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Absorption Spectra of Tetrahalodioxouranium(IV) Complexes at 4.2 K. II. Di(tetramethylammonium)uranyltetrabromide

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Single crystal polarized spectra of $(Me_4N)_2UO_2Br_4$ have been recorded at 4.2 K. Eleven electronic origins have been detected. The transition mechanism, the symmetry of the excited states and the vibrational structure are also assigned.

Introduction

The peculiar nature of the uranyl group gives a noticeable interest to studies of its electronic structure [1, 2]. Several attempts have been made to point out this structure by analyzing the electronic spectra of uranyl compounds; only recently studies of single crystal spectra at low temperature have been undertaken, owing to the more detailed data obtained with this method [3].

The main conclusion of these studies is that the spectral behaviour of the uranyl complexes is essentially due to electronic transitions located in the uranyl moiety. The intensity and the energy of transitions are slightly influenced by the coordinated ligands.

The polarized absorption spectra at 4.2 K of $Cs_2UO_2Cl_4$ single crystals lead to identify 12 electronic origins, all either of magnetic dipole or of electric quadrupole type [3].

Following a previous note, we have undertaken spectral studies at 4.2 K of compounds having general formula $(R_4N)_2UO_2X_4$ (where R = alkyl group; X = Cl, Br), in order to clarify the spectral behaviour of the uranyl group and the influence of the coordinated ligands. In this paper we report the spectra at 4.2 K of $(Me_4N)_2UO_2Br_4$, whose crystal structure has been determined previously by us [4].

Experimental

A solution of $(Me_4N)_2UO_2Br_4$ was prepared by the standard methods [2, 5, 6]. The crystals were grown by slow evaporation at room temperature. The orientation of the crystals was checked by means of Weissemberg photographs.

Single crystal spectra were measured as described elsewhere [2], with incident light orthogonal to the *c* crystallographic axis and the electric vector polarized respectively parallel and perpendicular to the *c* axis.

Results and Discussion

The polarized electronic spectra of single crystals at 4.2 K are reported in Fig. 1. The bands are strongly polarized with a clear vibrational fine structure. The observed frequencies are listed in Table I with our assignments of the vibronic progressions.

In the low energy region the spectra present low intensity bands. In the medium and high energy regions the bands have higher intensity and a more complicate pattern.

The crystal structure of $(Me_4N)_2UO_2Br_4$ is a $P4_2/$ mnm space group with two molecules per unit cell [7].

The relative positions of the UO_2 groups with respect to the crystallographic axes are shown in Fig. 2. Clearly there are two UO_2 groups per unit cell. Both are parallel to the *ab* plane and orthogonal to the *c* axis. Moreover one group is orthogonal to the other one. The site symmetry is D_{4h}.

TABLE I. Observed Frequencies (cm^{-1}) and Assignments.

$/\!/c$	$\perp c$		$/\!/c$	$\perp c$	
19.964 $\times 10^{-3}$	*19.965* $\times 10^{-3}$	I_1	22.133 $\times 10^{-3}$	22.143 $\times 10^{-3}$	$I_2 + 3\nu_3 + 2\nu_1$
19.989		I_2	22.190	22.185	$I_7 + \nu_1 + \nu_4$
	20.026	I_3		22.196	$I_3 + 3\nu_3 + 2\nu_1$
20.052	20.049	$I_1 + \nu_9$	*22.329*	*22.331*	I_9
20.214	*20.213*	I_4	22.363	22.363	$I_7 + \nu_1 + 2\nu_4$
20.236	20.236	$I_2 + \nu_3$	22.381		$I_2 + \nu_3 + 3\nu_1$
	20.279	$I_3 + \nu_3$		*22.418*	I_{10}
20.283		$I_2 + \nu_4 + \nu_8$		22.436	$I_3 + \nu_3 + 3\nu_1$
20.313	20.313	$I_4 + \nu_7$	22.481	22.484	$I_7 + \nu_1 + 2\nu_4 + \nu_7$
20.346	20.343	$I_1 + \nu_9 + \nu_4 + \nu_7$		22.504	$I_5 + \nu_3 + 2\nu_1 + 2\nu_4$
20.362	20.360	$I_1 + 2\nu_4$		22.521	$I_6 + \nu_3 + 2\nu_1 + 2\nu_4$
20.374	20.375	$I_4 + \nu_5$	22.543	22.542	$I_4 + 3\nu_1 + \nu_5$
	20.436	I_5		22.566	$I_8 + \nu_3 + \nu_1$
20.449	20.449	$I_1 + 2\nu_4 + \nu_7$	22.591	22.594	$I_1 + 2\nu_4 + \nu_7 + 3\nu_1$
	20.464	I_6	22.617	22.615	$I_7 + \nu_1 + 2\nu_4 + \nu_7 + \nu_5$
20.525	20.525	$I_1 + 2\nu_4 + \nu_5$	22.662	22.661	$I_1 + 2\nu_4 + \nu_5 + 3\nu_1$
	20.624	$I_6 + \nu_6$	22.694	22.694	$I_7 + 2\nu_1$
20.682		$I_1 + \nu_1$	22.717	22.718	$I_4 + 3\nu_1 + \nu_4 + \nu_5$
	20.690	$I_5 + \nu_3$	22.744	22.753	$I_7 + \nu_1 + 2\nu_4 + 2\nu_7 + \nu_5$
20.707		$I_2 + \nu_1$	22.815	22.816	$I_7 + 2\nu_1 + \nu_7$
	20.709	$I_6 + \nu_3$	22.852	22.845	$I_2 + 3\nu_3 + 3\nu_1$
20.735	20.733	$I_2 + 3\nu_3$		22.888	$I_3 + 3\nu_3 + 3\nu_1$
20.769		$I_1 + \nu_1 + \nu_9$	22.915	22.911	$I_7 + 2\nu_1 + \nu_4$
	20.786	$I_3 + 3\nu_3$	23.052	23.062	$I_9 + \nu_1$
20.930	20.932	$I_4 + \nu_1$	23.087	23.088	$I_7 + 2\nu_1 + 2\nu_4$
20.953	20.952	$I_2 + \nu_3 + \nu_1$		23.142	$I_{10} + \nu_1$
	20.994	$I_3 + \nu_3 + \nu_1$	23.195	23.191	$I_7 + 2\nu_1 + 2\nu_4 + \nu_7$
21.028	21.024	$I_1 + \nu_9 + \nu_5 + \nu_7 + \nu_1$		23.209	$I_5 + \nu_3 + 3\nu_1 + 2\nu_4$
21.063	21.061	$I_1 + \nu_9 + \nu_4 + \nu_7 + \nu_1$		23.224	$I_6 + \nu_3 + 3\nu_1 + 2\nu_4$
21.076	21.075	$I_1 + 2\nu_4 + \nu_1$	*23.232*	*23.232*	I_{11}
21.100	21.095	$I_4 + \nu_1 + \nu_5$	23.249	23.249	$I_4 + 4\nu_1 + \nu_5$
21.167	21.166	$I_1 + 2\nu_4 + \nu_7 + \nu_1$		23.277	$I_8 + \nu_3 + 2\nu_1$
	21.202	$I_6 + 3\nu_3$	23.307	23.316	$I_1 + 2\nu_4 + \nu_7 + 4\nu_1$
21.243	21.243	$I_1 + 2\nu_4 + \nu_5 + \nu_1$	23.340	23.333	$I_7 + 2\nu_1 + 2\nu_4 + \nu_7 + \nu_5$
21.281	*21.282*	I_7	23.380	23.380	$I_1 + 2\nu_4 + \nu_5 + 4\nu_1$
	21.342	$I_6 + \nu_6 + \nu_1$	23.466	23.474	$I_7 + 2\nu_1 + 2\nu_4 + 2\nu_7 + \nu_5$
21.395		$I_1 + 2\nu_1$	23.537	23.534	$I_7 + 3\nu_1 + \nu_7$
	21.402	$I_5 + \nu_3 + \nu_1$	23.565	23.548	$I_2 + 3\nu_3 + 4\nu_1$
	21.416	$I_6 + \nu_3 + \nu_1$	23.602	23.595	$I_{11} + 2\nu_4$
21.440	21.438	$I_2 + 3\nu_3 + \nu_1$	23.633	23.628	$I_7 + 3\nu_1 + \nu_4$
21.482		$I_1 + 2\nu_1 + \nu_9$	23.763	27.755	$I_9 + 2\nu_1$
	21.496	$I_3 + 3\nu_3 + \nu_1$	23.791	23.791	$I_{11} + 3\nu_4$
21.645	21.646	$I_4 + 2\nu_1$	23.809	23.809	$I_7 + 3\nu_1 + 2\nu_4$
21.666	21.665	$I_2 + \nu_3 + 2\nu_1$		23.853	$I_{10} + 2\nu_1$
	21.710	$I_3 + \nu_3 + 2\nu_1$	23.890	23.890	$I_7 + 3\nu_1 + 2\nu_4 + \nu_7$
21.737		$I_1 + \nu_9 + \nu_5 + \nu_7 + 2\nu_1$	23.918	23.918	$I_{11} + \nu_1$
	21.754	$I_8 + \nu_6$		23.950	$I_6 + \nu_3 + 4\nu_1 + 2\nu_4$
21.768		$I_1 + \nu_9 + \nu_4 + \nu_7 + 2\nu_1$	23.970	23.975	$I_4 + 5\nu_1 + \nu_5$
21.822	21.822	$I_4 + 2\nu_1 + \nu_5$	24.025	24.032	$I_1 + 2\nu_4 + \nu_7 + 5\nu_1$
	21.843	$I_8 + \nu_3$	24.097	24.091	$I_1 + 2\nu_4 + \nu_5 + 5\nu_1$
21.877	21.882	$I_1 + 2\nu_4 + \nu_7 + 2\nu_1$	24.121	24.121	$I_{11} + \nu_1 + \nu_4$
	21.914	$I_6 + 3\nu_3 + \nu_1$	24.184	24.184	$I_7 + 3\nu_1 + 2\nu_4 + 2\nu_7 + \nu_5$
21.955	21.955	$I_1 + 2\nu_4 + \nu_5 + 2\nu_1$	24.252	24.252	$I_7 + 4\nu_1 + \nu_7$
21.990	21.992	$I_7 + \nu_1$	24.286	24.286	$I_{11} + \nu_1 + \nu_4 + \nu_5$
22.008		$I_4 + 2\nu_1 + \nu_4 + \nu_5$	24.324	24.324	$I_{11} + \nu_1 + 2\nu_4$
	22.117	$I_5 + \nu_3 + 2\nu_1$	24.358	24.358	$I_7 + 4\nu_1 + \nu_4$
	22.127	$I_6 + \nu_3 + 2\nu_1$			

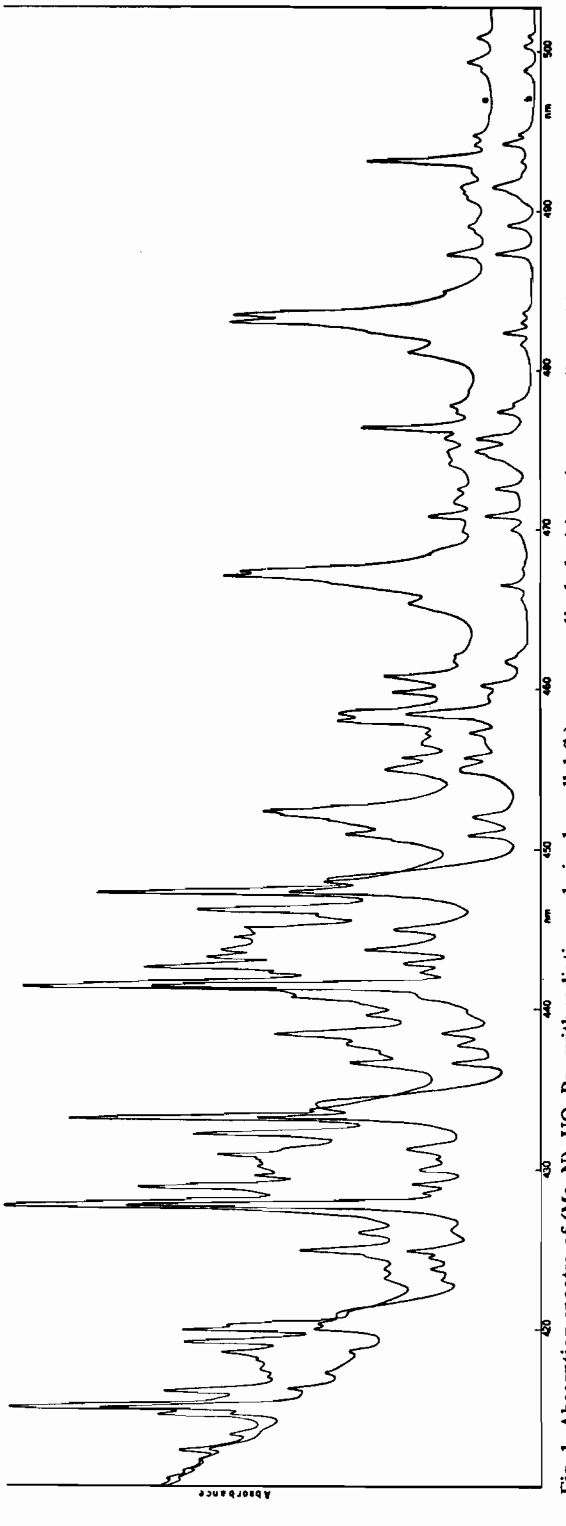

Fig. 1. Absorption spectra of $(Me_4N)_2UO_2Br_4$ with radiation polarized parallel (b) or perpendicularly (a) to the *c* crystallographic axis.

The electronic structure of UO_2^{2+} ion is a closed shell system [1]. This is substantiated experimentally by the temperature-independent paramagnetism and

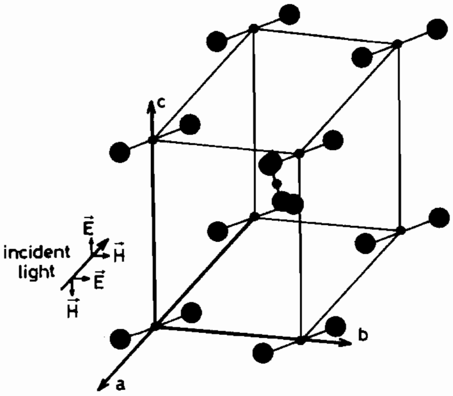

Fig. 2. Relative positions of UO_2 groups; $\vec{E}$, and $\vec{H}$ orientation.

leads to an assignment of the ground state as ${}^1A_{1g}$ in D_{4h} symmetry. In this symmetry the operators of the components of the electric dipole moment (μ) and magnetic dipole moment (m) transform like E (μ_x, μ_y), $A_{2u}(\mu_z)$ and E_g (m_x, m_y), A_{2g} (m_z) respectively.

Therefore if the spin–orbit coupling is neglected, the electronic transitions allowed by these mechanisms are the following:

$${}^1A_{1g} \dashrightarrow {}^1E_u$$

$${}^1A_{1g} \dashrightarrow {}^1A_{2u}$$

$${}^1A_{1g} \dashrightarrow {}^1E_g$$

$${}^1A_{1g} \dashrightarrow {}^1A_{2g}$$

Taking into account the spin–orbit coupling in D^*_{4h}

$$\Gamma_1^+ \dashrightarrow \Gamma_5^-$$

$$\Gamma_1^+ \dashrightarrow \Gamma_2^-$$

$$\Gamma_1^+ \dashrightarrow \Gamma_5^+$$

$$\Gamma_1^+ \dashrightarrow \Gamma_2^+$$

Moreover, electronic transitions, forbidden by electric dipole mechanism, can be allowed by vibration of appropriate symmetry via vibronic coupling.

Therefore we have measured the Raman and i.r. spectra and we have obtained the following vibrational frequencies:

TABLE II. Spectral Origins.

Origin	Excited State Symmetry	Wavenumber (cm^{-1}) $\vec{E}\parallel c$	$\vec{E}\perp c$	Transition Moment	Intensity Ratio
I	E_g	19.964×10^{-3}	19.965×10^{-3}	m (Q)	0.6, 1.5
II	A_{2g} or B_{2g}	19.989		m or Q	–
III	E_g		20.026	μ	
IV	E_g	20.214	20.213	m (Q)	0.6
V	E_g		20.436	μ	
VI	E_g		20.464	μ	
VII	E_g	21.281	21.282	m (Q)	0.6
VIII + ν_6	E_g		21.754	μ	
IX	E_u	22.329	22.331	μ	1.3
X	A_{2u}		22.418	μ	
XI	E_g	23.232	23.232	m (Q)	0.7

Mode	*Symmetry in D_{4h}*	*Type of vibration*	*cm^{-1}*
ν_1	a_{1g}	O–U–O sym. str.	833
ν_2	a_{2u}	O–U–O asym. str.	918
ν_3	e_u	O–U–O bend	254
ν_4	a_{1g}	U–Br sym. str.	195
ν_5	b_{1g}	U–Br str.	164
ν_6	e_u	U–Br str.	167
ν_7	b_{2g}	U–Br in plane bend	94
ν_8	e_u	U–Br in plane bend	98
ν_9	a_{2u}	U–Br out of plane bend	86
ν_{10}	b_{2u}	U–Br out of plane bend	–
ν_{11}	e_g	O–U–O rock	205

On the basis of the orientation of the uranyl groups in the unit cell it follows that:

1) with incident light orthogonal to the *c* axis and the electric vector parallel to *c*, $\vec{E}\parallel c$, the magnetic vector is necessarily orthogonal to *c*, $\vec{H}_{\perp}c$ and therefore

– $\vec{E}$ is orthogonal to both the UO_2 groups,

– $\vec{H}$ has complementary projections on the two UO_2 groups;

2) with incident light orthogonal to the *c* axis and $\vec{E}\perp c$, it must be $\vec{H}\parallel c$ and therefore

– $\vec{H}$ is orthogonal to both the UO_2 groups,

– $\vec{E}$ has complementary projections on the two UO_2 groups.

The consequences are:

a) If in case 2) there are magnetic dipole transitions, they must be present also in case 1) but with half intensity. It must be pointed out that in case 1) we can have magnetic dipole transitions forbidden in case 2);

b) If in case 1) there are electric dipole transitions, they must be present also in case 2) with half intensity. Again it must be pointed out that in case 2) we can have electric dipole transitions forbidden in case 1);

c) With incident light orthogonal to *c* axis, transitions allowed by an electric quadrupole mechanism behave as those allowed by a magnetic dipole mechanism, *i.e.* if there are electric quadrupole transitions in case 2), they must be present also in case 1) but with half intensity.

On the basis of the features of the spectrum we have identified 11 origins as reported in Table II. Moreover taking into account the polarization properties, the vibrational structure and the relative intensities we have assigned the transition mechanism and the symmetry of the excited state.

The origins IV, VII, XI, whose progressions are reported in Table I, are present in both polarizations. The intensity ratios, calculated for all the origins and along the progressions, are very close to the theoretical value which is 0.5. On the basis of the previous considerations, these bands are identified as bands due to a magnetic dipole or electric quadrupole mechanism, and are assigned to excited states of Eg symmetry.

The origins III, V, VI and VIII are present only in the polarization $\vec{E}\perp c$. The vibrational structures can be completely assigned by assuming for each peak an odd quantum number of $e_u(\nu_3, \nu_6)$ vibrational modes (Table I). The only other modes observed in the progressions are a_{1g} modes (ν_1, ν_4). This suggests that these transitions are forbidden according to an electric dipole mechanism, become allowed because of a vibronic coupling and finally the excited state belongs to the E_g symmetry.

The origin X is present only in the polarization $\vec{E}\perp c$. In this case only one mode, $\nu_1(a_{1g})$, is observed (Table I). This would suggest that the transition is allowed by an electric dipole mechanism and the excited state is of A_{2u} symmetry.

The origin IX is present in both polarizations with greater intensity for $\vec{E}/\!/c$. The only mode observed in the progression is $\nu_1(a_{1g})$ (Table I). This would suggest that the transition is allowed by an electric dipole mechanism and the excited state is of E_u symmetry.

The origin II is present only when $\vec{E}/\!/c$. However progressions connected with this origin are present in both polarizations according to $II + n_1\nu_1 + n_3\nu_3$ with $n_1 = 1,2,3,4$ and $n_3 = 1,3$. This fact seems to suggest that the transition is allowed by both a magnetic dipole (or electric quadrupole) and a vibronic-coupling mechanism. The excited state would be A_{2g} (B_{2g} in the case of an electric quadrupole mechanism). Unfortunately there is a remarkable overlapping of the peaks with those of the other progressions and it is impossible to make any consideration based on the relative intensity values.

The origin I is present in both polarizations. Connected with this origin there are two progressions. One is $I + n_1\nu_1 + 2\nu_4 + \nu_5$ and $I + n_1\nu_1 + 2\nu_4 + \nu_7$ with $n_1 = 0,1,2,3,4,5$.

With an intensity ratio $I/\!/c/I\perp c \cong 0.6$ this behaviour agrees with an excited state of symmetry E_g and a magnetic dipole or electric quadrupole transition mechanism. The other progression is $I + n_1\nu_1 + \nu_9 + \nu_7 + \nu_4$ and $I + n_1\nu_1 + \nu_9 + \nu_7 + \nu_5$ with $n_1 = 0,1,2$ and the intensity ratio is $I/\!/c/I\perp c \cong 1.5$. This progression can be explained by assuming a vibronic mechanism.

Conclusions

On the basis of the orientation of the UO_2 groups in the unit cell only few and well defined polarization behaviours can be expected which depend on the transition mechanism and on the symmetry of the excited state.

From the spectral analysis of the $(Me_4N)_2UO_2Br_4$ compound we have that the absorption spectrum can be interpreted as several overlapping progressions and that each of them belongs to one of the expected polarization behaviours. In this way we are able to give each progression an assignment for what concerns the symmetry of the excited state and of the vibrational structure.

These results seem to support further our original project to investigate systematically the absorption spectra of the series $(R_4N)_2UO_2X_4$ with R = CH_3, C_2H_5, C_3H_7, C_4H_9 and X = Cl, Br. In fact, although the spectra should be quite different because of the different lattice structure and different orientation of the UO_2 groups in the unit cell, we might expect that such spectra would be interpreted on the basis of a rather limited and common set of transitions.

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