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Optical and Magnetic Properties of Tetravalent
Actinide Ions and Compounds

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Summary

A survey will be given of the optical and magnetic data available for tetravalent actinide ions in a variety of single crystals and as pure compounds. Where possible, conclusions will be drawn from the values of the "free ion" parameters in crystals when compared with the values for the free ions in the gaseous phase. Problems with the theoretical model will be discussed.

1. Introduction

Optical spectra of the $4f^n$ and $5f^n$ ions (where n is equal to the number of equivalent electrons) are characterized by relatively sharp lines due to transitions between energy levels within the f^n configuration. The f^n electrons are inner shell electrons which are shielded from their surroundings by outer shell electrons ($5s^2 5p^6$ for the $4f^n$ ions, $6s^2 6p^6$ for the $5f^n$ ions). Thus, even in compounds, the f^n shell retains atomic-like properties. The comparison of the spectra of the free ion with that of the ion in the solid state provides information about the effects of its surroundings on the f^n ion [1-3].

For free ions, a perturbation treatment of the central field Hamiltonian has been widely used to calculate energy levels. This

approach entails treating the angular parts of the Hamiltonian exactly and the radial parts as parameters. The energy levels within an f^n configuration for an f^n ion in a crystal field may be written in terms of the atomic free ion (H_{FI}) and the crystal field Hamiltonians as follows:

$$H = H_{FI} + H_{CF}$$

where

$$H_{FI} = \sum_{k=0,2,4,6} f_k F^k(nf,nf) + \zeta_f a_{so} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{k=2,3,4,6,7,8} t_k T^k + \sum_{k=0,2,4} m_k M^k + \sum_{k=2,4,6} p_k P^k.$$

The $F^k(nf,nf)$'s and ζ_f represent, respectively, the radial parts of the electrostatic and spin-orbit interactions between f electrons, while f_k and a_{so} are the angular parts of the interactions, α , β , and γ are the parameters associated with the two-body effective operators of configuration interaction. For f^n configurations with $n = 3$ or greater, the T^k 's represent three-body electrostatic configuration interaction parameters. The M^k parameters represent the spin-spin and spin-other-

orbit interactions while the P^k parameters arise from electrostatic-spin-orbit interactions with higher configurations. States of the free ion are classified by the quantum numbers $\alpha'SLJ$ where $\vec{S} = \vec{s}_1$, $\vec{L} = \vec{l}_1$, $\vec{J} = \vec{L} + \vec{S}$, and α' represents additional quantum numbers. When the f^n ion is placed in a crystal the spherical symmetry of the free ion is lifted. This results in a splitting of the $2J+1$ levels for each free ion J level. The degeneracies of the $2J+1$ levels depend on the symmetry of the crystal field and whether there are an even or odd number of electrons. The crystal field Hamiltonian is written as

$$H_{CF} = \sum_i B_q^k (C_q^k)_i, \quad [C_q^k = (\frac{4\pi}{2k+1})^{1/2} Y_q^k]$$

where the B_q^k are empirical parameters which include the radial parts and the C_q^k are spherical tensors whose matrix elements can be evaluated and are related to the spherical harmonics.

The approach used in the analysis of f^n ions is to obtain the optical spectra, Zeeman splittings, and magnetic susceptibility data, and then adjust the parameters of the above Hamiltonian to obtain the best agreement between the experimental data and the calculated quantities (energy levels, g values, etc.) [1-3].

What kinds of results can one expect? For trivalent lanthanide ions in LaCl_3 one obtains rms deviations between calculated and

experimental energy levels of the order of $5\text{--}10\text{ cm}^{-1}$. For example in the analysis of Ho^{3+} in LaCl_3 , 128 levels were fit to an rms deviation of 5.2 cm^{-1} using a 20 parameter fit [4]. For the trivalent actinide ions in LaCl_3 deviations of approximately 20 cm^{-1} are found [5].

Very few data have been available for tetravalent actinide ions until recently. The fits that have been reported for these ions are significantly poorer (greater rms deviations) than for the trivalent ions. In this paper data for the tetravalent actinide ions will be reviewed. Compounds of Pa^{4+} ($5f^1$) are not included.

2. U^{4+} Ions

Spectroscopic studies on U^{4+} diluted in single crystals and in pure compounds have been reported for the past 30 years [6]. However the analyses of the earlier data have been unsatisfactory due to the poor agreement between the experimental and calculated levels. Recently, the complete optical spectrum of the U^{4+} free ion has been reported and analyzed [7]. The free ion parameters are given in Table 1. In addition, fluorescence transitions have been observed in some U^{4+} compounds [8,9]. The free ion analysis provided reasonable starting parameters for the reanalysis of some of the earlier data while the fluorescence data provided more level information. Thus there has been a number of recent papers reporting new data on old and new U^{4+} systems plus some reanalyses of earlier data.

2.1. U^{4+} in D_{2d} and D_2 Symmetry

Spectra of $U^{4+}/ThBr_4$ were first reported in 1977 along with a preliminary analysis of the energy levels in a D_{2d} site symmetry [10]. However it was noted in this paper that there were too many levels observed that could be assigned to zero-phonon electronic transitions of a $5f^2$ system. Subsequently it was determined that the host lattice undergoes a phase transition at $T_c = 95K$ to an incommensurate phase. Below T_c there is a continuous distribution of sites which vary from D_{2d} symmetry to a limiting D_2 symmetry. In a later paper, the sharp features of the optical spectrum were assigned to either a D_{2d} symmetry site or to the limiting D_2 site [8].

Based on the above assignments, a parametric analysis was performed, and it was found that for the D_{2d} site, 26 levels were assigned and fitted with an rms deviation $\sigma = 36 \text{ cm}^{-1}$. For the D_2 site, 38 levels were assigned with a $\sigma = 38 \text{ cm}^{-1}$. The parameters of the Hamiltonian are listed in Table 2. For $U^{4+}/ThBr_4$ the crystal field model provided a reasonable interpretation of the energy levels although the results were poorer than found for trivalent actinides and much poorer than found for the trivalent lanthanides [11].

U^{4+} exists in a similar environment (dodecahedral) to that of $ThBr_4$ in a number of crystals and in these systems the experimental optical

spectra is similar. Analyses or reanalyses of the optical spectra of U^{4+} in β $ThCl_4$, UCl_4 , $ZrSiO_4$, and $ThSiO_4$ have recently been published. The parameters of the Hamiltonian for these systems are listed in Tables 2 and 3. Note, however, that σ for these systems vary from 46 to greater than 100 cm^{-1} [12-14].

For U^{4+} in $ThBr_4$ it was determined by the optical selection rules that the ground state had to be of Γ_4 symmetry. The first excited state is of Γ_5 symmetry. The same energy level ordering has been found in UCl_4 . The Γ_4 state is nonmagnetic (to first order) while the Γ_5 state is paramagnetic. The temperature dependence of the magnetic susceptibility is very sensitive to the Γ_4 - Γ_5 energy difference. Recent inelastic neutron scattering experiments on UCl_4 have assigned the first Γ_5 level at 92 cm^{-1} and another Γ_5 level at 1125 cm^{-1} [15]. Single crystal magnetic susceptibility experiments were previously interpreted on the basis of the first Γ_5 level being at an energy of 110 cm^{-1} [16]. The introduction of an orbital reduction factor k reconciles these discrepancies.

The orbital reduction factor is defined by the following equation

$$g = 2\langle\psi|k\vec{L} + g_s\vec{S}|\psi\rangle$$

where $\vec{L} + g_s\vec{S}$ is the Zeeman operator ($g_s = 2.0023$) and k is a factor which takes into account the reduction of orbital angular momentum caused by covalent bonding. In d transition metals values of k are

found between .5 and .8 [17]. The effect of introducing k in calculating the magnetic susceptibility of UCl_4 is to lower the energy of the first Γ_5 level. Thus by using $E_{\Gamma_5} = 92 \text{ cm}^{-1}$ we evaluate the orbital reduction constant as $k = .95$. The experimental and calculated data are shown in Figure 1.

2.2. U^{4+} in T_d Symmetry

Following the successful analysis of the spectra for $U^{4+}/ThBr_4$ the high resolution optical data of Bernstein and Keiderling on $U(BD_4)_4/Hf(BD_4)_4$ were reexamined [18,19]. In this complex, the U^{4+} ion is at a site of T_d symmetry. Because of the lack of inversion symmetry, zero-phonon forced electric dipole transitions are expected to be quite intense. In addition, magnetic measurements on the monomeric molecular compound, $U(BH_3CH_3)_4$ were analyzed on the basis of the wavefunctions obtained from the optical analysis. Rajnak et al. [19] were able to assign 19 zero-phonon electronic origins with σ of 71 cm^{-1} or, given one alternative assignment, a σ of 53 cm^{-1} . The parameters of the best fit of the optical data are given in Table 1.

Rajnak et al. also fit the magnetic susceptibility data of $U(BH_3CH_3)_4$ in the temperature range 1.8-330K. They found the calculated susceptibility was strongly dependent on the energy of the magnetic T_1 state above the nonmagnetic (to first order) ground E state. With an

E-T₁ splitting of 215 cm⁻¹ and the orbital reduction factor $k = 0.85$, good agreement was found between the calculated and experimental values.

2.3. UX₆²⁻ Spectra (X = Br, Cl)

One of the most thoroughly studied tetravalent U systems is that of UX₆²⁻ (X = Cl, Br) in which the U⁴⁺ ion is octahedrally coordinated to six halide ions (or nearly so, as some crystals have slight distortions from O_h symmetry). Satten and his coworkers have reported and analyzed high resolution absorption spectra in numerous papers for almost 30 years [6]. Recently, Flint and Tanner have reexamined some of these systems and have reported laser-induced fluorescence measurements which complement the earlier absorption measurements [9,20,21].

In the optical spectra of these complexes, the intense spectra are due to vibronic transitions, that is a transition from the ground electronic and vibrational state to an excited electronic state plus a higher vibrational state. The reason for the absence of zero-phonon electronic transitions is because the uranium ion is at a site of inversion symmetry and electric dipole transitions are formally forbidden. Zero-phonon magnetic dipole transitions are allowed but are weak.

Despite the extensive studies on these systems, the parametric analysis described previously results in rms deviations of greater than 100 cm⁻¹. Table 1 lists the parameters of a representative analysis published by Satten, et al. [7]

2.4. Organometallic compounds of U^{4+}

Cp_3UCl ($Cp = C_5H_5$) was the first organoactinide compound synthesized by Reynolds and Wilkinson in 1956 [22]. In this paper a molecular orbital description by W. Moffitt was given for the cation Cp_3U^+ of D_{3h} symmetry which suggested that adducts of the type Cp_3UX or $[Cp_3UX_2]^q$ could easily be formed. Subsequently a number of such complexes have been reported [23,24].

Amberger and his coworkers have measured the optical spectra of the pseudo-tetrahedral compounds Cp_3UX where $X = Cp, BH_4$ and Cl and have attempted to analyze such data on the basis of an effective crystal field with T_d symmetry [25,26]. This work has been hampered by the lack of suitable single crystals with which to obtain polarized spectra.

Recently, absorption and magnetic circular dichroism (MCD) measurements of the pseudo-trigonal bipyramidal complexes of the type $[Cp_3UX_2]^-$ [$X = NCS, NCBH_3$] [27] have been reported. Here the effective crystal field is assumed to be of D_{3h} symmetry, and MCD measurements allow the assignments of some levels. Based on these assignments a preliminary analysis has been made. The fit is rather poor, $\sigma \sim 300$ cm^{-1} , but this appears to be primarily due to the free ion parameters being ill-defined. The crystal field parameters do not appear to be very sensitive to the values of the free ion parameters. Representative parameters for the analyses of $Cp_3U(NCS)_2^-$ and $Cp_3U(NCBH_3)_2^{-1}$ are listed

in Table 4. The magnetic susceptibility of $(C_4H_9)_4N[Cp_3U(NCBH_3)_2]$ was measured from 5-300K. With the wavefunctions obtained from the optical fit and assigning the first excited state at $\sim 600\text{ cm}^{-1}$ from a "hot" transition, good agreement was found between the calculated and experimental susceptibility values with an orbital reduction factor $k = 0.90$ [28].

3.0. Np⁴⁺ Ions

3.1. Np⁴⁺ in T_d Symmetry

Following the successful reanalysis of the $U(BD_4)_4/Hf(BD_4)_4$ optical spectrum, the $Np(BD_4)_4/Zr(BD_4)_4$ optical spectrum was analyzed. One of the criteria for the analysis was that the crystal field parameters of the Np^{4+} compound should be similar to those of the U^{4+} complex. Again a consistent set of vibrational energies was sought for each electronic origin assigned. Because of the lack of inversion symmetry it was expected that the zero-phonon electronic transitions would be most intense. However in the final assignment for this compound, for some transitions the strongest line in a group had to be assigned as a vibronic transition rather than as an origin. A total of 46 electronic levels were fit with $\sigma = 84\text{ cm}^{-1}$ [29]. The parameters are given in Table 5.

Magnetic susceptibility data on $\text{Np}(\text{BH}_3\text{CH}_3)_4$ and EPR data on both $\text{Np}(\text{BD}_4)_4$ and $\text{Np}(\text{BH}_3\text{CH}_3)_4$ could only be fit with the eigenvectors of the optical analysis with an orbital reduction factor $k = 0.885$ for $\text{Np}(\text{BD}_4)_4$ and $k = 0.862$ for $\text{Np}(\text{BH}_3\text{CH}_3)_4$.

3.2. Np^{4+} in Cubic Symmetry and Octahedral Symmetry (O_h)

The optical spectrum of Np^{4+} diluted in a single crystal of ThO_2 was first reported by Gruber and Menzel [30]. This spectrum has recently been reinvestigated by LaHalle and Krupa [31]. In this crystal, the Np^{4+} ion is at a site of inversion symmetry so that the spectrum is dominated by intense vibronic transitions as in the UCl_6^{2-} spectra discussed previously. Furthermore, a further complication in the analysis was the presence of Np^{3+} as an impurity. Nevertheless, LaHalle and Krupa have analyzed the spectrum, and have fit 15 levels with a σ equal to 74 cm^{-1} . The values of the parameters are given in Table 5.

Menzel and Gruber [32] have also reported the absorption spectrum of a single crystal of Cs_2NpCl_6 . They analyzed the data below 13000 cm^{-1} only in terms of a first order crystal field theory; that is each J is treated separately, and J mixing by the crystal field is neglected. Surprisingly they reported a number of zero-phonon electronic transitions were observed which they attributed to distortions from octahedral

symmetry which may have been caused by crystal defects or microscopic strains. This work is an interesting preliminary study.

3.3. Np^{4+} Compounds in D_{2d} Symmetry

Optical studies on Np^{4+} diluted in ThSiO_4 have recently been completed [31]. Polarized absorption spectra have been obtained and fluorescence experiments have permitted the identification of two of the excited levels of the ground $J = 9/2$ manifold. A total of 29 levels (plus the ground level) were utilized in fitting the Hamiltonian parameters of the $5f^3$ configuration in D_{2d} symmetry. The parameters are given in Table 5. The value of σ is equal to 47 cm^{-1} .

Our group has recently obtained and is analyzing the absorption spectra of $\text{Np}^{4+}/\text{ZrSiO}_4$ [33]. Two different crystals were measured with varying concentrations of tetravalent Np. Although the crystals appeared to be of good optical quality, the lines were very broad, $> 15 \text{ cm}^{-1}$ in half width. The broadness of the lines precluded observation of any Zeeman effect.

In D_{2d} symmetry for an f^3 ion, the Kramer's degenerate states are classified by the Γ_6 and Γ_7 representations. The selection rules are straightforward: $\Gamma_7 \leftrightarrow \Gamma_6$, π polarization; $\Gamma_6, \Gamma_7 \leftrightarrow \Gamma_6, \Gamma_7$, σ polarization. Based on a Γ_6 ground state, 37 absorption lines have been assigned. However in some cases the intensities of the absorption lines

with σ or π polarization were very weak, and for some transitions to excited Γ_7 levels for which strong π absorptions were observed, the lines disappeared completely under σ polarization. The results of a preliminary analysis for this system are listed in Table 5. For 37 levels, a σ of 75 cm^{-1} was obtained.

3.4. Np^{4+} in PbMoO_4 (S_4 Symmetry)

Sharma and Artman reported the absorption and fluorescence spectra of Np^{4+} in PbMoO_4 in 1969 [34]. The crystals were grown by the Czochralski method after the addition of sodium (in the form of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) along with NpO_2 powder to powdered PbMoO_4 . After growth, it appeared the Np^{4+} ions substituted for Pb^{2+} ions (S_4 symmetry site) in the lattice and charge neutrality was obtained by the creation of either oxygen or lead vacancies. The authors estimated their crystals contained 17 Np ions for every 10^6 Pb (or Mo) ions. In absorption the line widths varied from ~ 20 to 80 or 100 cm^{-1} and some lines that should have been present only in σ polarization also appeared in π polarization.

Sharma and Artman obtained data to 25000 cm^{-1} ; however they attempted to fit only their data below 12000 cm^{-1} to a first order crystal field model. They also estimated the effects of neglecting J mixing. Although the fitting results were not very satisfactory, this

work represents one of first Np^{4+} studies in an interesting crystal system.

4.0. Discussion

In d transition metal chemistry and spectroscopy, the Racah parameters B and C are usually used in place of the F^k 's to parameterize the electrostatic interaction. The F^k 's and B and C are linearly related. Crystal values of B are often compared to the free ion value via the ratio $\beta = B_{\text{crys.}}/B_{\text{FI}}$ where β is usually $0 < \beta \leq 1$ [35].

The amount to which β is less than 1 is usually taken as an indication of the degree of covalency. We have defined a similar quantity, $F_{\text{crys.}}^k/F_{\text{FI}}^k$ and also $\zeta_{\text{crys.}}/\zeta_{\text{FI}}$. The fourth order parameter F^4 , is much less reduced than the second order parameter on going from the free ion to the ion in a crystal, so the ratio F^4/F^2 is also a useful measure, especially for ions in which free ion data are not available. Data for the tetravalent actinide ions are listed in Table 6. We have used the parameter

$$N_V/\sqrt{4\pi} = \left[\sum_{k,q} \left(\frac{1}{2k+1} \right) (B_q^k)^2 \right]^{1/2}$$

of Auzel [36] as a measure of the relative crystal field strengths. Values of this quantity are also listed in Table 6.

From the values listed in Table 6 it appears $\text{U}(\text{BD}_4)_4$ is the most covalent compound. This molecule has the lowest value of $F_{\text{crys.}}^2/F_{\text{FI}}^2$ and

the largest value of $F_{\text{crys.}}^4 / F_{\text{crys.}}^2$. Comparable values are found for $\text{Np}(\text{BD}_4)_4$ although the Np compound appears less covalent than the uranium analog. This is supported by the orbital reduction factors where $\text{U}(\text{BH}_3\text{CH}_3)_4$ has a smaller value than $\text{Np}(\text{BH}_3\text{CH}_3)_4$. The values of the parameters for U^{4+} in D_{2d} symmetry are all comparable including (surprisingly) $\text{U}^{4+}/\text{ThSiO}_4$. The values for $\text{U}^{4+}/\text{ZrSiO}_4$ are questionable because of the rather large value of σ . It is interesting to note that the U^{4+} compounds which have the largest values for the crystal field strength also have the largest rms deviation σ . This correlation suggests the parametric model used to analyze the optical data might be inadequate under these conditions.

For the Np compounds, the situation is rather unsatisfactory. There does not seem to be much correlation between the U^{4+} and Np^{4+} values for the same host (except for the $\text{Np}(\text{BD}_4)_4$). Also there is no consistency among the various Np compounds. These facts suggest that the analyses must be treated with caution (i.e., see the discussion on $\text{Np}^{4+}/\text{ZrSiO}_4$) and that more systems should be investigated.

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Table 1. Parameter values for the U^{4+} free ion and in various high symmetry compounds. All parameters are in cm^{-1} .

	U^{4+} free ion ^a	$U(BD_4)_4/Hf(BD_4)_4$ ^b	UCl_6^{2-}	
		T_d	O_h	
F^2	51938(39)	41280(175)	41175 ^d	42266(760) ^e
F^4	42708(100)	40013(826)	40838	39604(3331)
F^6	27748(68)	22554(625)	28858	26360(2017)
ζ	1968(2)	1782(12)	1792	1760(28)
α	35.5(0.4)	38(2)		[31]
β	-664(25)	[-648]		[-644]
γ	744(26)	[1200]		[1200]
M^0	[0.99]	[0.99]		[0.99]
M^2	[0.55]	[0.55]		[0.55]
M^4	[0.38]	[0.38]		[0.38]
P^2	573(66)	[500]		[500]
P^4	524(144)	[500]		[500]
P^6	1173(321)	[500]		[500]
B_0^4		-2445(124) ^c	7656	7797(394)
B_0^6		-5371(81) ^c	1472	1344(230)

Table 1 continued.

	U^{4+} free ion ^a	$U(BD_4)_4/Hf(BD_4)_4$ ^b	UCl_6^{2-}
		T_d	O_h
No. of levels	13	19	23
σ	9.8	52	>150
			189

^aRef. 7. All parameters in square brackets held constant.

^bRef. 19.

^cFor T_d or O_h symmetry, $B_4^4 = (5/14)^{1/2} B_0^4$, $B_4^6 = -(7/2)^{1/2} B_0^6$.

^dFrom Ref. 6.

^eEnergy levels from Ref. 6. Parameters in square brackets held constant and are obtained from $U^{4+}/ThBr_4$ analysis.

Table 2. Parameter values for U^{4+} in various halide crystals. All parameters are in cm^{-1} .

	$U^{4+}/ThBr_4^a$		$U^{4+}/ThCl_4^b$	UCl_4^b
	D_{2d}	D_2	D_{2d}	D_{2d}
F^2	42253(127)	42264(84)	42752(162)	42561(236)
F^4	40458(489)	41159(407)	39925(502)	39440(634)
F^6	25881(383)	26018(237)	24519(479)	24174(609)
ζ	1783(7)	1774(5)	1808(8)	1805(8)
α	31(1)	[31]	30.4(2)	30.9(2)
β	-644(75)	[-644]	-492(84)	-576(168)
γ	[1200]	[1200]	[1200]	[1200]
B_0^2	-1096(80)	-1108(65)	-1054(117)	-903(151)
B_0^4	1316(146)	1358(137)	1146(200)	766(220)
B_4^4	-2230(85)	-2219(76)	-2767(147)	-3091(185)
B_0^6	-3170(379)	-3458(267)	-2135(404)	-1619(485)
B_4^6	686(246)	694(195)	312(227)	-308(280)
B_2^2		-78(30)		
B_2^4		318(122)		

Table 2 continued.

	$U^{4+}/ThBr_4^a$		$U^{4+}/ThCl_4^b$	UCl_4^b
	D_{2d}	D_2	D_{2d}	D_{2d}
B_2^6		136(101)		
B_6^6		123(125)		
No. of levels	26	38	25	26
σ	36	39	46	60

^aRef. 11.^bRef. 12.

Table 3. Parameter values for U^{4+} in silicate crystals. All parameters are in cm^{-1} .

	$U^{4+}/ThSiO_4^a$	$U^{4+}/ZrSiO_4^b$
	D_{2d}	D_{2d}
F^2	43110(245)	44258
F^4	40929(199)	40293
F^6	23834(639)	31287
ζ	1840(2)	1740
α	32.3(0.4)	23
β	-663(144)	
γ	[1200]	
B_0^2	-1003(127)	-2000
B_0^4	1147(281)	2000
B_4^4	-2698(251)	-5125
B_0^6	-2889(557)	-5792
B_4^6	-208(333)	427

Table 3 continued.

	$U^{4+}/ThSiO_4^a$	$U^{4+}/ZrSiO_4^b$
	D_{2d}	D_{2d}
No. of levels	25	30
σ	71	112

^aRef. 14. In this work the M^k and P^k parameters were set equal to zero.

^bRef. 13.

Table 4. Parameters for $[\text{Cp}_3\text{U}(\text{NCS})_2]^-$ and $[\text{Cp}_3\text{U}(\text{NCBH}_3)_2]^-$. All parameters are in cm^{-1} .

	$[\text{Cp}_3\text{U}(\text{NCS})_2]^{-\text{a}}$	$[\text{Cp}_3\text{U}(\text{NCBH}_3)_2]^{-\text{a}}$
F^2	45391	45609
F^4	44494	46116
F^6	19446	20780
ζ	1659	1664
α	$[31]^{\text{b}}$	$[31]^{\text{b}}$
β	$[-644]$	$[-644]$
γ	$[1200]$	$[1200]$
M^0	$[.99]$	$[.99]$
M^2	$[.55]$	$[.55]$
M^4	$[.38]$	$[.38]$
P^2	$[500]$	$[500]$
P^4	$[500]$	$[500]$
P^6	$[500]$	$[500]$
B_0^2	-2795(670)	-3121(824)
B_0^4	3039(1100)	3554(1526)
B_0^6	7659(968)	7250(1658)

Table 4 continued.

	$[\text{Cp}_3\text{U}(\text{NCS})_2]^{-a}$	$[\text{Cp}_3\text{U}(\text{NCBH}_3)_2]^{-a}$
B_6^6	-3064(723)	-2872(817)

^aRef. 28.^bValues of parameters in [] are held fixed at $\text{U}(\text{BD}_4)_4$ values.

Table 5. Parameter values for tetravalent Np compounds. For all calculations, the values of the parameters $M^0 = 0.88$, $M^2 = 0.49$, $M^4 = 0.34$, $P^2 = P^4 = P^6 = 500$, $T^2 = 278$, $T^3 = 44$, $T^4 = 64$, $T^6 = -361$, $T^7 = 434$, and $T^8 = 353 \text{ cm}^{-1}$ were used. Values in square brackets were held constant. All parameters are in cm^{-1} .

	$\text{Np}(\text{BD}_4)/\text{Zr}(\text{BD}_4)_4^a$	$\text{Np}^{4+}/\text{ThSiO}_4^b$	$\text{Np}^{4+}/\text{ZrSiO}_4^c$	$\text{Np}^{4+}/\text{ThO}_2^b$
	T_d	D_{2d}	D_{2d}	O_h (Cubic)
F^2	46689(415)	45196(716)	46259	49269(968)
F^4	43239(645)	38032(546)	44193	37662(1080)
F^6	26303(722)	28343(791)	25463	30937(1434)
ζ	2089(10)	2129(7)	2076	2175(13)
α	40(2)	15(3)		18(3)
β	[-600]	[-600]		[-600]
γ	[1200]	[1200]		[1200]
B_0^2		323(185)	-2104	
B_0^4	-2722(182)	1511(278)	4434	-854(281)
B_4^4		-3559(163)	-5251	
B_0^6	-5070(69)	-1871(372)	-4879	-994(142)
B_4^6		-801(197)	-79	

Table 5 continued.

	$\text{Np}(\text{BD}_4)/\text{Zr}(\text{BD}_4)_4$ ^a	$\text{Np}^{4+}/\text{ThSiO}_4$ ^b	$\text{Np}^{4+}/\text{ZrSiO}_4$ ^c	$\text{Np}^{4+}/\text{ThO}_2$ ^b
	T_d	D_{2d}	D_{2d}	O_h (Cubic)
No. of levels	46	29	37	16(24)
σ	84	47	75	74

^aRef. 29. In T_d or O_h symmetry $B_4^4 = (5/14)^{1/2} B_0^4$, $B_4^6 = -(7/2)^{1/2} B_0^6$.

^bRef. 31.

^cRef. 33.

Table 6. Comparison of various parameters for the tetravalent actinide ions.

Compound	$\frac{F_{\text{crys.}}^2}{F_{\text{FI}}^2}$	$\frac{F_{\text{crys.}}^4}{F_{\text{crys.}}^2}$	$\frac{\zeta_{\text{crys.}}}{\zeta_{\text{FI}}}$	k	$\frac{N_v^a}{(4\pi)^{1/2}}$ (cm ⁻¹)	σ^a (cm ⁻¹)
U ⁴⁺ /ThBr ₄	0.81	0.96	0.91	-	1544	36
U ⁴⁺ /ThCl ₄	0.82	0.93	0.92	-	1560	46
UCl ₄	0.82	0.93	0.92	0.95	1602	60
U ⁴⁺ /ThSiO ₄	0.83	0.95	0.93	-	1617	71
U ⁴⁺ /ZrSiO ₄	0.85	0.91	0.88	-	3113	112
UBD ₄ /Hf(BD ₄) ₄	0.79	0.97	0.91	0.85 ^b	4346	52
Cs ₂ UCl ₆ ²⁻	-	-	-	-	3562	189
[Cp ₃ U(NCS) ₂] ⁻	-	-	-	-	2923	>250
[Cp ₃ U(NCBH) ₃] ₂ ⁻	-	-	-	0.90	2943	>250
Np ⁴⁺ /ThO ₂	0.90	0.76	-	-	864	74
Np ⁴⁺ /ThSiO ₄	0.83	0.84	-	-	1859	47
Np ⁴⁺ /ZrSiO ₄	0.85	0.96	-	-	3321	75

Table 6 continued.

Compound	$\frac{F_{\text{crys.}}^2}{F_{\text{FI}}^2}$	$\frac{F_{\text{crys.}}^4}{F_{\text{crys.}}^2}$	$\frac{\zeta_{\text{crys.}}}{\zeta_{\text{FI}}}$	k	$\frac{N_v^a}{(4\pi)^{1/2}}$ (cm ⁻¹)	σ^a (cm ⁻¹)
<hr/>						
Np(BD ₄)/Zr(BD ₄) ₄	0.86	0.93	-	0.885(0.862) ^b	4151	84

^aIn cm⁻¹.

^bFor the methylborohydride compound.

Figure Caption

Figure 1. Fit of magnetic susceptibility data of Ref. 16 with the wavefunctions obtained from the optical analysis of $UC\ell_4$ (Ref 12). The $\Gamma_4-\Gamma_5$ splitting was adjusted empirically to 92 cm^{-1} . The solid lines are drawn for $k=1, 0.95, 0.94$, and 0.93 respectively from top to bottom.

Figure 1

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