

Luminescence Behaviour of Uranyl Nitrate Hydrates*

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Whilst the characteristic green luminescence of hydrated uranyl nitrate must be one of the most extensively studied areas of inorganic photophysics [1, 2], our detailed understanding of the emitting state(s) and decay pathways is still far from complete. For example, it is unclear why the luminescence lifetime of this compound in the solid state is over two orders of magnitude longer than in aqueous solution.

We have recently studied the decay of the uranyl nitrate luminescence in aqueous solution [3] under conditions where the dominant species is thought to be $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ [4]. The decay is sensitive to pH, uranyl concentration, temperature, excitation intensity and solvent deuteration. It is now generally recognized that hydrogen abstraction from water is one of the dominant decay routes for excited uranyl ion in water [3, 5, 6]. In addition, we feel that reversible crossing between two states via solvent exchange provides a ready explanation for the bi-exponential decay observed in these systems between pH 1 and 4 [3]. To obtain further information on the role of water in the photochemistry of the uranyl ion, we have been studying the luminescence spectra and decay of uranyl nitrate hydrates, $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ($x = 6, 3, \text{ or } 2$). In all cases UO_2^{2+} is coordinated to two water molecules and two bidentate

NO_3^- ligands. Other water molecules are present as relatively mobile structural molecules [7].

Tri- and di-hydrates were obtained by thermal decomposition of the hexahydrate [8]. The dihydrate was found to be highly hygroscopic, so that only the qualitative behaviour was studied in this case. At room temperature, the luminescence spectrum of the trihydrate consists of a series of bands starting at $20\,480\text{ cm}^{-1}$, with structure very similar to the hexahydrate [9], but blue shifted relative to it by *ca.* 30 cm^{-1} . The separation between the bands is $840(\pm 20)\text{ cm}^{-1}$, corresponding to the totally symmetric $\text{O}=\text{U}=\text{O}$ stretch vibration. The luminescence spectrum of the dihydrate is similar, except that the bands are blue shifted by a further *ca.* 40 cm^{-1} . On cooling to 77 K, each of the components of hexa-, tri- and di-hydrate luminescence is further split into multiplets [9–11]. Data for the trihydrate are given in Table I. In addition, it is worth noting that, although quantitative comparison is difficult, the overall intensity of the luminescence of the trihydrate at 77 K is very much greater than at room temperature. Similar splittings are observed in the fluorescence excitation spectrum, and we have observed at least 35 transitions between $20\,590$ and $31\,450\text{ cm}^{-1}$. These splittings have been interpreted either as splittings of the excited state [9], or as site symmetry effects [12]. On excitation of the luminescence of components at $23\,390$, $23\,190$ and $22\,900\text{ cm}^{-1}$ of one of the bands, the energies of the bands in the emission spectra were identical, but the relative intensities were somewhat different. Furthermore, the onset of the excitation spectrum ($20\,590\text{ cm}^{-1}$) is at lower energies than the first component in the emission spectrum ($20\,700\text{ cm}^{-1}$), clearly showing the presence of different emitting levels. Whether these have different electronic origin or are different crystallographic sites is unclear. It is worthy of note that a large number of components have been observed in the emission spectrum of various uranyl compounds at 77 K between $22\,000$ and $29\,000\text{ cm}^{-1}$ [13].

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TABLE I. Luminescence Spectrum of $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}^a$

	Wavenumber (cm^{-1}) ^b	
	Room temperature	77 K
(1)	20480	20700, 20520, 20450, 20270, 20210
(2)	19640	19760, 19580, 19410
(3)	18770	18900, 18740, 18550
(4)	17910	18040, 17870, 17680
(5)	17090	17190, 17090, 17010
(6)	16270	16330 ^c
(7)	15420	15470 ^c

^aExcitation wavelength 337 nm. ^b $\pm 20\text{ cm}^{-1}$. ^cSplittings not resolved.

TABLE II. Luminescence Lifetimes of Uranyl Nitrate

System	Lifetime (μs)
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, room temperature	595 ^a
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, room temperature	620 ^a
$\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 77 K	900 ^a
uranyl nitrate (0.02 mol dm^{-3}) in water, pH 3	1.77, 10.2 ^b
uranyl nitrate (0.03 mol dm^{-3}) in acetone	1.07 ^c
uranyl nitrate (0.07 mol dm^{-3}) in acetone	1.65 ^c
uranyl nitrate (0.03 mol dm^{-3}) in acetone/water (97%)	1.73 ^c

^aInitial rapid decay(s) also observed. ^bBiexponential.

^cInitial rapid grow-in of emission (<200 ns) observed.

The decay of the $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ luminescence, excited by a N_2 laser at 337 nm, shows an initial fast component followed by a slow first-order decay. The fast component is complex and is being further studied. Within the accuracy of our measurements, the lifetime of the slow decay is identical to that in the hexahydrate (Table II). A similar lifetime is also observed with the dihydrate, suggesting that coordinated ligands have a more significant role in the $(\text{UO}_2^{2+})^*$ decay than any lattice water. On cooling to 77 K, the lifetime of the trihydrate emission increases and there is a decrease in the intensity of the fast component.

Hydrated uranyl nitrate is also present in acetone solution as the $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ species [4, 14]. The luminescence decay under these conditions is first-order and very much faster. Interestingly, the lifetime decreases on decreasing uranyl nitrate concentration, and increases on adding water, suggesting some chemical process between excited uranyl and acetone. Support for this comes from the observation of an as yet unidentified precipitate on photolysis of uranyl nitrate in acetone. Furthermore, free

radicals have been observed on photolysis of uranyl perchlorate in acetone at 77 K [15].

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