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Absorption spectrum analysis of uranium(III) formate

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Abstract

The absorption spectrum of a thin film of uranium(III) formate was measured at 4 and 300 K in the 4000–23 000 cm^{-1} range. The energy levels of U^{3+} were assigned and fitted to a semiempirical Hamiltonian representing the combined atomic and crystal-field interactions at the C_{3v} symmetry site. Ten energy level parameters were varied simultaneously in least-squares adjustments yielding a mean error of 23 cm^{-1}. The analysis enabled the determination of the crystal-field parameters and the assignment of 49 crystal-field levels. The calculated total splitting of the ground level is equal to 520 cm^{-1}. An analysis of the $5f^3 \rightarrow 5f^3$ band intensities based on the Judd–Ofelt theory is presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Uranium(III) formate; Uranium(3+); Absorption spectra; Crystal-field analysis; Intensity analysis

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1. Introduction

In previous papers we have reported an analysis of the ‘‘free ion’’ energy level scheme as well as intensity calculations of the $5f^3 \rightarrow 5f^3$ transitions in the absorption spectrum of solid uranium triformate [1] and U^{3+} in anhydrous formic acid [2]. The results of intensity calculations were considered in the problem of the L′J′S′ level assignment. X-ray powder diffraction analysis demonstrated that the compound crystallizes in the rhombohedral lattice of gadolinium(III) formate which possesses the C_{3v} point group [3]. In this paper the assignment of a number of crystal-field levels and the determination of the crystal-field parameters for U^{3+} in uranium(III) formate are presented. On the basis of the obtained wave function we have calculated a new set of $U^{(\lambda)}$ matrix elements which were included in the intensity calculations.

2. Experiment

The absorption spectrum was recorded using a Cary-5 UV–VIS–NIR spectrophotometer in the 4000–23 000 cm^{-1} range. Uranium(III) formate was prepared according to the procedure reported in Ref. [3]. In order to obtain the electronic absorption spectrum, a well-ground mixture of the compound with some chlorinated naphthalene oil (index of refraction 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 Instrument Model CF1204 cryostat. The absorption spectrum was recorded at 4.2 and 300 K.

3. Energy level calculations

The effective operator model, applied for the energy level calculations, is discussed in numerous articles [4–6] and will not be presented here in detail. The eigenvectors and eigenvalues of the crystal-field levels were obtained by simultaneous diagonalization of the combined ‘‘free ion’’ and crystal-field energy matrices. The Hamiltonian includes the following terms:

$$\begin{aligned} H = H_0 &+ \sum_{k=0,2,4,6} F^k(nf,nf) f_k + \zeta_{5f} A_{SO} + \alpha L(L+1) \\ &+ \beta G(G_2) + \gamma G(R_7) \sum_{i=2,3,4,6,7,8} T^i t_i + \sum_{f=2,4,6} P^f p_f \\ &+ \sum_{h=0,2,4} M^h m_h + \sum_{k,q,i} B^k_q C^k_q(i) \qquad (1) \end{aligned}$$

where H_0 is the spherically symmetric one-electron part of the Hamiltonian, $F^k(nf,nf)$ and ζ_{5f} represent the radial parts of the electrostatic and spin–orbit interactions, while f_k and A_{SO} are the angular parts of these interactions, respectively. The parameters α, β and γ are associated with the two-body corrections terms. $G(G_2)$ and $G(R_7)$ are Casimir's operators for the groups G_2 and R_7. L is the total orbital angular momentum. The three-particle configura-

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tion interaction is expressed by $T^i t_i$ ($i = 2,3,4,6,7,8$), where T^i are parameters and t_i are three-particle operators. The electrostatically correlated spin–orbit perturbation is represented by the P^f parameters and those of the spin–spin and spin–other-orbit relativistic corrections by the M_h parameters. The operators associated with these parameters are designated m_h and $p_{f,}$ respectively. The last term of the Hamiltonian represents the crystal-field interactions, where $C_q^k(i)$ is a spherical tensor of rank k and B_q^k are crystal-field parameters. For the C_{3v} symmetry the terms of this Hamiltonian may be written as

$$H_{\mathrm{CF}} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_3^4 (C_{-3}^{(4)} - C_3^{(4)}) + B_0^{(6)} C_0^{(6)} + B_3^6 (C_{-3}^{(6)} - C_3^{(6)}) + B_6^6 (C_{-6}^{(6)} + C_6^{(6)}) \qquad (2)$$

where C_q^k are intraconfigurational unit tensor operators [4].

The experimental energy levels were fitted to the parameters of the phenomenological Hamiltonian described above. The ‘‘free ion’’ parameters obtained by Crosswhite et al. for U^{3+}:$LaCl_3$ [7] were applied as starting points in the fitting procedure. Initially, only the electrostatic (F^k) and the spin–orbit parameter (ζ_{5f}) were determined by taking into account the centers of gravity of the L′S′J′ multiplets. The obtained values were close to those obtained in the prior investigations [1]. In the next step the four crystal-field parameters obtained by Crosswhite et al. [7] were varied in fitting to well-defined crystal-field levels, whereas the remaining two, B_3^4 and B_3^6, were fixed at zero. In the subsequent fit these four crystal-field parameters were fixed at their received values and the remaining two determined. In the final step the first seven ‘‘free ion’’ (see Eq. (1)) and the six crystal-field parameters were treated as adjustable parameters in least-squares adjustments to 49 experimental crystal-field levels. The experimental and calculated energy level values are listed in Table 1, whereas the obtained best set of parameters is given in Table 2.

4. Results and discussion

4.1. Crystal-field effects

The absorption spectra recorded at 4 and 300 K are similar to those reported previously [1] and will not be presented in this paper. One may note, however, some small differences in the number and energies of the observed absorption lines.

The relatively small errors obtained (Table 2) permit us to conclude that the ‘‘free-ion’’ and crystal-field parameters are well determined. The sequence of the ‘‘free ion’’ levels (L′S′J′ multiplets, see Table 1) follows the previously determined order [1], but differs somewhat from that reported by Carnall et al. [5]. One may note also that the reported [1] temperature-dependent satellite lines centered at about 300 cm^{-1} from one of the electronic lines corresponds with the calculated energy (270 and 293 cm^{-1}, see Table 1) of the first two crystal-field components of the ground multiplet. In addition, the correctness of the obtained crystal-field values may be checked by measurement of the magnitude of the total crystal-field strength, expressed by the scalar parameter [8]

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

The calculated N_v value for $U(HCOO)_3$ is 3658 cm^{-1} (largest total splitting value $\Delta = 520$ cm^{-1}) and is as expected for oxygen ligands larger than that determined for U^{3+}:$LaCl_3$ [5] ($N_v = 2144$ cm^{-1}, $\Delta = 451$ cm^{-1}) at a similar site symmetry. These values also correspond with those reported in our previous spectroscopic studies for U^{3+}:Cs_2NaYCl_6 ($N_v = 5816$ cm^{-1}, $\Delta = 626$ cm^{-1}) [9], U^{3+}:Li_2NaYCl_6 ($N_v = 5496$ cm^{-1}, $\Delta = 595$ cm^{-1}) [9] and RbY_2Cl_7:U^{3+} ($N_v = 4354$, $\Delta = 567$ cm^{-1}) [10].

4.2. Intensity considerations

For intensity considerations the Judd–Ofelt theory [11–13] of intra-f–f transitions was applied. On the basis of the obtained wave function a new set of $U^{(\lambda)}$ matrix elements was computed and included in the intensity calculations which followed the procedure described in Refs. [1,2,14]. Since one could not determine the uranium(3+) concentration in the sample it was possible to calculate quantities (T_λ) proportional to the τ_λ parameters only [1]. The first six well-separated absorption bands [1] (Table 3) were used for computation of the parameters. In the 8650–10 240 cm^{-1} and 10 530–12 280 cm^{-1} absorption range it was not possible to separate the band areas of a particular S′L′J′ multiplet. In these cases the whole area was measured and compared with $\Sigma_i \nu_{\mathrm{av}} [\tau_2 \times U(2)_i + \tau_4 \times U(4)_i + \tau_6 \times U(6)_i]$, where ν_{av} corresponds to the average center of gravity of all the i energy levels (S′L′J′ multiplets) included in the band area. In spite of very precise measurements and calculations, no agreement with experiment could be obtained in the fitting procedures with the inclusion of all six band areas [1,2,14]. The calculations show that the main reason for this discrepancy is the too large band area of the $^4I_{13/2}$ multiplet and the somewhat too small band area of $^2H_{9/2} + {}^4F_{5/2}$. Since the exclusion of any one of these band areas from the calculation did not improve the results, in the subsequent fits we combined the two band areas and made a comparison with the appropriate sum of matrix elements. It is interesting to note that only in this case an agreement with the experimental data could be obtained (Table 3).

5. Conclusions

An analysis of the absorption spectrum of $U(HCCO)_3$ at 4 and 300 K is presented. For the first time the analysis

Table 1
Calculated and experimental energy levels for $U(HCOO)_3$

$^{2S+1}L_J$ [a]	Crystal field level[b]	Eigenvectors (%)	Calculated energy (cm^{-1})	Experimental energy (cm^{-1})	$E_{calc.} - E_{exp.}$ (cm^{-1})
$^4I_{9/2}$	Z_1	$85\ ^4I_{9/2} + 12\ ^2H2_{9/2}$	38.75	0	−38.75
	Z_2	$84\ ^4I_{9/2} + 13\ ^2H2_{9/2}$	270	–	
	Z_3	$84\ ^4I_{9/2} + 14\ ^2H2_{9/2}$	292	–	
	Z_4	$81\ ^4I_{9/2} + 14\ ^2H2_{9/92}$	505	–	
	Z_5	$81\ ^4I_{9/2} + 14\ ^2H2_{9/2}$	518	–	
$^4I_{11/2}$	Y_1	$93\ ^4I_{11/2} + 3\ ^2H2_{11/2}$	4415	–	–
	Y_2	$93\ ^4I_{11/2} + 4\ ^2H2_{11/2}$	4472	4485	13
	Y_3	$93\ ^4I_{11/2} + 3\ ^2H2_{11/2}$	4540	4526	−14
	Y_4	$93\ ^4I_{11/2} + 4\ ^2H2_{11/2}$	4616	4597	−19
	Y_5	$93\ ^4I_{11/2} + 4\ ^2H2_{11/2}$	4672	4654	−18
	Y_6	$93\ ^4I_{11/2} + 4\ ^2H2_{11/2}$	4710	4718	7
$^4F_{3/2}$	X_1	$63\ ^4F_{3/2} + 21\ ^2D1_{3/2} + 6\ ^2P_{3/2} + 4\ ^2D2_{3/2} + 2\ ^4S_{3/2}$	7106	7142	36
	X_2	$62\ ^4F_{3/2} + 18\ ^2D1_{3/2} + 5\ ^2P_{3/2} + 4\ ^2D2_{3/2} + 2\ ^4S_{3/2}$	7184	7193	9
$^4I_{13/2}$	W_1	$92\ ^4I_{13/2} + 5\ ^2K_{13/2}$	8049	–	–
	W_2	$91\ ^4I_{13/2} + 6\ ^2K_{13/2}$	8160	8118	−42
	W_3	$90\ ^4I_{13/2} + 5\ ^2K_{13/2}$	8190	–	–
	W_4	$91\ ^4I_{13/2} + 6\ ^2K_{13/2}$	8268	8280	12
	W_5	$91\ ^4I_{13/2} + 5\ ^2K_{13/2}$	8317	8356	39
	W_6	$90\ ^4I_{13/2} + 5\ ^2K_{13/2}$	8418	–	–
	W_7	$91\ ^4I_{13/2} + 6\ ^2K_{13/2}$	8495	–	–
$^2H_{9/2}$	A_1	$26\ ^2H2_{9/2} + 16\ ^2G1_{9/2} + 13\ ^4I_{9/2} + 12\ ^2G2_{9/2} + 12\ ^4F_{9/2}$	9344	–	–
	A_2	$29\ ^2H2_{9/2} + 17\ ^2G1_{9/2} + 13\ ^2G2_{9/2} + 12.1\ ^4I_{9/2} + 12\ ^4F_{9/2}$	9389	9417	28
	A_3	$30\ ^2H2_{9/2} + 17\ ^2G1_{9/2} + 12\ ^2G2_{9/2} + 12\ ^4F_{9/2} + 11\ ^4I_{9/2} + 7\ ^4G_{9/2}$	9497	–	–
	A_4	$31\ ^2H2_{9/2} + 17\ ^2G1_{9/2} + 13\ ^2G2_{9/2} + 11\ ^4I_{9/2} + 10\ ^4F_{9/2} + 7\ ^4G1_{9/2}$	9649	–	–
	A_5	$33\ ^2H2_{9/2} + 18\ ^2G1_{9/2} + 13\ ^2G2_{9/2} + 11\ ^4F_{9/2} + 10\ ^4I_{9/2} + 6\ ^4G1_{9/2}$	9750	9739	−11
$^4F_{5/2}$	B_1	$58\ ^4F_{5/2} + 20\ ^4G_{5/2} + 7\ ^2D1_{5/2}$	9933	–	–
	B_2	$64\ ^4F_{5/2} + 13\ ^4G_{5/2} + 7\ ^2D1_{5/2}$	10 028	–	–
	B_3	$71\ ^4F_{5/2} + 8\ ^2D1_{5/2} + 6\ ^4G_{5/2}$	10 095	10 080	−15
$^4G_{5/2} + {}^4S_{3/2} + {}^4F_{7/2} + {}^4I_{15/2}$	C_1	$59\ ^4G_{5/2} + 7\ ^4F_{5/2} + 6\ ^4F_{7/2} + 5\ ^4S_{3/2}$	10 887	10 892	5
	C_2	$26\ ^4I_{15/2} + 21\ ^4F_{7/2} + 18\ ^4I_{15/2} + 8\ ^4G_{5/2} + 6\ ^2G_{7/2} + 5\ ^2K_{15/2}$	11 049		
	C_3	$32\ ^4S_{3/2} + 25\ ^4I_{15/2} + 12\ ^2P_{3/2} + 11\ ^4G_{5/2} + 7\ ^4F_{3/2}$	11 137	11 119	−18
	C_4	$28\ ^4G_{5/2} + 16\ ^4F_{7/2} + 14\ ^4S_{3/22} + 9\ ^4F_{5/2} + 8\ ^4I_{15/2}$	11 176		
	C_5	$49\ ^4I_{15/2} + 13\ ^4F_{7/2} + 9\ ^4G_{5/2} + 9\ ^4S_{3/2} + 5\ ^2K_{15/2}$	11 283	11 259	−24
	C_6	$51\ ^4I_{15/2} + 11\ ^4G_{5/2} + 9\ ^2K_{15/2} + 8\ ^4F_{7/2} + 5\ ^4G_{7/2}$	11 318		
	C_7	$31\ ^4S_{3/2} + 17\ ^4I_{15/2} + 10\ ^4F_{7/2} + 7\ ^4F_{3/2} + 7\ ^2P_{3/2}$	11 363	11 344	−19
	C_8	$47\ ^4G_{5/2} + 14\ ^4F_{5/2} + 9\ ^4F_{7/2} + 6\ ^4S_{3/2} + 5\ ^4I_{15/2}$	11 510		
	C_9	$62\ ^4I_{15/2} + 12\ ^2K_{15/2} + 11\ ^4G_{5/2}$	11 515	11 497	−18
	C_{10}	$43\ ^4I_{15/2} + 19\ ^4F_{7/2} + 9\ ^2G1_{7/2} + 6\ ^4S_{7/2} + 5\ ^2G_{7/2}$	11 595		
	C_{11}	$40\ ^4I_{15/2} + 18\ ^4G_{5/2} + 10\ ^4F_{7/2} + 7\ ^2K_{15/2} + 5\ ^4F_{3/2} + 5\ ^4I_{15/2}$	11 617	11 603	−14
	C_{12}	$36\ ^4I_{15/2} + 31\ ^4F_{7/2} + 10\ ^2G1_{7/2} + 7\ ^2K_{15/2} + 7\ ^2G2_{7/2}$	11 621		
	C_{13}	$35\ ^4I_{15/2} + 11\ ^4F_{7/2} + 11\ ^4G_{5/2} + 6\ ^2G1_{7/2} + 6\ ^2K_{15/2} + 6\ ^4S_{3/2}$	11 765		
	C_{14}	$63\ ^4I_{15/2} + 9\ ^4F_{7/2} + 9\ ^2K_{15/2}$	11 791	11 788	−3
	C_{15}	$37\ ^4F_{7/2} + 18\ ^2G1_{7/2} + 15\ ^4I_{15/2} + 11\ ^2G2_{7/2} + 6\ ^4G_{7/2}$	11 848	11 852	4
	C_{16}	$75\ ^4I_{15/2} + 14\ ^2K_{15/2}$	11 986	11 980	−6
	C_{14}	$76\ ^4I_{15/2} + 15\ ^2K_{15/2}$	12 082		
$^4G_{7/2}$	D_1	$64\ ^4G_{7/2} + 19\ ^4F_{7/2}$	13 214	13 269	55
	D_2	$66\ ^4G_{7/2} + 18\ ^4F_{7/2}$	13 339	13 348	9
	D_3	$66\ ^4G_{7/2} + 25\ ^4F_{7/2}$	13 346	13 402	56
	D_4	$65\ ^4G_{7/2} + 23\ ^4F_{7/2}$	13 587	13 635	48
$^4F_{9/2}$	E_1	$57\ ^4F_{9/2} + 18\ ^2H2_{9/2}$	14 520		
	E_2	$56\ ^4F_{9/2} + 20\ ^2H2_{9/2} + 5\ ^4G_{9/2} + 5\ ^2G1_{9/2}$	14 572	14 582	10
	E_3	$58\ ^4F_{9/2} + 23\ ^2H2_{9/2}$	14 614	14 643	29
	E_4	$55\ ^4F_{9/2} + 25\ ^2H2_{9/2}$	14 683		
	E_5	$59\ ^4F_{9/2} + 21\ ^2H2_{9/2} + 6\ ^2G1_{9/2}$	14 814	14 786	−28

Table 1. Continued

$^{2S+1}L_J$[a]	Crystal field level[b]	Eigenvectors (%)	Calculated energy (cm^{-1})	Experimental energy (cm^{-1})	$E_{\mathrm{calc.}} - E_{\mathrm{exp.}}$ (cm^{-1})
$^{2}H2_{9/2} +$ $^{4}K_{13/2} +$ $^{4}D_{3/2}$	F_1	$46\ {}^{2}H2_{11/2} + 22\ {}^{4}G_{11/2} + 13\ {}^{2}K_{13/2} + 5\ {}^{2}I_{11/2}$	15 223		
	F_2	$54\ {}^{2}H2_{11/2} + 24\ {}^{4}G_{11/2} + 5\ {}^{2}K_{13/2}$	15 317	15 302	−14
	F_3	$46\ {}^{2}H2_{11/2} + 22\ {}^{4}G_{11/2} + 5\ {}^{2}K_{13/2}$	15 325	15 347	22
	F_4	$55\ {}^{2}H2_{11/2} + 22\ {}^{4}G_{11/2}$	15 404		
	F_5	$60\ {}^{2}K_{13/2} + 14\ {}^{2}H2_{11/2} + 6\ {}^{4}I_{13/2}$	15 445		
	F_6	$44\ {}^{2}H2_{11/2} + 17\ {}^{4}G_{11/2} + 16\ {}^{2}K_{13/2} + 6\ {}^{4}F_{9/2}$	15 532	15 578	46
	F_7	$33\ {}^{2}H2_{11/2} + 31\ {}^{2}K_{13/2} + 14\ {}^{4}G_{11/2}$	15 610	15 637	27
	F_8	$35\ {}^{2}K_{13/2} + 21\ {}^{2}H2_{11/2} + 13\ {}^{4}G_{11/2}$	15 669		
	F_9	$63\ {}^{2}K_{13/2} + 5\ {}^{4}I_{13/2}$	15 773		
	F_{10}	$32\ {}^{2}K_{13/2} + 11\ {}^{4}D_{3/2} + 10\ {}^{2}H2_{11/2} + 8\ {}^{4}S_{3/2} + 6\ {}^{2}D2_{3/2}$	15 896		
	F_{11}	$63\ {}^{2}K_{13/2} + 5\ {}^{2}H2_{11/2} + 5\ {}^{4}I_{13/2}$	15 899		
	F_{12}	$21\ {}^{4}D_{3/2} + 13\ {}^{2}D2_{3/2} + 13\ {}^{4}S_{3/2} + 10\ {}^{4}F_{3/2} + 10\ {}^{2}K_{13/2} + 9\ {}^{2}H2_{11/2} + 9\ {}^{2}D1_{3/2}$	15 943		
	F_{13}	$70\ {}^{2}K_{13/2} + 9\ {}^{2}I_{13/2}$	16 038	16 024	−14
	F_{14}	$71\ {}^{2}K_{13/2} + 4\ {}^{2}I_{13/2} + 4\ {}^{2}G1_{7/2}$	16 212	16 240	28
	F_{15}	$61\ {}^{2}K_{13/2} + 7\ {}^{4}I_{13/2} + 5\ {}^{4}G_{9/2}$	16 292		
$^{2}P_{1/2}$	G_1	$33\ {}^{4}D_{1/2} + 29\ {}^{2}P_{1/2} + 14\ {}^{2}K_{13/2}$	16 579	16 520	59
$^{4}G_{9/2} +$ $^{2}G_{7/2}$	H_1	$60\ {}^{4}G_{9/2} + 5\ {}^{2}H1_{9/2}$	16 741		
	H_2	$63\ {}^{4}G_{9/2} + 5\ {}^{2}H2_{9/2} + 5\ {}^{2}G1_{7/2}$	16 760		
	H_3	$31\ {}^{2}G1_{7/2} + 20\ {}^{2}G2_{7/2} + 18\ {}^{4}F_{7/2} + 14\ {}^{4}G_{7/2} + 11\ {}^{2}K_{13/2}$	16 779	16 799	20
	H_4	$53\ {}^{4}G_{9/2} + 7\ {}^{2}H2_{9/2} + 6\ {}^{2}H1_{9/2}$	16 843		
	H_5	$56\ {}^{4}G_{9/2} + 9\ {}^{2}G1_{7/2} + 7\ {}^{2}G2_{7/2} + 6\ {}^{2}H2_{9/2} + 5\ {}^{4}F_{7/2}$	16 860	16 862	2
	H_6	$22\ {}^{2}G1_{7/2} + 17\ {}^{4}G_{9/2} + 14\ {}^{2}G2_{7/2} + 14\ {}^{4}F_{7/2} + 9\ {}^{2}K_{13/2} + 8\ {}^{4}G_{7/2}$	16 930		
	H_7	$67\ {}^{4}G_{9/2} + 7\ {}^{2}K_{13/2} + 5\ {}^{2}H1_{9/2}$	17 018		
	H_8	$27\ {}^{2}G1_{7/2} + 18\ {}^{4}F_{7/2} + 16\ {}^{2}G2_{7/2} + 12\ {}^{4}G_{7/2} + 11\ {}^{4}G_{9/2}$	17 168		
	H_9	$23\ {}^{2}G1_{7/2} + 25\ {}^{4}G_{9/2} + 17\ {}^{4}F_{7/2} + 14\ {}^{2}G2_{7/2} + 11\ {}^{4}G_{7/2}$	17 305		
$^{4}D_{5/2}$	I_1	$45\ {}^{4}D_{5/2} + 25\ {}^{2}D2_{5/2} + 9\ {}^{4}G_{9/2}$	17 433	17 458	25
	I_2	$41\ {}^{4}D_{5/2} + 24\ {}^{2}D2_{5/2} + 11\ {}^{4}G_{9/2}$	17 644	17 610	−34
	I_3	$46\ {}^{4}D_{5/2} + 29\ {}^{2}D2_{5/2}$	17 806	17 760	−46
$^{2}K_{15/2}$	K_1	$42\ {}^{2}L_{15/2} + 34\ {}^{2}K_{15/2} + 14\ {}^{4}I_{15/2}$	18 027	17 992	−35
	K_2	$39\ {}^{2}L_{15/2} + 39\ {}^{2}K_{15/2} + 13\ {}^{4}I_{15/2}$	18 115		
	K_3	$42\ {}^{2}K_{15/2} + 41\ {}^{2}L_{15/2} + 13\ {}^{4}I_{15/2}$	18 367	18 402	35
	K_4	$42\ {}^{2}K_{15/2} + 41\ {}^{2}L_{15/2} + 13\ {}^{4}I_{15/2}$	18 553		
	K_5	$40\ {}^{2}K_{15/2} + 38\ {}^{2}L_{15/2} + 13\ {}^{4}I_{15/2}$	18 672		
	K_6	$52\ {}^{2}K_{15/2} + 39\ {}^{2}L_{15/2} + 13\ {}^{4}I_{15/2}$	18 874		
	K_7	$37\ {}^{2}K_{15/2} + 35\ {}^{2}L_{15/2} + 11\ {}^{4}I_{15/2}$			
	K_8	$42\ {}^{2}K_{15/2} + 39\ {}^{2}L_{15/2} + 12\ {}^{4}I_{15/2}$	18 918		
$^{4}D_{3/2}$	L_1	$33\ {}^{4}D_{3/2} + 20\ {}^{2}D1_{3/2} + 14\ {}^{2}P_{3/2} + 9\ {}^{4}S_{3/2} + 9\ {}^{2}D2_{3/2}$	19 094	19 060	−34
	L_2	$31\ {}^{4}D_{3/2} + 18\ {}^{2}D1_{3/2} + 13\ {}^{2}P_{3/2} + 7\ {}^{2}D2_{3/2} + 7\ {}^{2}L_{15/2} + 6\ {}^{2}\mathrm{K}_{15/2} + 6\ {}^{4}\mathrm{S}_{3/2}$	19 146		
$^{2}H1_{11/2}$	M_1	$48\ {}^{2}H1_{11/2} + 19\ {}^{4}G_{11/2} + 14\ {}^{2}I_{11/2} + 9\ {}^{2}H2_{11/2}$	19 499		
	M_2	$39\ {}^{2}H1_{11/2} + 26\ {}^{4}G_{11/2} + 9\ {}^{2}H2_{11/2} + 8\ {}^{2}D1_{5/2} + 7\ {}^{2}I_{11/2}$	19 638		
	M_3	$44\ {}^{2}H1_{11/2} + 26\ {}^{4}G_{11/2} + 8\ {}^{2}H2_{11/2} + 7\ {}^{2}I_{11/2}$	19 647		
	M_4	$41\ {}^{2}H1_{11/2} + 28\ {}^{4}G_{11/2} + 8\ {}^{2}H2_{11/2} + 8\ {}^{2}D1_{5/2} + 7\ {}^{2}I_{11/2}$	19 688		
	M_5	$46\ {}^{2}H1_{11/2} + 31\ {}^{4}G_{11/2} + 8\ {}^{2}I_{11/2} + 7\ {}^{2}H2_{11/2}$	19 753	19 744	−9
	M_6	$45\ {}^{2}H1_{11/2} + 32\ {}^{4}G_{11/2} + 8\ {}^{2}H2_{11/2} + 7\ {}^{2}I_{11/2}$	19 818		
$^{2}D1_{5/2} +$ $^{2}I_{11/2} +$ $^{4}D_{1/2}$	N_1	$64\ {}^{2}D1_{5/2} + 7\ {}^{2}H1_{11/2} + 7\ {}^{4}G_{11/2} + 6\ {}^{2}F_{5/2} + 6\ {}^{4}D_{5/2}$	20 141	20 145	4
	N_2	$70\ {}^{2}D1_{5/2} + 8\ {}^{4}F_{5/2} + 5\ {}^{4}D_{5/2} + 5\ {}^{4}G_{11/2}$	20 319		
	N_3	$25\ {}^{2}I_{11/2} + 14\ {}^{2}G1_{9/2} + 12\ {}^{4}G_{11/2} + 11\ {}^{2}H2_{9/2} + 9\ {}^{2}G2_{9/2} + 9\ {}^{4}F_{9/2}$	21 090	21 082	−8
	N_4	$47\ {}^{2}I_{11/2} + 35\ {}^{4}G_{11/2} + 7\ {}^{2}H2_{11/2}$	21 131		
	N_5	$24\ {}^{2}I_{11/2} + 15\ {}^{4}G_{11/2} + 14\ {}^{2}G1_{9/2} + 11\ {}^{2}H2_{9/2} + 10\ {}^{2}H1_{9/2} + 10\ {}^{4}F_{9/2}$	21 152		
	N_6	$32\ {}^{4}D_{1/2} + 32\ {}^{2}P_{1/2} + 7\ {}^{2}I_{11/2}$	21 349	21 325	−24
	(. . .)				

[a] Nominal quantum numbers for the atomic state associated with the group (major component of eigenvector).

[b] The symbols follow partially the nomenclature of Ref. [7].

Table 2
Free ion and crystal-field parameters for U(HCOO)$_3$

Parameter	Parameter value[a] (cm^{-1})	Parameter	Parameter value[a] (cm^{-1})
E_{av}	19 488 (38)	M^0	[0.67]
F^2	39 746 (133)	M^2	[0.37]
F^4	32 457 (23)	M^4	[0.26]
F^6	23 232 (242)	P^2	[1216.00]
ζ	1612 (11)	P^4	[608.0]
α	30 (6)	P^6	[122.0]
β	−951 (40)	B^2_0	1360 (43)
γ	999 (129)	B^4_0	−1345 (70)
T^2	[293.0]	B^6_0	1059 (67)
T^3	[50.0]	B^4_3	−1443 (68)
T^4	[183.0]	B^6_3	−553 (70)
T^6	[−183.0]	B^6_6	932 (72)
T^7	[407.0]	n[b]	49
T^8	[300.0]	σ[c]	33

[a] Numbers in parentheses indicate errors in determination of the parameter value. Those in square brackets were kept constant in the fitting procedure.

[b] Number of levels included in the fitting procedure.

[c] Deviation $\sigma = \Sigma[(\Delta_i)^2/(n-p)]^{1/2}$, 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.

enabled the determination of the crystal-field parameters and the assignment of the crystal-field levels in a relatively large spectral range. Good agreement with theory was obtained in the intensity analysis of the 5f^3→5f^3 transitions only if some of the experimental band areas were combined.

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Table 3
Intensity correlation

Spectral region[a] (cm^{-1})	Center of band energy (cm^{-1})	Level assignment[b] L′S′J′	Relative band area	
			Obs.	Calc.[c]
4150–5000	4433	$^4I_{11/2}$	8.3	8.21
7000−7350	7191	$^4F_{3/2}$	0.97	0.54
7400–10 300	8937	$^4I_{13/2}$ $^2H_{9/2}$ $^4F_{5/2}$	27.6	27.82
10 300–12 300	11 014	$^4S_{3/2}$ $^4G_{5/2}$ $^4I_{15/2}$ $^4F_{7/2}$	51.0	50.94
12 500–14 000	13 260	$^4G_{7/2}$	6.4	6.16

[a] Range encompassing observed band(s).

[b] Major component of eigenvector.

[c] In the fitting process the following values proportional to the τ_λ parameters were obtained: $T_2 = 0.03783(0.0009)$, $T_4 = 0.0048293(0.0011)$, $T_6 = 0.016010(0.0005)$; numbers in parentheses indicate errors in determination of the parameter value. Deviation $\sigma = \Sigma[(\Delta_i)^2/(n-p)]^{1/2} = 0.39$, where Δ_i is the difference between the observed and calculated absorption band areas, n is the number of fitted areas and p is the number of T_λ parameters.