ces dernières sont classifiées en dipôle électrique, dipôle magnétique, transitions vibroniques- électroniques et électriques quadrupolaires. Nous avons calculé les probabilités de transition électroniques correspondantes par la méthode de Van Vleck. Des différences importantes ont pu être observées entre les spectres des ions La^{3+} et Ce^{3+} dans différents solvants à cause de l'existence d'électron 4f dans l'ion de cérium(III). Par contre, les spectres des ions solvatés de Th^{4+} sont très semblables à ceux des ions de La^{3+} . Nous avons effectué des calculs ab initio sur l'ion libre Ce^{3+} et sur l'ion $[Ce(H_2O)_6]^{3+}$, en supposant une symétrie T_h pour l'ion hexaaquo-cérium(III). Nous avons calculé la population des orbitales atomiques Mulliken pour l'ion Ce dans $Ce(H_2O)_6^{3+}$ comme étant : $4f^{0.75}5d^{0.49}6s^{0.49}6p^{0.32}$, la densité de charge des différents atomes étant pour Ce = +2.45, O = -0.78 et H = +0.43. La superposition atomique Mulliken calculée indique l'absence de lien π entre l'ion Ce^{3+} et les atomes O de $[Ce(H_2O)_6]^{3+}$.

Abstract

The electronic absorption spectra of La^{3+} , Ce^{3+} and Th^{4+} ions have been investigated in different solvents. The observed spectra show a number of overlapping bands that were analyzed using Gaussian analysis and assigned to the corresponding electronic transitions. The observed absorption bands correspond to both allowed as well as forbidden transitions. The latter are classified as electric dipole, magnetic dipole, vibronic- electronic and electric quadrupole transitions. The corresponding transition probabilities were calculated using the Van Vleck method. Marked differences are observed between the spectra of solvated La^{3+} and Ce^{3+} ions in the different solvents as a result of the existence of the 4f-electron in cerium(III) ion. On the other hand, the spectra of solvated Th^{4+} ions are very similar to those of solvated La^{3+} ions. Ab initio calculations were performed on free Ce^{3+} ion and on $[Ce(H_2O)_6]^{3+}$ ion, assuming a T_h symmetry for aqueous cerium(III) ion. The Mulliken atomic orbital population is calculated for the Ce ion in $Ce(H_2O)_6^{3+}$ and found to be: $4f^{0.75}5d^{0.49}6s^{0.49}6p^{0.32}$. The charge density on the different atoms is Ce = +2.45, O = -0.78 and H = +0.43. The calculated Mulliken atomic overlap indicates the absence of π -bonding between Ce^{3+} ion and O-atoms in $[Ce(H_2O)_6]^{3+}$.

Keywords: lanthanum, cerium, thorium, solvation, absorption spectra, ab initio

Introduction

The uniqueness of the chemistry of lanthanides resides

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in the structure of their individual atoms and ions. The elements are the first members of the 4-d type transition series. The problem with lanthanides primarily concerns the presence or absence of a 5d-electron. The 5d and 4f orbitals have so nearly the same energy that distinction between the two is difficult. Whether the fundamental configuration is $4f^n 5d^1 6s^2$ or $4f^{n+1} 6s^2$ is of far less chemical than physical significance, since the energy differences are too small to alter many chemical properties.

Fast electron energy loss spectroscopy (FEELS) was used to study the 3p to 6p spectra of LaF_3 and many other lanthanide elements or their salts (1). At high energies, 4d-lanthanide and 5-d actinide spectra are compared using photo absorption measurements. Mandelbaum (2) found that many X-ray spectra emitted by laser-irradiated high-Z elements are dominated by the intense pseudo-continuum originating from 3d-4f inner-shell resonance transitions. Some of the particular properties of the 3d-4f inner-shell excited levels were presented, and their implications for the interpretation of the observed spectra were discussed..

Lanthanum 5p photo emission spectra under 4d-4f resonant excitation were studied both experimentally and theoretically, and the interference of the emission via the 1P_1 and 3D_1 states was discussed (3). The polarized analysis and fluorescence spectra of (0.01-5%) Np^{3+} doped into single crystal- LaCl_3 were measured at moderate and high resolution in the range of 50,000 cm^{-1} at 298.27 and 4K, and the crystal field components were identified. A similar study was performed on LaCl_3 (4).

Several La(III)- hydroxy carboxylate complexes were studied using the ^{139}La chemical shift and line-width measurements (5). The technique is a useful component of the study of complex formation in these systems. In the very concentrated aqueous solutions of LaCl_3 , the inner coordination sphere of La^{3+} is occupied exclusively by oxygen, even when the solvent is 10 normal hydrochloric acid (6). The results of X-ray diffraction gave an average La-O distance of 2.48 Å, and, on average, each La^{3+} has eight nearest neighbor oxygens in these solutions. It may be concluded that La^{3+} greatly prefers oxygen to chloride as an inner-sphere ligand.

Frey and Horrocks (7) measured the luminescence spectra of Ce^{3+} in aqueous solution and assigned it to d-f electronic transitions. Band intensity and quantum yield were the measured parameters to determine the

stoichiometry of the Ce(III) ion-complex.

Absorption, emission and excitation spectra, in addition to the fluorescence decay phenomena, were studied for a Ce^{3+} doped GdAlO_3 single crystal (8). The energy levels of Ce^{3+} and Gd^{3+} were determined, and the effect of various transfer processes on Ce^{3+} fluorescence decay and fluorescence intensity was discussed.

The 4f orbital is highly localized in all the rare earths except in cerium, where the degree of localization is reduced and the 4f wave function is of an extended nature (9). The electronic transition $4d^{10}4f^1 \rightarrow 4d^9 4f^2$ has been investigated in the spectrum of cerium; the multiplicity and band intensity were investigated, and the correspondence with the experimental results was adequate (10). The gas phase He-photoelectron spectra of the tetrahalides UF_4 , ThF_4 , UCl_4 and ThCl_4 were recorded by Dyke *et al.* (11). The spectra were consistent with an effective tetrahedral geometry.

In this work, the electronic absorption spectra of lanthanum (III), cerium (III) and thorium (IV) nitrates have been investigated using a number of solvents. The nature of the observed electronic transitions is interpreted in terms of allowed as well as forbidden transitions. The values of band intensity for the observed f-f, f-d,(d-f), p-d, or s-p transitions must be different from the value of a band intensity of a charge transfer transition. The electronic states of the studied ions were analyzed through the L-S coupling. The existence of a 4f¹ electron in Ce^{3+} leads to a spectrum that differs significantly from that of La^{3+} and that of Th^{4+} .

Electronic transitions can be electric dipole, magnetic dipole or electric quadropole. All the types may play a role. It is difficult to interpret the spectra without any theoretical guidance about the positions of the energy levels. This is because the selection rules for polarization combined with a knowledge of the splitting of the energy level under the influence of a specific field do not, in general, lead to an unambiguous assignment of the transitions. This is why it is important to investigate the electronic structure of lanthanides through the experimental study of the spectra and the theoretical calculations of band intensity.

Experimental

Lanthanum nitrate, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99% purity, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% purity and $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, 97% purity, are BDH reagents and were used without

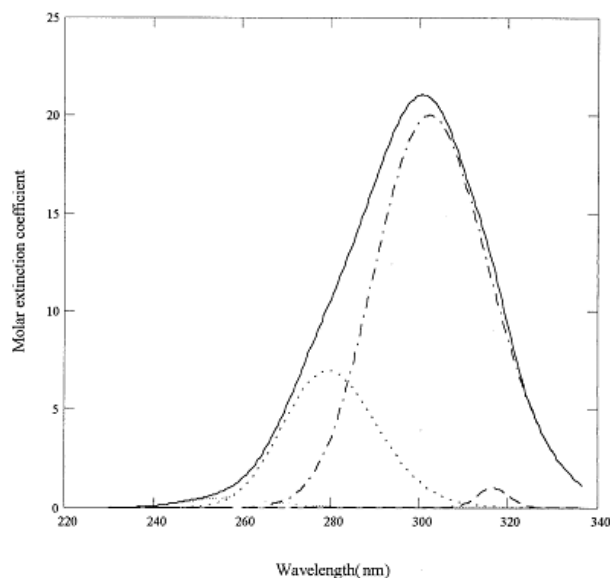


Figure 1. Electronic absorption spectrum of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in water (—) and its Gaussian analysis (---, -.-.-, ...)

further purification. Methanol and ethanol (Merck), isopropyl alcohol, isobutyl alcohol and ethylene glycol are BDH analar reagents were used without further purification. Spectra were scanned on a Perkin Elmer Lambda 4B recording spectrophotometer using 1.0cm fused silica cells. The instrument records linearly over the range 190-900nm

Molecular orbital calculations were carried out using a GAMESS program; smaller programs were developed for fine analysis of the outputs without incorporation of the original code.

Results and Discussion

Electronic Absorption Spectra

Lanthanum (III)- ion in different matrices

Lanthanum (III)- ion has a $[\text{Xe}]$ inert gas configuration, leading to a $^1\text{S}_0$ ground state. Excited states can arise from a p-d transition leading to the electronic configuration: $\dots 5s^2 5p^5 5d^1$ which gives rise to the singlet $^1\text{P}_1$, $^1\text{D}_2$ and $^1\text{F}_3$ and the triplet $^3\text{P}_1$, $^3\text{D}_2$ and $^3\text{F}_3$ states. The energies of these states are (12):

$$\begin{aligned} ^1\text{P}, ^3\text{P} &= F_0 + 7F_2 \pm (G_1 + 63G_2) \\ ^1\text{D}, ^3\text{D} &= F_0 - 7F_2 \pm (3G_1 + 21G_2) \\ ^1\text{F}, ^3\text{F} &= F_0 + 7F_2 \pm (6G_1 + 3G_2) \end{aligned}$$

Using means to eliminate the G's and give a theoretical ratio:

$$(\text{P-F})/(\text{F-D}) = 5/9$$

The theoretical ratio varies between 0.28 (in the case of Ge 1:4p4d) and 3.58 (in the case of Zn III: 5p4d) instead of the theoretical value of 0.555. The values of F_0 , F_2 , G_1 , and G_2 are dependent on each ion.

The electronic absorption spectra of $[\text{La}(\text{L})_n]^{3+}$, L = solvent molecule or ligand, may contain M→L and L→M charge transfer transitions in addition to the different M→M transitions. Charge transfer transitions are very intense, and their band maxima are sensitive to the change in solvent polarity. Abrahamer and Marcus (13) studied the interaction of lanthanide ions with varying numbers of f electrons and nitrate ion in different solvents. In aqueous media, both inner and outer sphere nitrate complexes are obtained (14,15). The degree of interaction between La^{n+} and the solvent varies as (13)



Conductivity measurements (16) have indicated the existence of a 1:1 electrolyte formulated as $[\text{Ln}(\text{DMF})_n]^{3+}(\text{NO}_3)_2]^{+}\text{NO}_3^-$.

Figure 1 shows the electronic absorption spectrum of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in water as a solvent. A relatively broad and weak band is obtained which, on Gaussian analysis (Mathcad package, version 7), gave three main bands; the minimum residue method is used to perform band analysis. Assuming that the excited states of the La^{3+} ion result from a p-d transition and the crystal field surrounding the ion is approximated by an O_h field, the lowest energy transition, $^1\text{S}_0 \rightarrow ^1\text{D}_2$, is represented by band I in table 1 and is a Laporte forbidden transition, $^1\text{A}_{1g} \rightarrow ^1\text{E}_g$. The second and third transitions arise from a $^1\text{S}_0 \rightarrow ^1\text{F}_3$ transition which splits into the Laporte allowed $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1u}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2u}$ transitions, $e=20$ and 7, respectively (bands II and III in table 1). The spectra of lanthanum nitrate were scanned in different solvents and were similarly analyzed; results are given in table 1.

The electronic absorption spectra of rare-earth ions in a crystal field are classified by Van Vleck (17) to result from: (1) electric-quadrupole transition, (2) magnetic dipole transition, (3) vibronic electric transitions and (4) electric dipole transitions. Only the last transition is allowed. For the allowed transition, the transition probability is given by:

$$\sigma_{\text{allowed}} = 64\pi^4 \omega^3 q^2 / h = 7.24 \times 10^{-10} \omega^3 q^2$$

and for the forbidden transitions:

Table 1. Band Maxima and molar extinction coefficient in different solvents.

Solvent	Band	La(NO ₃) ₃ ·6H ₂ O	Th(NO ₃) ₄ ·6H ₂ O
DMF	I	*314(6)**	*306(11)**
	II	288(27)	280(36)
	III	---	263(23)
Dioxane	I	314(3)	---
	II	283(36)	---
Ethanol	I	319(4)	300(9)
	II	281(37)	271(57)
Methanol	I	314(7)	300(9)
	II	285(26)	273(44)
Isopropanol	I	310(5)	302(13)
	II	282(27)	270(65)
Acetonitrile	I	---	300(13)
	II	285(39)	280(46)
	III	272(23)	271(25)
Ethylene glycol	I	---	309(8)
	II	293(21)	280(29)
Water	I	318(2)	318(2)
	II	302(20)	300(26)
	III	279(7)	279(12)
Isobutyl alcohol	I	---	320(6)
	II	---	283(33)
	III	---	277(57)
	IV	---	268(39)

* Band Maxima, nm. ** Molar extinction coefficient, mol⁻¹ L (values in parentheses)

$$\sigma_1 = 32\pi^6 e^2 \omega^5 Q^2 / 5h$$

$$\sigma_2 = 64\pi^4 \omega^3 M^2 / 3h$$

$$\sigma_3 = \sigma_{\text{allowed}} [V_{\text{hem}} / h \bar{\nu}]^2$$

where ω is the band maximum in cm⁻¹ (the wave number of the radiation in question) and q^2 is of the order of magnitude of the mean square radius $\langle r^2 \rangle_{\text{av}}$ of the orbit. The term Q is the quadrupole and is comparable dimensionally with the mean square radius of the orbit; it is estimated by $Q = \langle r^2 \rangle_{\text{av}}$. M is the matrix element of the magnetic moment which connects the states between which the electron transition occurs, and it is of the order of Bohr magneton. The matrix element of the hemihedral part of the crystal field is V_{hem} . Tanabe and Sugano (18) used a value of 10^5 cm⁻¹ for $\bar{\nu}$ and calculated V_{hem} from:

$$V_{\text{hem}} = (R / \langle r_{\text{av}} \rangle) V_0$$

where R is the zero point amplitude of the nuclear vibration and is estimated from:

$$2\pi^2 \mu v_0^2 (R^2) = 1/2 h v_0$$

and μ is the reduced mass of the vibrating ion and is of the order of the mass of the central metal ion, La³⁺. The fundamental frequency (18) of vibration, v_0 , of the ion [Ln(H₂O)₆]³⁺ is of the order of 10^5 cm⁻¹, and the value of V_0 is taken as 104 cm⁻¹. The value of R is calculated and found to be of the order of 0.39×10.9 cm⁻¹. The value of $\langle r \rangle_{\text{av}}$ is estimated (16) from:

$$\langle r \rangle = (360 a_0^2 Z^2)^{1/2}$$

where Z is the effective nuclear charge, 10.05 for La³⁺ ion, and a_0 is the Bohr radius. The calculated V_{hem} is 338 cm⁻¹.

The oscillator strength f , is given by:

$$f = 4.315 \times 10^{-4} \int \epsilon_{\text{max}} v(dv)$$

$$\int \epsilon_{\text{max}} v(dv) = \epsilon_{\text{max}} (1.0645) h$$

where h is the half-band width in cm⁻¹.

For lanthanum nitrate in different solvents, the values of ϵ_{max} and λ_{max} are given in table 1. Band maxima and intensity are sensitive to both polarity and refractive index of the solvent, yet there is no regular shift in band maxima with solvent polarity.

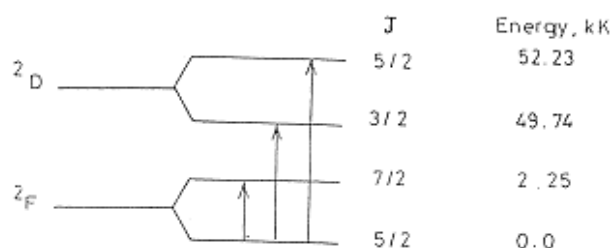
Table 1 shows that λ_{max} of band I of La³⁺ ion is at 318 nm when water is the solvent and varies from 310-314 nm in the other solvents. Similarly, band II has a maximum around 300 nm when water is the solvent and varies from 293-282 nm in other solvents. These results indicate a strong electronic interaction between H₂O molecules and La³⁺ ion. The contribution of the allowed and forbidden transitions to the lowest-energy transition of La³⁺ (band I) is indicated by the values of σ_{all} , σ_1 , σ_2 and σ_3 (table 2). The values of σ_{all} were calculated for the other transitions. The values of the oscillator, f_1 are calculated from the relation

$$f_1 = \sigma_1 / \sigma_{\text{allowed}}$$

The variation of band intensity of the second electronic transition of La³⁺ (band II) with solvent is not in the same direction as the variation of band maximum. The highest

Table 2. Transition probabilities and oscillator strength for La (NO₃)₃·6H₂O in different solvents.

Solvent	Band	$\sigma_{\text{all}} \times 10^{-8} (\text{sec}^{-1})$	$\sigma_1 (\text{sec}^{-1})$	$\sigma_2 (\text{sec}^{-1})$	$\sigma_3 (\text{sec}^{-1})$	$f_1 \times 10^7$	$f_2 \times 10^7$	$f_3 \times 10^7$
DMF	I	2.337	6.99	869.3	3527.2	0.299	37.197	150.9
	II	3.055	---	---	---	---	---	---
Dioxane	I	2.337	6.99	869.3	3527.2	0.299	37.197	150.9
	II	3.159	---	---	---	---	---	---
Ethanol	I	2.229	6.46	829.1	3364.3	0.299	36.2	150.9
	II	3.259	---	---	---	---	---	---
Methanol	I	2.337	6.99	869.3	3527.2	0.299	37.197	150.9
	II	3.119	---	---	---	---	---	---
Isopropanol	I	2.429	7.46	903.4	3557.0	0.307	37.18	150.9
	II	---	---	---	---	---	---	---
Acetonitrile	I	---	---	---	---	---	---	---
	II	3.109	---	---	---	---	---	---
	III	3.580	---	---	---	---	---	---
Water	I	2.188	6.63	813.8	3302.4	0.303	37.19	150.9
	II	2.670	---	---	---	---	---	---
	III	4.072	17.62	1513.7	6145.8	433	37.17	150.9
Ethylene glycol	I	---	---	---	---	---	---	---
	II	3.259	---	---	---	---	---	---
	III	---	---	---	---	---	---	---

Figure 2. Energy level diagram for gaseous Ce³⁺ ion.

intensity is observed when acetonitrile, isopropyl alcohol, or dioxane (polar and nonpolar) are the solvents ($\epsilon = 39.0$), whereas the weakest intensity is when water is the solvent ($\epsilon = 21.0$). This result indicates that band intensity is directly related to the extent of distortion in symmetry of the solvated La³⁺ ion.

The different transition probabilities and oscillator strength were calculated for band I in the spectrum of [La(solvent)_n]³⁺ ion using different solvents, and the results are given in table 2. Since band II is assigned to the allowed ¹A_{1g} → ¹T_{1u} transition, σ_{all} was only calculated for this band. A general comparison of the values of σ_1 , σ_2 and σ_3 indicates that: $\sigma_1 \ll \sigma_2 < \sigma_3$. The weakest contribution to the intensity of a forbidden transition comes from the electric quadrupole contribution.

Cerium(III) ion in Different Solvents

The existence of a 4f¹ electron in Ce³⁺ configuration [Xe] 4f¹5d⁶s markedly affects the electronic spectra of the ion. The ground state is the ²F_{7/2, 5/2} state, and the first excited state configuration is: [Xe]4f⁵d¹6s, leading to the ²D_{5/2, 3/2} state. In the presence of an external field, the splitting of the energy levels leads to the situation shown in figure 2, wherein the values of energies are for gaseous Ce³⁺ as given by Jorgenson (19). Three electronic transitions are possible. The lowest energy transition, ²F_{5/2} → ²F_{7/2} (2.25 cm⁻¹), is a Laporte forbidden $\mu \rightarrow \mu$ transition and corresponds to an fⁿ → fⁿ transition. The other two transitions, ²F_{5/2} → ²D_{3/2, 5/2}, are Laporte allowed nf → n-1fd transitions. The f → f transition is of low energy and is expected to appear in the IR region ($\lambda_{\text{max}} \sim 440\text{nm}$), whereas the f → d transitions are observed in the UV region ($\lambda \sim 190\text{-}300\text{nm}$). The aqua Ce³⁺ ion is probably nine coordinated with a trigonal micro symmetry that is approximated to a linear symmetry. The excited orbitals are $\sigma_{1/2}$, $\delta_{3/2}$, $\delta_{5/2}$, $\pi_{1/2}$ and $\pi_{3/2}$, with energies (kK) 13.7, 39.6, 41.7, 45.1 and 47.4, respectively (19). The extinction coefficient of the first transition is only 16, indicating a symmetry forbidden transition. The spin-orbit coupling constant ζ_{5d} of Ce³⁺ is only 1.00 kK, which explains the weak splitting of the energy levels.

Jorgensen (20) suggested that Ce(III) aqua ions might

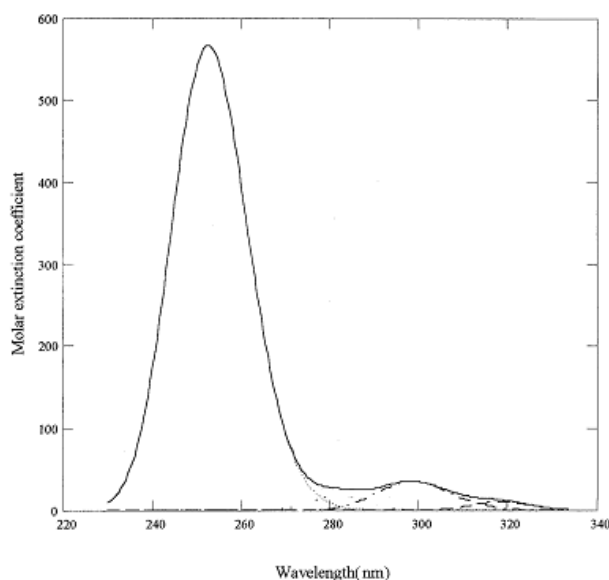


Figure 3. Electronic absorption spectrum of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in water (—) and its Gaussian analysis (---, -.-., ...)

exist with a lower coordination number, producing the weak band. The intensity of the weak band is strongly dependent on the temperature, the presence of the other ion, and even the substitution of heavy water as a solvent. A comparison of the energy difference $4f-5d$ is about 28 percent in complexes of ethylene-diaminetetraacetate, citrate and chloride, representing the same analogy to the nephelauxetic effect as the $s^2 \rightarrow sp$ transitions.

In this work, the electronic absorption spectra of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ have been studied using different solvents. The spectrum in water is shown in figure 3. The overlapping bands were resolved using Gaussian analysis, and three resolved bands are designated, starting from the lowest energy, as bands I, II and III, respectively. This result agrees with the predictions of Ce^{3+} energy level-splitting assuming that the lowest transition ($f^n \rightarrow f^n$) appears in the IR region. The intensity of band I indicates a forbidden transition ($\epsilon=10$), whereas the intensity of bands II and III indicate that both represent allowed transitions.

The spectra of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ have been investigated in a number of solvents. In dioxane, band I is not observed (table 3), and a red shift of the maxima of bands II and III is observed. The weak interaction between Ce^{3+} and dioxane molecules leads to a weak splitting of the energy levels of the metal ion. When DMF was the solvent, bands I, II and III were red shifted and intensified. Dimethyl formamide is a strong polar solvent

Table 3. Band Maxima and molar extinction coefficient of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in different solvents.

Solvent	Band	λ_{max} (nm)	ϵ_{max} (M^{-1}L)	$\sigma_{\text{all}} \times 10^{-8} \text{sec}^{-1}$
DMF	I	337	80	29.674
	II	308	180	32.468
	III	275	930	36.364
Dioxane	I	---	---	---
	II	315	120	31.745
	III	262	550	38.168
Ethanol	I	328	70	30.488
	II	298	150	35.557
	III	262	480	38.168
Methanol	I	329	60	30.395
	II	299	140	33.445
	III	255	670	39.216
Isopropanol	I	340	50	29.412
	II	310	150	32.258
	III	263	530	38.023
Acetonitrile	I	348	30	28.736
	II	308	130	32.468
	III	---	---	---
Ethylene glycol	I	---	---	---
	II	298	40	33.557
	III	249	350	40.161
Water	I	319	8	31.348
	II	295	42	33.898
	III	251	580	39.841

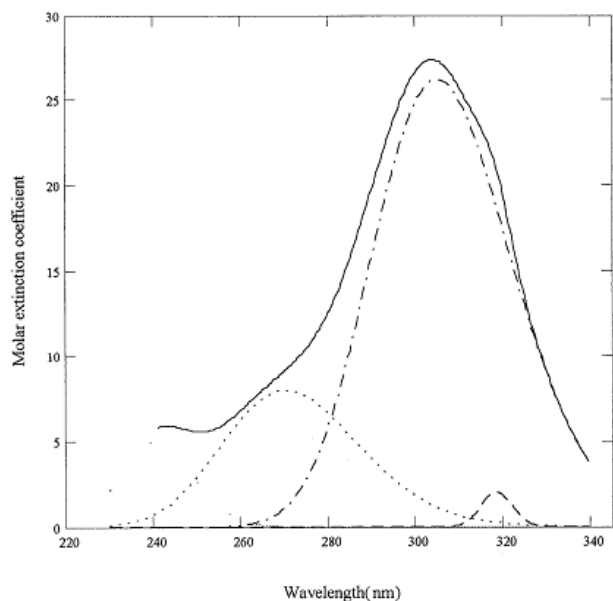
and is effective in replacing nitrate ions from the inner coordination sphere of the Ce^{3+} ion; thus, the absorbing species differs when water is the solvent from when DMF is the solvent. Hence, both the distortion of symmetry of the solvated Ce^{3+} and the type of solvent in the inner coordination sphere have led to the intensification of bands, and symmetry forbidden transitions are rendered allowed. This results is confirmed when investigating the spectrum of Ce^{3+} in isopropyl alcohol: the intensity of the three bands has increased, and their maxima are red shifted (table 3) compared with their values when water is the solvent.

The electronic absorption spectra of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ have been investigated using methanol, ethanol, acetonitrile and ethylene glycol as solvents. The variations of band maxima indicate that the electrostatic field of the solvent molecules, and consequently the Ce^{3+} ion-solvent interaction, vary in the order: DMF > isopropyl alcohol > water > methanol > ethanol > ethylene glycol > acetonitrile. The values of band maxima, λ_{max} , and molar extinction coefficients, ϵ , are given in table 3.

The allowed transition probability, σ_{all} , was calculated for all the resolved transitions, and the results are given

Table 4. Transition probabilities and oscillator strength for Th(NO₃)₃·6H₂O in different solvents

Solvent	Band	$\sigma_{\text{all}} \times 10^{-8} (\text{sec}^{-1})$	$\sigma_1 (\text{sec}^{-1})$	$\sigma_2 (\text{sec}^{-1})$	$\sigma_3 (\text{sec}^{-1})$	$f_1 \times 10^7$	$f_2 \times 10^7$	$f_3 \times 10^7$
DMF	I	2.085	12.04	939.30	2539.30	0.578	45.05	121.80
	II	2.721	---	---	---	---	---	---
	III	3.284	---	---	---	---	---	---
Ethanol	I	2.212	5.98	996.79	2694.73	0.270	45.06	121.80
	II	2.991	---	---	---	---	---	---
Methanol	I	2.212	5.98	996.79	2694.73	0.270	45.06	121.80
	II	2.952	---	---	---	---	---	---
Isopropanol	I	2.025	11.47	912.21	2466.06	0.0567	45.06	121.80
	II	3.035	---	---	---	---	---	---
Acetonitrile	I	2.212	13.30	996.79	2694.73	0.600	45.06	121.80
	II	2.721	---	---	---	---	---	---
	III	3.001	---	---	---	---	---	---
Ethylene glycol	I	2.025	11.47	912.21	2466.06	0.57	45.06	121.80
	II	2.721	---	---	---	---	---	---
Water	I	1.789	9.33	806.12	2179.26	0.522	45.06	121.80
	II	2.212	---	---	---	---	---	---
	III	2.841	---	---	---	---	---	---
Isobutyl alcohol	I	1.821	4.24	820.66	2218.58	0.238	45.06	121.80
	II	2.642	---	---	---	---	---	---
	III	2.801	---	---	---	---	---	---
	IV	3.099	---	---	---	---	---	---

Figure 4. Electronic absorption spectrum of Th(NO₃)₃·6H₂O in water (—) and its Gaussian analysis (---, -.-.-, ...).

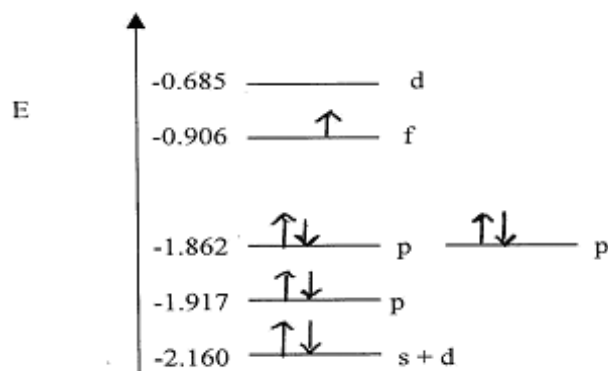
in table 3. The forbidden transition probabilities σ_1 , σ_2 and σ_3 were calculated for band I when water was the solvent, and the results are 35.0, 821.4 and 5530 sec⁻¹, respectively. The highest contribution to the intensity of

a forbidden transition comes from the electric-vibronic contribution. The fundamental frequency of vibration, ν_0 , of Ce(H₂O)₆³⁺ is taken as 10⁵ cm⁻¹, and the value (18) of V_0 is taken as 10⁴ cm⁻¹. The zero-point amplitude of nuclear vibration, R , is calculated and found to be 0.449 × 10⁻⁹ cm. The effective nuclear charge of Ce³⁺ is 8.0, and the calculated V_{hem} is 0.326 × 10³ cm⁻¹.

Thorium(IV) ion in Different Solvents

The electronic configuration of Th⁴⁺ is [Rn], leading to a ¹S₀ ground state. The lowest electronic excitation leads to a 6s²6p⁵6d¹ configuration, and L-S coupling gives the ^{1,3}P, ^{1,3}D and ^{1,3}F states. In aqueous medium, the absorbing ions is Th(H₂O)_n⁴⁺ and, assuming n=6 and the crystal field surrounding the Th⁴⁺ ion is an O_h field, the energy levels splitting will be the same as in the case of La(H₂O)₆³⁺. In group theoretical notation, the lowest energy transition is the ¹A_{1g} → ¹E_g Laporte forbidden transition (band I, table 4). The next two transitions are the Laporte allowed ¹A_{1g} → ¹T_{1u} and ¹A_{1g} → ¹T_{2u} (bands II and III in table 4).

The electronic absorption spectra of Th(NO₃)₃·6H₂O have been investigated using different solvents. When

Figure 5. Ab initio atomic orbitals of the Ce³⁺ ion.

using water as a solvent (figure 4), one broad asymmetric band is observed in the 240-340nm region. Gaussian analysis leads mainly to three bands; λ_{\max} and ϵ are given in table 1. When using DMF as a solvent, the spectrum of the solvated Th⁴⁺ ion shows a broad band that is easily resolved into three overlapping transitions. The spectrum is blue shifted and more intensified compared to that obtained in water as a solvent. Intensification of bands is further observed when isobutyl alcohol is the solvent.

The spectra of Th(NO₃)₄·6H₂O were studied in methanol, ethanol and ethylene glycol as solvents, and only two bands were observed. The lowest energy band corresponds to the Laporte forbidden transition with a molar extinction coefficient of 9.0. The second band corresponds to the Laporte allowed ¹A_{1g} → ¹T_{1u} transition 57.0 > ϵ > 29.0. When acetonitrile is the solvent, the spectrum of Th⁴⁺ consists of a broad band with a long-wavelength shoulder. The band is resolved into two transitions with λ_{\max} around 270 and 280 nm. The spectral observations indicate that the field strength of the used solvents varies in the order DMF > acetonitrile > H₂O. Table 1 gives the values of band maxima and intensity for the observed transitions.

Table 4 gives the values of the different transition probabilities calculated for band I (forbidden transition). the largest component contributing to the intensity of the forbidden transition is that due to the electric dipole coupled with vibration, transition probability σ_3 . For the allowed transitions, bands II and III, only σ_{all} was calculated.

Molecular Orbital Calculations

Ab initio calculations were performed on the free Ce³⁺ ion using a GAMESS program (21). The total energy

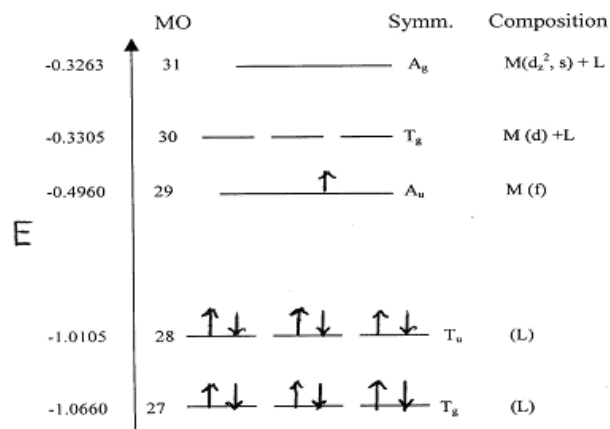
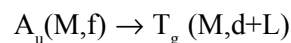


Figure 6. A non-scale MO Energy diagram for [Ce(H₂O)₆]³⁺ assuming T_h symmetry. The highest three MOs are: T_g and T_u (localized on the ligands) and the A_u is a pure metal f atomic orbital. The lowest two vacant MOs are: T_g (localized on the metal, d orbitals and the ligands), A_g (localized on the metal and ligands).

obtained is -36.83025787 a.u. after twenty-nine iterations. The resulting energy level diagram is shown in figure 5. The highest occupied orbital is a pure 4f atomic orbital.

Calculations were repeated for the [Ce(H₂O)₆]³⁺ ion, adopting a T_h symmetry point group. The obtained energy levels diagram is shown in figure 6. Some important and interesting results are evident. The highest occupied orbital in [Ce(H₂O)₆]³⁺ is a pure f orbital with A_u symmetry. The lowest vacant molecular orbital has a main contribution from d-orbitals of Ce³⁺ (92%) and some contribution (8%) from the ligand (H₂O) molecular orbitals. Consequently, one would expect a lowest energy allowed and intense transition which is:



According to the symmetry properties of the T_h group, the electric dipole vector, **er**, transforms as T_u. Consequently, transitions from T_u or to T_u levels are symmetry allowed, and the transitions T_u → A_u, T_u → A_g and T_u → T_g are all symmetry allowed. The transition T_u → A_u is Laporte forbidden, whereas the other two transitions are Laporte and symmetry allowed. Experimentally, the observed lowest energy transitions of Ce(NO₃)₃·6H₂O in water as a solvent is relatively weak, $\epsilon=8$. This result indicates that aquated Ce³⁺ has a distorted symmetry, and the forbidden transition has a degree of allowance. Distortion of symmetry results in the observation of the forbidden transitions T_u → A_u,

$T_g \rightarrow A_g$ and $T_g \rightarrow T_g$ (figure 6).

The electronic spectrum of Ce^{3+} in water as a solvent (Figure 3) shows three well-defined bands corresponding to three electronic transitions. Both L-S coupling and MO calculations show that all the transitions have a degree of allowance.

Mulliken atomic orbital population was calculated for Ce^{3+} in $[Ce(H_2O)_6]^{3+}$ assuming a T_h symmetry; the result is $4f^{0.72}5d^{0.49}6s^{0.49}6p^{0.32}$. There is a drag of electronic charge from the ligand to the metal ion. Mulliken atomic overlap between cerium and oxygen atoms in $[Ce(H_2O)_6]^{3+}$ has the same value, 0.0767, which indicates the absence of any π -bonding between the cerium ion and any of the oxygen atoms and that only a covalent σ -bond is formed. The calculated charge distribution on the different atoms of the complex ion $[Ce(H_2O)_6]^{3+}$ is $Ce=+2.45$, $O=-0.78$ and $H=+0.43$.

Conclusions

The difference in the electronic configuration of the La^{3+} ion: $[Xe]5d6s$ and the Th^{4+} ion: $[Rn]6d7s$ on one side and that of the Ce^{3+} ion: $[Xe]4f^15d6s$ on the other side has led to detectable differences in the spectra of the different solvated ions. The electronic spectra of $[La(solvent)_n]^{3+}$ ion and $[Th(solvent)_n]^{4+}$ showed mainly weak forbidden transitions, whereas that of $[Ce(solvent)_n]^{3+}$ ion gave mainly strong allowed transitions. The extent of the solvent-solute electronic interaction was dependent on the solvent and the specific metal ion. As a result, values of band maxima varied with the solvent for the same metal ion. The electronic spectra of the studied aquated ions show a high extent of band overlap, and Gaussian analysis was used for resolution. The observed band intensity can differentiate clearly between allowed (ϵ up to 900) and forbidden (ϵ as low as 2) transitions.

Transition probabilities were calculated for allowed as well as for forbidden transitions using the Van Vleck method. Experimentally, band intensity is found to be directly proportional to the type of solvent and to the extent of distortion of the absorbing ion; $[Ln(isopropyl alc.)_n]^{3+}$ ion absorbs light more strongly than $[Ln(H_2O)_n]^{3+}$ ion. On the other hand, a general red shift of band maximum of the absorbing species is observed with increasing polarity of the solvent.

The transition probabilities of the three types of forbidden transitions, quadrupole transition, magnetic

dipole transition and vibronic-electronic transition, contribute to the intensity of the forbidden transitions of the studied ions. The main contribution to intensity comes from the vibronic electronic transition, and the least contribution to intensity comes from the quadrupole transition ($\sigma_3 \gg \sigma_1$).

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