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Absorption spectrum analysis of uranium trichloride heptahydrate

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Abstract

A good quality absorption spectrum of a powdered sample of $UCl_3 \cdot 7H_2O$ was obtained at 4.2 K in the 4000–30 000 cm^{-1} range. Analysis of the spectrum enabled the determination of the crystal-field parameters and assignment of 94 crystal-field levels. The energies of the levels were computed by applying a simplified angular overlap model as well as a semi-empirical Hamiltonian representing the combined atomic and crystal-field interactions. © 2001 Elsevier Science B.V. All rights reserved

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1. Introduction

This paper presents a crystal-field level analysis performed on the basis of the low-temperature absorption spectrum of polycrystalline samples of $UCl_3 \cdot 7H_2O$. Spectroscopic crystal-field studies of trivalent uranium, due to experimental difficulties, have so far been exclusively carried out on single-crystal hosts of simple and complex lanthanide halides [1–10] and a polycrystalline $U(HCOO)_3$ sample [11]. Most of these investigations, however, exhibit a substantial drawback depending on the appearance of strong, Lapporte-allowed f–d bands in the spectra at energies as low as about 16 000–18 000 cm^{-1}. As a result, the energy level structure of U^{3+} in different environments is relatively well established in the 0–16 500 cm^{-1} region only. Hence, we turned our attention to uranium(III) compounds in polycrystalline form, for which good quality absorption spectra could also be recorded in the 15 000–30 000 cm^{-1} range.

2. Experimental

The compound was prepared according to the procedures reported in Ref. [12]. The electronic absorption spectrum of a thin film of the compound was recorded on a Cary 5 NIR–Vis–UV spectrophotometer in the 4000–30 000 cm^{-1} range. In order to obtain the spectrum, a well-ground mixture of the compound with some chlorinated naphthalene oil (refraction index 1.635) was placed between two quartz windows, approximately 0.8 cm in diameter, pressed to obtain a transparent layer, and placed in the cell compartment of an Oxford Instruments Model CF1204 cryostat. The spectrum was recorded at 4.2 and 300 K.

3. Parameterization of the crystal-field potential

Since no qualitative differences were found [12] between the X-ray powder diffraction data of $UCl_3 \cdot 7H_2O$ and $LaCl_3 \cdot 7H_2O$ it was assumed that these compounds are isostructural and form similar $[(H_2O)_7Me\langle^{Cl}_{Cl}\rangle Me(H_2O)_7]Cl_4$ dimers, where Me=U or La. The coordination polyhedron approximates two single-capped square antiprisms which share an equitorial edge formed by the bridging chloride atoms [13]. The other four chloride atoms are not bound to the metal ion. The cells are triclinic with space group $P\bar{1}$. Due to the lack of symmetry elements at the metal site in the compound under consideration as many as 27 independent crystal-field parameters describe the crystal-field (CF) potential. Preliminary estimation of their values is difficult in view of the fact that the first coordination sphere, being of major importance for the CF effect, is especially complex [12,13]. All ligands, i.e. the two chlorine ions and seven oxygens, are non-equivalent in the sense that any two of

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them cannot be interchanged by a rotation only, leaving the system invariant. To simplify the phenomenological description of the system, the angular overlap model (AOM) [14], known to be especially efficient in cases of low-symmetry systems (see, for example, Ref. [15]), was applied. In this model the CF potential V is partitioned into certain spatial contributions attributed to ligands. The usual B_q^k CF parameters are then expressed in terms of the so-called intrinsic e_μ^t parameters, which correspond to the above-mentioned contributions and the specific $W_{kq}^{\mu t}$ factors, which depend on the geometry of the metal ion surroundings:

$$B_q^k = \sum_t \sum_\mu W_{kq}^{\mu t} e_\mu^t \quad (1)$$

The index t identifies ligands and μ represents the absolute value of the magnetic quantum number of a 5f electron in the local coordination system, taking values of 0, 1, 2, denoted also by σ, π, δ. Thus there are three e_μ^t AOM parameters per ligand. The total number of AOM parameters depends on the number of non-equivalent ligands, being equal to 27 (3×9) for the considered hydrate. The characteristic properties of the AOM parameters allow one to reduce the number of independent parameters to a few only. We fixed the metal–ligand distance dependence of the parameters in the form

$$e_\mu^t = e_\mu^0 \left(\frac{R_0}{R_t}\right)^{\alpha_\mu} \quad (2)$$

as well as the ratios between them, using the α_μ exponents in the above formula and the $e_\mu^t/e_\mu^{t'}$ ratios from Ref. [15]. The $W_{kq}^{\mu t}$ coefficients were calculated on the basis of the crystallographic (X-ray) data reported in Ref. [13] for isostructural $PrCl_3 \cdot 7H_2O$.

The parameterization is a quite severe simplification in the cases of systems containing water molecules [16]. Nevertheless, this exceptionally compact description of the intricate CF potential is practically indispensable in the initial steps of the interpretation of complex spectra. Moreover, despite the apparent shortcomings, the model has been shown to work quite satisfactorily for hydrates [16].

4. Phases of interpretation

The fitting procedure was divided into a number of steps, starting from a raw single-parameter AOM approach to the standard CF Hamiltonian. In the first step of the calculations we only took into account crystal-field levels which could be assigned unambiguously. The remaining levels were gradually identified and included in the fitting procedure as the calculations proceeded. The initial values of the AOM parameters and their ratios were taken from the above ab initio calculations. In this calculation step a single-parameter approximation was introduced through the following constraints:

1. $e_\delta^O = e_\delta^{Cl} = 0$;
2. $e_\pi^O = 0.363 e_o^O$, $e_\pi^{Cl} = 0.339 e_o^{Cl}$;
3. $e_o^{Cl} = 0.67 e_o^O$

The e_μ^O and e_μ^{Cl} parameters are defined as averaged quantities over all ligands of a given type, with weights determined from the ab initio calculations. According to the above equations, e_o^O becomes the only free parameter to be varied in the first step of the fitting procedure. The initial value of the e_o^O parameter was estimated at 800 cm^{-1}.

In the second step, constraint 3 was relaxed and the two e_o^O and e_o^{Cl} parameters, which separately describe the U–Cl and U–O interactions, were freely varied. In the next step, we released the e_o^O and e_o^{Cl} parameters with the initial values obtained from the second step as well as the e_δ^O and e_δ^{Cl} parameters with the starting value equal to 0. Constraints 2 were still maintained. Since the release of the e_δ^{Cl} parameter resulted in a parameter value different from the calculated value, this parameter was not included in further fitting procedures. In the final AOM phase the e_σ^O, e_π^O, e_δ^O, e_σ^{Cl} and e_π^{Cl} parameters were treated as independent variables with the initial values of e_σ^O and e_σ^{Cl} determined from the third step and those of e_π^O and e_π^{Cl} from the relation in constraint 2. The final values of the AOM parameters (Table 1) were determined with a relatively small error and were consistent with the applied model. At this stage the largest difference between the computed and experimental crystal-field levels did not exceeded 122 cm^{-1} and the r.m.s error was 42.6 cm^{-1}.

However, since the applied conventional AOM approach does not precisely reflect the polarization effects, which are expected to be important for the investigated compound, we switched to the B_q^k parameterization. Thus, in the next steps of the fitting procedure, all the usual CF parameters were varied paying special attention to the B_q^2 parameters, which are especially sensitive to the electric polarization of the surroundings. Their initial values were determined according to Eq. (1) from the obtained AOM parameters listed in Table 1. In the next two steps we released the crystal-field parameters with the largest absolute values, i.e. the B_1^6, Im B_2^6, B_4^6, Im B_4^6, Im B_5^6 and B_0^2, Im B_1^2, B_2^2, Im B_2^2 parameters, respectively. At this stage of the calculations, all computed values exhibit relatively small changes and parameter errors. In the final fit, seven 'free

Table 1
AOM parameters (cm^{-1}) for $UCl_3 \cdot 7H_2O$

e_σ^{Cl}	e_σ^O	e_π^{Cl}	e_π^O	e_δ^{Cl}	e_δ^O
547 (92)[a]	1126 (86)	154 (81)	422 (78)	[0][b]	111 (58)

[a] Values in parentheses are parameter errors.
[b] Parameters not varied in the fitting procedure.

Table 2
Free ion and crystal-field parameters for $UCl_3 \cdot 7H_2O$

Parameter[a,b]	(cm^{-1})	Parameter[a,b]	(cm^{-1})
E_{avg}	19 827 (17)	B_4^4	[374]
F^2	40 488 (58)	Im B_4^4	[−491]
F^4	32 544 (81)	B_0^6	[−130]
F^6	22 866 (75)	B_1^6	428 (90)
α	28 (5)	Im B_1^6	[−77]
β	−622 (35)	B_2^6	[171]
ζ	1622 (10)	Im B_2^6	133 [100]
B_0^2	−126 (76)	B_3^6	[−251]
B_1^2	[−109]	Im B_3^6	[−14]
Im B_1^2	−423 (47)	B_4^6	−489 (110)
B_2^2	−209 (53)	Im B_4^6	−1832 (81)
Im B_2^2	−350 (55)	B_5^6	[160]
B_0^4	188 (106)	Im B_5^6	1197 (96)
B_1^4	[−99]	B_6^6	−498 (98)
Im B_1^4	[−81]	Im B_6^6	−241 (91)
B_2^4	[−66]		
Im B_2^4	[−238]	σ[c]	36
B_3^4	[136]	n	94
Im B_3^4	−529 (83)		

[a] The values of the free ion parameters which were kept constant during the fitting procedures were: $\gamma = 1148$; $T^2 = 306$, $T^3 = 42$, $T^4 = 188$, $T^6 = -242$, $T^7 = 447$, $T^8 = 300$; $M^0 = 0.672$, $M^2 = 0.372$, $M^4 = 0.258$; $P^2 = 1216$, $P^4 = 608$, $P^6 = 122$.

[b] Values in parentheses are parameter errors. Values of the crystal-filed parameters in brackets were obtained by deconvolution of AOM parameters and were kept constant during the fitting procedures.

[c] r.m.s. deviation: $\sigma = \Sigma[\Delta_i/(n-p)]^{1/2}$, where Δ_i is the difference between the observed and calculated energies, n is the number of levels fitted and p is the number of parameters freely varied.

ion' and 13 crystal-field parameters were varied simultaneously (Table 2). Relaxing of the remaining crystal-field parameters led either to large errors in the determination of parameter values or to large deviations from the initial values and usually also to larger r.m.s. errors.

5. Results and discussion

The absorption spectrum recorded at 4.2 K is presented in Figs. 1 and 2. The near-IR and visible part of the spectrum consists of relatively intense, sharp and well-separated absorption lines. The low site symmetry of U^{3+} results in the absence of distinct vibronic lines and the appearance of $(2J+1)/2$ lines for each multiplet. Hence, the recorded lines may be assigned to transitions from the lowest component of the $^4I_{9/2}$ ground level to the components of the excited $^{2S+1}L_J$ multiplets. In addition to some very weak features of unknown origin, the observed number of lines does not exceed $(2J+1)/2$, which is indicative of single uranium sites in the compound.

The conventional parametric Hamiltonian requires 26 real and imaginary B_q^k parameters. For such low site symmetries a least-square routine may lead to a false minimum of no physical meaning. To limit the space of the possible solutions we decided to apply the AOM constraints. In this phase of interpretation, we obtained somewhat larger r.m.s. errors, but the parameters retained their physical meaning.

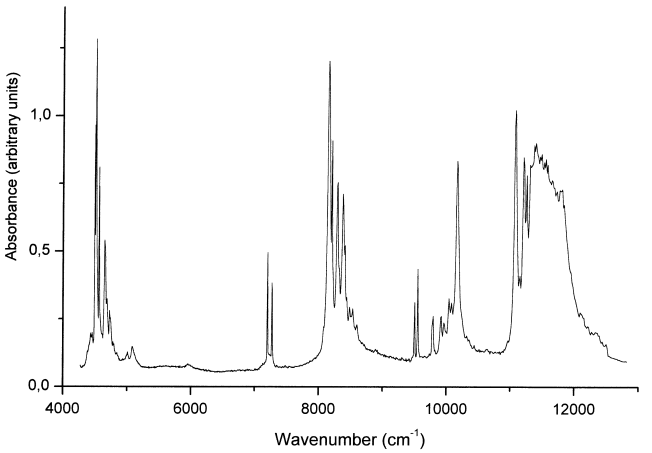

Fig. 1. Absorption spectrum of $UCl_3 \cdot 7H_2O$ at 4 K in the 4000–13 000 cm^{-1} range.

In the calculations, seven 'free ion' and 13 crystal-field parameters were allowed to vary freely. As can be seen from Table 3 almost all absorption bands were recorded and assigned. In comparison with earlier analyses [1–11] the number of levels included in the calculations is larger. Finally, we could identify 94 crystal-field levels (Table 3).

The relatively small r.m.s deviation of 36 cm^{-1} (Table 2) as well as the good relationship between the computed and theoretical parameters allowed us to conclude that the obtained values retained their physical meaning. To the best of our knowledge these are not only the first crystal-field calculations for such uranium(III) systems, but also one of the first for hydrated nf^N electron compounds of very low site symmetry.

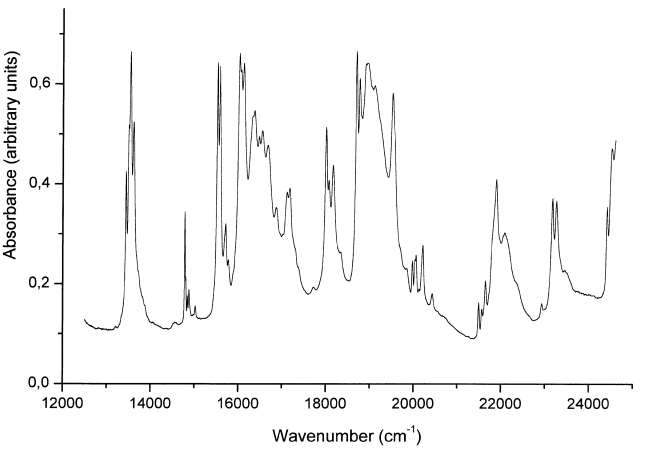

Fig. 2. Absorption spectrum of $UCl_3 \cdot 7H_2O$ at 4 K in the 13 000–25 000 cm^{-1} range.

Table 3
Calculated and experimental energy levels for $UCl_3 \cdot 7H_2O$

$^{2S+1}L_J$ [a]	Calculated energy (cm^{-1})	Experimental energy (cm^{-1})	$E_{exp.} - E_{calc.}$ (cm^{-1})
$^4I_{9/2}$	21	0	−21
	167	170	3
	329		
	546		
	704		
$^4I_{11/2}$	4455	4494	39
	4507	4511	4
	4576	4561	−15
	4622	4649	−38
	4724	4686	−38
	4789	4725	−64
$^4F_{3/2}$	7177	7198	21
	7268	7270	2
$^4I_{13/2}$	8098	8150	51
	8204	8202	−2
	8260	8288	28
	8316	8376	60
	8440	8483	43
	8525	8530	5
	8604	8595	−9
$^2H2_{9/2}$	9538	9506	−32
	9604	9551	−53
	9753	9794	41
	9881	9915	34
	9941	9962	21
$^4F_{5/2}$	10 020	10 038	18
	10 083	10 080	−3
	10 144	10 165	21
$^4S_{3/2} + {}^4G_{5/2} + {}^4F_{7/2} + {}^4I_{15/2}$	11 039	11 072	33
	11 140	11 142	2
	11 188	11 200	12
	11 245	11 246	1
	11 397	11 309	−88
	11 433	11 379	−54
	11 488	11 457	−31
	11 548	11 551	3
	11 627		
	11 672	11 659	−13
	11 737		
	11 788	11 778	−10
	11 873		
	11 999	11 960	−39
	12 118	12 116	−2
	12 268	12 221	−47
	12 365	12 348	−17
$^4G_{7/2}$	13 482	13 441	−41
	13 582	13 539	−43
	13 630	13 613	−17
	13 754	13 724	−30
$^4F_{9/2}$	14 725	14 785	60
	14 787	14 808	21
	14 811	14 844	33
	14 871	14 880	9
	14 968	15 020	52
$^2H2_{11/2}$	15 463		
	15 543	15 522	−22
	15 584	15 577	−7
	15 674	15 711	37
	15 744	15 774	30
	15 879	15 883	4
$^2K_{13/2} + {}^4D_{3/2} + {}^4D_{1/2}$	16 038	16 021	−17
	16 107	16 062	−45
	16 170	16 120	−50
	16 273		
	16 310	16 319	9
	16 363	16 367	4
	16 426	16 471	45
	16 512	16 544	32
	16 688	16 670	−18
	16 920	16 868	−52

Table 3. Continued

$^{2S+1}L_J$ [a]	Calculated energy (cm^{-1})	Experimental energy (cm^{-1})	$E_{exp.} - E_{calc.}$ (cm^{-1})
$^2G1_{7/2} + {}^4G_{9/2}$	16 972	16 952	−21
	17 029	17 017	−12
	17 089		
	17 114	17 109	−5
	17 193	17 170	−23
	17 245	17 251	5
	17 271	17 298	27
	17 382	17 371	−11
	17 510		
$^4D_{5/2}$	17 945	18 002	55
	18 030	18 064	34
	18 162	18 159	−3
$^2L_{15/2} + {}^4D_{3/2}$	18 653	18 694	40
	18 744	18 762	18
	18 834		
	18 921	18 935	14
	19 070		
	19 116	19 105	−11
	19 202		
	19 359		
	19 470		
	19 513	19 531	17
$^2H1_{11/2}$	19 934		
	19 977	19 972	−5
	20 028	20 030	2
	20 067	20 054	−13
	20 100	20 122	22
	20 143	20 209	66
$^2D1_{5/2}$	20 496	20 422	−74
	20 650		
	20 764		
$^2G1_{9/2} + {}^2I_{11/2} + {}^2P_{1/2}$	21 389		
	21 467	21 486	19
	21 569	21 564	−6
	21 640	21 641	1
	21 753		
	21 789		
	21 878	21 888	10
	21 941		
	22 026		
	22 084	22 082	−2
	22 239		
	22 378	22 382	4
$^4D_{7/2} + {}^2D2_{3/2}$	22 675		
	22 897	22 934	37
	23 019		
	23 079		
	23 179	23 174	−5
	23 264	23 259	−5
$^2I_{13/2} + {}^2L_{15/2} + {}^2H1_{9/2} + {}^2F2_{5/2}$	24 453	24 414	−39
	24 571	24 512	−60
	24 660		
	24 683		
	...		

[a] Nominal quantum numbers for the atomic state associated with the group.

6. Conclusions

The obtained good-quality low-temperature absorption spectrum of a powdered sample of $UCl_3 \cdot 7H_2O$ enabled a successful crystal-field analysis in the 0–25 000 cm^{-1} absorption range. Compared with earlier analyses of other uranium(III) systems the number of levels included in the calculations is larger and the r.m.s. deviation is relatively small. The AOM model was found to be useful in the determination of the initial values for the B_q^k parameterization.

References

[1] J. Drożdżyński, in: A.J. Freeman, C. Keller (Eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 6, Elsevier, 1991, p. 282.
[2] H.M. Crosswhite, H. Crosswhite, W.T. Carnall, A.P. Paszek, J. Chem. Phys. 72 (1980) 5103.
[3] W.T. Carnall, H.M. Crosswhite, ANL-84-90, Optical spectra and electronic structure of actinide ions in compounds and solutions, Argonne National Laboratory, 1985.
[4] E. Simoni, M. Louis, J.Y. Gesland, S. Hubert, J. Lumin. 65 (1995) 153.
[5] M. Karbowiak, K.M. Murdoch, J. Drożdżyński, N.M. Edelstein, S. Hubert, Acta Phys. Polon. A 90 (2) (1996) 371.
[6] M. Karbowiak, E. Simoni, J. Drożdżyński, S. Hubert, Acta Phys. Polon. A 90 (2) (1996) 367.
[7] H.P. Andres, K. Krämer, H.-U. Güdel, Phys. Rev. 54 (1996) 3830.
[8] M. Karbowiak, J. Drożdżyński, K.M. Murdoch, N.M. Edelstein, S. Hubert, J. Chem. Phys. 106 (1997) 3067.
[9] M. Karbowiak, J. Drożdżyński, S. Hubert, E. Simoni, W. Stręk, J. Chem. Phys. 108 (1998) 10181.
[10] M. Karbowiak, N. Edelstein, Z. Gajek, J. Drożdżyński, Spectrochim. Acta A 54 (1998) 2035.
[11] M. Karbowiak, J. Drożdżyński, J. Alloys Comp. 300/301 (2000) 329–333.
[12] J. Drożdżyński, Inorg. Chim. Acta 109 (1985) 79.
[13] A. Habenschuss, F.H. Spedding, Cryst. Struct. Comm. 7 (1978) 535.
[14] Z. Gajek, J. Mulak, M. Faucher, J. Phys. Chem. Solids 48 (1987) 947.
[15] Z. Gajek, J. Mulak, J. Phys. Condens. Matter 4 (1992) 427.
[16] M. Karbowiak, Z. Gajek, J. Drożdżyński, Chem. Phys. 261 (2000) 301.