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Analyses of the excited $5f^1$ optical spectra of Th^{3+} compounds

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Abstract

The electronic structure of $Th(Cp'')_3$ ($Cp'' = \eta^5\text{-}C_5H_3(SiMe_3\text{-}1,3)$, a molecule which has a $6d^1$ ground configuration and an excited $5f^1$ configuration beginning approximately 14,000 cm^{-1} higher, is reexamined. The ground state of the $6d^1$ configuration in a crystal field of D_{3h} symmetry is shown to be an orbitally quenched $^2A_1'$ state, best described as a pure $^2D_{1/2}$ state. Electric dipole selection rules from this state to the states for the $5f^1$ configuration in a D_{3h} crystal field result in the $5f^1$ truncated optical spectrum observed. The optical spectrum of the square planar Th^{3+} compound $[Li(THF)_4][Th(OAr')_4]$, where ($OAr' = OC_6 H_2^t Bu_2\text{-}2,6\text{-}Me\text{-}4$), is discussed.

Introduction

The first crystal structure of a trivalent Th^{3+} compound, $Th(Cp'')_3$, was reported by the Lappert group in 1986[1], over thirty years ago. Shortly afterwards, the $Th(Cp'')_3$ solution optical spectrum and its electron paramagnetic resonance(epr) spectrum at room temperature and 77K were published.[2] The observation of the 300K epr spectrum with a g value near 2.0 established that the ground configuration of $Th(Cp'')_3$ was from the $6d^1$ configuration. This assignment was not completely surprising since for the Th^{3+} free ion (Th(IV), the separation between the ground $5f^1$ ground level and the first $6d^1$ level is 9193 cm^{-1}.[3] As explained by Kot et al., large shifts of the relative energies of d and f configurations take place when the free ion is placed in a crystalline field. Such is the case for 6d and 5f configurations of Th^{3+} with the result that the two configurations overlap in the $Th(Cp'')_3$ molecule with the ground state of $6d^1$ character. However the original optical spectrum contained three bands energetically close together and a fourth band approximately 10000 cm^{-1} higher. Recently Wedal et al[4] reported the epr and solution optical spectrum of a new $Th(Cp')_3$ ($Cp' = C_5H_4SiMe_3$) molecule which had very similar values to that of the original Lappert compound except that the highest energy band was not present. In the lower energy region where the 6d to 5f bands are expected, the observed optical spectrum resembled closely the original spectrum of Cp''_3Th. Therefore, we have reexamined the expected optical spectrum for $Th(Cp'')_3$ by use of ligand field and intensity calculations.

The Evans group have also reported the synthesis and characterization of a new compound, square planar $[Li(THF)_4][Th(OAr')_4]$ ($OAr' = OC_6 H_2{}^tBu_2$-2,6-Me-4), which has an epr spectrum at room temperature with a g value of 1.84 and a glassy spectrum at 77K with $g_\parallel = 1.99$ and $g_\perp = 1.79$.[5] They compiled a table of the known Th^{3+} compounds and listed the g values of the measured epr spectra. In all cases for the Th^{3+} complexes with approximate D_{3h} symmetry, the room temperature solution g value is within the range 1.90±.03. For three of these D_{3h} symmetry compounds measurements at 77K or 100K have given $g_\parallel = 1.97±.01$ and $g_\perp = 1.88±.03$. The epr g values of the Th^{3+} compounds and their solution spectra, obtained at room temperature in solution or as glassy samples at 77K, or for the epr spectra as powders at room temperature or at 77K, are consistent with the published crystal structures of these compounds.

Crystal field calculations

In a crystal field of D_{3h} symmetry, the d^1 configuration will split into one A_1' (Γ_2) level (d_{z2}), and two E' (Γ_6) levels (d_{xy} and d_{x2-y2}) and two E'' (Γ_5) levels (d_{xz} and d_{yz}). Each of these five levels is doubly degenerate (Kramers degeneracy). A detailed group theory description of the splitting of a d electron in a strong crystal field of D_{3h} symmetry in the $|m_L, m_S>$ representation (with L =2, S =1/2 for all d states) has been given by Becker, Meek and Dunn[6] and is shown in Table 1. We reproduce part of their Table 5 in our Table 1 (using our group theory representation for the labels).

Single group	Double Group	Wavefunction
$^2A_1'$ or Γ_1	$E_{1/2}$ or Γ_{7a}	$= |0,-1/2\rangle$
$^2A_1'$ or Γ_1	$E_{1/2}$ or Γ_{7b}	$= -|0,-1/2\rangle$
$^2E'(1)$ or Γ_6	$E_{5/2}$ or Γ_{8a}	$= |2, ,1/2\rangle$
$^2E'(2)$ or Γ_6	$E_{5/2}$ or Γ_{8a}	$= |-2,-1/2\rangle$
$^2E'(3)$ or Γ_6	$E_{3/2}$ or Γ_{9a}	$= |-2,1/2\rangle$
$^2E'(4)$ or Γ_6	$E_{3/2}$ or Γ_{9a}	$= |2,-1/2\rangle$
$^2E''(1)$ or Γ_5	$E_{1/2}$ or Γ_{7a}	$= |-1,1/2\rangle$
$^2E''(2)$ or Γ_5	$E_{1/2}$ or Γ_{7b}	$= -|1,-1/2\rangle$
$^2E''(3)$ or Γ_5	$E_{3/2}$ or Γ_{9a}	$= |-1,-1/2\rangle$
$^2E''(4)$ or Γ_5	$E_{3/2}$ or Γ_{9a}	$= |1,1/2\rangle$

[a] Wavefunctions taken from Table V of reference 6. Group theory notation from Altman et al.[7] and from Koster et al.[8] for D_{3h} symmetry.

Table 1 Wavefunctions for the d^1 configuration in a strong crystal field in the $|m_L,m_s\rangle$ basis with L = 2, S = ½.

Under D_{3h} symmetry the crystal field Hamiltonian for a single d electron is

$$H_{CF} = B_0^2(d)(C_0^2) + B_0^4(d)(C_0^4) \qquad\qquad (1)$$

where $B_0^2(d)$ and $B_0^4(d)$ represent the d electron crystal field parameters and the (C_0^k)'s represent angular operators whose matrix elements can be evaluated exactly. In this paper we use exclusively the Wybourne definition of the crystal field operators.[9] The correct relationship between the Wybourne definition[10] and the older operator equivalent definition has been given by Kassman,[11] among others.

We may use any of the wavefunctions for each of the A_1', E', and E'' groups in Table 1 and calculate the crystal field levels for the d^1 configuration in a crystal field of D_{3h} symmetry. This calculation can easily be done with the above Hamiltonian using the Steven's operator equivalent method with the L,M_L values of the wave functions in Table 1. The appropriate tables are given in in the appendices of Abragam and Bleaney,[12] and the table from Kassman to change from the operator equivalent crystal field parameters to the Wyboune definitions. The crystal field energies for three levels in terms of the $B^2_0(d)$ and $B^4_0(d)$ are given in Table 3.

Level	Energy
A_1'	$(2/7)\,B_0^2(d) + (2/7)\,B_0^4(d)$
E'	$(1/7)\,B_0^2(d) - (4/21)\,B_0^4(d)$
E''	$(-2/7)\,B_0^2(d) + (1/21)\,B_0^4(d)$

Table 2 Crystal field energies for a d^1 configuration in D_{3h} symmetry

In order to have some idea of the $6d^1$ energy levels in this molecule we utilize the results of the non-relativistic and relativistic discrete variational-Xα calculations on [Th(η-Cp)$_3$] of Kaltsoyannis and Bursten.[13] Although they used C_{3v} symmetry and calculated their results for the non-relativistic and the relativistic cases, we will approximate their results for the [ThCp$_3$] 6d electron configuration with the non-relativistic D_{3h} nomenclature. The energies given by the Kaltsoyannis, Bursten calculation are from their Table 3 and result in the ground state 6d1 A_1' at 0 cm-1 , the first excited $^2E'$ state at ~7200 cm-1 and the second excited state $^2E''$ at ~ 25500 cm^{-1}. With these approximate energies we find $B_0^2(d) = -43750$ cm^{-1} and $B_0^4(d) = -2100$ cm^{-1}. We have assumed the ground A_1' state is 100% d_z^2 wavefunction and therefore the calculated g factors are $|g_{\parallel}| = |g_{\perp}| = 2.00$. We may write this $^2D_{1/2}$ state in terms of the S,L.J,M_J representation where S=1/2 and L=2 for both terms (which are not included in the ket) as follows:[6]

$$\text{sqrt}(3/5)|5/2,-1/2\rangle - \text{sqrt}(2/5)|3/2,-1/2\rangle$$

where the numbers in the ket represent $|J, M_J\rangle$. Note that this wavefunction is just half of the Kramers doublet which has the same energy.

We note the thorium free ion (Th^{3+} or ThIV) spectrum was reported by Klinkenberg and Lang[3] where they determined the spin-orbit coupling constants for $\zeta_{6d} = 2117.2$ cm^{-1} and $\zeta_{5f} = 1235.7$ cm^{-1} with the ground term of $5f^1$ origin.

From this point on we use the SLJM$_J$ and the powerful tools described by Wybourne[9] which easily allows the addition of crystal field mixing between energy levels and the addition of spin-orbit coupling. Using the SLJMJ basis set we find the same energies as found previously with no spin-orbit mixing for the d^1 configuration under a D_{3h} crystal field. We also calculate the energy levels and g values for two values of the ζ_{6d} as shown in Table 3. Note that the experimental g values for Th(Cp$_3''$) as mentioned earlier are much closer to the calculation for $\zeta_{6d} = 0$. Despite the value of $\zeta_{6d} = 2117.2$ cm^{-1} for the Th^{3+} (ThIV) free ion, the best fit for the measured g values for Th(Cp$_3''$) is when the orbital angular momentum is almost quenched completely. This result does not depend on our choice of crystal field parameters. We conclude it is a good approximation to assume the ground state of Cp$_3''$Th is a pure A_1' (Γ_1 state). It is clear that the orbital angular momentum is quenched in this particular case which is reasonable for a d^1 ion in

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a strong D_{3h} crystal field with the A_1' state lowest, and with an E′ doublet as the next highest state.

Param. (cm^{-1})	E(cm^{-1})	E(cm^{-1})	E(cm^{-1})
B_0^2(d)	-43750	-43750	-43750
B_0^4(d)	-2100	-2100	-2100
ζ(d)	0	200	728
A_1'	0	0	0
2E′	7250	7004	6929
		7356	7511
2E″	25500	25461	25577
		27053	27003
$\lvert g_\parallel \rvert$	2.0	2.0	2.0
$\lvert g_\perp \rvert$	2.0	1.8	1.3

[a]When ζ(d) is included in the calculation, the E′ and E″ levels each split into two doublets, which together with the A_1' level, are each doubly degenerate.

Table 3– Calculated energies and g values for the $6d^1$ configuration in Th(Cp″)$_3$[a]

The $5f^1$ state

The $5f^1$ excited state levels for Th(Cp″)$_3$ can be derived from the following Hamiltonian

$$H = H_{cf} + H_{so} \tag{2}$$

where for D_{3h} symmetry

$$H_{cf} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_6^6 (C_6^6 + C_{-6}^6) \tag{3}$$

and $H_{so} = \zeta_{5f}\mathbf{s}\cdot\mathbf{l}$.

We are now writing the crystal field parameters for the f^1 configuration as B_0^2, B_0^4, B_0^6, and B_6^6 to differentiate them from the B_0^2(d) and B_0^4(d) parameters which are only for the $6d^1$ configuration.

With the above Hamiltonian for the $5f^1$ configuration in a D_{3h} crystal field, we can classify the states by group theory using the double group nomenclature or by μ values, which for D_{3h} symmetry for an f^n configuration where n is odd, are the same. Thus $\mu = \frac{1}{2} = \Gamma_7$, $\mu = 3/2 = \Gamma_9$, and $\mu = 5/2 = \Gamma_8$.

The eigenfunctions for the three μ values are given schematically in Table 4.

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μ value

| 1/2 | a1*\|5/2, -1/2> | b1*\|7/2, -1/2> |
| | a1*\|7/2, -1/2> | -b1*\|5/2, -1/2> |

| 3/2 | a2*\|5/2, -3/2> | b2*\|7/2, -3/2> |
| | a2*\|7/2, -3/2> | -b2*\|5/2, -3/2> |

5/2	a3*|5/2, -5/2>	b3*|7/2, -5/2>	c3*|7/2, 7/2>
	a4*|5/2, -5/2>	b4*|7/2, -5/2>	c4*|7/2, 7/2>
	a5*|5/2, -5/2>	b5*|7/2, -5/2>	c5*|7/2, 7/2>

Table 4. Schematic eigenfunctions for the $5f^1$ matrix with spin-orbit coupling and a D_{3h} crystal field. All states are from the ^2F configuration with S=1/2 and L =3, J = 5/2 or 7/2. Values within the kets are \|J, M_J> and are given for each μ value. The a, b, c s are coefficients of the wavefunctions and are dependent on the values of the crystal field parameters and ζ_{5f}.

Selection rules for the intensities of the allowed 6d to 5f transitions

The theory needed to calculate the oscillator strength for a polarized electric dipole transition between the initial d state \|d> and a final f state \|f> was developed by Axe[14] and utilized by Williams et al.[15] for the calculation of 4f to 5d states for Ce^{3+} diluted in $LuPO_4$. The equation for summed oscillator strengths is proportional to the dipole matrix elements describing the electronic states for the Th^{3+} ion. These matrix elements can be easily evaluated by expressing the operator $\mathbf{e \cdot D}$ as linear combinations of the spherical electric dipole operators, D_q^1 as given by the following equation:

$$< f_e|D_q^1|i_e> = <6d|r|5f><2||C^{(1)}||3> \sum_{J,M_J} \sum_{J',M_{J'}} a_{i_eJM_J} a*_{f_eJ'M_{J'}}$$

$$X \; (-1)^{J'-M_J} \begin{pmatrix} J & 1 & J \\ -M_{J'} & q & M_J \end{pmatrix}$$

$$X \; (-1)^{L'+S'+J+1}(2J+1)^{1/2}(2J'+1)^{1/2} \begin{Bmatrix} J' & 1 & J \\ L & S & L' \end{Bmatrix} <L'||U^1||L>. \quad (4)$$

The parts of this equation that we need for this discussion are the 3 j and 6j symbols.

The 6j symbol must satisfy certain triangular conditions and results in the following selection rule[10]

$$\Delta S = 0, \quad \Delta L = 0, \pm 1, \quad \text{and} \quad \Delta J = 0, \pm 1, \text{ but not } 0 \leftrightarrow 0. \quad (5)$$

For the 3j symbol to be not zero the sum

$$-M_{J'} + q + M_J = 0 \qquad (6)$$

which leads to the following selection rules for $q = 0, \pm 1$,

$$\Delta M_J = 0, \pm 1. \qquad (7)$$

Now for the 5d state in Th(Cp″)$_3$ we have shown the ground state to be a $M_J = \pm 1/2$. In order to obey that above selection rules, the only allowed transitions from the ground $6d^1$ $\mu = 1/2$ states to the 5f levels are the following:

from $^2D_{3/2,5/2}$ $M_J = \pm 1/2 \rightarrow$ $^2F_{5/2,7/2}$ $M_J = \pm 1/2$, $\pm 3/2$. \qquad (8)

From these restrictions we see there are no allowed transitions to the $\mu = 5/2$ states of the excited $5f^1$ of Th(Cp″)$_3$ as this μ value contains eigenvectors components that are sums of $|J, M_J\rangle$ $= a|5/2,-5/2\rangle$, $b|7/2,-5/2\rangle$, and $c|7/2,+7/2\rangle$, see Table 4. The crystal field Hamiltonian for the $\mu = 1/2$ and $3/2$ levels do not include the B_6^6 term as only $\mu = 5/2$ levels have this term in the energy matrix. Thus, there are at most four possible transitions that may be observed from a d^1, $\mu = \frac{1}{2}$ state out of the seven possible transitions, and these levels do not depend directly on the B_6^6 term.. If we assume two of the four possible transitions overlap, we can explain why only the three transitions are observed. These selection rules do not depend on our assignment of the pure $^2D_{1/2}$ state as the ground state. All that is needed for the selection rules to apply is that a $\mu = \frac{1}{2}$ state be the lowest d^1 state in D$_{3h}$ symmetry.

Discussion

We can fit the observed spectrum shown in Fig. 1 to three Gaussian functions. The fit is shown in Fig. 1 and the parameters of the fit are given in Table 5.
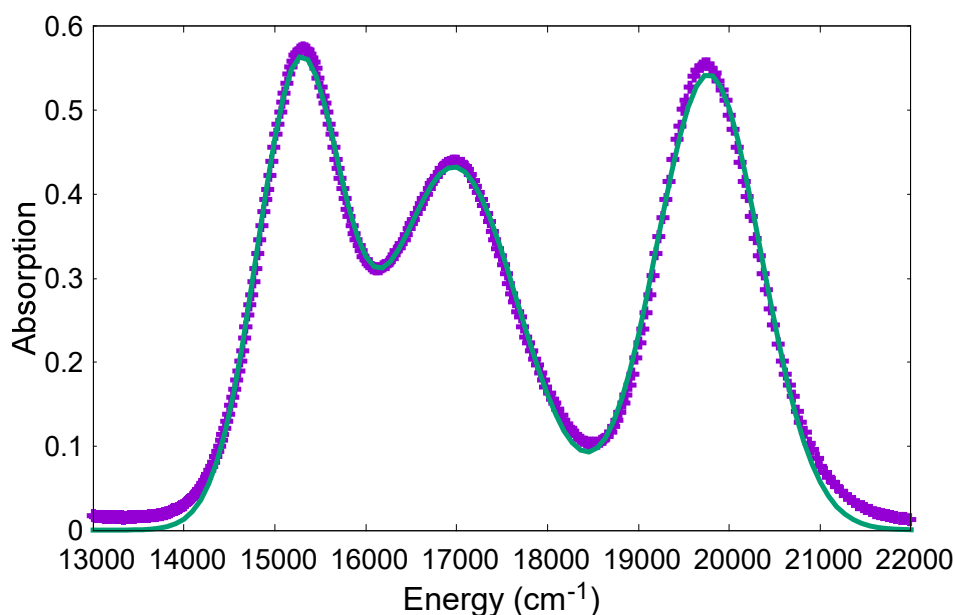
Figure 1 Fit of the 5f^1 optical spectrum of Th(Cp″)$_3$ to three Gaussian functions, dotted line – experimental data, continuous line – fit of the three Gaussian functions.

Energy cm^{-1}	Relative Energy cm^{-1}	Relative area	Half-width cm^{-1}
15264.	0.00	1.00	464.
16972.	1708.	1.25	721.
19771.	4507.	1.26	579.

Table 5 Results from the fitting of three Gaussian functions to the observed 5f^1 optical spectrum of Th(Cp″)$_3$.

The expectation for the 6d to 5f optical spectra is rather sharp zero phonon lines on the order of a few cm^{-1} surrounded by vibrational progressions. These features have been observed at liquid helium temperatures in high resolution solid state studies at octahedral sites of Pa^{4+} diluted in Cs$_2$ZrCl$_6$ [16-17] and Ce^{3+} in Cs$_2$NaCeCl$_6$ and Ce^{3+} diluted in Cs$_2$NaYCl$_6$ [18-19]. What we have observed in the room temperature optical spectra of Th(Cp″)$_3$ are very broad lines on the order of 500 cm^{-1} half-width, likely composed of the zero phonon lines broadened by vibrational features. The absorption spectrum we have observed is also composed of just four transitions that are allowed by an electric dipole transition from the ground $\mu = \frac{1}{2}$ 6d ground state of Th(Cp′)$_3$.   The energy levels of the 5f^1 configuration in D$_{3h}$ symmetry depend on four crystal field parameters and the 5f^1 Th^{3+} spin-orbit coupling constant. The free ion spin-orbit coupling constant is known

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which puts an upper limit on its molecular value. However the levels we observe arise only from the $\mu = \frac{1}{2}$ and $\mu = 3/2$ matrices and consist of admixtures from the $M_J = \frac{1}{2}$ or $M_J = 3/2$ states from the J =5/2 and J=7/2 manifolds. Absent is any contribution from the $M_J = 5/2$ or $M_J = 7/2$ states (see Table 4). The B_6^6 term arises only for the $\mu = 5/2$ submatrix, so the possible energy levels observed do not have any direct dependence on this term. Therefore, it is impossible to determine this parameter from the present spectrum. Nevertheless the actual levels of the 5f[1] configuration for Th(Cp″)$_3$ depend on all four crystal field parameters as the value of B_6^6 term affects the energies of the three $\mu = 5/2$ states and the values of other crystal field parameters and the molecular spin-orbit coupling constant. Thus we have decided not to try to fit this spectrum due to insufficient data.

The Th^{3+} compound [Li(THF)$_4$][Th(OAr′)$_4$]

This compound was reported recently by the Evans group and its epr and optical spectrum were recorded.[5] Of interest here is the fact that this compound has the Th^{3+} ion in a square planar complex for which the Th^{3+} ion is at a site of D$_4$ symmetry. The ground 6d[1] state is of A$_1$ (or Γ_1 for D$_4$) symmetry which means the $\mu = \frac{1}{2}$ level is the ground state. For D$_4$ symmetry the crystal field Hamiltonian for a d[1] ion is

$$H_{cf} = B_0^2(d)(C^2{}_0) + B_0^4(d)\, C_0^4 + B_4^4(d)(\, C_4^4 + C_{-4}^4) \tag{9}$$

and the $\mu = \frac{1}{2}$ wavefunctions for 6d[1] ion, the D$_4$ symmetry wavefunctions will consist of eigenvectors similar to the D$_{3h}$ wavefunctions

$$a'|5/2,-1/2> - b'|3/2,-1/2> \tag{10}$$

where a′ and b′ depend on the values of the B_q^k(d) parameters.

For the f[1] ion in a crystal field of D$_4$ symmetry the Hamiltonian is

$$H_{cf} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4(C_4^4 + C_{-4}^4) + B_0^6 C_0^6 + B_4^6(C_4^6 + C_{-4}^6) \tag{11}$$

with eigenvectors as shown schematically in Table 6

μ value

1/2	a1*|5/2, -1/2>	b1*|7/2, -1/2>	c1*|7/2, 7/2>	
	a2*|7/2, -1/2>	b2*|5/2, -1/2>	c2*|7/2, 7/2>	
	a3*|7/2, -1/2>	b3*|5/2, -1/2>	c3*|7/2, 7/2>	

3/2	a4*|5/2, -3/2>	b4*|7/2, -3/2>	c4*|5/2, 5/2>	d4*|7/2, 5/2>
	a5*|5/2, -3/2>	b5*|7/2, 3-/2>	c5*|5/2, 5/2>	d5*|7/2, 5/2>
	a6*|5/2, -3/2>	b6*|7/2, -5/2>	c6*|5/2, 7/2>	d6*|7/2, 5/2>
	a7*|5/2, -3/2>	b7*|7/2, -5/2>	c7*|5/2, 7/2>	d7*|7/2, 5/>2

Table 6 Schematic eigenfunctions for the 5f^1 matrix with spin-orbit coupling and a D$_4$ crystal field. All states are from the ^{2}F configuration with S=1/2 and L =3, J = 5/2 or 7/2. Values within the kets are |J, M$_J$> and are given for each μ value. The a, b, c s are coefficients of the wavefunctions and are dependent on the values of the crystal field parameters and ζ$_{5f}$.

The selection rules are the same as discussed previously but in the D$_4$ crystal field case all wavefunctions of the 5f^1 case have at least one component which will allow a 6d^1 to 5f^1 transition from the μ = ½ 6d state. Thus the solution optical spectrum of [Li(THF)$_4$][Th(OAr′)$_4$ as shown by Huh, et al. [5] should represent all the 5f^1 levels. In their spectrum there are two broad lines centered at 483 nm and 581nm (20,704 cm^{-1} and 17218 cm^{-1}) in the visible region representing the 5f^1 configuration of the Th^{3+} complex. For the 5f configuration of the Th^{3+} free ion, the spin-orbit splitting between the J=5/2 and J = 7/2 states is equal to 7/2* ζ$_{5f}$. If we assume the crystal field is relatively small compared with the spin-orbit splitting we may approximate the value of ζ$_{5f}$ in [Li(THF)$_4$][Th(OAr′)$_4$ from the difference between the peaks of the two absorption lines . This difference is ~ 3500 cm^{-1}. Thus ζ$_{5f}$ is ~ 1000 cm^{-1} for this Th^{3+} compound, which is quite a reasonable value when compared to the Th^{3+} free ion value of 1235.7 cm^{-1}.

Conclusion

We have shown that the sparse spectrum observed for the 6d^1 to 5f^1 transitions for the molecule Th(Cp″)$_3$ is due to the electric dipole selection rules. However for the D$_4$ symmetry of the Li(THF)$_4$][Th(OAr′)$_4$ molecule all transition from the ground 6d^1 state are allowed to some extent to all the 5f^1 levels of this molecule. To date, no 5f to 6d fluorescent transitions for any Th^{3+} compound have been reported. The most probable reason for this is non-radiative relaxation from the fluorescent state as there are high energy vibronic transitions associated with the hydrogen atoms near the Th^{3+} ion. The best candidate molecule with which to observe fluorescence is Li(THF)$_4$][Th(OAr′)$_4$. If a small amount of this molecule were dissolved in a deuterated solvent and proton exchange took place between the solvent and the molecule, it is likely that fluorescence could be observed. Also if deuterated Li(THF)$_4$][Th(OAr′)$_4$ could be isolated it is quite possible that high resolution laser optical studies at low temperatures of the 5f to 6d fluorescence would be able to observe the zero phonon 5f states and the vibronic structure.

Acknowledgments

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Table of Contents – Graphic

Allowed
^{2}D J=3/2, M$_J$ = -1/2 → ^{2}F J=5/2, M$_J$= -1/2, -3/2
^{2}D J=3/2, M$_J$ = -1/2 → ^{2}F J=7/2, M$_J$= -1/2, -3/2
Not allowed
^{2}D J=3/2, M$_J$ = -1/2 ↛ ^{2}F J=5/2, M$_J$= -5/2
^{2}D J=3/2, M$_J$ = -1/2 ↛ ^{2}F J=7/2, M$_J$= -5/2+7/2
6d^1 to 5f^1 electric dipole transitions for D$_{3h}$ symmetry

Allowed

^{2}D J=3/2, M$_J$ = -1/2 $\longrightarrow$ ^{2}F J=5/2 or 7/2, M$_J$= -1/2, -3/2

Not allowed

^{2}D J=3/2, M$_J$ = -1/2 $\nrightarrow$ ^{2}F J=5/2, M$_J$= -5/2

^{2}D J=3/2, M$_J$ = -1/2 $\nrightarrow$ ^{2}F J=7/2, M$_J$= -5/2+7/2

6d^1 to 5f^1 electric dipole transitions for D$_{3h}$ symmetry