

Negative Stern–Volmer Deviations in the Quenching of Uranyl Luminescence by Silver Ion

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It is generally reported that quenching of the uranyl ion luminescence by various perturbors gives good Stern–Volmer (SV) plots, meaning that over a reasonable range of quencher concentration:

$$k_{SV} = k_q \tau_0 \quad (1a)$$

is invariable, and

$$\lim(I_L/I_L^0)_{[Q]=0} = 1 \quad (2a)$$

Recently, however, Matsushima *et al.* reported negative deviations in the quenching of uranyl luminescence by some arylaldehydes in 60 vol.% aqueous acetone containing 0.1 M HClO₄, but this point has not been discussed by the authors [1].

Actually, whether the SV law is derived by photostationary relations or by a stochastic formulation of rate equations [2], the validity of (1a), (2a) implies specificity of a quencher to interact with only one vibronic state (which is emissive) of a definite excited species and therefore deviations have to occur when these conditions are not fulfilled.

For organic molecules, SV deviations generally occur when both lowest excited singlet and triplet states are quenched by external perturbors [3], but in the case of UO₂²⁺ such a possibility cannot be substantiated, since optical excitation and emission take place to and from the same electronic state $\pi_u^3(5f, \delta_u \text{ or } \phi_u)$ [1].

On the other hand, as shown in Figure 1A, the gradient of the SV plot starts to decrease for a Ag⁺ concentration quite lower than the UO₂²⁺ concentration, while most frequently SV deviations appear for a large excess of perturber over the perturbed molecule.

In previous work [4–6], we proposed a photo-physical scheme more involved than the one generally adopted for UO₂²⁺ in aqueous solution, with additional excited-state chemical paths leading to (UO₂H²⁺)^{*}, (UO₂)^{*}, (U₂O₄H⁴⁺)^{*} species and thus accounting for the observation of dual luminescence, for self-quenching, for D₂O and pH effects and for quenching by foreign molecules.

Judging from the most probable configurations and conformations of the above excited uranyl species, it would be a quite exceptional happening

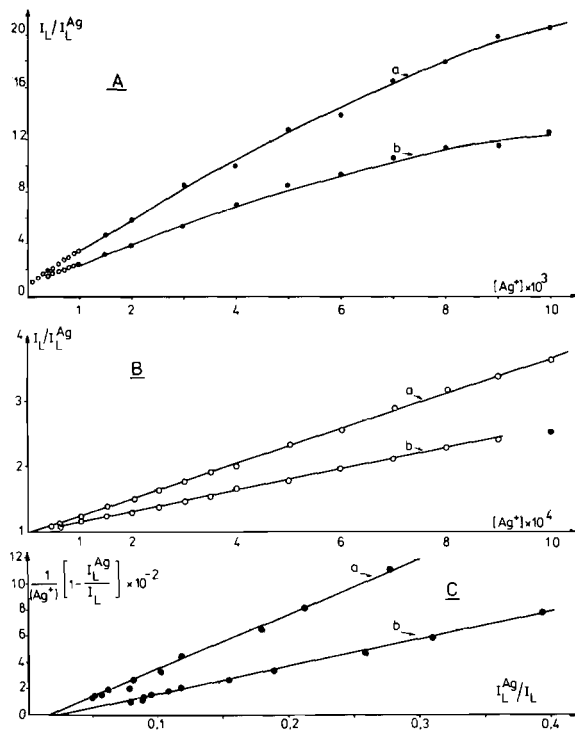
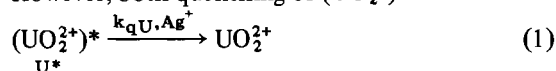


Fig. 1. A and B: Stern–Volmer plots; $[UO_2^{2+}] = 2.4 \times 10^{-2} M$, $[Ag^+] = 4 \times 10^{-5}$ to $10^{-2} M$, pH = 1.94 (HNO₃), T = 25 °C. Exc.: 406; Em: 510 nm (very low exc. intensity used (see [5])). A: $(UO_2^{2+}) = 3.84 \times 10^{-3}$, μ (ionic strength) = 0.437 (constant for all solutions, by added NO₃Na). B: $(UO_2^{2+}) = 8.41 \times 10^{-3}$, $\mu = 0.087$; activity coefficients calculated by Güntelberg's formula [9]. C: graphical analysis of SV deviations.

for a quencher like Ag⁺ to interact only with the linear (UO₂²⁺)^{*}.

In fact, one has to consider possible paths involving Ag⁺ and the chemically formed in the excited-state uranyl species. Nevertheless, under our experimental conditions (HNO₃ = 10⁻², $[UO_2^{2+}] = 2.4 \times 10^{-2}$, $0.087 \leq \mu \leq 0.587$) it would be implausible to think of any interaction between (U₂O₄H⁴⁺)^{*} and Ag⁺, since this would require excessive suppression of charge activity. In fact, kinetic schemes including a (U₂O₄H⁴⁺)^{*}–Ag⁺ interaction in order to account for the anomalies in the SV plots, leave our experimental data completely unfitted. This happens also to be the case when, implausibly enough, a catalytic action of Ag⁺ is suspected in the excited-state formation of (UO₂H²⁺)^{*}, (UO₂)^{*} or (U₂O₄H⁴⁺)^{*}.

However, both quenching of (UO₂²⁺)^{*}:



and of either (UO₂H²⁺)^{*}:

TABLE. Parameters from the Analysis of I_L/I_L^{Ag} vs. Silver Ion Activity (Ag^+).

$(UO_2^{2+}) \times 10^3$	μ	$k_{SV(1)}^a$	y_1^a	r_1	$k_{SV(2)}^b$	$-y_2^b$	r_2
8.414	0.087	2040	1.02	0.9993	2089	-34.1	0.998
5.620	0.212	3019	0.98	0.9997	2881	-47.5	0.997
4.815	0.287	3550	1.03	0.9998	3685	-45.2	0.999
4.103	0.387	3981	1.00	0.999	3729	-49.2	0.998
3.839	0.437	4252	0.99	0.9996	4296	-59.1	0.999
3.255	0.587	4763	1.00	0.9991	4910	-51.2	0.999

^aFrom relation (7).^bFrom relation (8). y_1 : intercept; r_1 : linear regression coefficient.or $(UO_2^+)^*$:can account for the whole I_L/I_L^{Ag} vs. $[Ag^+]$ variation.

In fact, as for the exciplex formation ([4], [5]), so for kinetics of paths (1) and (2) or (3), quencher activities are obviously adequate in deriving photo-stationary relations and from reactions (1) to (5), (2'), (2'') and expressions (8) to (14) in ref. [5], together with (1) and (2) or (3), the following expression is obtained:

$$\frac{I_L}{I_L^{Ag}} = \frac{1 + ([A + k_E K_E(U)] + (k_U + k_{qU}(Ag^+) + k_{XU})k_{q2}k_{qU}^{-1})k_{qU}D^{-1}(Ag^+)}{1 + k_{q2}(Ag^+)[A + k_E K_E(U)]^{-1}} = k_{SV} \frac{I_L^{Ag}}{I_L} - y_2 \quad (8)$$

with:

$$\begin{aligned} k_{q2} &= k_{qX} \text{ or } k_{qY} K_Y [H^+]^{-1}; \\ K_Y &= [(UO_2^+)^*][H^+] / [(UO_2H^{2+})^*] \end{aligned} \quad (5)$$

and where I_L^{Ag} is the emission intensity of UO_2^{2+} (measured at the 510 nm vibronic component) in the presence of Ag^+ ; (U) and (Ag^+) stand for activities and where the significance of the other symbols can be found in ref. [5].

Before discussing whether it is $(UO_2H^{2+})^*$ (2) or $(UO_2^+)^*$ (3) whose degradation is enhanced in the presence of Ag^+ , it can be seen from relation (4) that, if $k_{qU} > k_{q2}$, then:

$$\frac{I_L}{I_L^{Ag}} = \frac{1 + [A + k_E K_E(U)] k_{qU}(Ag^+)D^{-1}}{1 + k_{q2}(Ag^+)[A + k_E K_E(U)]^{-1}}, \quad (6)$$

since (see [5]) $A + k_E K_E(U) = k_{UX} + k_{nrx} + k_{nry} K_Y [H^+]^{-1} + k_E K_E(U)$ is larger than $k_U + k_{qU}(Ag^+) + k_{XU}$.

Now, it is expected that for low (Ag^+) , $k_{q2}(Ag^+)[A + k_E K_E(U)]^{-1}$ (but not $k_{qU}(Ag^+)[A + k_E K_E(U)]^{-1}$) becomes much lower than unity, in which case (6) reduces to (see Fig. 1B):

$$\frac{I_L}{I_L^{Ag}} = 1 + [A + k_E K_E(U)] k_{qU} D^{-1} (Ag^+) = 1 + k_{SV}(Ag^+) \quad (7)$$

and this latter relation has been recently shown [5] to explain the anomalous decrease of k_{SV} with uranyl concentration, observed by Burrows *et al.* [7] (also see Table).

For high (Ag^+) , however, relation (6) remains valid and it is noteworthy that if (6) is taken in the following form (see Fig. 1C):

$$\frac{1}{(Ag^+)} \left[1 - \frac{I_L^{Ag}}{I_L} \right] = k_{SV} \frac{I_L^{Ag}}{I_L} - k_{q2} [A + k_E K_E(U)]^{-1} = k_{SV} \frac{I_L^{Ag}}{I_L} - y_2 \quad (8)$$

k_{SV} values determined by (7) (low (Ag^+)) and by (8) (high (Ag^+)) are in striking agreement (Table). Figure 2A also shows the validity of the intercept y_2 of (*), $1/y_2$ being indeed a linear function of uranyl activity (Fig. 2A), thus bringing further evidence in favour of the exciplex formation [4, 5].

It can be seen from relation (5) that k_{q2} must be pH insensitive, if $k_{q2} = k_{qX}$. But if $(UO_2^+)^*$ is the other excited species quenched by Ag^+ , k_{q2} has to depend on pH.

Figure 2B shows that when the pH is lowered from 1.94 to 0.14, SV linearity extends to higher silver ion activities, indicating that k_{q2} in relation (4) has been decreased and thus strongly suggesting that $(UO_2^+)^*$ is the quenched species.

It is also noteworthy that there is an about three-fold increase in k_{SV} when pH is changed from 1.94 to 0.14 (compare k_{SV} given in the table for $(UO_2^{2+}) = 4.81 \times 10^{-3}$ and 4.1×10^{-3} , with $k_{SV} = 11580$ (Fig. 2B) for $(UO_2^{2+}) = 4.48 \times 10^{-3}$ at pH = 0.14).

According to (7), the form of k_{SV} (also see [5]) is:

$$k_{SV}(M^{-1}) = \frac{k_{QU}[k_{UX} + k_{nrX} + k_{nrY}K_Y[H^+]^{-1} + k_E K_E(U)]}{k_U(k_{UX} + k_{nrX}) + k_{XU}k_{nrX} + (k_U + k_{XU})[k_{nrY}K_Y[H^+]^{-1} + k_E K_E(U)]}$$

and, as we are going to show in a further paper:

$$k_{UX} + k_{nrX} = 120 k_{nrY}K_Y.$$

k_{SV} , which is then:

$$k_{SV} = \frac{k_{QU}[(120 + [H^+]^{-1})k_{nrY}K_Y + k_E K_E(U)]}{M + N[k_{nrY}K_Y[H^+]^{-1} + k_E K_E(U)]}$$

has to increase when pH is lowered from 1.94 to 0.14, since the relative decrease in $k_{nrY}K_Y[H^+]^{-1}$ is far more important than that of $(120 + [H^+]^{-1})k_{nrY}K_Y$.

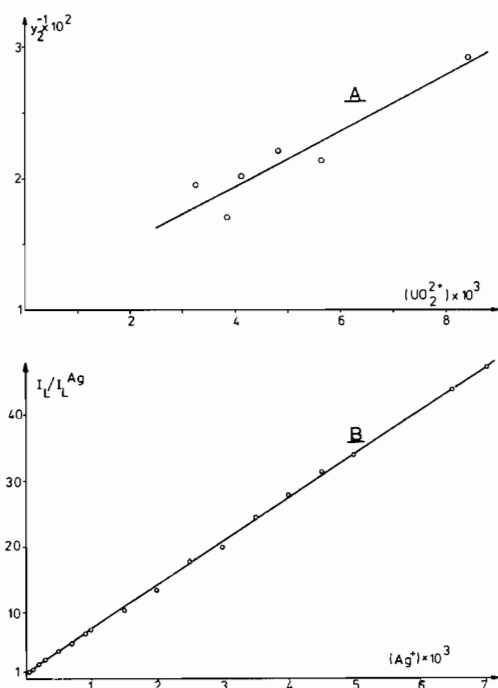


Fig. 2. A: Plot of y_2^{-1} vs. uranyl ion activity (U) (linear regression coefficient = 0.927); B: Stern-Volmer plot for uranyl quenched by Ag^+ at pH = 0.14. $(UO_2^{2+}) = 4.48 \times 10^{-3}$.

This, in addition to a possible uranyl ion activity (U) effect (if k_{SV} is determined with two different (U)), undoubtedly explains the discrepancy between Matsushima *et al.*'s value ($k_{SV(Ag)} = 5.2 \times 10^5$, $[UO_2^{2+}] = 10^{-3} M$ in $0.67 M H_3PO_4$) [8] with the value of Burrows *et al.* ($k_{SV(Ag)} = 4350$, $[UO_2^{2+}] = 2 \times 10^{-2} M$, pH = 2–2.5, with HNO_3) [7].

However, our present data are insufficient to make any proposition as to the mechanism of quenching of species $(UO_2^+)^*$. $d_{Ag^+} \longrightarrow \pi_u(UO_2^+)^*$ electron transfer actually appears as the most plausible mechanism of $(UO_2^+)^*$ quenching and it cannot be excluded that Ag^+ acts as two-way quencher, also perturbing $(UO_2^+)^*$ by a $s_{Ag^+}^0 \longleftarrow \pi_u(UO_2^+)^*$ E.T.

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