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Luminescence of Uranyl Ions in Phosphate Glass and Phosphoric Acid, Spontaneous Reduction to Uranium(IV) and New Description of the Electron Transfer Bands

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The absorption and emission spectra of the uranyl ion in phosphate glass and in 85 percent phosphoric acid are similar to the dilute aqueous solution, but the luminescence yield is far higher and small concentrations of uranium(IV) occur, possibly as a quasi-stationary equilibrium with free oxygen. The quantum numbers Ω *of the excited states are discussed, based on "weak-field" coupling between* $^2F_{5/2}$ *and* $\omega = 3/2$ *or* $1/2$ *of* π_u*. Detailed variations of band positions are related to U–O bond length modification, also in borate and germanate glasses. The excited uranyl ion may perform energy transfer to lanthanides, conceivably applicable to lasers.*

Though the luminescence of uranyl salts was studied by Brewster in 1833 and formed the basis for Stokes' law, and in spite of a huge spectroscopic effort during the Manhattan project [1], the understanding of the corresponding excited states progressed slowly. One of us [2] discussed the strong effects of spin–orbit coupling on the electron transfer spectrum, where an electron is excited from two M.O. (presumably of symmetry type π_u) consisting almost exclusively of oxygen 2p in the L.C.A.O. model, to the empty 5f shell of the uranium atom. We remarked later [3] that the frequently discussed question [4] whether the first excited state is a triplet or a singlet has no physical significance in this specific case, because of the combination of two conditions, the almost identical one-electron energies of (at least) four among the seven 5f orbitals and the large spin–orbit separation between $^2F_{7/2}$ and $^2F_{5/2}$ which is now known [5] to be 7609 cm^{-1} in gaseous U^{+5} though it is recognized to be decreased about 10 percent in uranium(V) compounds by a relativistic nephelauxetic effect. We return below to the theoretical treatment of this question.

The absorption spectra of the uranyl ion in vitreous materials show weak bands above 20000 cm^{-1} (below 500 nm) but the emission spectra of luminescence fall in two categories: the conventional silicate glasses, as well as phosphate glasses [6, 7] show a series of roughly equidistant, narrow bands, whereas borate and germanate glasses only provide a broad structure, rather similar to the octahedrally coordinated perovskites studied by Blasse [8, 9]. We want here to compare the luminescence of uranyl ions in concentrated phosphoric acid (85% Frutarom Laboratory C.P., passing the test for the presence of reducing agents; thus, titrations with KMnO$_4$ show less than a-tenth of the reducing equivalents needed to form the concentration of U(IV) discussed below) and in phosphate glasses. Matsushima *et al.* [10] previously noted that the quantum yield (and the corresponding life-time) is higher in 0.67 *M* H$_3$PO$_4$ than in dilute aqueous solution. There is one problem, difficult to avoid, in the constitution of very strong phosphoric acid (even of the highest conceivable purity) that pyrophosphate or oligomeric metaphosphates may be present in low concentrations, forming strong complexes with dissolved cations. The bulk of the phosphate glass is a metaphosphate network-forming anion formed by dehydration of NaH$_2$PO$_4$ by heating to 850 °C for 2 hours. The typical environment of a given phosphorus atom in such a glass consists of two terminal and two bridging oxygen atoms. The dissolved net-

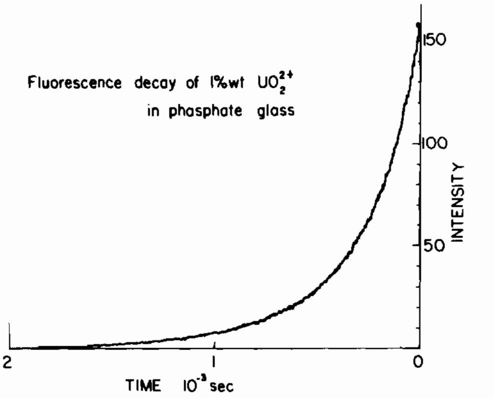

Figure 1. Decay of uranyl luminescence in phosphate glass.

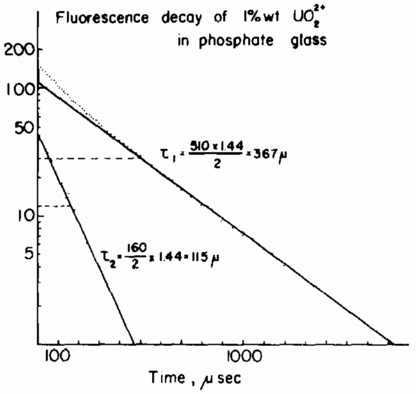

Figure 2. Resolution of decay curve of luminescence in two exponential curves.

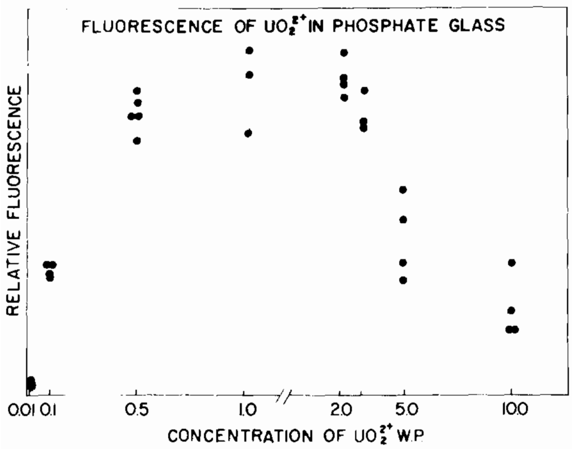

Figure 3. Relative steady-state luminescence intensity (for a large number of measurements) as a function of the weight percentage of uranyl ions in phosphate glass.

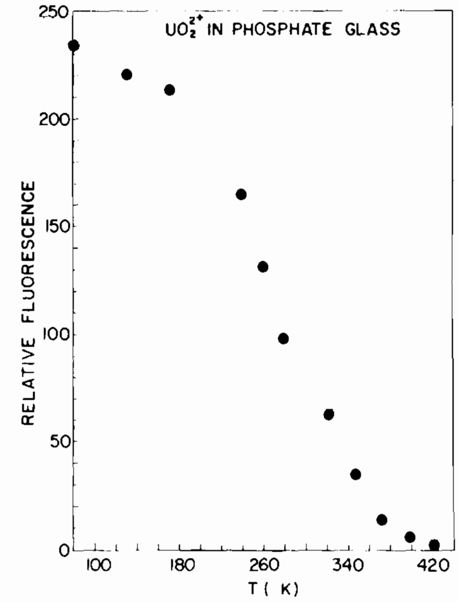

Figure 4. Relative steady-state luminescence intensity as a function of the absolute temperature.

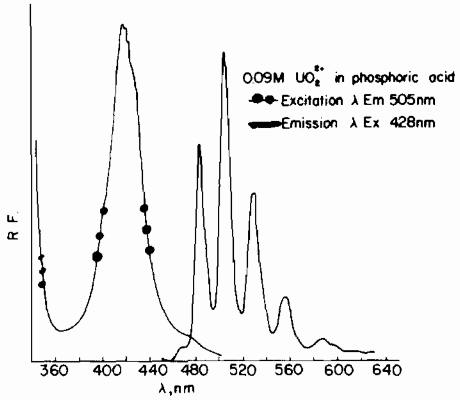

Figure 5. Excitation and emission spectra of 0.09 molar uranyl solution in 85 percent phosphoric acid.

work-modifying cations have closest contacts to the terminal oxygen atoms of several phosphate groups. Whereas the absorption spectra of cobalt(II), nickel(II) and chromium(III) are similar [11] to octahedral species, such as the aqua ions, there is hardly any evidence available for the symmetry of the long uranium-oxygen bonds probably distributed close to the equatorial plane perpendicular on the uranyl ion.

Fig. 1 shows the decay of the fluorescence of a phosphate glass containing 1 weight percent uranyl ions measured with a spectrofluorimeter, to which was fitted an EGG-FX-6 AU flash lamp (pulse duration 3×10^{-6} s) and a 162 P.A.R. boxcar averager combined with a 164 P.A.R. gated integrator, at room temperature (300 °K). As seen on Fig. 2, the decay is not exponential, but can be satisfactorily described as a superposition of two exponential curves, a short-lived with the life-time τ_2 = 0.115 ms (millisecond) and about a-quarter of the initial intensity, and a longer-lived, more intense component with τ_1 = 0.367 ms. Comparison with other luminescent uranyl compounds makes it unlikely that τ_2 is connected with an excited state slightly above the first excited state, but rather that a small concentration of uranyl pairs with a characteristic short U–U distance is formed during the vitrification of the molten glass by cooling. Such pairs were also recently described by Marcantonatos [12] as excimers (having a slightly different emission spectrum) detected as kinetic intermediates in aqueous solution at pH = 2 (where the concentration of dimeric hydroxo complexes is rather negligible).

Self-quenching of the uranyl fluorescence in phosphate glass occurs already at low uranyl concentrations, and Fig. 3 shows a broad maximum of intensity around 1 weight percent as a function of the concentration between 0.1 and 10. The temperature has an influence shown on Fig. 4, a quite characteristic behaviour of many luminescemt samples.

TABLE I. Vibrational Components of the Absorption Spectrum of the Uranyl Ion in 15 *M* Phosphoric Acid Compared with the Uranyl Aqua Ion [13] in Dilute Perchloric Acid. Wavelengths λ (nm) and Wave-numbers ν and Their Consecutive Difference Δν (cm^{-1}).

Phosphoric Acid			Perchloric Acid		
λ	ν	Δν	λ	ν	Δν
491.5	20350		485.9	20580	
		700			750
475	21050		468.8	21330	
		690			720
460	21740		453.6	22050	
		630			670
447	22370		440.0	22720	
		730			680
433	23100		427.3	23400	
		650			710
421	23750		414.8	24110	
		700			710
409	24450		403.0	24820	
		680			700
398	25130		391.8	25520	
		720			720
(387)	25850		381.1	26240	

TABLE II. Emission Spectra of the Uranyl ion in Various Environments. Notation as in Table I.

Environment	λ	ν	Δν
15 *M* H_3PO_4	(467)	(21410)	
			740
	483.8	20670	
			840
	504.3	13830	
			910
	528.4	18920	
			870
	554	18050	
			980
	586	17070	
			290
	(596)	(16780)	
Phosphate glass	487	20530	
			820
	507.2	19710	
			870
	530.9	18840	
			890
	557	17950	
			880
	586	17070	
Borax glass	525	19050	–
Germanate glass	531	18830	–

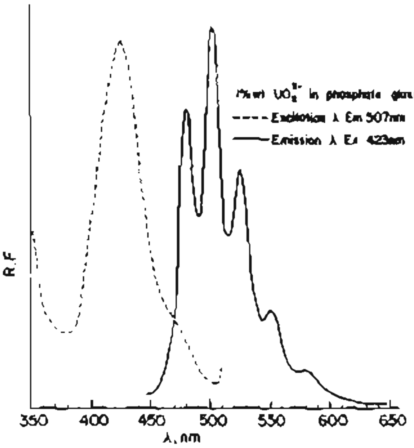

Figure 6. Excitation and emission spectra of uranyl ions in phosphate glass.

Fig. 5 shows the excitation spectrum (monitored by emission at 505 nm) and the emission spectrum (excited at 428 nm) of a solution 0.09 *M* (1.4 weight percent) in 15 *M* phosphoric acid. As also seen from Table I (comparing with the absorption spectrum of the aqueous perchlorate solution measured by Bell and Biggers [13]) and Table II (comparing with the emission spectra of several of our glasses) it is not evident whether the electronic origin corresponds to the weak emission at 21400 cm^{-1} or the stronger emission at 20670 cm^{-1} though arguments in favour of the second alternative are that it fits to a roughly equidistant progression, and that uranyl salts rarely show this origin above 20700 cm^{-1}. In the phosphate glass (Fig. 6) it is not easy to detect the origin in absorption, but the rather intense emission band at 20540 cm^{-1} is a plausible candidate. Though the distances between the approximately equidistant emission bands are open to some experimental uncertainty, they are seen in Table II to be about 900 cm^{-1} in phosphoric acid and close to 880 cm^{-1} in the phosphate glass. These values are somewhat higher than the symmetric stretching frequency in the electronic ground state 855 ± 20 cm^{-1} [13] to be compared with 715 ± 18 cm^{-1} in the first excited state presumably having lower force constants. Denning, Snellgrove and Woodwark [14] made a careful study of the absorption spectrum of $Cs_2UO_2Cl_4$ in polarized light (and performing oxygen-18 substitution). The two symmetric stretching frequences are here 831 and 709 cm^{-1} excepting the first origin at 20096 cm^{-1} with 714.7 cm^{-1}. A detailed study [15] of the photochemical decomposition of the hydrated formiate $UO_2(HCO_2)_2 \cdot H_2O$ also involved the measurement of the luminescence spectrum (origin at 20568 cm^{-1}) with the symmetric stretching frequency of the ground state 864 cm^{-1}. It seems to be a general trend that going from very weak to moderately strong bonding of the neighbour

TABLE III. Mean Life-times τ (in the unit 10^{-6} s) of the Uranyl Ion in the Various Environments (measured at room temperature). When the decay curve can be resolved in two exponential functions, two τ values are given.

Environment	Concentration	τ
15 M H_3PO_4	0.09 M	20
Phosphate glass	0.02 weight %	408
	0.01 "	408
	0.1 "	429
	1 "	115 and 367
	5 "	229
Borax glass	1 "	150
Germanate glass	1 "	150

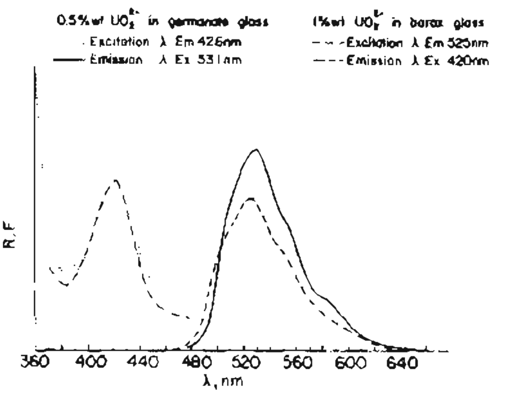

Figure 7. Excitation and emission spectra of uranyl ions in germanate and borate glasses.

atoms in the equatorial plane (in our examples aqua ion < phosphate glass < formiate < phosphoric acid < $UO_2Cl_4^{-2}$) the wave-number of the origin decreases some 600 cm^{-1} and the stretching frequency in the electronic groundstate decreases from 900 to 831 cm^{-1} both (rather moderate) effects suggesting a slight inductive elongation of the two (very short) U–O distances.

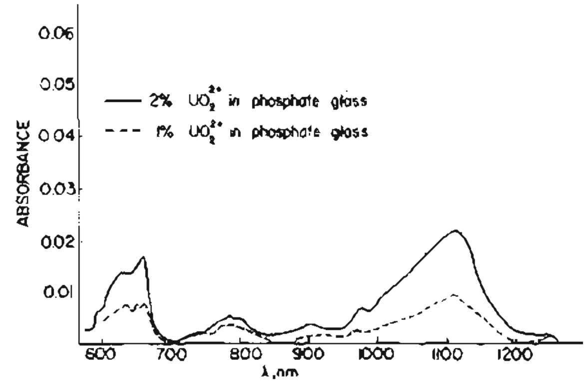

Figure 8. Absorption spectra showing the presence of uranium(IV) in two phosphate glasses.

A situation approaching the regular octahedral UF_6 discussed elsewhere [16–18] are the mixed oxides [8, 9] containing octahedral chromophores $U(VI)O_6$ where the origin occurs perceptibly lower than in the linear uranyl ion. The borate and germanate glasses illustrated on Fig. 7 and in Table II show two or more broad features not forming a Franck–Condon projection having approximately Gaussian shape, such as the vibrational structure in Figures 5 and 6. Table III compiles the life-time measurements of various glasses under differing conditions. Though the broadened emission spectrum of borax and germanate glasses might have suggested highly inequivalent sites, only one exponential with τ = 0.15 ms is observed.

A quite unexpected feature of the phosphate glasses is the observation (Fig. 8) of weak narrow absorption bands in the red and near infra-red, manifestly due to the $5f^2$ transitions of uranium(IV).

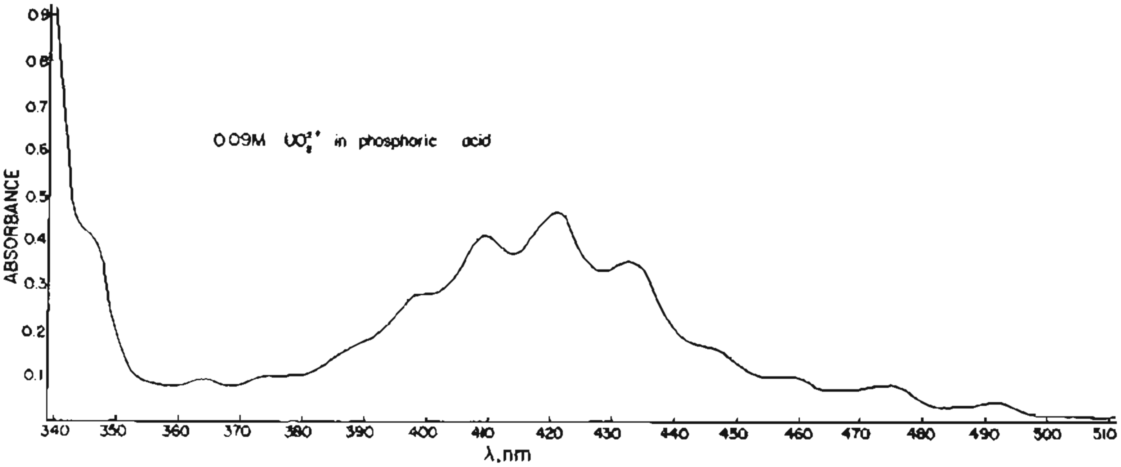

Figure 9. Absorption spectrum showing the weak electron transfer bands of 0.09 molar uranyl ions in 85 percent phosphoric acid.

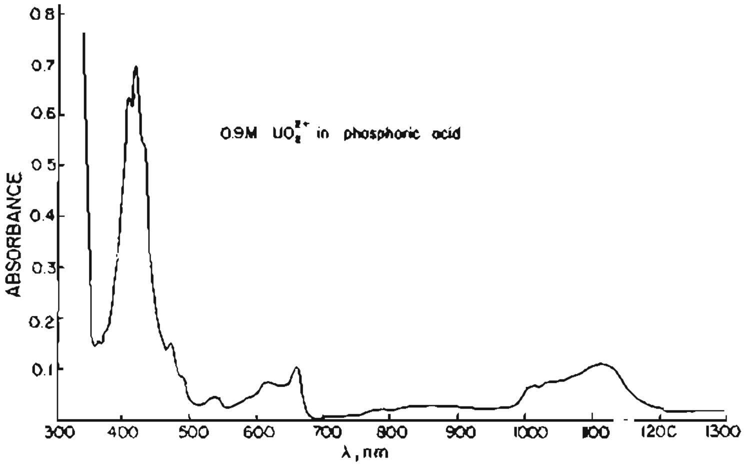

Figure 10. Absorption spectrum showing the presence of uranium(IV) in the uranyl solution in 85 percent phosphoric acid.

Whereas the spectrum (Fig. 9) of the solution in phosphoric acid below 500 nm is closely similar to uranyl aqua ions [13] the higher wave-lengths (Fig. 10) clearly demonstrate the presence of U(IV). Since reducing impurities were carefully excluded, the most probable explanation is a photochemical reduction with molecular oxygen as the other product. The excited state of the uranyl ion [4, 18] can be calculated to be as oxidizing as if the standard oxidation potential E^0 is +2.6V, slightly below that of free fluorine. The photoelectron spectra of solid phosphates [19, 20] suggest a vertical ionization energy I of the loosest bound M.O. close to 10 eV (relative to vacuum). The extrapolated adiabatic I = 8.5 eV corresponds to E^0 = +4V relative to the hydrogen electrode, but on the other hand, there is no reason to expect that E^0 for evolution of O_2 is tremendously in excess of 1.3 eV known for dilute acid. The polymeric phosphates may possess highly delocalized M.O. among which a few have unusually low I.

A quasi-stationary situation seems to dominate the formation of U(IV). A nearly constant ratio of concentrations U(VI)/U(IV) can be inferred from the ratio of optical densities at 420 and 650 nm being 21.7 for phosphate glass containing 2 weight percent uranyl, 26 for 1 and 19.5 for 0.5 percent, whereas this ratio is 6.6 for 0.09M UO_2^{+2} in phosphoric acid, ϵ of the uranyl ion at 420 nm has been measured to be 7.8 in phosphoric acid, 20.6 in the phosphate glass, 39.2 in germanate and 44.6 in borate glass. The uranium(IV) aqua ion [21] has ϵ = 55 at 650 nm, and [22] 31.6 at 630 and 38.2 at 670 nm in 1.8 to 4.8 *M* phosphoric acid. The order of magnitude of U(IV)/U(VI) concentrations seems to be 0.03 in phosphoric acid and 0.02 in phosphate glass. It is highly probable [4, 15, 23] that the primary photochemical product is U(V) containing one 5f electron, but it is expected to disproportionate rapidly, in view of the known large affinity of U(IV) to phosphate ligands.

Previously, we have given the arguments [3] why the first excited state of the uranyl ion, lacking one of the four feasible π_u electrons in the loosest bound M.O. (consisting almost exclusively of oxygen 2p in the L.C.A.O. model) and having this electron transferred to the empty 5f shell on the uranium atom, does not have well-defined S and Λ (in linear symmetry) in contrast to almost all other chemical species being reasonably good approximations to Russell–Saunders coupling [24, 25]. It was also shown [3] which Ω values are found among the 56 states (4 times 14) and suggested that the lowest energy level consists of two states having Ω = 4. An abundant variety of other proposals have been made in recent literature, but we maintain that it has no physical significance to discuss whether the luminescent level is a triplet (S = 1) or a singlet (S = 0). One study [14] based on a considerable amount of experimental data considers the loosest bound M.O. to have the symmetry σ_u. We do not find this likely (when comparing with all kinds of triatomic molecules) in spite of relativistic Dirac–Slater calculations [26] indicating σ_u as the loosest bound of 6 Kramers doublets originating in the oxygen 2p shells (with a total spreading 3 eV of energy). On the other hand, we accept the magnetic dipole character of the first origin at 20096 cm^{-1} in $Cs_2UO_2Cl_4$ to indicate Ω = 1 rather than 4.

This is not as great a revolution as one might think. It is becoming clear that the lower excited levels of the uranyl ion are well described in linear symmetry [24] by a coupling scheme between $^2F_{5/2}$ and ω = 3/2 or 1/2 of the π_u orbitals. The two lowest Ω values of $^2F_{5/2}$ are 5/2 and 3/2 whereas the last, Ω = 1/2 contains so much 5fσ character [2] that it readily may have higher energy than the lowest-lying Ω = 7/2 of $^2F_{7/2}$ corresponding to pure 5fϕ. The four

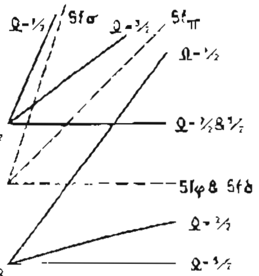

Figure 11. The energy levels of one 5f electron in linear symmetry as a function of increasing π-anti-bonding (and thrice as strong σ-anti-bonding) effect on the one-electron energies, given as dashed lines. It may be noted that the two levels with $\Omega = 5/2$ do not have the same asymptotic positions as they would, if the 5fφ and 5fδ one-electron energies were not assumed to coincide. Also, the asymptotic eigenvectors remain mixtures of the two latter λ values.

alternatives at low energy produce nine levels with Ω values

$5/2 \oplus 3/2$: 1 and 4
$3/2 \oplus 3/2$: $0^+, 0^-$ and 3
$5/2 \oplus 1/2$: 2 and 3
$3/2 \oplus 1/2$: 1 and 2

(electron transfer of σ_u with $\omega = 1/2$ produces the last four levels, but it would be difficult to explain why $\Omega = 1$ then has lowest energy).

The two levels with $\Omega = 1$ and 4 may differ slightly in the diagonal elements of interelectronic repulsion, as kindly pointed out to us by Dr. Denning. The energy difference between $\Omega = 3/2$ and 5/2 of $^2F_{5/2}$ assuming [3] essentially identical one-electron energies of 5fφ and 5fδ is due to the moderate amount (below 2/7) of 5fπ character in the former case as seen on Fig. 11. If the π-anti-bonding of 5fπ is 5000 cm^{-1}, this would explain an energy increase around 1000 cm^{-1}, the asymptotic value ζ_{5f} being 2000 cm^{-1}. Quite generally [2] the squared amplitudes of the two 5fλ values in a given asymptotic "weak-field limit" is $1/2 \pm \Omega/7$ where the plus sign applies to the higher $\lambda = \Omega + 1/2$ and the minus sign to $\lambda = \Omega - 1/2$ for the three Ω values of $^2F_{5/2}$ whereas it is the other way round for $^2F_{7/2}$. The energy difference between $\Omega = 3/2$ and 1/2 of $(\pi_u)^3$ would be very small, ζ_{2p} (= 150 cm^{-1} in the oxygen atom) if the two π_u consist exclusively of O2p, but it is very sensitive to small uranium-centered contributions. Thus ζ_{7p} is 8544 cm^{-1} (= 1.06 eV) in gaseous Th^{+3} and [5] 15030 cm^{-1} (= 1.89 eV) in U^{+5}; and the last closed shell has ζ_{6p} around 5 eV according to photoelectron spectra. Hence, 10 percent U7p character or a few percent U6p character [27] would be sufficient to separate the two Ω values of $(\pi_u)^3$ about 1000 cm^{-1}. Denning *et al.* [14] find six electronic origins in the interval from 20406 to 22750 cm^{-1}. Together with the level ($\Omega = 1$) at 20096 cm^{-1}, these seven levels are, in our opinion, included among the nine levels mentioned above. The two states in $\Omega = 2$ or 4 may separate their energy in the tetragonal symmetry of the chloro complex. The two next origins [14] reported at 26197 and 26247 cm^{-1} already may show $^2F_{7/2}$ character, as is almost certainly the case for the origins at 27719 and 27758 cm^{-1}. It is, of course, possible that not all the origins have been detected. Seven origins [28] are found between 19979 and 23111 cm^{-1} in $[N(CH_3)_4]_2[UO_2Cl_4]$ followed by the next at 26330 cm^{-1}.

Measurements of the relative intensity of fluorescence of phosphate glasses and phosphoric acid show a ratio of 13.5 ± 1.5 for each of the four strong emission bands, indicating a considerably higher quantum yield in the glass. Such glasses have been used [6, 7] for energy transfer to the luminescent state $^5D_0$ of europium(III) and might conceivably be useful in lasers [29]. Similar energy transfer has also been observed [30] in aqueous solutions containing uranyl and europium salts.

A rather fundamental problem is the presence of multiple sites in glasses [29]. By selective excitation with monochromatic laser light, Lam and Leung [31] found distinct variations of finer details of the emission spectra of uranyl ions in sodium calcium silicate glasses, showing origins at so low wave-numbers as 19374 and 19738 cm^{-1}. Another question is whether the typical τ for solid uranyl compounds (without competing processes) is as high as 1.6 ms [32]. Since this value is in excess of the radiative life-time derived from Einstein's 1917 formula [29] if the whole oscillator strength in the blue is taken into account, it is a compelling conclusion that the lowest-lying electronic transition has a considerably lower oscillator strength. Recent experiments by Marcantonatos [33] suggest that low values of τ around 0.01 ms found in aqueous solution are due to competition with abstraction of hydrogen atoms from the ambient water molecules. However, it is not obvious whether a "natural" value of τ is approximately invariant for uranyl ions in differing environments. We hope to clarify these two questions by further experiments.

References

1 E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds", Pergamon Press, Oxford (1964).
2 C. K. Jørgensen, *Acta Chem. Scand.*, *11*, 166 (1957).
3 C. K. Jørgensen and R. Reisfeld, *Chem. Phys. Letters*, *35*, 441 (1975).
4 H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev. (London)*, *3*, 139 (1974).
5 V. Kaufman and L. J. Radziemski, *J. Opt. Soc. Am.*, *66*, 599 (1976).

6 R. Reisfeld, N. Lieblich-Sofer, L. Boehm and B. Barnett, *J. Luminescence, 12,* 749 (1967).

7 R. Reisfeld, *Structure and Bonding, 22,* 123 (1975) and *30,* 65 (1976).

8 J. T. W. de Hair and G. Blasse, *Chem. Phys. Letters, 36,* 111 (1975).

9 G. Blasse, *Structure and Bonding, 26,* 43 (1976).

10 R. Matsushima, H. Fujimori and S. Sakuraba, *J. Chem. Soc. Faraday Trans., I, 70,* 1702 (1974).

11 R. J. Landry, J. T. Fournier and C. G. Young, *J. Chem. Phys., 46,* 1285 (1967).

12 M. Marcantonatos, *Inorg. Chim. Acta, 24,* L37 and L53 (1977).

13 J. T. Bell and R. E. Biggers, *J. Mol. Spectr., 18,* 247 (1965) and *25,* 312 (1968).

14 R. G. Denning, T. R. Snellgrove, D. R. Woodwark, *Mol. Phys., 32,* 419 (1976).

15 H. Sautereau, *Thèse I-DE-76008,* Institut National des Sciences Appliquées, Lyon (1976).

16 R. McDiarmid, *J. Chem. Phys., 65,* 168 (1976).

17 W. B. Lewis, L. B. Asprey, L. H. Jones, R. S. McDowell, S. W. Rabideau, A. H. Zeltmann and R. T. Plane, *J. Chem. Phys., 65,* 2707 (1976).

18 C. K. Jørgensen, *Revue Chimie minér. (Paris), 14,* 127 (1977).

19 R. Prins, *J. Chem. Phys., 61,* 2580 (1974).

20 J. Weber, *Chem. Phys. Letters, 40,* 275 (1976).

21 C. K. Jørgensen, *Mat. fys. Medd. Danske Vid. Selskab (Copenhagen), 29,* No. 7 (1955).

22 C. F. Baes, *J. Phys. Chem., 60,* 805 (1956).

23 S. Sostero, O. Traverso, C. Bartocci, P. Di Bernardo, L. Magon and V. Carassiti, *Inorg. Chim. Acta, 19,* 229 (1976).

24 C. K. Jørgensen, "Modern Aspects of Ligand Field Theory", North-Holland, Amsterdam (1971).

25 C. K. Jørgensen, *Adv. Quantum Chem., 11,* (1978) in press.

26 P. F. Walch and D. E. Ellis, *J. Chem. Phys., 65,* 2387 (1976).

27 C. K. Jørgensen, *Structure and Bonding, 30,* 141 (1976).

28 L. Di Sipio, E. Tondello, G. Pelizzi, G. Ingletto and A. Montenero, *Inorg. Chim. Acta, 22,* 23 (1977).

29 R. Reisfeld and C. K. Jørgensen, "Lasers and Excited States of the Rare Earths", Springer-Verlag, Berlin (1977).

30 B. D. Joshi, A. G. I. Dalvi, T. R. Bangia, *J. Luminescence, 10,* 261 (1975).

31 K. L. Lam and A. F. Leung, *J. Non-Crystalline Solids, 23,* 385 (1977).

32 G. C. Joshi, *India J. Pure Appl. Phys., 14,* 180 (1976).

33 M. Marcantonatos, *Inorg. Chim. Acta, 25,* L87 and L101 (1977) and *26,* 41 (1978).