Dual Luminescence of Uranyl and Self-quenching in Aqueous Acidic Solution

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Dual luminescence of uranyl in aqueous solution is observed. The second emittive component is attributed to exciplex formation between $(UO_2H^{2+})^*$ and OUO^{2+}. Unusual concentration quenching effects also support this attribution and indicate a far more versatile behaviour of $(OUO^{2+})^*$ than generally admitted.

Introduction

Several important aspects of uranyl photophysics and photochemistry remain unclarified. Thus, answers to fundamental questions, such as orbital energy ordering in the ground and excited states, the symmetry species and multiplicity of the lowest excited state and the nature of optical transitions, are controversial (see [1] and also [2–5]). Similarly, the mechanism of self-quenching [6, 7] or of the large isotopic effect produced by deuterated alcoholic quenchers, are not known conclusively [1] and intriguing manifestations of the photoexcited uranyl ion, such as two-component lifetime in phosphate glasses [2, 8], or non-exponential emission decay under high photoexcitation of uranyl crystals [1], have not as yet received satisfactory explanations.

The origin of the present work was our growing interest in uranyl photophysics stimulated by discussions with C. K. Jørgensen, by one of his recent papers with R. Reisfeld on this subject [2], and by the recent review of uranyl photochemistry by H. D. Burrows and T. J. Kemp [1]. Our first intention was to investigate the intimate mechanism of quenching of the uranyl luminescence by metal ions, since despite the correlation of $\log K_q$ with I_p (metal ion ionization potential) [6] (which is rather rough), the probability of metal ion electron delocalisation to the π_u MO of the excited uranyl in its f, π_u E.T. state, seems by far more important [9].

It appeared, nevertheless, from our first experiments that luminescence intensity of uranyl solutions in 10^{-2} HNO_3, without metal ion quencher, is a quite peculiar function of I_m (the rate of light absorption) when emission is measured at 544 and 554 nm. Moreover, unusual and unexpected self-quenching effects were superimposed on the above phenomena.

Experimental

Luminescence measurements at 25 °C were made with a Perkin–Elmer MPF-2A spectrofluorometer. Incident light intensities (406 nm) $I_o' = SI_o(Nh\nu/min)$ were measured by a ferric oxalate actinometer and varied by varying S.

A check of possible apparatus effects was made using the Zeiss fluorescent standard and diluted solutions of fluoresceine. At the working wavelengths for emission measurements of the uranyl solutions (478, 544, 554 nm), as well as at several others, fluorescence intensity of standards *vs.* I_o' were perfectly linear. These graphs were regularly used to check the I_o' values together with periodical actinometric determinations.

At the different working wavelengths, inner-filter effects were systematically checked. For the uranyl concentrations used auto-absorptive losses of emission intensity were negligible.

Uranyl solutions in 10^{-2} HNO_3 were always freshly prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ "*Analar*" B.D.H., HNO_3 "*suprapur*" Merck and tridistilled (in a quartz apparatus) pre-boiled H_2O.

The pH of all the UO_2^{2+} solutions studied was 1.94 ± 0.02.

Results and Discussion

For a given uranyl concentration [U], the luminescence (406 nm excited) intensity $I_{L\lambda}$ (at $\lambda(1) = 478$, $\lambda(2) = 544$, $\lambda(3) = 554$ nm) variations with I_m (average number of $Nh\nu$ absorbed in unit volume and unit time $= I_o' V^{-1} [1 - \exp(-2.303\epsilon_{406} [U] l)]$) are shown in Fig. 1 to 2.
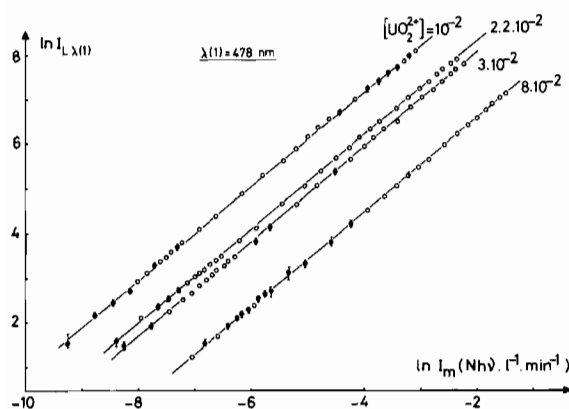
Figure 1. Logarithmic plot of UO_2^{2+} luminescence intensity I_L in 10^{-2} HNO$_3$ vs. I_m (exc. 406 nm); each point is the mean of 6 independent determinations with extreme values shown in the Figure.
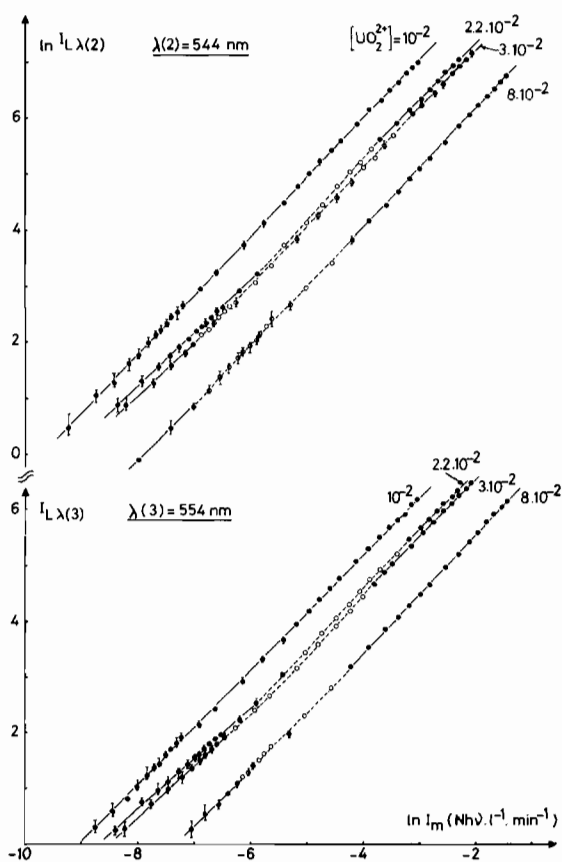

Figure 2. ln I_L vs. ln I_m (exc. 406 nm) in 10^{-2} HNO$_3$.

It is seen that:

(i) for $[U] \leqslant 10^{-2}$, ln $I_{L\lambda(1,2,3)}$ vs. ln I_m are linear as normally exped by:

$$I_{L\lambda(1,2,3)} = q_{(1,2,3)} k_{rU} [U^*] = q_{(1,2,3)} \Phi_{rU} I_m \quad (1)$$

q being an apparatus constant. However, for higher concentrations, remarkable deviations occur when I_L is measured at $\lambda(2) = 544$ and $\lambda(3) = 554$ nm. Thus:

(ii) for $[U] > 10^{-2}$, ln $I_{L\lambda(1)}$ vs. ln I_m ($\lambda(1) = 478$) is always linear, but ln $I_{L\lambda(2,3)}$ are peculiar functions of ln I_m, presenting for low I_m and high I_m two linear parts of different intersection y for ln $I_m = 0$, with $y^{(h)} > y^{(l)}$. ($y = \ln \phi$, $\phi =$ apparent luminescence efficiency, $\phi =$ slope of I_L vs. I_m).

(iii) as $[U]$ increases, the departure from linearity of ln $I_{L\lambda(2,3)}$ against ln I_m (characterized by $y^{(l)}$) takes place at lower I_m and simultaneously:

(iv) the intersection difference $y^{(h)} - y^{(l)}$ first increases and then diminishes (see also Table I).

As there was no indication of any uranyl species other than the aquo linear one (as evidenced by insignificant deviations in ϵ: $\epsilon_{357} = 2.78 \pm 0.03$, $\epsilon_{406} = 7.21 \pm 0.15$, $\epsilon_{422} = 6.17 \pm 0.19$, $\epsilon_{434} = 3.76 \pm 0.06$, from 195 absorbance measurements of $8 \times 10^{-3} \leqslant UO_2^{2+} \leqslant 10^{-1}$ solutions), there cannot be any doubt that the above features cannot be explained by the usually expected decay routes of the photoexcited linear uranyl.

In fact, since augmented population of the lowest excited state of UO_2^{2+} by increasing I_m only, results in an increase of Φ_{rU} in (1), excited state formation of some emitting uranyl species other than the linear $(UO_2^{2+})^*$ has to be considered.

Any assumption of emission from two different electronic states of the same species, to account for the observed anomalous luminescence, may be highly implausible. For such a hypothesis to be correct, one has to argue a non-equilibrium distribution between these two states, which can only occur in the highly improbable case of emission being faster than internal conversion between these states.

Anyhow, our results, especially in relation to quenching, do not support this possibility and it will also be excluded by many other points in the discussion.

Theoretically a number of different mechanisms could be considered to account for the peculiar $(UO_2^{2+})^*$ behaviour. We examined various possibilities and found the following scheme, the most consistent and the only one to fit our results:
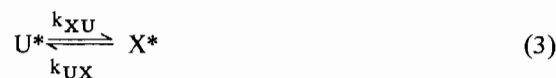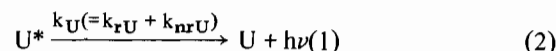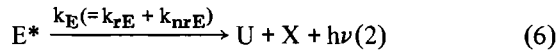
$$U^* \xrightarrow{k_U(=k_{rU} + k_{nrU})} U + h\nu \quad (2)$$

$$U^* \underset{k_{UX}}{\overset{k_{XU}}{\rightleftharpoons}} X^* \quad (3)$$

$$X^* \xrightarrow{k_{nrX}} X \quad (4)$$

TABLE I. Characteristics of the ln I_L vs. ln I_m Functions (see Figs. 1, 2).[a]

$[UO_2^{2+}]$ × 10^2	478 nm		544 nm						
	p	r	$p^{(l)}$	$r^{(l)}$	$y^{(l)}$	$p^{(h)}$	$r^{(h)}$	$y^{(h)}$	$y^{(h)} - y^{(l)}$
1.0	1.05	0.9998	1.06	0.9999	10.2	$p^{(l)}$	$r^{(l)}$	$y^{(l)}$	0
2.2	1.06	0.9999	0.95	0.9997	8.86	1.06	0.9995	9.57	0.71
3.0	1.05	0.9998	0.90	0.9994	8.26	1.07	0.9996	9.44	1.18
8.0	1.05	0.9999	0.96	–	7.65	1.07	0.9999	8.36	0.71

$[UO_2^{2+}]$ × 10^2	554 nm						
	$p^{(l)}$	$r^{(l)}$	$y^{(l)}$	$p^{(h)}$	$r^{(h)}$	$y^{(h)}$	$y^{(h)} - y^{(l)}$
1.0	1.04	0.998	9.37	$p^{(l)}$	$r^{(l)}$	$y^{(l)}$	0
2.2	0.91	0.999	7.93	1.03	0.9994	8.78	0.85
3.0	0.93	0.998	7.93	1.05	0.9998	8.70	0.77
8.0	1.04	0.996	7.62	1.07	0.9999	7.74	0.12

[a] r: linear regression coefficient; p : slope of ln I_L vs. ln I_m; $y^{(l)}$: intersection (ln I_m = 0) of ln I_L vs. ln I_m, for low I_m; $y^{(h)}$: as $y^{(l)}$, but for high I_m.

$$X^* + U \underset{k_{XE}}{\overset{k_{EX}}{\rightleftharpoons}} E^* \qquad (5)$$

$$E^* \xrightarrow{k_E(=k_{rE} + k_{nrE})} U + X + h\nu(2) \qquad (6)$$

With r and nr standing for radiative and radiationless transitions, U* and E* for the excited linear uranyl and an excited emitting complex, photostationary concentrations are:

$$[E^*] = k_{EX}[X^*][U]/k_{XE} + k_E = K_E[X^*][U] \qquad (7)$$

$$[X^*] = k_{XU}[U^*]/k_{UX} + k_{nrX} + k_E K_E[U] \qquad (8)$$

$$[U^*] = I_m/k_U + k_{XU}(k_{nrX} + k_E K_E[U])$$
$$(k_{UX} + k_{nrX} + k_E K_E[U])^{-1} = \Phi_{rU} I_m k_{rU}^{-1} =$$
$$\phi(q k_{rU})^{-1} I_m \qquad (9)$$

and the emission intensity is given by:

$$I_L = q(k_{rU}[U^*] + k_{rE}[E^*]) \qquad (10)$$

As, at 478 nm or with low I_m, the emission of E* is very low:

$$\ln I_{L\lambda(1,2,3)} = \ln q_{(1,2,3)}\Phi_{rU} + \ln I_m = y^{(l)} +$$
$$\ln I_m \qquad (11)$$

but at 544 and 554 nm or for high I_m this is no longer the case and (10) leads to:

$$\ln I_{L\lambda(2,3)} = \ln(\phi_{rU} + \phi_{rE})I_m = \ln \frac{q_{(2,3)}k_{rU}(k_{UX} + k_{nrX}) + q_{(2,3)}(k_{rU}k_E + k_{rE}k_{XU})K_E[U]}{k_U(k_{UX} + k_{nrX}) + k_{XU}k_{nrX} + (k_U + k_{XU})K_E[U]} \qquad I_m =$$

$$= \ln \phi_{(2,3)} + \ln I_m,$$

with $\ln \phi_{(2,3)} = y^{(h)}$.

$$(12)$$

Results (i) are satisfied by (11) and both expressions (11) and (12) account well for results (ii). Moreover, from (7), (8), (9):

$$[E^*] = k_{XU}K_E[U]I_m[k_U(k_{UX} + k_{nrX}) +$$
$$k_{XU}k_{nrX} + (k_U + k_{XU})k_E K_E[U]]^{-1},$$

showing that for a given I_m, [E*] increases with [U] ; thus E* emission is visible at lower I_m for higher concentrations, accounting for results (iii) also.

Results (iv) (last column of Table I) clearly indicate concentration quenching effects. Figures 1 and 2, however, do not allow a quantitative comparison of $I_{L\lambda}$ variations with [U], owing to different sensitivity arrangements of the apparatus, but a whole quantitative picture of a unusual case of self-quenching is given in Figures 3A, B, E and F.

As can be seen (Fig. 3A and B), results at 478 nm fit relation (9). This, taken in the form:

$$\phi_{(1)} =$$

$$\frac{q_{(1)}k_{rU}(k_{UX} + k_{nrX}) + q_{(1)}k_{rU}k_E K_E(U)}{k_U(k_{UX} + k_{nrX}) + k_{XU}k_{nrX} + (k_U + k_{XU})k_E K_E(U)} =$$

$$= \frac{A + B(U)}{C + D(U)} \qquad (13)$$

with (U) standing for activity, leads to:

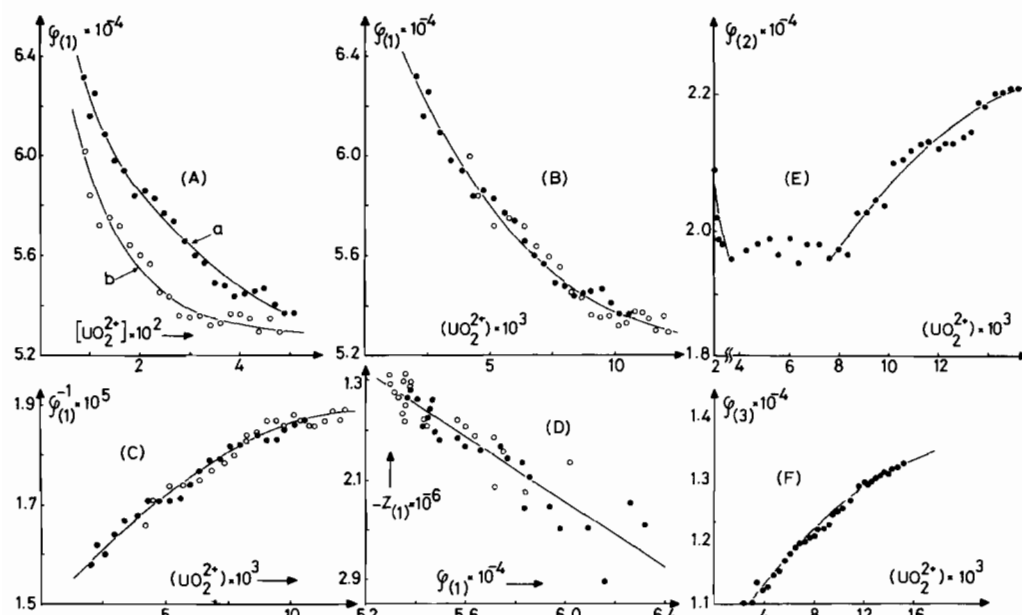$$\frac{\phi_{(1)} - (AC^{-1})}{(U)} = Z_{(1)} = BC^{-1} - \phi_{(1)}DC^{-1}, \qquad (14)$$

Figure 3. Concentration quenching of uranyl luminescence in 10^{-2} HNO$_3$. [ ]: concentrations, ( ): activities (calculated by means of the Davies formula [12]). $\phi = I_L I_m^{-1}$: apparent luminescence efficiency (exc. 406 nm). Each point is the mean of four independent determinations and the highest statistical errors are about ±10%. $\phi_{(1)}$ (478 nm), $\phi_{(2)}$ (544 nm) with $I'_o = 9.6 \times 10^{-6}$ N$h\nu$ min^{-1}, $\phi_{(3)}$ (554) with $I'_o = 6.2 \times 10^{-4}$ N$h\nu$ min^{-1}. o- UO$_2^{2+}$ in 10^{-2} HNO$_3$; ● plus NaNO$_3$; linear regression coefficient of $Z_{(1)}$ $vs.$ $\phi_{(1)}$: 0.915.

($AC^{-1} = \lim \phi_{(1)}$ for (U) $\rightarrow$ 0), which is verified (Fig. 3D).

This latter point excludes emitting excimer EX* formation via:

$$\xleftarrow{k_e(= k_{re} + k_{nre})} EX^* \underset{k_{Ue}}{\overset{k_{eU}, U}{\rightleftharpoons}} U^* \qquad (15)$$
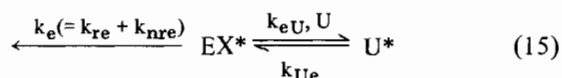
since in this case it is readily shown that:

$$\phi_{(1)}^{-1} = k_U(q_{(1)}k_{rU})^{-1} + k_e K_e(U)(q_{(1)}k_{rU})^{-1},$$

which is not satisfied (see Fig. 3C).

Another interesting point is that activities (U), rather than concentrations [U] satisfy (13) and (9) (compare points of curves in Fig. 3a and b, standing for different ionic strenghts μ, with points in Fig. 3B and C), as expected from the nature of path (5).

It is also conclusive that Burrows et $al.$ [6] found, from luminescence measurements (at 510 nm) of low uranyl concentrations ([U] < 10^{-2}), that k_{SV} of (UO$_2^{2+}$)* by Ag$^+$ increase when [U] is lowered or μ augmented. This is in striking agreement with expression (13), since according to (13) k_{SV} must have the form $k_{SV} = [a + b(U)] [C + D(U)]^{-1}$ (see (13)), with $a = k_{q(Ag)} (k_{UX} + k_{nrX})$ and $b = k_{q(Ag)}k_E K_E$. We found that all eight values of k_{SV} obtained by Burrows et $al.$ [6] for different [U] and μ nicely fit this latter relation, thus giving an explanation of the findings of the above authors.

Again $\phi_{(2,3)}$ (λ(2) = 544, λ(3) = 554 nm) variations with (U) (Fig. 3E and F) are in agreement with relations (10) and (12). Note the very significant

excited-state situation already pointed out (results (ii) and relation (11)), that for low I'_o and (U), $I_{L\lambda(2)} \simeq q_{(2)}k_{rU}$ (U) and $\phi_{(2)}$ varies with (U) approximately as $\phi_{(1)}$. However, as (U) increases and [E*] becomes appreciable, relation (12) operates (Fig. 3E). Obviously, for high I'_o the applicability of (12) is already seen for lower (U) (Fig. 3F). Moreover, using relation (12), $\phi_{(3)}$ (Fig. 3F) and the higher part of $\phi_{(2)}$ (Fig. 3E) can be readily linearised, thus further showing the consistency of the proposed scheme (2) to (6).
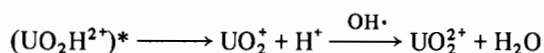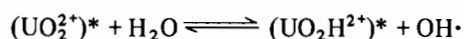
The remarkable central point of importance in this scheme is species X*. Exciplex formation by its interaction with UO$_2^{2+}$ may not be surprising, since excited complex formations are actually known to be very common degradation routes of photoexcited molecules. It is however remarkable that it is the species X* which forms an excited complex and not the linear (UO$_2^{2+}$)* and this point will be briefly discussed subsequently.

As far as X* is concerned, we cannot favour a bent isomer of (OUO^{2+})*. If, and this is what we think, the lowest excited state of this latter is reached by a parity-forbidden f $\leftarrow$ π_u transition [2, 9, 10], repulsion owing to f orbital occupancy by one electron can weaken the UO axial bonds, but it is doubtful whether this repulsion is strong enough to bend them in an appreciable extent.

From our present picture of uranyl photochemistry, the most favoured candidate for X* is (UO$_2$H^{2+})*, resulting from (UO$_2^{2+}$)* hydrogen abstraction from water.

Production of $(UO_2H^{2+})^*$ in the primary path of $(UO_2^{2+})^*$ interaction with many organic compounds can presently be considered as a quite trivial aspect of uranyl photochemistry and there is now direct spectroscopic evidence for U(V) species photoformation [4]. U(V) complexes have also recently been photoprepared [11] from UO_2^{2+} ones.

It can be readily shown that E_o of $(UO_2^{2+})^*$ is as high as 2.6 V [9] and Benson *et al.* [7] found that the activation energy of concentration quenching of $(UO_2^{2+})^*$ in aqueous acidic solution refers rather to the chemical quenching $(UO_2^{2+})^* + H_2O \rightarrow UO_2^+ + H^+ + OH\cdot$ than to a photophysical process. As already pointed out [1, 7], failure to observe $OH\cdot$ as yet may merely imply rapid back reaction between U(V) species and $OH\cdot$ so that the possibility (see paths (3), (4)):

$$(UO_2^{2+})^* + H_2O \rightleftharpoons (UO_2H^{2+})^* + OH\cdot$$

$$(UO_2H^{2+})^* \longrightarrow UO_2^+ + H^+ \xrightarrow{OH\cdot} UO_2^{2+} + H_2O$$

can only be objected to on a phenomenological basis.

It may be significant that rate constants of physical and chemical deactivation of $(UO_2^{2+})^*$ by active alcohols such as CH_3OH, C_2H_5OH, $(CH_3)_2$-CHOH, are of the same order of magnitude [4], and as k_1 for

$$(UO_2^{2+})^* \xrightarrow{k_1} UO_2^{2+} + h\nu$$
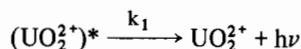
was found to be much lower than either of the quenching constants, H-abstraction by $(UO_2^{2+})^*$ must be a highly efficient path.

It can certainly be argued that H_2O may not be comparable to the above favorable cases, since H mobility in H_2O is expected to be, simply on bond strenght considerations, much lesser than the above

active alcohols. But for the whole argument to be valid, in comparing $(UO_2^{2+})^*$ reactivity towards H_2O and alcohols, one is forced to consider a H-abstraction from H_2O by a bimolecular path. However, this may not be a mechanistic restriction, since we cannot see any special hindrance to the violent $(UO_2^{2+})^*$ moiety in its f, πu state, intramolecularly abstracting a H from one of the equatorial aquo-ligands.

Indirect but strong evidence in favour of such an intramolecular primary act will come in a further paper where we shall discuss lifetimes and photochemistry of crystalline uranyls and where we shall present an explanation of the intriguing fact that luminescence exaltation occurs in $UO_2SO_4\cdot3H_2O$ (but not in $K_2UO_2(SO_4)_2\cdot2H_2O$) crystals when H_2O is replaced by D_2O [1].

From our present results E^* (path (5)) seems to be $(U_2O_4H^{4+})^*$ and it is noteworthy that there is already evidence in favour of the formation of a $U_2O_4^{3+}$ species [1]. Note that the emission spectrum (Fig. 4) of the second uranyl species is not in contradiction with the $(U_2O_4H^{4+})^*$ assumption. It is vibrationally structured and obviously one would not expect loss or even serious blurring of vibrational structure from UO_2^{2+} to $U_2O_4H^{4+}$. Relative to the total emission (Fig. 4a), dominated by the $(UO_2^{2+})^*$ luminescence, the E^* emission is red shifted and interestingly enough the rate constant of $E^* \rightarrow E + h\nu(2)$ is temperature independent (compare Fig. 3b with c) as is, in general, the case of complexes formed in the excited state [13]. Compared to the total emission, there is a ~120 cm^{-1} shortening of the vibrational progression in the spectrum of E^*, suggesting that, in its non-relaxed ground state, there is a weakening of the UO bonds, as expected for a species like $U_2O_4H^{4+}$. Moreover, when temperature is lowered a red shift occurs in the emission of E^* and this, if there is a H-like

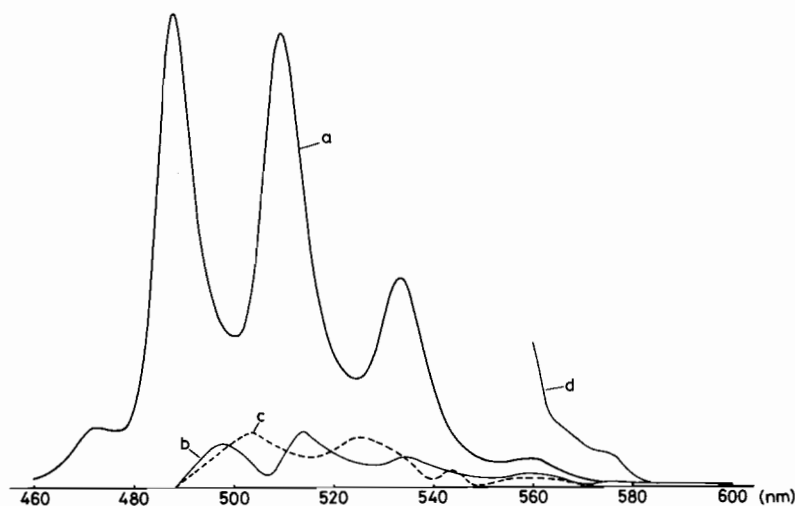Figure 4. (a) Emission of 6×10^{-2} UO_2^{2+} in 10^{-2} HNO_3 at 25 °C (exc.: 406 nm), (b) after normalizing at 488 nm and substracting from (a) the emission of 10^{-2} UO_2^{2+} in 10^{-2} HNO_3 at 25 °C, (c) as (b), but the spectra of 6×10^{-2} and 10^{-2} UO_2^{2+} were taken at 4 °C; for emissions b and c, same scale as for a; (d) as (b), but augmented excitation intensity and apparatus sensitivity.

bond in E*, is also in agreement with the $(U_2O_4H^{4+})^*$ assumption.

However, in the actual state of our work any further attempt to present a mechanism of the $(U_2O_4H^{4+})^*$ formation or to show how it gains sufficient binding energy would be highly speculative, since further investigations, primarily of its emission and together, if possible, with theoretical calculations, are necessary.

There remains one important question which may not be easily answered: why and how $(U_2O_4H^{4+})^*$ decays radiatively, since in the proposed mechanism $(UO_2H^{2+})^*$ was assumed to degrade without irradiation. The possibility emerges that $(UO_2H^{2+})^*$ decays also radiatively but with a probability much lower than that of $(UO_2^{2+})^*$. Being, moreover, highly reactive and probably exhibiting emittive spectral characteristics close to those of $(UO_2^{2+})^*$, its emission may not be distinguishable and may not appreciably contribute to the total luminescence. In that case, the main process, strictly responsible for the chemical quenching of $(UO_2^{2+})^*$ by organic H donors for example, must be the formation of $(UO_2^+)^*$. In aqueous solutions this requires rapid hydrolysis of $(UO_2H^{2+})^*$ and our first results from present studies of the influence of pH on the uranyl luminescence in aqueous acidic media strongly suggest such an excited-state path. Conclusively enough, we found that by favouring the hydrolysis of $(UO_2H^{2+})^*$ there is a marked suppression in the yield of the second emitting species.

Thus the final species in the proposed mechanism are most probably UO_2H^{2+} and UO_2^+. UO_2H^{++} has to hydrolyse and UO_2^+ must rapidly disproportionate to UO_2^{2+} and U(IV) species, the latter being reoxidized in the presence of oxygen.

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