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On The Mechanism of Quenching of Uranyl Ion Luminescence by Metal Ions

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Quenching of lowest excited states by metal ions has been much investigated in aromatics. The well-defined photophysics of these molecules and the knowledge of their lowest excited electronic configurations and sometimes conformations, has led to a rather comprehensive built-up of the quenching mechanism.

Excited configurations of inorganic molecules are obviously far more numerous, and for orbitally versatile inorganic compounds the quantum chemical approach does not always lead to an unambiguous ordering of M.O.'s. Moreover, emittive states reached by photoexcitation may often be of a quite involved nature and lowest excited-state geometries may only be inferred.

A striking example is the uranyl ion, whose $\pi_u \rightarrow 5f$ excitation involves fifty-six mutually orthogonal states [1]. Also, although near OUO linearity in $(UO_2^{2+})^*$, as in UO_2^{2+}, may in principle be argued from the constancy of the vibrational progression of its emission, the OUO angle in $(UO_2^{2+})^*$ may not be exactly identical to (UO_2^{2+}).

One electron occupation of the ϕ_u or of the δ_u M.O.'s, with virtually atomic $f_{x,y,z}$ and $f_{z(x^2-y^2)}$ components of this latter, both expanding at 45° to the $(6_g^+)^2$, $(6_u^+)^2$, $(\pi_g)^4$, $(\pi_u)^3$, manifold, may result in a slight OUO bend owing to some repulsion, particularly as the 5f expansion of uranium (0.95 a.u.) may not be dramatically contracted in $(UO_2^{2+})^*$.

Quenching of the UO_2^{2+} luminescence by transition and non-transition metal ions has been investigated by Burrows *et al.* [2] and Matsushima *et al.* [3]. The most interesting general point arising from these investigations is the violent free-radical behaviour of $(UO_2^{2+})^*$, owing to the π_u hole which not only can extract a strongly bound d electron from the quencher, but also can abstract a H atom by C–H disruption from organic molecules. Obviously, such a reactivity suggests more than strongly that all of the electron density of the π_u optical electron has been centered in the uranium 5f by the absorption process [1, 4].

Electron transfer from metal ions to $(UO_2^{2+})^*$ is therefore a most plausible mechanism accounting for the quenching of its luminescent state, but the attempt [2, 3] to correlate quenching constants k_q to ionization energies I_p of gaseous metal ions seems, at least for $(UO_2^{2+})^*$, rather unjustified.

In fact, all I_p of the metal ions already investigated are larger than the π_u energy in $(UO_2^{2+})^*$. Moreover, the calculated energy (~23 eV) [5, 6] of this latter M.O. may be suspected to be overestimated, in which case the highest occupied orbitals (HOMO) of M^{z+} will be placed much lower than the accepting π_u M.O. of $(UO_2^{2+})^*$.

Chemical ionization energies I_c of aquo-metallic cationic complexes are therefore a much more appropriate choice for HOMOs energies.

It can immediately be seen, from the $I_c = 36$ kK + 0.807 E_okK relation, where E_o is the one-electron standard oxidation potential of M_{ag}^{z+} [7], that $I_c < I_p$, thus placing the HOMO above the π_u of $(UO_2^{2+})^*$. For instance, calculated from E_o [8] I_c are for aquo-: $Ag^+ \cong 6.16$, $Fe^{2+} \cong 5.23$, $Hg_2^{2+} \cong 5.37$, $Mn^{2+} \cong 5.98$, $Co^{2+} \cong 6.31$, $Ce^{3+} \cong 6.06$ *e.V*, which are far lower than the I_p of: $Ag^+ = 21.5$, $Fe^{2+} = 30.6$, $Hg_2^{2+} = 26$, $Mn^{2+} = 33.7$, $Co^{2+} = 33.5$, $Ce^{3+} = 33.3$ *e.V.*

The above I_c do not, however, satisfy any relation such as $\ln k_q = A - BI_p$, as seen from the values of $\ln k_q$ for: $Ag^+ = 21.97$, $Fe^{2+} = 20.32$, $Hg_2^{2+} = 20.72$, $Mn^{2+} = 15.04$, $Co^{2+} = 16.09$, $Ce^{3+} = 12.62$ M^{-1} sec^{-1} [2].

In their study of $(UO_2^{2+})^*$ quenching by metal ions, Burrows *et al.* used the Evans [9] mechanistic approach which can be applied to uncharged organics and which can be summarised by the relations:

$$\ln y = \ln(k_q/k_d - k_q) \propto \Delta G^{\ddagger} \text{ and } \Delta G^{\ddagger} \propto I_p + C$$

for:

$$A^s + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (A^s/Q) \xrightarrow{k_r} (\bar{A}\cdot\overset{+}{Q}\cdot),$$

where: A^s is the excited molecule, Q the quencher, (A^s/Q) the proximity pair, k_d the rate constant of diffusion to form (A^s/Q), k_d the rate constant for diffusion of (A^s/Q) out of the solvent cavity, $\Delta G^{\ddagger}$ the energy of activation for the electron transfer reaction and C comprises terms related to the solvation of a pair of ions.

To obtain a relation such as $\ln k_q = A - BI_p$, which has been suggested [2] as rationalizing the quenching effect on $(UO_2^{2+})^*$ of various metal ions, one must use the above relations as:

$$y = e^{-\alpha\Delta G^{\ddagger}}, \Delta G^{\ddagger} = B(I_p + C),$$

giving:

$$\ln k_q = -BI_p + \ln[\alpha/(1 - \gamma)k_d] - BC,$$

where $\gamma = k_q k_{\bar{d}}^{-1}$.

Even if hydration is assumed to contribute only slightly to the overall energy change [2], it is not easy to assert that γ is of the same size for all the metal ions studied in [2] and [3]. For instance, it can be reasonably anticipated that k_d for Co^{2+}_{aq} and Fe^{2+}_{aq} is of the same order of magnitude, but k_q for Co^{2+}_{aq} is 9.7×10^6 and k_q for Fe^{2+}_{aq} 6.7×10^8 M^{-1} sec^{-1}. It may be argued that $\gamma << 1$ for weak quenchers, but in that case it would be implausible to assume, for example, that k_d is approximately the same for Ce^{3+}_{aq} and Cu^{2+}_{aq}.

Practically, M^{z+}_{aq} to $(UO_2^{2+})^*$ electron transfer requires overlap of the donating metal ion orbital with M.O.'s of the excited uranyl ion and it can be easily seen that one-electron d orbitals can nicely match the π_u M.O. of $(UO_2^{2+})^*$, and that filled d or p orbitals can simultaneously overlap with the π_u M.O. and one of the virtually atomic $f_{x,y,z}$ or $f_{z(x^2-y^2)}$ components of the δ_u M.O. of $(UO_2^{2+})^*$.

Efficient overlap can then lead to exciplex formation, following a $(UO_2^{2+})^*$ encounter with M^{z+} and giving a $(UO_2^+)^*$ solvated pair with $M^{(z+1)+}$ before degradation takes place.

These latter paths can be supported by the very interesting result of Burrows *et al.*, revealing the formation of Mn^{3+} in the presence of photo-excited UO_2^{2+}.

Consequently, at least for the M^{z+} studied in [2] and for some of those investigated in [3], a plausible mechanism would be:

$$(UO_2^{2+})^* + M^{z+} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (UO_2^{2+})^*\text{---}M^{z+}$$

$$\underset{k_{-E}}{\overset{k_E}{\rightleftharpoons}} (UO_2^+ - M^{(z+1)+})^*$$

$$\downarrow k_s$$

$$\xleftarrow{k_c} (UO_2^+)^*\text{---}M^{(Z+1)+}$$

for which

$$k_q = K_{dE}k_s = k_{SV}\,\tau^{-1}$$

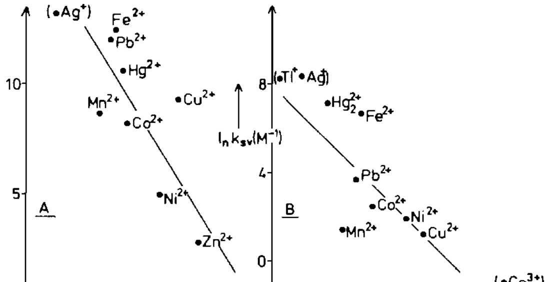

Figure 1. Semilogarithmic plot of Stern–Volmer constant k_{SV} versus $E_{\rho'}$. A: Matsushima's *et al.* data for electron transfer quenching [3]; B: Burrows *et al.* data [2]; linear regression coefficient: 0.729 for A, 0.659 for B.

with k_q then depending on the energy ΔG^e of formation of the exciplex from $(UO_2^{2+})^*$ and M^{z+} and on the activation energy ΔG^* for the $(UO_2^+)^*\text{---}M^{(z+1)}$, formation.

$\Delta G^e = I_c - E_A - E_f + E_{\rho'}$, where I_c is the chemical ionisation energy of M^{z+}_{aq}, E_A the 5f electron affinity and E_f the $\pi_u \rightarrow$ 5f excitation energy. The additional term $E_{\rho'}$ represents the energy necessary to overcome electrostatic repulsion and bring the partners to a suitable distance for orbital overlap.

This energy term $E_{\rho'}$ can be given by:

$$E_{\rho'} = (z + 1)e^2/\epsilon_{\rho'},$$

where ϵ is the solvent dielectric constant and where ρ' can, as a limiting distance, be taken as the sum of radii of maximum density of the 5f U in $(UO_2^{2+})^*$ (ρ_U) and of the d or p orbital in M^{z+}_{aq} (ρ_M).

$\ln k_{SV}$ ($= \ln k_q\tau$) is then expressed by:

$$\ln k_{SV} = -\frac{\Delta G^e + \Delta G^*}{RT} + \ln(\alpha\tau)$$

$$= \ln(\alpha\tau) + \frac{(E_A + E_f)}{RT} - \frac{(I_c + \Delta G^*)}{RT} - \frac{(z + 1)e^2}{RT\epsilon\rho'}$$

where α is the pre-exponential factor in the k_s, ΔG^* relation and where $I_c + \Delta G^*$ may not vary significantly for one metal ion to another, since the lower the I_c (and therefore the larger the electron donnor orbital expansion) and the better the overlap (and therefore the more robust the exciplex), the higher the activation energy ΔG^*.

To check this assumption $\ln k_{SV}$ was expressed as a function of $E_{\rho'}$ only.

ρ' values were obtained by taking (on the basis of the value 0.95 a.u. for 5fU [10]) as a reasonable ρ_U value 0.4 a.u. and adding to this ρ_M values for isolated M^{2+}. ρ_M were calculated by the X^a method for Ag^+ ($4d^{10}$), Cu^{2+} ($3d^9$), Hg^{2+} ($5d^{10}$), Zn^{2+} ($3d^{10}$), Mn^{2+} ($3d^5$) and Ce^{3+} (4f), and the ρ_M values for the other M^{z+} were taken as those of the corresponding atoms and corrected for orbital contraction on the basis of calculated ρ_M for the previous cations. ρ_M value for Fe^{3+} has not been calculated, since k_q value for this ion is not sure [2].

As can be seen from fig. 1A and 1B, the ln k_{SV} vs $E_{\rho'}$ is quite well obeyed, when Matsushima's *et al.* data are taken for all ions quenching $(UO_2^{2+})^*$ by electron transfer, except Ag^+.

With Burrows *et al.* [2] data, Ce^{3+} deviates seriously as well as Ag^+ and Tl^+. Ce^{3+} deviation cannot be easily explained. For all M^{z+} the actual $\rho_M(M^{z+}_{aq})$ are certainly larger than the X^a calculated ρ_M (M^{z+}), and it is possible that for Ce^{3+}_{aq}, ρ_M $(M^{z+}_{aq})/\rho_M$ (M^{z+}) is larger than is the same ratio for the other M_{aq}^{z+}. This (but with an opposite effect) may also be the reason of the Ag_{aq}^{+} and Tl_{aq}^{+} deviations. Till being higher than 1, the ρ_M $(M_{aq}^{+})/\rho_M$ (M^{+}) for these cations are expected to be lower than the analogous ratios for the other M_{aq}^{z+}, owing to a different aquo-field (*i.e.* $Ag(OH_2)_2^+$ to compare with $M(OH_2)_6^{z+}$).

Interestingly enough, the slope (40.2 eV^{-1}) of the $\ln k_{SV}$ *vs.* $E_{\rho'}$ plot with Matsushima's *et al.* data (except Ag^+) gives R = 1.92 cal (deg. mol)$^{-1}$ and that (25.1 eV^{-1}) of the plot with Burrows *et al.* data (except Ag^+, Tl^+, Ce^{3+}) gives R = 3.08 cal (deg. mol)$^{-1}$, which is not unsatisfactory.

As we already mentioned, the actual ρ_M for M_{aq}^{z+} must be larger than the ρ_M (M^{z+}) which were taken for the present calculations. Nevertheless, this does not greatly affect the value of the slope of $\ln k_{SV}$ *vs.* $E_{\rho'}$, but only alters the value of the intercept.

Finally, it is seen that k_{SV} values are for most quenchers higher in [3] than in [2]. As pointed out in [2], this comes mainly from the uranyl ion concentration, which was lower in [3] and, in fact, explanations of this effect can be found in two recent papers [11].

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