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Luminescence and Vibrational Spectra of the $UO_2Br_4^{2-}$ Ion

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The infrared, Raman, and luminescence spectra of single crystals of $Cs_2UO_2Br_4$ have been measured at low temperatures. Ten of the expected eleven internal anion modes have been identified. In the infrared spectrum ν_2, the O–U–O antisymmetric stretch, shows a unit cell group splitting which is not present in the luminescence spectra, and the reason for this is discussed. The well-resolved luminescence spectrum of Cs_2ZrBr_6:$UO_2Br_4^{2-}$ has also been measured and analyzed.

Introduction

Within the last few years, Denning[1–4] has developed a description of the electronic structure of the uranyl ion which accounts for most of the chemical and spectroscopic properties of this ion. The model was derived from a thorough investigation of the electronic absorption spectra of $Cs_2UO_2Cl_4$ and $CsUO_2(NO_3)_3$. Recently we have shown that this model also accounts for the main features of the luminescence spectra of a series of compounds containing the $UO_2Cl_4^{2-}$ and $UO_2F_5^{3-}$ ions.[5–9]

There is current interest in the energy-transfer and photochemical behaviour of the uranyl ion.[10–12] We have therefore undertaken a study of the luminescence and absorption spectra of crystals containing the uranyl ion in a range of coordination geometries and with a variety of in-plane ligands in order to further test the Denning model and to provide some experimental data on the range of phenomena which is available for exploitation. In this paper we report the luminescence properties of the UO_2^{2+} ion in the stoichiometric compound $Cs_2UO_2Br_4$ and as an impurity ion in the cubic crystal Cs_2ZrBr_6. So that the luminescence spectra could be interpreted, a thorough analysis of the vibrational properties of this ion has been performed.

Some features in the luminescence spectrum of $Cs_2UO_2Br_4$ have been reported at high resolution but low sensitivity by Wong.[13] Temperatures down to 1.4 K were employed, and the spectra were dominated by a large number of bands due to trap emission which partly masked regions of the intrinsic luminescence. The many conflicting observations in previous studies of the vibrational spectra of the $UO_2Br_4^{2-}$ ion[13–19] necessitated a reinvestigation of the infrared (including single-crystal measurements) and Raman spectra of this species. Di Sipio[20] has reported the absorption spectrum of $(Me_4N)_2UO_2Br_4$. Our experimental measurements and analysis of the absorption spectrum of this compound are not in agreement with their study but are consistent with the results presented in this paper. We shall report our study of $(Me_4N)_2UO_2Br_4$ elsewhere.

Table I. C_{2h} Unit Cell Group Analysis of $Cs_2UO_2Br_4$

	Raman active		IR active	
mode	α_g	β_g	α_u	β_u
acoustic	0	0	1	2
translational	3	3	5	4
rotational	3	3	0	0
internal	6	6	9	9

internal mode	molecular sym D_{4h}	site sym C_i	unit cell group sym C_{2h}
$\nu_1 \nu_s$(O–U–O)	α_{1g}	α_g	α_g, β_g
$\nu_4 \nu_s$(U–Br)	α_{1g}	α_g	α_g, β_g
$\nu_2 \nu_{as}$(O–U–O)	α_{2u}	α_u	α_u, β_u
$\nu_9 \delta$(Br–U–Br)	α_{2u}	α_u	α_u, β_u
$\nu_3 \delta$(O–U–O)	ϵ_u	$2\alpha_u$	$2(\alpha_u, \beta_u)$
$\nu_6 \nu_{as}$(U–Br)	ϵ_u	$2\alpha_u$	$2(\alpha_u, \beta_u)$
$\nu_8 \delta$(Br–U–Br)	ϵ_u	$2\alpha_u$	$2(\alpha_u, \beta_u)$
$\nu_5 \nu_{as}$(U–Br)	β_{2g}	α_g	α_g, β_g
$\nu_7 \delta$(Br–U–Br)	β_{1g}	α_g	α_g, β_g
$\nu_{10} \delta$(Br–U–Br)	β_{1u}	α_u	α_u, β_u
$\nu_{11} \rho$(O–U–O)	ϵ_g	$2\alpha_g$	$2(\alpha_g, \beta_g)$

Experimental Section

Hydrated uranium trioxide (BDH) was dissolved in concentrated aqueous HBr, and a solution of CsBr in dilute aqueous HBr was added. This solution deposited large crystals of $Cs_2UO_2Br_4$ on slow evaporation in the absence of light. These crystals contained appreciable concentrations of water, and the single-crystal infrared spectrum showed a sharp band at 839 cm^{-1} due to ν_1(^{16}O–U–^{16}O) at a defect site. These features were absent in crystals recrystallized three times from 2 M HBr in the dark which were used for the luminescence measurements. These crystals however still contained luminescence traps which could not be removed by further recrystallization. Blassé[21] has estimated the concentration of these uranyl traps at 1% in his crystals. As far as we can judge from our luminescence and vibrational spectra, the concentration of traps in our multiply recrystallized material is lower than this. Single crystals of Cs_2ZrBr_6:$UO_2Br_4^{2-}$ containing ca. 1 mol% $UO_2Br_4^{2-}$ were prepared by passing a finely ground, carefully dried mixture of Cs_2ZrBr_6 and $Cs_2UO_2Br_4$ in vacuo in a sealed silica tube through a Bridgman furnace at 800 °C. Experimental procedures have been described elsewhere.[5,6]

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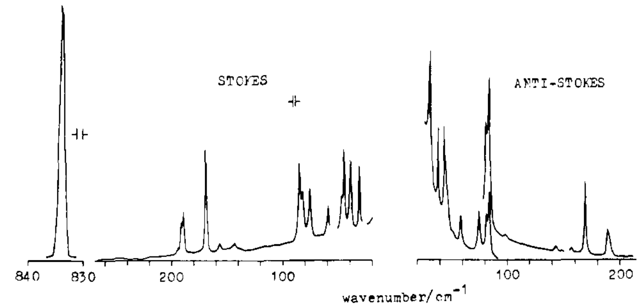

Figure 1. 120 K Stokes and anti-Stokes Raman spectrum of $Cs_2UO_2Br_4$. (Note the change of scale near ν_1 and the scale discontinuities.)

Structural Data and Vibrational Spectra

$Cs_2UO_2Br_4$ crystallizes[22] in the space group $P2_1/a\text{-}C_{2h}^5$ with two formula units in the Bravais cell. The $UO_2Br_4^{2-}$ ions are at sites of C_i symmetry with a U–O distance of 170 pm and U–Br distances of 280 and 283 pm. The shortest U–U distances are 641.5 pm between translationally equivalent ions and 699 pm between rotationally equivalent ions. A significant correlation field splitting of the internal modes of the complex ion is therefore expected, and their dispersion may also be appreciable. A unit cell group analysis is given in Table I. The notation for the internal modes follows that of Denning,[1] who has also given diagrams for the symmetry coordinates. Since both the uranyl ion and the unit cell are centrosymmetric, no modes will appear in both the infrared and Raman spectra.

The 120 K Raman spectrum of $Cs_2UO_2Br_4$ is well resolved with many line widths of the order of 1 cm^{-1} (Figure 1). Even at this resolution, no unit cell group splitting of the feature ν_1 at 834 cm^{-1} could be detected (the measured fwhH is 1.2 cm^{-1}). The most intense feature in this region, at 169 cm^{-1}, is assigned from its polarization behavior and lack of an ^{18}O shift as ν_4. The ratio of the ν_4 wavenumber in $Cs_2UO_2Cl_4$ and $Cs_2UO_2Br_4$ is then reasonable at 1.56. The bands at 189, 191, and 194 cm^{-1} shift to lower energy in $Cs_2U^{18}O_2Br_4$ and are assigned to ν_{11}. The triple structure may be due to partially resolved unit cell group splitting, but there may also be a Fermi resonance with ν_5 + 45, 47. The two weak features at 157 and 144 cm^{-1} have not been previously reported. Following the assignment for $Cs_2UO_2Cl_4$ a very weak band due to ν_5 is expected in this region. Features corresponding to this band occur between 138 and 142 cm^{-1} in several other salts of the $UO_2Br_4^{2-}$ ion, and we therefore assign ν_5 at 144 cm^{-1} and the 157-cm^{-1} mode as a combination. The remaining Raman-active internal mode ν_6 is assigned to the strong band at 85 cm^{-1}. To low energy, 7 of the 12 expected lattice modes are observed.

Our mull infrared spectrum is much better resolved than those of previous studies. The intense doublet at 917 and 925 cm^{-1} is assigned as the unit cell group split components of the ν_2 mode. A weaker feature at 903 cm^{-1} is due to ν_2 of the $^{16}O\text{–}U\text{–}^{18}O$ ion. No orientational or correlation field splitting of this mode is expected. These features are both sample and temperature independent. Some intensity in this region may also arise from resonance with the combination $\nu_1 + \nu_9$. Strong bands at 248 and 258 cm^{-1} are assigned to ν_3.

We have not reexamined the far-infrared region; however, all previous studies have assigned ν_6 at ca. 170 cm^{-1}. We expect ν_9 to occur near 90 cm^{-1}. Ohwada has reported a feature in this region although agreement with other far-infrared studies is poor. Additional features observable in the single-crystal infrared spectrum are $\nu_1(^{16}O\text{–}U\text{–}^{18}O)$ and numerous combination modes (Table II), those involving the uranyl group being the most intense.

Table II. Vibrational Spectra of $Cs_2UO_2Br_4$[a]

Raman	IR: mull	IR: single-crystal	assignt
		2575 vw	$2\nu_1 + \nu_2$
	1749 vw	*1750* s	$\nu_1 + \nu_2$
		1738 ms	
		1109 s	$\nu_{11} + \nu_2$
		1090 sh	$\nu_1 + \nu_3$
		1086 s	$\nu_4 + \nu_2$
		1013 vw	$\nu_1 + \nu_6$
	925 vs	tot abs	$\nu_2\nu_{as}$(O–U–O)
	917 vs		
	903 vw		$\nu_2(^{16}OU^{18}O)$
834 s			$\nu_1\nu_s$(O–U–O)
		802 m	$\nu_1(^{16}OU^{18}O)$
		785 b sh	ν_1 – lattice 49
		752 m	$\nu_2 - \nu_4$
		740 m	$\nu_1 - \nu_9$
		728 mw	$\nu_2 - \nu_{11}$
		583 ms	$\nu_1 - \nu_3$
		575 sh	
		447 s	$\nu_{11} + \nu_3$
		436 ms	
		399 w	$\nu_5 + \nu_3$
	(273 vw)		$(\nu_{11} + \nu_{10})$
	258 s		$\nu_3\delta$(O–U–O)
	248 s		
194 w			ν_5 + lattice 45 and 47
191 ms			
189 ms			$\nu_{11}\rho$(O–U–O)
	170[b]		$\nu_6\nu_{as}$(U–Br)
169 s			$\nu_4\nu_s$(U–Br)
157 w			lattice 76 + 82, 85
144 w			$\nu_5\nu_{as}$(U–Br)
	89[b]		$\nu_9\delta$(Br–U–Br)
85 s			$\nu_7\delta$(Br–U–Br)
82 ms			lattice
76 ms			
59 ms			
47 w			
45 s			
39 s			
31 s			

[a] Italicized bands were measured at 85 K (infrared) and 120 K (Raman). [b] Reference 18.

Luminescence Spectrum of $Cs_2UO_2Br_4$. At very low temperatures, the luminescence spectrum of $Cs_2UO_2Br_4$ is dominated by emission from traps. The intrinsic emission is best observed at about 20 K. The two intrinsic origins (I, II) $E_g \rightarrow A_{1g}$ (D_{4h}) are assigned as features at 19 665 and 19 674 cm^{-1} coincident with bands observed in the polarized absorption spectrum by Snellgrove.[4] Wong has reported that the emission from these levels is in thermal equilibrium.[13] The trap emission prevented any detailed study of the weak lattice modes based on these origins.

Strong sharp features at 250 and 920 cm^{-1} below both of these origins are assigned as ν_2 and ν_3 vibronic origins. These bands were observed at 251 and 920 cm^{-1} by Wong.[13] In contrast to the infrared spectra, no vibrational splittings of the vibronic origins were detected although the experimental slit width and the observed half-height width of the lines were sufficient to resolve the splitting. The splittings of the electronic origins and vibronic origins were equal, and the two components had the expected temperature dependence. In the absence of correlation field splittings, the $E_g \rightarrow A_{1g} + \nu_3$ transition would be expected to show two components $B_{2g} \rightarrow A_g + \beta_{3u}$ and $B_{3g} \rightarrow A_g + \beta_{2u}$ in D_{2h} symmetry, but if the electronic and vibrational splittings are comparable, the splitting of the vibronic origin should not be equal to the splitting of the electronic origin. For ν_2, the wavenumber

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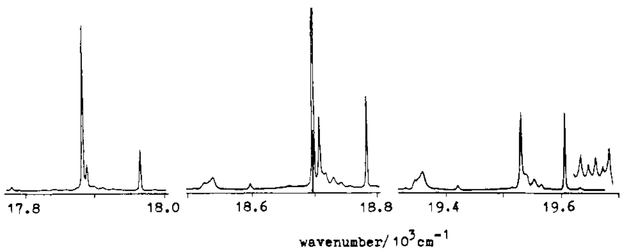

Figure 2. First three groups of bands in the 457-nm excited luminescence spectrum of $Cs_2ZrBr_6:UO_2Br_4^{2-}$ (200:1) at 20 K (the anti-Stokes lattice mode region is at 35 K; note the scale discontinuities).

observed in the luminescence spectra is intermediate between those of the infrared spectrum. In the electronic spectrum, the vibrational wavevector of the terminal state need not be zero so that the phase distinction between the correlation field split components of the vibrations is no longer important. So far as we are aware, there are no detailed calculations of dispersion curves for this type of system.

The intense features at 77, 81 cm^{-1} below I, II do not vary in intensity with temperature, and, by analogy with the $Cs_2UO_2Cl_4$ luminescence spectrum, these bands are associated with the ν_{10} mode strongly coupled to lattice modes. Much weaker bands at 170 and 173 cm^{-1} below I, II correspond to ν_6. The intensity mechanism of these features has been discussed for $Cs_2UO_2Cl_4$ by Denning, and it is consistent that Snellgrove has reported intense features at 165 and 168 cm^{-1} above origin III in the 4 K absorption spectrum of $Cs_2UO_2Br_4$.

To low energy, strong progressions in ν_1 (835 cm^{-1}) based on all of these features are observed; the nonzero anharmonicity constants are $x_{11} = -1.4 \pm 0.3$ and $x_{12} = -6.1 \pm 0.1$ cm^{-1}. First members of very much weaker progressions in ν_{11} are also detected.

Luminescence Spectrum of $Cs_2ZrBr_6:UO_2Br_4^{2-}$. The first three groups of bands in the 20 K luminescence spectrum of $Cs_2ZrBr_6:UO_2Br_4^{2-}$ are shown in Figure 2. Similar results were obtained for $Cs_2SnBr_6:UO_2Br_4^{2-}$ and are therefore not reported. The crystallographic and vibrational data for these host lattices have been given.[23] Most of the spectral features are sharp (fwhH < 4cm^{-1}), and emission from traps or impurities is weak. The intense feature at highest energy (19 605 cm^{-1}) is the $E_g \rightarrow A_{1g}$ (D_{4h}) electronic origin. This feature moves by 11 cm^{-1} to high energy on cooling from 85 to 20 K. Strong bands at 75, 244, and 908 cm^{-1} and a weaker band at 185 cm^{-1} from the origin correspond to the ν_{10}, ν_3, ν_2, and ν_6 vibronic origins, ν_2 also being observed at 908 cm^{-1} in the 300 K infrared absorption spectrum of the same crystal. The weak band at 26 cm^{-1} above the origin increases in relative intensity

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Table III. Wavenumbers (cm^{-1}) of Internal $UO_2Br_4^{2-}$ Modes from the Luminescence of $Cs_2UO_2Br_4$ and $Cs_2ZrBr_6:UO_2Br_4^{2-}$

compd mode	$Cs_2UO_2Br_4$	$Cs_2ZrBr_6:UO_2Br_4^{2-}$
ν_1	835	823
ν_2	922	908
ν_3	250	244
ν_6	170, 173	185
ν_{10}	77, 81	76
ν_{11}[a]	189	184

[a] From progressions on vibronic origins.

as the concentration of the $UO_2Br_4^{2-}$ ion increases and is assigned to emission from pairs. A similar feature has been assigned to pair emission in $Cs_2SnCl_6:UO_2Cl_4^{2-}$. At 85 K, weak bands are observed at 23–25 cm^{-1} below the electronic origin and all vibronic origins and progressions thereupon. These bands disappear on cooling and correspond to the first members of the sequence $E_g + \nu_{11} \rightarrow A_{1g} + \nu_{11}$. The derived wavenumber of ν_{11} in the E_g state is 166 cm^{-1}. Lattice modes observed at 39, 52 and 66 cm^{-1} below the origin are assigned analogously[24] to $Cs_2ZrBr_6:ReBr_6^{2-}$ although the perturbation of the lattice must be rather different. A weaker feature at 90 cm^{-1} may be associated with the host ν_6 mode.

Strong progressions in ν_1 (823 cm^{-1}) and weaker progressions in a mode of 184 cm^{-1} are observed on the electronic and vibronic origins. The latter interval is probably ν_{11} from comparison with $Cs_2UO_2Br_4$ and $Cs_2SnCl_6:UO_2Cl_4^{2-}$, although ν_4 is also expected at about this wavenumber.

Conclusions

The assignments for the ν_4, ν_5, and ν_{11} vibrations of the $UO_2Br_4^{2-}$ ion deduced in this study differ from those given earlier, but are consistent with the analyses of the vibrational behavior of $Cs_2UO_2Cl_4$ and $Cs_3UO_2F_5$. The luminescence spectrum of $Cs_2UO_2Br_4$ is interpreted in a way similar to that of $Cs_2UO_2Cl_4$. The splitting of the E_g excited state is 8 cm^{-1}. Dispersion eliminates the unit cell group ν_2 splitting.

The $UO_2Br_4^{2-}$ ion in Cs_2ZrBr_6 occupies a site with fourfold symmetry, and no splitting of the doubly degenerate first excited state is detected in luminescence. The relatively high intensity of the electronic origin suggests that the ion does not occupy the O_h Zr^{4+} site but lies slightly off center. Since the Zr–Br distance in Cs_2ZrBr_6 is greater than the U–O distance and less than the U–Br distance in $Cs_2UO_2Br_4$, we expect axial elongation and equatorial compression of the $UO_2Br_4^{2-}$ ion to occur in Cs_2ZrBr_6 compared to $Cs_2UO_2Br_4$. This is supported by the frequencies of the internal modes (Table III).

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Registry No. $Cs_2UO_2Br_4$, 18324-47-5; Cs_2ZrBr_6, 36407-58-6.

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