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### Publication Date

1992-06-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## CHEMICAL SCIENCES DIVISION

To be presented at the Rare Earths 1992 Conference, Kyoto, Japan,  
June 1-5, 1992, and to be published in the Proceedings

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June 1992



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of Tetravalent Pa and Trivalent Th Compounds

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Abstract

At the beginning of the actinide series, the 5f and 6d configurations are very close in energy. Consequently, both the 5f and 6d energy level splittings may be observed experimentally in Pa<sup>4+</sup> and Th<sup>3+</sup> compounds. The available magnetic and optical data on these systems are reviewed.

Introduction

Before 1940, the elements Th, Pa, and U (atomic numbers 90-92) were placed below their 5d counterparts Hf, Ta, and W (atomic numbers 72-74) in the Periodic Table because of the similarity of their chemical properties to those 5d elements. However it had long been predicted theoretically that a new transition series should begin somewhere around uranium in the Periodic Table, and many early studies suggested this shell should consist of 5f electrons [1]. Today it

is known experimentally that the first appearance of 5f electrons in the free gaseous atoms of the present-day actinide series occurs at element 91, Pa, whose ground configuration is  $5f^2 6d 7s^2$  outside the closed radon shell. For all the early actinide gaseous atoms and ions, there are a number of low-lying electron configurations [2]. Placing these ions in compounds or crystals, can cause perturbations to the relative energies of these configurations due to the effects of the crystal field. The most notable example is for the one structurally characterized compound of trivalent Th,  $\text{Cp}_3\text{Th}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_3\text{-(SiMe}_3)_2$ ) [3]. In the free trivalent Th ion, the lowest configuration is  $5f^1$  with the  $6d^1$  configuration starting at  $9192.84 \text{ cm}^{-1}$ . In  $\text{Cp}_3\text{Th}$ , the ground configuration is  $6d^1$  with the  $5f^1$  configuration beginning at  $15,350 \text{ cm}^{-1}$ . Thus placing the  $\text{Th}^{3+}$  ion into this compound results in a stabilization of the lowest 6d energy level by greater than  $24,000 \text{ cm}^{-1}$ . Similar, though less dramatic, effects occur in Pa compounds. In this paper, electronic and magnetic studies on  $\text{Pa}^{4+}$  and  $\text{Th}^{3+}$  compounds will be reviewed.

#### $\text{Pa}^{4+}$ Magnetism and Spectroscopy

The near infra-red spectrum of  $\text{Pa}^{4+}$  ( $5f^1$ ) diluted into the host crystal  $\text{Cs}_2\text{ZrCl}_6$  was measured originally by Axe [4]. He and coworkers also reported the EPR (electron paramagnetic resonance) spectrum of the ground state [5].  $\text{Pa}^{4+}$  in this crystal is at a site of  $\text{O}_h$  symmetry and the energy level scheme is shown in Fig. 1. As will be discussed later it is appropriate to think of the active species as the

$\text{PaCl}_6^{2-}$  anion. Axe was the first to use  $\text{Cs}_2\text{ZrCl}_6$  as a host crystal and this crystal has now been studied extensively with  $\text{U}^{4+}$  as the dopant ion [6], as well as with the  $\text{Np}^{4+}$  ion [7]. Axe also observed strong transitions in the visible region but did not give these bands a definite assignment.

The optical and magnetic data for  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  were analyzed in terms of the crystal and spin-orbit interactions for an  $f^1$  electron. The Hamiltonian for the energy levels of an  $f$  electron in octahedral symmetry may be written as

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{CF}} \\ \mathcal{H}_{\text{SO}} &= \zeta_l(r) \mathbf{l} \cdot \mathbf{s}, \quad (1) \\ \mathcal{H}_{\text{CF}} &= B_0^4 [C_0^4 + \left(\frac{5}{14}\right)^{1/2} (C_{-4}^4 + C_4^4)] \\ &\quad + B_0^6 [C_0^6 - \left(\frac{7}{2}\right)^{1/2} (C_{-4}^6 + C_4^6)].\end{aligned}$$

The effects due to the radial part of the  $5f$  wavefunctions are contained in the crystal field parameters  $B_0^4$  and  $B_0^6$ , and the spin-orbit coupling constant  $\zeta_{5f}(r)$ , which are evaluated empirically. The matrix elements for the angular momentum operators,  $s$  and  $l$ , and the tensor operators,  $C_q^k$ , depend only on the angular coordinates and are evaluated by standard techniques [8].

Under the effect of the octahedral crystal field at the  $\text{Pa}^{4+}$  site, the seven degenerate  $f$  orbitals (of the free ion) decompose into two triplet states,  $t_{1u}$  and  $t_{2u}$ , and one singlet state,  $a_{2u}$  ( $O_h$  point group). When the electron spin is considered, each orbital becomes doubly degenerate and the double group representations  $\Gamma_{6u}$ ,  $\Gamma_{7u}$ , and  $\Gamma_{8u}$  become the proper labels for the eigenstates and energy levels. Because the spin-



orbit coupling interaction is large compared to the crystal field interaction, the crystal field levels fall in two groups which can be described (approximately) by the term labels  ${}^2F_{5/2}$  and  ${}^2F_{7/2}$  (Fig. 1).

Although the 5f radial wavefunction is more extended than its 4f counterpart  $\text{Ce}^{3+}$ , it is still shielded from the surrounding environment by the  $6s^2$  and  $6p^6$  filled electron shells. The radial wavefunction of the 6d configuration extends significantly beyond the filled  $6s^2 6p^6$  shells of the Rn core. Thus, the 6d electron experiences a crystal field that is much larger than the 6d spin-orbit coupling. The octahedral ( $O_h$ ) crystal field of  $\text{PaCl}_6^{2-}$  splits the 6d configuration into two levels, a  $t_{2g}$  lower state (triply degenerate) and an  $e_g$  upper state (doubly degenerate). When the 6d spin-orbit interaction is included, the  $t_{2g}$  level splits into a  $\Gamma_{8g}$  (a degenerate quartet with the inclusion of spin) state and a higher-lying  $\Gamma_{7g}$  (Kramers doublet) state. The higher-lying  $e_g$  level also transforms as a  $\Gamma_{8g}$  quartet when the spin-orbit coupling is considered (Fig. 1).

The EPR data can be fit with a spin-Hamiltonian of the form:

$$\mathcal{H} = g \beta \vec{H} \cdot \vec{S} + A \vec{I} \cdot \vec{S}. \quad (2)$$

For the case of  ${}^{231}\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ ,  $I$  (the nuclear spin) is equal to  $3/2$ , and both  $g$  and  $A$  are isotropic because the ground state is a  $\Gamma_7$  doublet ( $O_h$  symmetry). The values of  $\zeta$ ,  $B_0^4$ ,  $B_0^6$  and  $g$ , as obtained by Axe, et al. are given in Table 1 [5].

Additional near infra-red data have been reported for the pure hexahalocompounds at 85°K and room temperature [9,10]. These data were analyzed with the above model. The parameters and measured

values for two of the measured compounds,  $(\text{Et}_4\text{N})_2\text{PaCl}_6$  and  $(\text{Et}_4\text{N})_2\text{PaF}_6$ , are also shown in Table 1.

$\text{Pa}^{4+}$  diluted in single crystals of  $\text{ThBr}_4$  and  $\text{ThCl}_4$  has been thoroughly studied by near-infra-red emission and absorption spectroscopy and by EPR [11]. In addition, strong visible fluorescence in these crystals was observed and assigned to transitions from the  $6d^1$  configuration to the  $5f$  levels [12]. The  $5f \rightarrow 6d$  absorption spectra of  $\text{Pa}^{4+}/\text{ThBr}_4$  and of  $\text{Pa}^{4+}$  in solutions of the hexachloro- and hexabromo-salts also have been measured and analyzed [13].

Recently, visible fluorescence has been reported for the system,  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  at 4.2K when excited with the 488 nm line of an argon ion laser [14]. This fluorescence arises from the lowest state in the  $6d^1$  configuration ( $6d\Gamma_{8g}$ , see Fig. 1) to all five crystal field levels of the  $5f^1$  configuration. The fluorescence shows highly structured sidebands with the most prominent feature arising from vibronic progressions of the  $310\text{ cm}^{-1}$  totally symmetric stretching mode ( $\nu_1$ ) of the  $\text{PaCl}_6^{2-}$  complex. Most of the other vibronic peaks can be assigned to even parity vibrations of the  $\text{PaCl}_6^{2-}$  complex or the host lattice.

A study of the high-resolution absorption spectrum of  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  has appeared [15]. Extensive vibrational structure was observed in the first  $6d$  band ( $6d\Gamma_{8g}$ ) and this structure has been compared with that found in the emission spectra. The emission spectra probe the details of the potential surface for the  $5f^1$  configuration of the  $\text{PaCl}_6^{2-}$  complex, while the absorption spectrum probes the potential surface of the  $6d^1$  configuration. The major differences between the

absorption and the emission spectra were the absence of features due to  $e_g$  and  $t_{2g}$  normal modes in the absorption spectrum, and a very dramatic broadening of the higher energy vibronic features in the higher harmonics of the  $\nu_1$  vibration as shown in Fig. 2.

From the absorption spectrum of  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ , assignments have been made for the three 6d energy levels expected for a  $6d^1$  electron in an  $O_h$  crystalline field. These levels are shown in Fig. 1 and tabulated in Table 1. The analyses of the energy levels of both the 6d and 5f configurations of  $\text{Pa}^{4+}$  in  $\text{ThBr}_4$  and in  $\text{Cs}_2\text{ZrCl}_6$  allow the change in the relative shifts of the centers of gravity of these two configurations to be compared with the free ion. This comparison is shown in Fig. 3, which also includes data for  $\text{Ce}^{3+}$  free ion ( $4f^1, 5d^1$ ) [16] and for  $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$  [17,18]. Note these shifts in the relative energy difference between the d and the f configurations are approximately  $17,400 \text{ cm}^{-1}$  to  $22,000 \text{ cm}^{-1}$  for  $\text{Pa}^{4+}$  in the halide hosts, while it is approximately  $14,400 \text{ cm}^{-1}$  for  $\text{Ce}^{3+}$  in  $\text{Cs}_2\text{NaYCl}_6$ . Thus, extrapolating to the  $\text{Th}^{3+}$  free ion where the 6d configuration is only approximately  $10,000 \text{ cm}^{-1}$  above the 5f configuration in the free ion, the 6d configuration could plausibly be the ground configuration in  $\text{Th}^{3+}$  compounds.

From the data given in Table 1, the parameters of the Hamiltonian, Eq. 1, are overdetermined. The best fit parameters for  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  are shown in Table 1. The crystal field parameters agree fairly well with those obtained from the analysis of the extensive experimental studies of  $\text{U}^{4+}/\text{Cs}_2\text{ZrCl}_6$  ( $5f^2$  configuration) [6]. Nevertheless, the simple crystal

field model is not adequate for the  $5f^1$  system. For the analyses of the  $U^{4+}/Cs_2ZrCl_6$  and  $U^{4+}/Cs_2ZrBr_6$  systems ( $5f^2$ , in which the Slater parameters and the Trees parameter are included) Flint and Tanner report a root-mean-square (rms) deviation of  $\sim 150\text{ cm}^{-1}$  and greater for a large number of assigned levels [6]. Further calculations on the same energy levels sets using the parametric Hamiltonian as in the  $UBD_4/HfBD_4$  study [19] did not significantly improve the fits [20]. These results are in contrast to analyses of other tetravalent transprotactinium ion systems where the rms deviations are less than  $100\text{ cm}^{-1}$  [21,22,23]. For the trivalent actinide ions in  $LaCl_3$ , the rms deviations are on the order of  $18\text{-}22\text{ cm}^{-1}$  for most of the series [24]. However for  $U^{3+}/LaCl_3$  the rms deviation was  $29\text{ cm}^{-1}$  and Carnall has noted that the  $U^{3+}$  free ion parameters do not fit with the systematics of the rest of the series.

In general parametric fits for the tetravalent transuranium ions have an rms deviation greater than  $35\text{ cm}^{-1}$ . The major difference between the trivalent and tetravalent ions in crystals or compounds is that the crystal field interaction is much larger for the latter series, especially in the host crystal,  $Cs_2ZrCl_6$ . There are a number of possibilities for the sources of these analysis problems at the beginning of both the trivalent and tetravalent actinide ion series. First of all, the  $5f$  orbitals are most extended at the beginning of series which results in greater  $5f$ -ligand interaction. Secondly, the  $5f^{n-1}6d^1$  excited configuration is at its lowest relative energy in this region. Thus the parametric theory used to fit  $5f^n$  optical spectra may be lacking

parameters which can take into account important interactions which occur at the beginning of the actinide series and the effects of a strong crystal field interaction.

### Th<sup>3+</sup> Magnetism and Spectroscopy

Although the energies of the low-lying configurations of the Th<sup>3+</sup> free ion have been measured, almost nothing is known about the electronic structure of Th<sup>3+</sup> in compounds. The one structurally characterized Th<sup>3+</sup> compound, Cp<sub>3</sub>Th has been shown to have a 6d<sup>1</sup> ground state from EPR measurements as a function of temperature. The spectra are shown in Fig. 4. Recently Lukens and Andersen [25] have measured the EPR spectrum of Cp<sub>3</sub>Zr where Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> (a 4d<sup>1</sup> complex which is also assumed to have approximately D<sub>3h</sub> symmetry) and its spin-Hamiltonian parameters are consistent with those of Cp<sub>3</sub>Th when the much smaller spin-orbit coupling is considered. By contrast, the EPR spectrum of Cp<sub>3</sub>Ce (a 4f<sup>1</sup> complex with approximate D<sub>3h</sub> symmetry) gives quite different values for the spin-Hamiltonian parameters and no room temperature spectrum is observed [26]. If D<sub>3h</sub> symmetry about the Th<sup>3+</sup> ion in Cp<sub>3</sub>Th is assumed, the 6d orbitals will split into an orbital singlet A' and two orbital doublets, E' and E". The A' orbital (or 6d<sub>z<sup>2</sup></sub>) is lowest in energy because it most successfully avoids the electron density of the Cp rings. This assignment is the only consistent one with the observed EPR spectrum [3].

The complex Cp<sub>3</sub>Th (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) has also been reported previously. Kanellakopulos and coworkers reported a purple compound with a room temperature magnetic moment of 0.331 μ<sub>B</sub> (μ<sub>B</sub>

= Bohr magneton) and Marks and coworkers reported a green compound with  $\mu_{\text{eff}} = 0.403 \mu_{\text{B}}$  [27,28]. Photolysis of solutions of  $\text{Cp}_3\text{ThR}$ ,  $(\text{MeCp})_3\text{R}$ , and  $(\text{C}_9\text{H}_7)_3\text{ThR}$  ( $\text{MeCp} = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ,  $\text{C}_9\text{H}_7 = \eta^5\text{-C}_5\text{H}_3\text{C}_4\text{H}_4$ ) liberated gaseous alkanes and alkenes and the solutions became strongly colored [28]. Pulse radiolysis experiments on the compound  $\eta^5(\text{C}_5\text{Me}_5)_2\text{ThCl}_2$  also produced a transient spectrum attributed to the species  $(\eta^5\text{-C}_5\text{Me})_2\text{ThCl}_2^-$  followed by a more stable species assigned to  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ThCl}$ . The latter species had an optical spectrum similar to the one obtained by the photolysis of a  $(\text{MeCp})_3\text{Th}$  alkyl attributed to  $(\eta^5\text{-C}_5\text{H}_4\text{Me})_3\text{Th}$  [29]. The room temperature optical spectrum of  $\text{Cp}_3^*\text{Th}$  is shown in Fig. 5. Three very strong bands are observed in the 15000-20000  $\text{cm}^{-1}$  region along with a fourth peak at  $\sim 27000 \text{ cm}^{-1}$  that overlaps a very broad absorption edge. Assuming  $D_{3h}$  symmetry, four allowed electric dipole transitions are expected from the ground  $6d A_1'$  state to the 5f levels. It is expected the total span of the 5f configuration in  $\text{Th}^{3+}$  would be less than 6000  $\text{cm}^{-1}$  (for  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  it is  $\sim 8000 \text{ cm}^{-1}$  with a larger spin-orbit coupling constant). Thus it is likely the fourth allowed  $6d \rightarrow 5f$  transition is masked by the three observed bands. The band at 27000  $\text{cm}^{-1}$  is tentatively assigned as  $6d \rightarrow 7s$  or  $7p$  [27].

Bursten and coworkers have carried out quasi-relativistic X- $\alpha$  SW calculations on the molecules  $\text{Cp}_3\text{M}$  ( $\text{M} = \text{Th}, \text{Pa}, \text{U}, \text{Np}, \text{and Pu}$ ) [30]. Their results agree with the assigned  $6d^1$  ground state for  $\text{Cp}_3^*\text{Th}$  (assuming  $\text{Cp}_3\text{Th}$  is similar to  $\text{Cp}_3^*\text{Th}$ ). Interestingly, Bursten, et al. point out the  $6d_{z^2}$  orbital will be destabilized by the addition of a Lewis

base to a  $\text{Cp}_3\text{Th}$  molecule and predict for a hypothetical (to date)  $\text{Cp}_3\text{Th}\cdot\text{L}$  molecule ( $\text{C}_{3v}$  symmetry about the  $\text{Th}^{3+}$  ion) a  $5f^1$  ground state. They also predict the hypothetical  $\text{Cp}_3\text{Pa}$  molecule would have a  $5f^16d^1$  ground state. Their calculations give approximately equal energies for the  $5f^3$  and  $5f^26d^1$  configurations for the molecule  $\text{Cp}_3\text{U}$  although experimental magnetic and optical data clearly indicate the ground state is  $5f^3$  for  $\text{Cp}_3\text{U}$  with the start of the  $5f^26d^1$  configuration greater than  $20000\text{ cm}^{-1}$  [31].

Although no  $\text{Cp}_3\text{Th}\cdot\text{L}$  compounds (where L is a Lewis base) are known, the analogous  $\text{Cp}_3\text{Ce}$  and  $\text{Cp}_3\text{Ce}\cdot\text{CN}^t\text{Bu}$  compounds have been synthesized and crystallographically characterized [32]. The symmetry about the  $\text{Ce}^{3+}$  ion in each compound is approximately  $\text{D}_{3h}$  and  $\text{C}_{3v}$ , respectively. For  $\text{Ce}^{3+}$  compounds the ground state is unequivocally  $4f^1$  and the first 5d level can vary from  $\sim 20,000$  to  $40,000\text{ cm}^{-1}$  in energy depending on the ligands about the  $\text{Ce}^{3+}$  ion [33]. Measurements of the  $4f \rightarrow 5d$  transitions for the two  $\text{Ce}^{3+}$  compounds given above show a shift of about  $6000\text{ cm}^{-1}$  to higher energy for the first 5d level of  $\text{Cp}_3\text{Ce}\cdot\text{L}$  as compared to the base-free compound [26]. It is possible this effect might be considerably larger in the analogous Th complex.

EPR experiments have been performed on the photolysis product of  $(\text{C}_9\text{H}_7)_3\text{ThCH}_3$ . If the photolysis product (which is highly colored) is  $(\text{C}_9\text{H}_7)_3\text{Th}$  and has the same structure as  $(\text{C}_9\text{H}_7)_3\text{U}$ , then this compound would have the pentahapto indenyl rings surrounding the  $\text{Th}^{3+}$  ion in a trigonal manner [34]. Thus the electronic structure should

be similar to that of  $\text{Cp}_3\text{Th}$ . A room temperature EPR signal was observed upon photolysis with a  $g$  value of 1.953. Measuring the frozen solution at 80K gave an axial spectrum consistent with a  $6d^1$  configuration. Although the signal was weak due to the limited solubility of the  $(\text{C}_9\text{H}_7)_3\text{ThCH}_3$  and the low quantum yield of the photolysis step, this experiment does confirm the assignment of the  $6d^1$  configuration in these types of molecules [26].

### Conclusion

At the beginning of both the actinide and lanthanide series, the  $5f(4f)$  and  $6d(5d)$  configurations are rather close in energy. Optical and EPR studies have been utilized to explore the relative energies of these two configurations. Does the unusual bonding of the early actinide ions arise from the extended nature of the  $5f$  orbitals at the beginning of the series? Or does it arise from the relatively close proximity of the  $6d$  configuration? Theoretical calculations on organometallic molecules do indicate the  $6d$  orbitals play a dominant role [35]. More extensive studies on  $\text{Th}^{3+}$  and  $\text{Pa}^{4+}$  compounds may help in answering the above questions.

### Acknowledgement.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.



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Energy Levels	Pa <sup>4+</sup> /Cs <sub>2</sub> ZrCl <sub>6</sub> [4,5]		(Et <sub>4</sub> N) <sub>2</sub> PaCl <sub>6</sub> [9]		(Et <sub>4</sub> N) <sub>2</sub> PaF <sub>6</sub> [10]		Pa <sup>4+</sup> /Cs <sub>2</sub> ZrCl <sub>6</sub> [15,16]	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
6d $\Gamma_{8'g}$ (cm <sup>-1</sup> )							40000	40000
6d $\Gamma_{7g}$ (cm <sup>-1</sup> )							23000	23000
6d $\Gamma_{8g}$ (cm <sup>-1</sup> )							19954	19954
5f $\Gamma_{6u}$ (cm <sup>-1</sup> )	8000	8121	8011	8029	11446	11537	8173	8215
5f $\Gamma_{8u}$ (cm <sup>-1</sup> )	7085	6954	7022	6988	9708	9586	7272	7210
5f $\Gamma_{7u}$ (cm <sup>-1</sup> )	5215	5215	5330	5347	5698	5717	5330	5413
5f $\Gamma_{8u}$ (cm <sup>-1</sup> )		1912		1867		3708	2108	2133
5f $\Gamma_{7u}$ (cm <sup>-1</sup> )	0	0	0	0	0	0	0	0
g values								
$g_{\Gamma_{7u}}$	11.1411	-1.141		-1.115		-0.705	11.1411	-0.979
Parameters								
B <sub>0</sub> <sup>4</sup> (5f)(cm <sup>-1</sup> )		7104		6665		14740		7244
B <sub>0</sub> <sup>6</sup> (5f)(cm <sup>-1</sup> )		6708		394		1423		66.1
$\zeta_{5f}$ (cm <sup>-1</sup> )		1490		1523		1508		1511.2
B <sub>0</sub> <sup>4</sup> (6d)(cm <sup>-1</sup> )								39050
$\zeta_{6d}$ (cm <sup>-1</sup> )								1856.5
E <sub>Ave</sub> (6d)(cm <sup>-1</sup> )								28582

Table 1. Spectroscopic data and fits for various Pa<sup>4+</sup> octahedral systems.

## Figure Captions

- Figure 1. Schematic energy level diagram of  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ .
- Figure 2. An absorption ( $5f \rightarrow 6d$ ) and an emission ( $6d \rightarrow 5f$ ) band of  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ . The continuous vertical lines at the bottom represent the 0-0 line and the  $a_{1g}$  progression of the  $\text{PaCl}_6^{2-}$  complex. The long dashed lines and the short dashed lines show the features assigned to the  $t_{2g}$  and  $e_g$  vibrations, respectively. The data are plotted relative to the 0-0 line.
- Figure 3. Energy level diagrams for the  $\text{Pa}^{4+}$  free ion, some Pa compounds, the  $\text{Ce}^{3+}$  free ion, and  $\text{Cs}_2\text{NaCeCl}_6$ . The arrows represent the energy differences between the centers of gravity of the f and d configurations.
- Figure 4. EPR spectra of  $\text{Cp}_3\text{Th}$  in methylcyclohexane (freezing point 147K) as a function of temperature. All data were obtained at 9.255 GHz.
- Figure 5. Room temperature absorption spectrum of  $\text{Cp}_3\text{Th}$  in methylcyclohexane (concentration =  $7.8 \times 10^{-4}\text{M}$ , pathlength 1 cm).

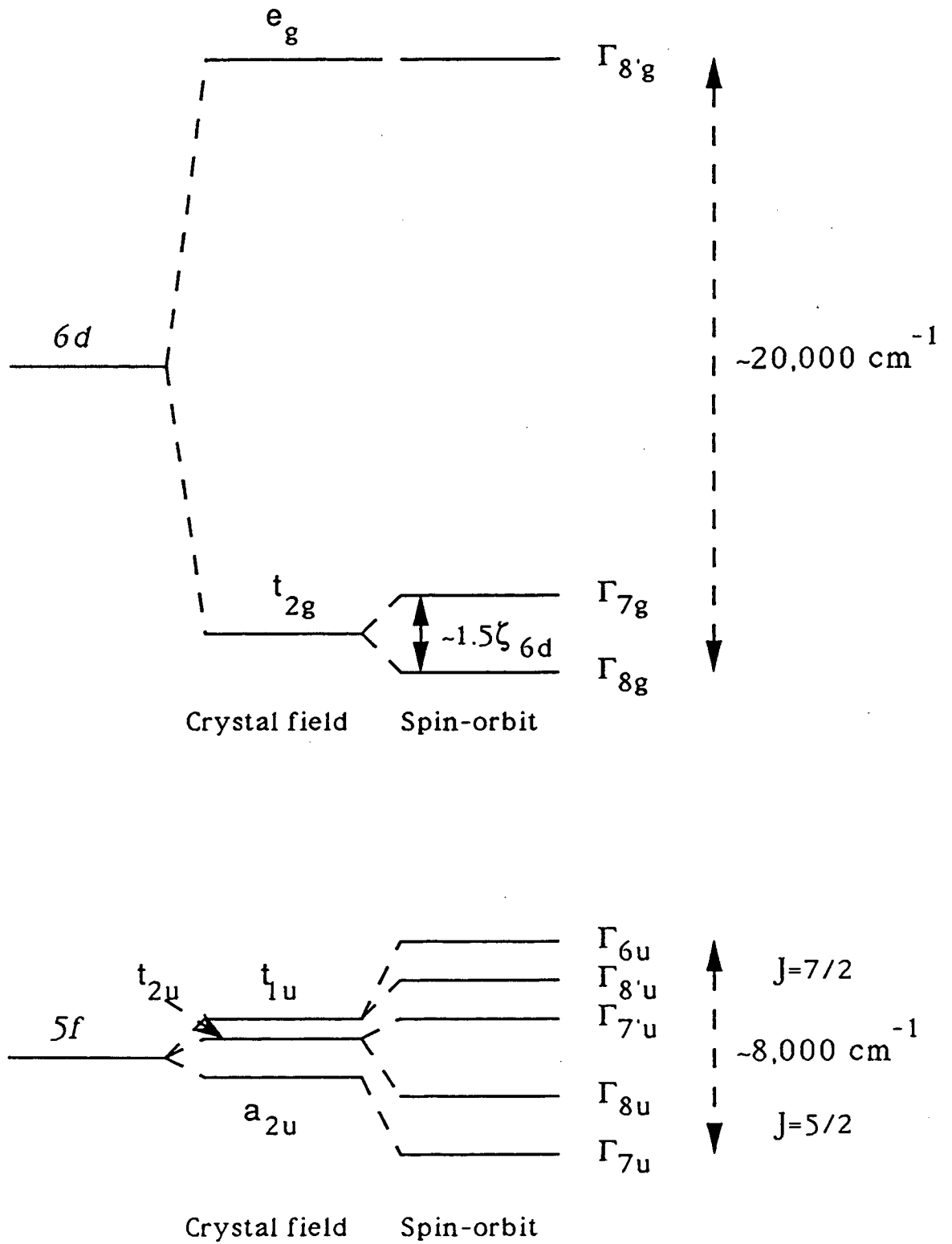


Figure 1

## Relative Emission

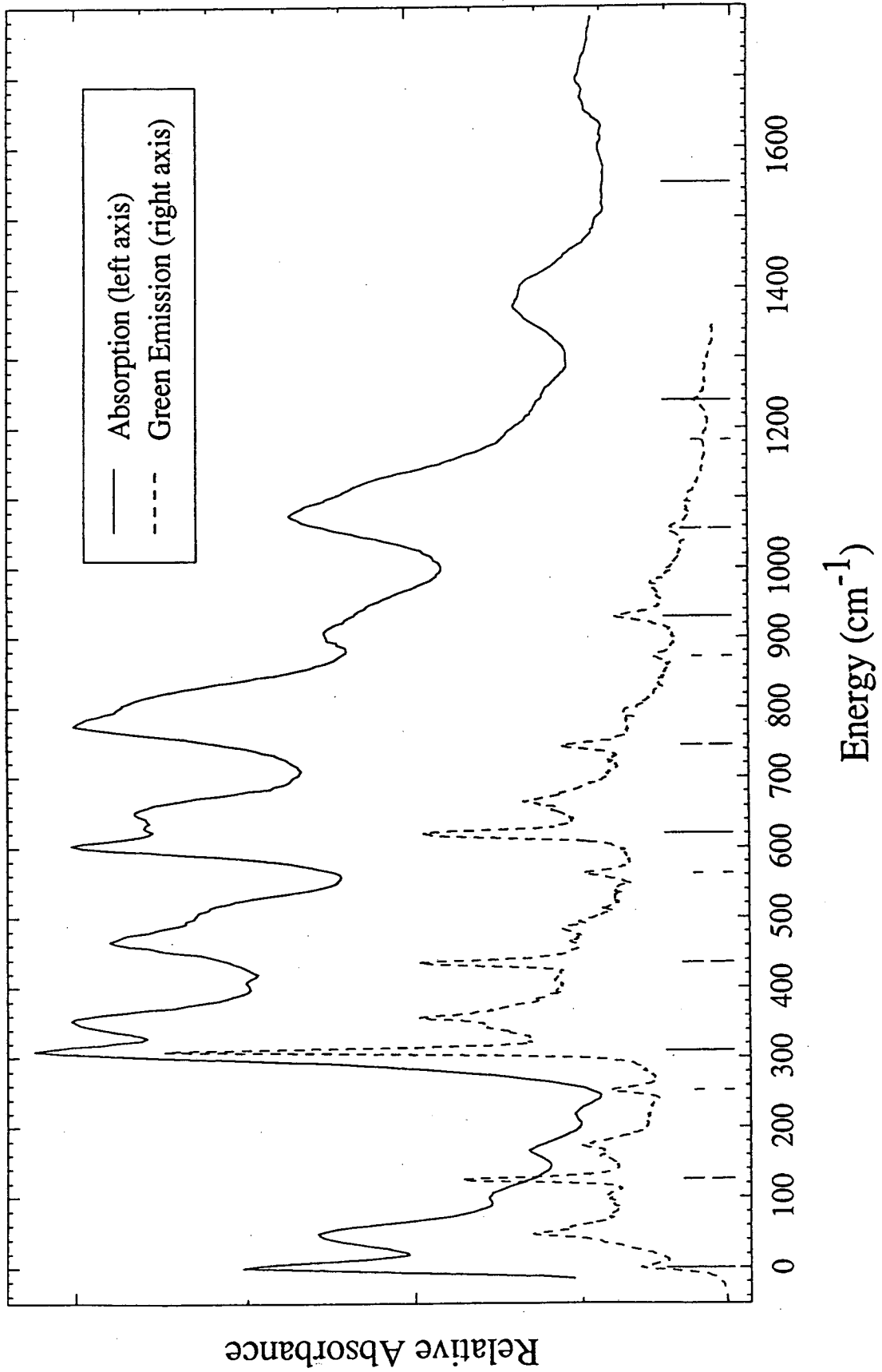


Figure 2

# Pa<sup>4+</sup> and Ce<sup>3+</sup> Energy Levels

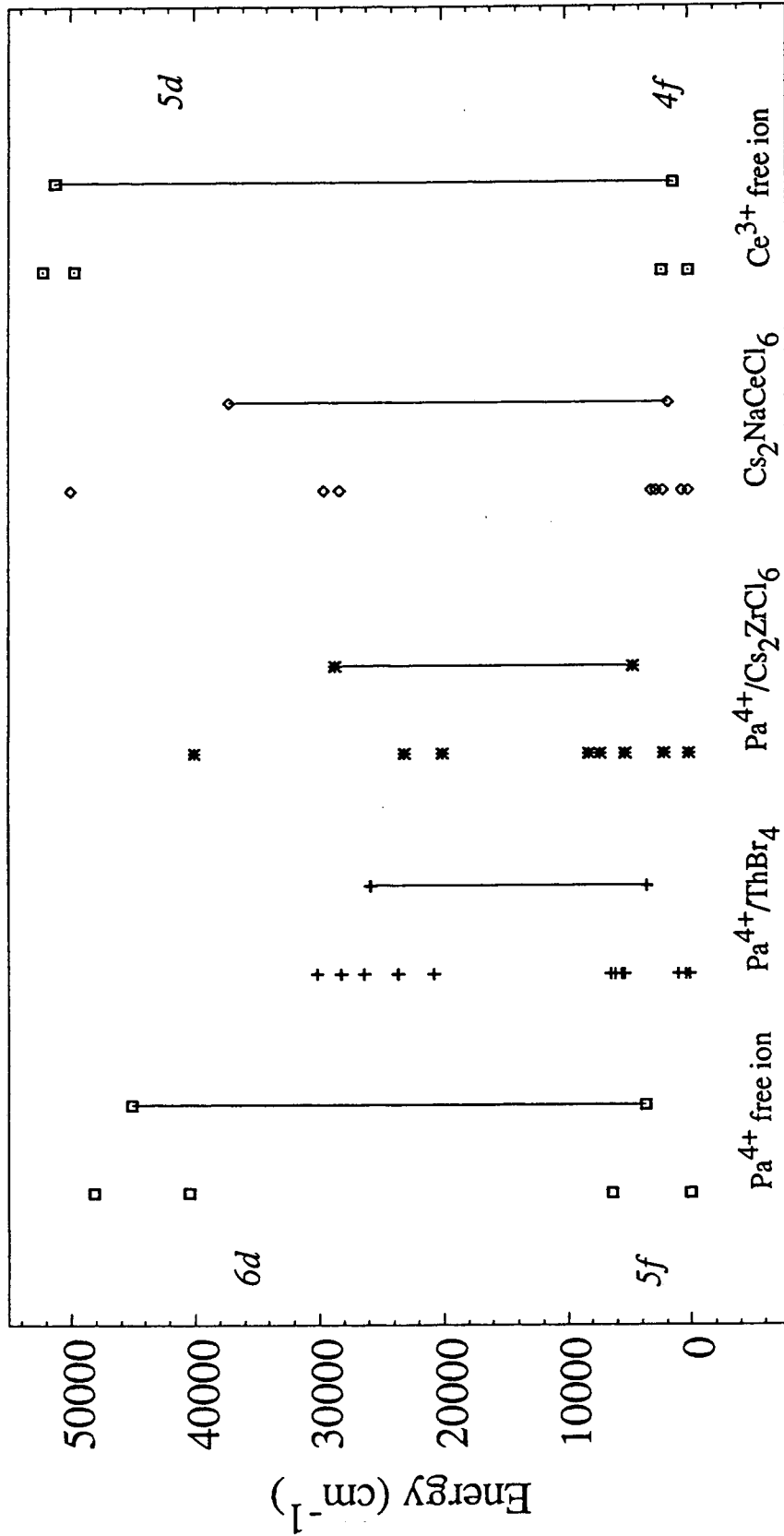


Figure 3



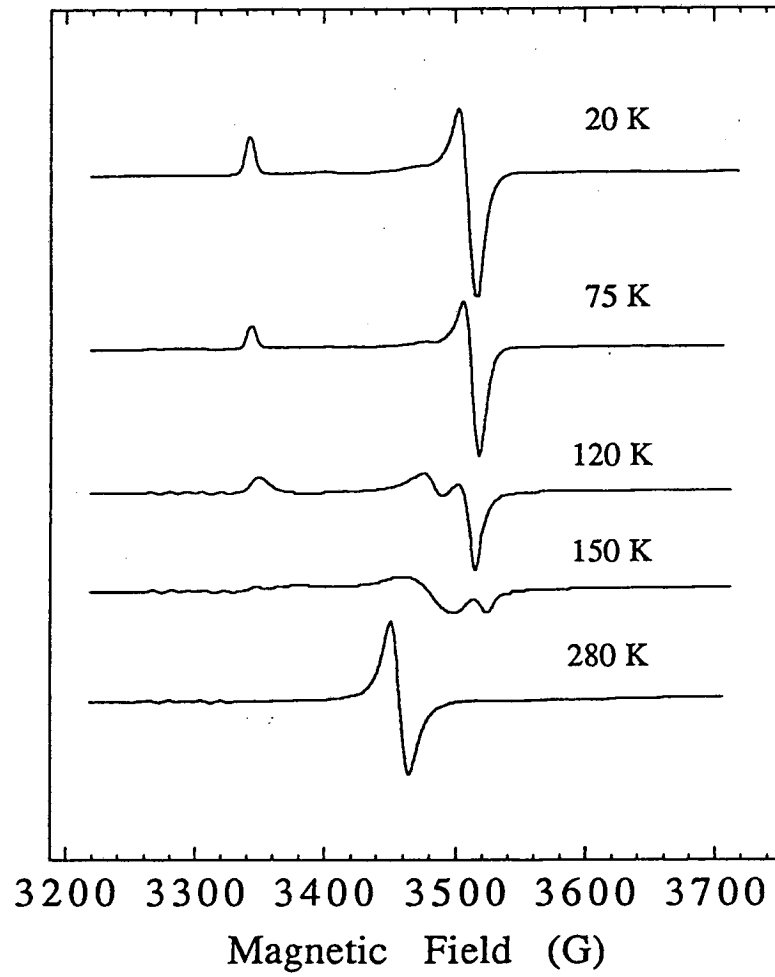


Figure 4

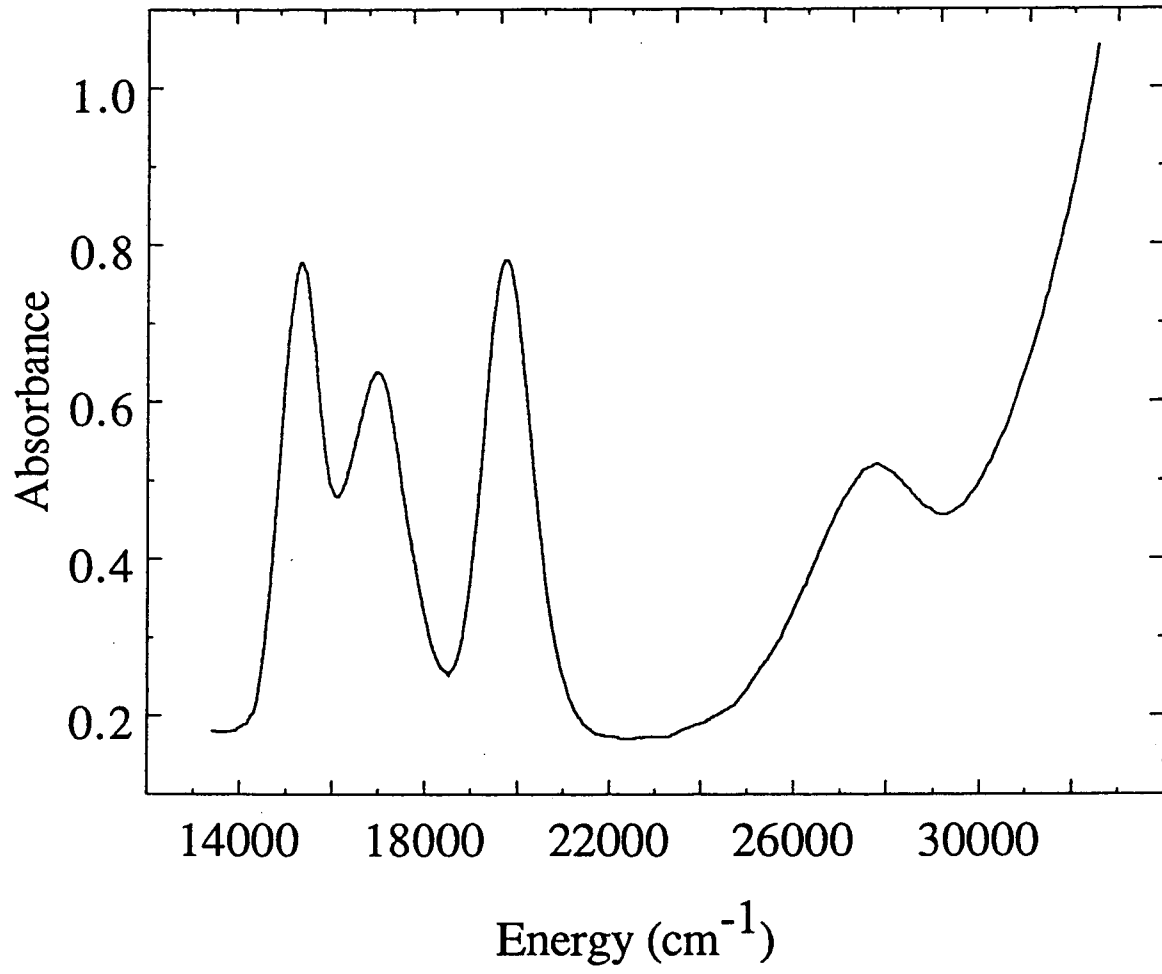


Figure 5

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