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Crystal field superposition model analyses for tetravalent actinides

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Abstract. Intrinsic, or single ligand parameters, are derived for Cl^- , Br^- and O^{2-} ligands. These allow the approximate prediction of crystal field parameters for any site where the atomic positions are known. Several instances where published parameters are apparently incorrect have been discovered. Derived parameter ratios support the argument that the simple molecular orbital description of crystal fields breaks down for the tetravalent actinides.

1. Introduction

Crystal field analyses of the optical spectra of Pa^{4+} , U^{4+} and Np^{4+} in a variety of host crystals have been carried out, but published work on the heavier tetravalent actinides is sparse (see e.g. Krupa 1987). Even in the case of the lighter actinides, considerable difficulty has been experienced in correctly assigning the electronic transitions, and significant root mean square deviations between fitted and observed energy levels are commonplace. Some doubts remain, therefore, concerning the significance of the fitted parameters, even to the extent that the validity of the one-electron crystal field model for such systems has been questioned (Carnall 1986).

The aim of this work is to use the superposition model to assess the validity of published parameter sets and to investigate its usefulness in estimating initial values of crystal field parameters before fitting to data. Attention will also be directed to interpreting the values of the intrinsic (or single ligand) crystal field parameters as these can throw light on the processes coupling the 5f electrons with their crystalline environment.

2. Analysis of data

Available sets of crystal field parameters are primarily of two types: B_0^4 , B_0^6 for cubic crystals and sets of five parameters B_0^2 , B_0^4 , B_4^4 , B_0^6 , B_4^6 for crystals with sites of D_{2d} symmetry. In the former case the parameters are related directly to the intrinsic parameters \bar{A}_k by (Chen and Newman 1981):

$$B_0^4 = 28 \bar{A}_4 \quad (\text{sixfold or octahedral coordination})$$

$$= -(224/9) \bar{A}_4 \quad (\text{eightfold or cubal coordination})$$

$$B_0^6 = 12 \bar{A}_6 \quad (\text{sixfold or octahedral coordination})$$

$$= (256/9) \bar{A}_6 \quad (\text{eightfold or cubal coordination})$$

Table 1. Coordination factors K_q^k for paramagnetic ions in D_{2d} host crystals. R_1, R_2 refer to the spacing of the two sets of neighbouring ligands from the paramagnetic ion. The calculations are based on ligand positions given in the literature.

System	Metal-ligand spacing (\AA)	K_0^2	K_0^4	K_4^4	K_0^6	K_6^6
^a β -ThCl ₄	2.90 (= R_2)	4.42	-3.27	-1.49	-26.44	-13.42
	2.72 (= R_1)	-3.48	7.07	-15.32	-4.12	10.78
^a β -ThBr ₄	3.12 (= R_2)	4.48	-2.90	-1.44	-26.34	-13.09
	2.95 (= R_1)	-3.42	6.49	-15.14	-2.43	9.43
^a UCl ₄	2.869 (= R_2)	4.51	-2.72	-1.42	-26.29	-12.94
	2.638 (= R_1)	-3.48	7.03	-15.30	-3.99	10.67
^a α -ThCl ₄	2.89 (= R_2)	3.39	-8.80	-2.47	-23.40	-19.13
	2.85 (= R_1)	-2.57	-0.32	-12.98	13.73	-5.43
^a α -ThBr ₄	3.02 (= R_2)	3.47	-8.44	-2.38	-23.93	-18.70
	2.91 (= R_1)	-2.53	-0.61	-12.88	14.26	-6.03
^b ZrSiO ₄	2.268 (= R_2)	4.55	-2.44	-1.38	-26.18	-12.69
	2.131 (= R_1)	-3.54	7.58	-15.47	-5.61	11.94
^b ThSiO ₄	2.50 (= R_2)	5.25	2.69	-0.88	-21.71	-8.82
	2.46 (= R_1)	-3.26	5.11	-14.73	1.38	6.32

^a Taylor (1976).

^b Vishwamittar and Puri (1974b).

(Note that the \bar{A}_k are expressed in Stevens' normalisation, while the B_q^k are expressed in Wybourne normalisation, which is usual in the literature.) In the case of sites of D_{2d} symmetry there are eight coordinated ligands and two different metal-ligand spacings. It is thus necessary to employ the more complicated superposition model expression (see e.g. Newman and Urban 1972)

$$B_q^k = [K_q^k(1) + K_q^k(2)(R_1/R_2)^{t_k}] \bar{A}_k$$

where $K_q^k(i)$ are the angular coordination factors for the four equidistant ions at R_i , and $R_2 > R_1$. Formulae for single-ion coordination factors have been given by Newman and Urban (1975) and Rudowicz (1987). Calculated values of the coordination factors for the host crystals β -ThCl₄, β -ThBr₄, UCl₄, α -ThCl₄, α -ThBr₄, ZrSiO₄ and ThSiO₄ are given in table 1.

Spectroscopically determined crystal field parameters B_q^k for a number of systems are given in tables 2–5, together with values of \bar{A}_k derived using table 1 and the trial values $t_k = 5, 10$. Because of quoted fitting errors in the crystal field parameters and the fact that no allowance has been made for local distortions in the neighbourhood of substituted ions, completely consistent results cannot be expected even if the superposition model hypotheses hold precisely. We can hardly expect, given the present state of our knowledge, to determine the *accuracy* of the superposition model as applied to these systems.

3. Results

We consider, first, the fits to parameters for D_{2d} system given in tables 2–4. The experimental parameters are quoted with $B_4^4 < 0$, although this sign (but not the relative sign of B_4^4 to B_6^6) is indeterminate in fits to optical data. We have therefore chosen the coordinate axes used for superposition model analyses to be consistent with this sign. It

Table 2. Crystal field parameters B_q^k and derived intrinsic parameters \bar{A}_k for tetravalent actinide ions in D_{2d} sites with chlorine ligands (cm^{-1}). Fitting errors are quoted where available (in brackets). σ is the RMS deviation (cm^{-1}) and n is the number of fitted levels. The \bar{A}_k are derived for two different values of power law exponent t_k .

System	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6	σ	n
$^a\beta\text{-ThCl}_4:\text{U}^{4+}$ (A)	-1054 (117)	1146 (200)	-2767 (147)	-2135 (404)	-312 (227)	46	25
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 3861 915	 244 207	 169 172	 99 128	 299 84		
$^b\beta\text{-ThCl}_4:\text{U}^{4+}$ (B)	-1129 (94)	1793 (154)	-2617 (94)	-3016 (323)	342 (246)	—	—
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 4135 980	 381 335	 160 163	 129 167	 -328 -92		
$^c\beta\text{-ThCl}_4:\text{Pa}^{4+}$	-1405 (50)	1749 (94)	-2440 (98)	-2404 (607)	-195 (267)	24	7
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 5147 1220	 372 327	 149 152	 103 133	 187 52		
$^d\text{UCl}_4$ (A)	-903 (151)	766 (220)	-3091 (185)	-1619 (482)	-308 (280)	60	26
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 1757 590	 146 131	 190 194	 76 105	 -142 -61		
$^e\text{UCl}_4$ (B)	-1008 (198)	1730 (362)	-2704 (193)	-2705 (665)	346 (436)	32	18
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 1961 658	 330 295	 166 170	 127 176	 160 68		

^a Malek *et al* (1986a).

^b Carnall and Crosswhite (1985).

^c Krupa *et al* (1983).

^d Malek *et al* (1986b).

^e Gamp *et al* (1983).

should be emphasised that intrinsic parameters are expected to be positive on the basis of extensive work on the lanthanides (see e.g. Newman 1978). One aim of the present analysis is to detect any consistent breakdown of this expectation.

Table 3. Crystal field parameters B_q^k and derived intrinsic parameters \bar{A}_k for tetravalent actinide ions in D_{2d} sites with bromine ligands (cm^{-1}). Fitting errors are quoted where available (in brackets). σ is the RMS deviation (cm^{-1}) and n the number of fitted levels. The \bar{A}_k are derived for two different values of power law exponent t_k .

System	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6	σ	n
$^a\beta\text{-ThBr}_4:\text{U}^{4+}$	-1096 (80)	1316 (146)	-2230 (85)	-3170 (379)	686 (246)	36	26
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 1933 683	 283 248	 139 142	 165 242	 622 166		
$^b\beta\text{-ThBr}_4:\text{Pa}^{4+}$	-1047 (52)	1366 (138)	-1990 (102)	-1162 (541)	623 (174)	19	7
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 1845 652	 294 257	 124 127	 61 89	 565 151		
$^c\alpha\text{-ThBr}_4:\text{U}^{4+}$	-382 (73)	-3262 (197)	-1734 (164)	-851 (334)	-1828 (163)	77	30
\bar{A}_k $\left\{ \begin{array}{l} t_k = 5 \\ t_k = 10 \end{array} \right.$	 -1073 2894	 428 507	 117 119	 151 377	 85 97		

^a Delamoye *et al* (1983).

^b Krupa *et al* (1983).

^c Simoni *et al* (1987).

Table 4. Crystal field parameters B_k^q and derived intrinsic parameters \bar{A}_k for tetravalent actinide ions in D_{2d} sites with oxygen ligands (cm^{-1}). Fitting errors are quoted where available (in brackets). σ is the RMS deviation (cm^{-1}) and n the number of fitted levels. The \bar{A}_k are derived for two different values of power law exponent t_k .

System	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6	σ	n
$^a\text{ZrSiO}_4:\text{U}^{4+}$	-2000	2000	-5125	-5792	427	112	30
$\bar{A}_k \begin{cases} t_k = 5 \\ t_k = 10 \end{cases}$	9662 1821	345 319	311 316	234 295	161 83		
$^b\text{ZrSiO}_4:\text{Np}^{4+}$	-2537 (101)	2304 (208)	-5281 (149)	-5065 (150)	642 (125)	33	31
$\bar{A}_k \begin{cases} t_k = 5 \\ t_k = 10 \end{cases}$	12256 2311	398 367	320 326	204 258	242 125		
$^c\text{ThSiO}_4:\text{U}^{4+}$	-1003 (127)	1147 (281)	-2698 (251)	-2889 (557)	-208 (333)	71	25
$\bar{A}_k \begin{cases} t_k = 5 \\ t_k = 10 \end{cases}$	-631 -829	151 155	174 174	155 167	114 175		
$^d\text{ThSiO}_4:\text{Np}^{4+}$	323 (185)	1511 (278)	-3559 (163)	-1871 (372)	-801 (197)	47	29
$\bar{A}_k \begin{cases} t_k = 5 \\ t_k = 10 \end{cases}$	203 267	195 204	229 230	100 109	439 674		

^a Vance and Mackey (1978).

^b Poirot *et al* (1988).

^c Malek *et al* (1986c).

^d Krupa (1987).

Table 5. Superposition model analysis for tetravalent actinides in sites of cubic symmetry. All parameters are given in cm^{-1} . Crystal field parameters are taken from Krupa (1987), tables IX and X. σ is the RMS deviation (cm^{-1}).

System	B_0^4	B_0^6	\bar{A}_4	\bar{A}_6	σ
UCl_5^{2-}	7797 (394)	1344 (230)	278	112	189
$\text{ThO}_2:\text{Np}^{4+}$	-854 (281)	-994 (142)	34	-35	74
$\text{Np}(\text{BD}_4)_4$	-2722 (182)	-5070 (69)	219	-356	84
$\text{U}(\text{BD}_4)_4$	-2445 (124)	-5371 (81)	196	-378	52

In the case of $\beta\text{-ThCl}_4:\text{U}^{4+}$, parameter set A (see table 2) is clearly superior to B in providing a consistent set of positive intrinsic parameters. This can be explained by the fact that Carnall and Crosswhite (1985) *estimated* the crystal field parameters in set B. Although consistent \bar{A}_4 -values are not obtained for $t_4 < 10$, we can estimate the range of uncertainty as $\bar{A}_4 = 190 \pm 20 \text{ cm}^{-1}$. A consistent value of $\bar{A}_6 = 120 \pm 10 \text{ cm}^{-1}$ is found for $t_6 \sim 9$. On the basis of previous work on the lanthanides, it is expected that $t_2 < 10$, giving $\bar{A}_2 > 1000 \text{ cm}^{-1}$. All these parameters correspond to a $\text{U}^{4+}\text{-Cl}^-$ spacing close to the nearest neighbour $\text{Th}^{4+}\text{-Cl}^-$ spacing in $\beta\text{-ThCl}_4$, i.e. 2.72 \AA .

The $\beta\text{-ThCl}_4:\text{Pa}^{4+}$ crystal field parameters (see table 2) give a value of \bar{A}_2 consistent with that just determined for U^{4+} and a very similar value of $\bar{A}_6 = 115 \pm 10 \text{ cm}^{-1}$. The \bar{A}_4 -values determined from B_4^4 and B_0^4 are inconsistent and comparison with the U^{4+} result suggests that B_0^4 is not well determined. (We are puzzled by the fact that Krupa *et al* (1983) quote mean square deviations for their fits of five crystal field parameters and one spin-orbit parameter to the six independent energy level differences in these systems. Presumably some further unspecified constraints were placed on the

parameters.)

Two sets of results for UCl_4 are shown in table 2. The better defined B_4^4 parameters in both sets give $\bar{A}_4 = 180 \pm 15 \text{ cm}^{-1}$ which is reasonably consistent with the result above, although now the nearest neighbour $\text{U}^{4+}-\text{Cl}^-$ spacing is 2.64 \AA . This suggests that the Cl^- ions move towards the U^{4+} ion substituted into $\beta\text{-ThCl}_4$. Rank-6 parameters are poorly determined for this system, but the results are reasonably consistent with the value for \bar{A}_6 determined above. If we assume that $t_2 > 5$, then $\bar{A}_2 < 2000 \text{ cm}^{-1}$ which, combined with the $\beta\text{-ThCl}_4$ result provides the result $\bar{A}_2 = 1500 \pm 500 \text{ cm}^{-1}$.

Results for $\beta\text{-ThBr}_4:\text{U}^{4+}$ given in table 3 do not provide consistent values of \bar{A}_4 . Following the UCl_4 analyses we accept the \bar{A}_4 -value based on B_4^4 (i.e. approximately 140 cm^{-1}) as being the most reliable. It is unlikely that \bar{A}_6 is greater than \bar{A}_4 , but the analysis suggests a value greater than 160 cm^{-1} . The $\beta\text{-ThBr}_4:\text{Pa}^{4+}$ analysis also gives inconsistent intrinsic parameter values, but the value of $\bar{A}_4 \sim 130 \text{ cm}^{-1}$ based on B_4^4 is consistent with that just derived for $\beta\text{-ThBr}_4:\text{U}^{4+}$. Both sets of data for the $\beta\text{-ThBr}_4$ host crystal provide an estimate of $A_2 = 1300 \pm 600 \text{ cm}^{-1}$, or slightly smaller than the Cl^- result. Again the derived intrinsic parameters for $\alpha\text{-ThBr}_4:\text{U}^{4+}$ show inconsistencies. None of the superposition model fits for Br^- ligands is satisfactory, and it seems likely that some incorrect assignments of energy levels have been made.

The data for ZrSiO_4 and ThSiO_4 hosts (see table 4) give more consistent results than the halide systems considered above. $\text{ZrSiO}_4:\text{U}^{4+}$ gives $\bar{A}_4 = 320 \pm 10 \text{ cm}^{-1}$ and $t_4 \sim 11$. Given $t_2 < 10$, we expect $\bar{A}_2 > 2000 \text{ cm}^{-1}$. Taking the B_6^6 -value as being the most reliable and $t_6 \sim 10$, we estimate $\bar{A}_6 = 280 \pm 50 \text{ cm}^{-1}$. This gives an unusually large ratio \bar{A}_6/\bar{A}_4 when compared with lanthanide data (see e.g. Newman 1978) and this will be discussed in the next section. The $\text{ZrSiO}_4:\text{Np}^{4+}$ results are reasonably consistent with those for U^{4+} , although $\bar{A}_6 (=230 \pm 50 \text{ cm}^{-1})$ is slightly smaller in this case. It should be noted that Np^{4+} and U^{4+} are a very tight fit in the ZrSiO_4 lattice, so a considerable distortion of the lattice may be taking place. Zr^{4+} has a smaller ionic radius than Th^{4+} , so we expect the intrinsic parameters for $\text{ThSiO}_4:\text{U}^{4+}$ to be much smaller than those derived for ZrSiO_4 . This is borne out by the results given in table 4, where we see that $\bar{A}_4 = 165 \pm 10 \text{ cm}^{-1}$, $\bar{A}_6 = 160 \pm 20 \text{ cm}^{-1}$ for $\text{ThSiO}_4:\text{U}^{4+}$. The negative value obtained for \bar{A}_2 in this system suggests that either local distortion is significant or that long-range electrostatic contributions cannot be neglected. $\text{ThSiO}_4:\text{Np}^{4+}$ gives a positive, but very small value of \bar{A}_2 , which we cannot take literally. In this system $\bar{A}_4 = 215 \pm 20 \text{ cm}^{-1}$ but \bar{A}_6 is not well determined.

A superposition model analysis for the system $\text{PbMoO}_4:\text{Np}^{4+}$ was carried out by Vishwamittar and Puri (1974a). Their results are in agreement with results obtained using the methods described in this work, namely

$$\bar{A}_2 = 2100 \pm 200 \text{ cm}^{-1} \quad \bar{A}_4 = 290 \pm 50 \text{ cm}^{-1} \quad \bar{A}_6 = 180 \pm 50 \text{ cm}^{-1}$$

for an interionic spacing of 2.6 \AA . These parameters show a similar tendency to those obtained for lanthanides in scheelite and zircon structure crystals in that, for a given oxygen distance, both \bar{A}_4 and \bar{A}_6 are larger in the scheelites. The most interesting feature of this system, however, is that it permits a very accurate determination of \bar{A}_2 .

Superposition model analyses for several systems with cubic symmetry are given in table 5. The results for UCl_6^{2-} are similar to those obtained for $\beta\text{-ThCl}_4:\text{U}^{4+}$ and UCl_4 , although \bar{A}_4 is significantly greater. This presumably reflects the small $\text{U}^{4+}-\text{Cl}^-$ spacing in this system. The remaining results in table 5 give negative \bar{A}_6 -values, too large to be explained by strong interpenetration effects as has been suggested previously (Newman 1983, Newman and Ng 1985). In any case, such an explanation would be inconsistent

with the results of our analyses of the D_{2d} systems described above. This suggests that these three sets of parameters correspond either to false minima in the fitting space or that they are based on some misidentification of spectral lines.

Finally we consider the $\text{CaF}_4:\text{Bk}^{4+}$ results of Jursich *et al* (1987). Taking the common coordination angle for all the F^- ions as 59.26° (in accord with the x-ray data) we derive

$$\bar{A}_2 = -62 \text{ cm}^{-1} \quad \bar{A}_4 = 352 \text{ cm}^{-1} \quad \bar{A}_6 = 52 \text{ cm}^{-1}.$$

Comparison with O^{2-} results suggests that their value of $B_0^4 = -6898 \text{ cm}^{-1}$ is approximately correct, while B_0^2 should be positive (rather than -107 cm^{-1}) and that their value of $B_0^6 = 2084 \text{ cm}^{-1}$ is too small. It should be emphasised, however, that the superposition model prediction of the signs of B_0^4 and B_0^6 is in accord with the results of Jursich *et al* (1987).

4. Discussion

We have derived consistent positive intrinsic parameter values for the tetravalent actinides (Pa^{4+} , U^{4+} , Np^{4+}) with Cl^- ligands as follows:

$$\bar{A}_2 = 1500 \pm 500 \text{ cm}^{-1} \quad \bar{A}_4 = 190 \pm 30 \text{ cm}^{-1} \quad \bar{A}_6 = 120 \pm 15 \text{ cm}^{-1}$$

with slightly smaller values for Br^- ligands. These correspond to an interionic spacing of about 2.7 \AA for Cl^- and about 2.9 \AA for Br^- . Power law exponents have not been determined accurately, but seem to be similar to those already derived for lanthanide systems, namely $t_2 \sim 7$, $t_4 \sim 11$, $t_6 \sim 8$.

Tetravalent actinides (U^{4+} , Np^{4+}) intrinsic parameters with O^{2-} ligands are, again, positive. They show a strong dependence on the ionic radius of the substituted ion which can be explained in terms of power law dependences with positive t_k . We have obtained for $R_0 \sim 2.45 \text{ \AA}$,

$$\bar{A}_2 = 1500 \pm 1000 \text{ cm}^{-1} \quad \bar{A}_4 = 190 \pm 30 \text{ cm}^{-1} \quad \bar{A}_6 = 160 \pm 30 \text{ cm}^{-1}$$

and for $R_0 \sim 2.3 \text{ \AA}$,

$$\bar{A}_2 = 2500 \pm 500 \text{ cm}^{-1} \quad \bar{A}_4 = 320 \pm 40 \text{ cm}^{-1} \quad \bar{A}_6 = 250 \pm 50 \text{ cm}^{-1}.$$

We believe that the intrinsic parameter values given above should provide a useful starting point in future crystal field analyses.

The most interesting conclusion of these analyses is that the ratios \bar{A}_6/\bar{A}_4 are generally so large as to be difficult to explain using a simple molecular orbital model. In that model the $m_l = 0$ (or σ) and $m_l = \pm 1$ (or π) orbital interaction energies are related to intrinsic parameters as follows (Ellis and Newman 1967):

$$\varepsilon_\sigma = \frac{56}{11} (\bar{A}_4 + \frac{4}{13} \bar{A}_6) \quad \varepsilon_\pi = \frac{112}{33} (\bar{A}_4 - \frac{18}{13} \bar{A}_6).$$

As $\varepsilon_\pi > 0$ in the molecular orbital model and is expected to be a significant fraction of ε_σ , it is clearly difficult to reconcile this model with intrinsic parameter ratios \bar{A}_6/\bar{A}_4 of the order unity. Recent *ab initio* calculations for 4f electron crystal fields (Ng and Newman 1988) suggest that significant contributions to \bar{A}_6 in actinides also come from $5f \rightarrow nf$ configuration interaction but we have yet to produce good quantitative results that could determine \bar{A}_6/\bar{A}_4 ratios. This is supported by the fact that the molecular orbital calculations of Gajek *et al* (1987) underestimate the rank six parameters (for example see the UCl_4 results in table 7 of that work). We conclude, therefore, that *ab*

initio molecular orbital models are inadequate to explain the relatively large \bar{A}_6 -values obtained in this work, and that these probably originate from configuration interaction effects.

Although most of the data we have analysed give reasonably consistent and positive \bar{A}_k -values, several sets of published parameters have been shown to give negative \bar{A}_k -values and therefore are very likely to be erroneous. It would be interesting to attempt new analyses of the spectra in these cases, starting from parameters based on superposition model predictions.

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