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Uranyl fluoride luminescence in acidic aqueous solutions

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Abstract

Luminescence emission spectra and decay rates are reported for uranyl species in acidic aqueous solutions containing HF or added NaF. The longest luminescence lifetime, 0.269 ± 0.006 ms, was observed from uranyl in 1 M HF + 1 M $HClO_4$ at 296 K and decreased with increasing temperature. Based on a luminescence dynamics model that assumes equilibrium among electronically excited uranyl fluoride species and free fluoride ion, this long lived uranyl luminescence in aqueous solution is attributed primarily to UO_2F_2. Studies on the effect of added $LiNO_3$ or $Na_2WO_4 \cdot 2H_2O$ showed relatively weak quenching of uranyl fluoride luminescence which suggests that high sensitivity determination of the UF_6 content of WF_6 gas should be feasible via uranyl luminescence analysis of hydrolyzed gas samples of impure WF_6.

Keywords: uranyl, luminescence, speciation, uranium analysis, uranyl fluoride

1. Introduction

Determination of trace levels of uranium, present as UF_6, in WF_6 gas is challenging due to the chemically aggressive nature of transition metal hexafluorides. The presence of UF_6 in WF_6 is technologically important because WF_6 is used to deposit tungsten metal in the

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manufacture of integrated circuits (see, for example, [1]). Impurity UF_6 in WF_6 can result in deposition of uranium species which, due to radioactive decay, give rise to alpha particle-induced single event upsets that degrade integrated circuit reliability [2]. During the course of assessing the applicability of luminescence analysis for U as uranyl in aqueous solutions resulting from hydrolysis of impure WF_6 in diluted nitric acid, we observed uranyl luminescence decay times that increased with increasing amount of hydrolyzed gas. We were surprised because W(VI) in 1 M H_3PO_4 [3] is known to quench uranyl luminescence and decrease its luminescence lifetime. Prompted by this result, and because hydrolysis of WF_6 generates both W(VI) and HF, we investigated the influence of fluoride ion on uranyl luminescence lifetime in solutions of molar acidity.

Ours is not the first work on the influence of fluoride ion, F^-, on uranyl luminescence. Enhancement of uranyl luminescence in aqueous solution via F^- has long been exploited for analytical purposes. The study of Kaminski and coworkers[4] provides an example of such work and they cite earlier analytical studies. Moriyasu and coworkers[5] carried out a systematic study of the influence of fluoride on the luminescence lifetimes of 0.01 M uranyl solutions. They reported that the uranyl luminescence decay rate at 298 K decreased with increasing fluoride concentration to a value, 6667 s^{-1}, that remained constant from 0.06 M to 1 M fluoride and concluded that UO_2F_2, $UO_2F_3^-$, and $UO_2F_4^{2-}$ have the same luminescence lifetimes. Billing and coworkers reported that the luminescence decay rate of 0.01 M uranyl in 0.5 M NaF at pH 7.4 is 6250 ± 78 s^{-1} and ascribed the luminescence to the $UO_2F_4^{2-}$ [6]. During the course of the present investigation, Moulin and coworkers reported that the luminescence decay rate of uranyl in 0.67 M HF is 3333 s^{-1} at 293 K [7] and assigned the luminescence to $UO_2F_3^-$ and $UO_2F_4^{2-}$. The nature of the luminescing state (or states) of uranyl and its complexes remains controversial. See

Azenha and coworkers[8] for a recent review of several interpretations of uranyl luminescence as well as references to earlier studies and reviews.

2. Experimental Details

Reagent grade or more highly purified chemicals and Type 1 reagent grade water (per ASTM D1193) were used to prepare solutions. Stock solutions that contained HF were stored in high density polyethylene containers. Uranium was added as uranyl (UO_2^{2+}) using a stock solution of uranyl in diluted nitric acid. Salts such as sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) and $LiNO_3$ were added in weighed amounts to an aliquot of a given acid stock solution. Based on weight changes, acidic 1 M HF solutions slowly attacked the fused silica cuvettes used for luminescence studies, although no visible etching was observed. Sample solutions were in contact with fused silica for at most a few hours, exhibited no discernible trend as to the influence of residence time on observed luminescence decay rate, and were discarded after undergoing analysis. The concentration stated for a particular chemical compound, such as $Na_2WO_4.2H_2O$, in a given solution is the total (analytical) concentration of the stated material in the solution. Speciation calculations were carried out using a simplex minimization algorithm[9]. The stability constants of Ahrland and Kullberg[10] for fluoride-containing uranyl solutions of ionic strength 1 at 298 K were used, unless otherwise stated.

The excitation light source was a 337 nm nitrogen laser (~2 mJ/pulse). Emission spectra were recorded using a time-gated, intensified, optical multichannel analyzer mounted on a spectrograph (0.5954 nm per datum) and have not been corrected for the spectral response of the detection system. Luminescence decays were recorded using optical filters that passed wavelengths longer than 470 nm, a cooled GaAs photomultiplier, a variable value load resistor, and a signal averaging digital storage oscilloscope that was interfaced to a personal computer.

The load resistance was varied to alter the response time of the detection system and thereby optimize signal-to-noise ratio. Nonlinear least squares fitting was carried out using either a single exponential decay model, $I(t) = A\exp(-k_1 t)$, where $I(t)$ is the observed luminescence intensity at time t following the laser pulse and A and k_1 are parameters whose value was adjusted or a double exponential decay model, $I(t) = A\exp(-k_1 t) + B\exp(-k_2 t)$, where A, k_1, B, and k_2 are parameters whose value underwent nonlinear adjustment. The stated uncertainties in adjusted model parameters correspond to 95% confidence limits based on replicate determinations.

3. Results

The gated emission spectrum of uranyl in 1 M HF + 1 M $HClO_4$ is shown in Fig. 1. The observed spectra consist of vibronic bands (846 cm^{-1} average spacing) that are attributed to emission from uranyl fluoride complexes (primarily UO_2F_2, as discussed below). The observed luminescence decay of uranyl ion in the same solution and corresponding best fit decay curve are shown in Fig. 2. The luminescence decay rate was temperature dependent: $k_1 = 3717 \pm 86\ s^{-1}$ at 296 K and $4149 \pm 138\ s^{-1}$ at 301 K

Serial addition of weighed amounts of NaF to a solution initially containing 3×10^{-6} M uranyl in 0.1 M $HClO_4$ was carried out and the luminescence decay of uranyl was recorded after each addition of NaF. The slowest decay rate ($k_1 = 3846 \pm 89\ s^{-1}$ at 299 K) was found for 1.3×10^{-1} M added NaF with faster decays observed at lower and higher concentrations of added NaF (see Fig. 3). To probe the influence of NO_3^- on the luminescence of uranyl fluorides, serial addition of $LiNO_3$ to a solution of uranyl in 1 M HF + 1 M $HClO_4$ was carried out and luminescence decay data were recorded after each addition of $LiNO_3$. Addition of 0.14 M, 0.27 M, and 0.58 M $LiNO_3$ resulted in increasingly rapid luminescence decays whose curves were better fit by the double exponential decay model although with decay rate constants that differed by less than 35% for a given $LiNO_3$ concentration. A final addition to give 0.98 M $LiNO_3$ resulted in a luminescence decay curve that was well fit by a single exponential decay model ($k_1 = 64700 \pm 940\ s^{-1}$). Analyzing the observed decays for 0.14 M, 0.27 M, and 0.58 M added $LiNO_3$ as single exponential and carrying out a Stern-Volmer plot of that data gave a quenching rate parameter, k_q, of $(1.1 \pm 2) x 10^4\ M^{-1}\ s^{-1}$ for addition of $LiNO_3$ to uranyl in 1 M HF + 1 M $HClO_4$ at 301 K. This value for quenching of uranyl fluoride luminescence by NO_3^- is somewhat smaller than the $(4.7 \pm 0.8) x 10^4\ M^{-1}\ s^{-1}$ value reported for quenching of UO_2^{2+} by NO_3^- in nitric acid[11]. An emission spectrum (Fig. 1) recorded after the final $LiNO_3$ addition was found to consist of a band identical to that of uranyl in 1 M HF + 1 M $HClO_4$ and a broad, relatively featureless, band that contained 24% of the total observed emission band area and is similar to that reported by Deniau and coworkers for uranyl in 1.6 M HNO_3 [12].

The luminescence decay and emission spectrum of uranyl in 1 M HF + 1 M HNO_3 at 295 K, following 337 nm excitation, were recorded before and after addition of $2.9 x 10^{-2}$ M $Na_2WO_4 \cdot 2H_2O$ to probe the influence of W(VI) on uranyl fluoride luminescence. The absence of new emission bands and faster decay upon addition of sodium tungstate argues that its primary effect is to collisionally quench uranyl luminescence. Based on the observed increase in uranyl luminescence decay rate, k_q for dissolved tungstate (likely a present as a fluorotungstate complex[13]) is $1.7 x 10^5\ M^{-1}\ s^{-1}$ in 1 M HF + 1 M HNO_3 at 295 K This differs little from the $k_q = 1.6 x 10^5\ M^{-1}\ s^{-1}$ value reported by Moriyasu and coworkers for W(VI) in 1 M H_3PO_4 at 298 K[3].

4. Discussion

In Fig. 1, the observed luminescence bands agree , within experimental error, with the maxima reported by Billing and coworkers [6] as occurring from uranyl in 0.5 M NaF at pH 2 and the uranyl in 0.67 M HF at 293 K spectrum reported by Moulin and coworkers[7]. The bands do differ from the reported emission spectrum of UO_2F^+ [14]. Using literature stability constants for 298 K and ionic strength 1 [10], we calculate that the predominant uranyl fluorides, as to mole fraction, X, in 1 M HF + 1 M $HClO_4$ are UO_2F^+ (X =0.200), UO_2F_2 (X = 0.607), and $UO_2F_3^-$ (X=0.182). For 0.01 M total uranyl in 0.5 M NaF at pH 2, the majority uranyl species are $UO_2F_3^-$ (X = 0.447) and $UO_2F_4^{2-}$ (X= 0.509). Using stability constants for ionic strength 0 at 298 K [15,16] for uranyl in 0.67 M HF, the calculated dominant species are UO_2F_2 (X = 0.244) and $UO_2F_3^-$ (X= 0.683). Based on these speciation calculations, it not evident why uranyl in 1 M HF + 1 M $HClO_4$, in 0.67 M HF, and in 0.5 M NaF at pH 2 gives rise to such similar emission spectra. Similar spectra would be expected if the equilibria among uranyl fluorides and free F^- is sufficiently different for electronically excited uranyl complexes in comparison with those reported for ground state uranyl complexes[10] and such equilibria are established on a time scale shorter than the observed luminescence decay. As discussed below, this interpretation is supported by luminescence lifetime studies.

Moriyasu and coworkers studied the effect of fluoride concentration on uranyl luminescence decay at 298 K (see their Fig. 2) [5]. They reported that the luminescence decay rate of UO_2F^+ is 13333 s^{-1} and the decay rates of UO_2F_2, $UO_2F_3^-$, and $UO_2F_4^{2-}$ are the same (6667 s^{-1}) to within an unstated error limit. In contrast, we have observed a luminescence decay rate of 3717 s^{-1} from uranyl in 1 M HF + 1 M $HClO_4$ at 296 K and Moulin and coworkers reported 3333 s^{-1} for uranyl in 0.67 M HF at 293 K [7]. Prompted by these differing values, we calculated uranyl speciation for the solution composition of Fig. 1 of Moriyasu and coworkers' paper[5] using the more recent stability constants of Ahrland and Kullberg[10]. Our values, shown in Fig. 4a, differ little from Fig. 1 of Moriyasu and coworkers. However, given the technical difficulties of pH measurement and ionic strength adjustment in solutions containing significant amounts of HF, Moriyasu and coworkers may have carried out serial addition of NaF to an 0.01 M uranyl solution that initially was pH = 1 and ionic strength = 1. In such a case, solution pH would have varied from acidic to near neutral. Our calculations for this case are shown in Fig. 4b (we did not correct for increased ionic strength due to addition of fluoride as NaF). In Fig. 4b, UO_2F_2 is the dominant uranyl fluoride species over a smaller fluoride concentration range and most uranyl at 1 M total fluoride is $UO_2F_4^{2-}$ rather than UO_2F_2. The 6667 s^{-1} decay rate reported by Moriyasu and coworkers and the dominance of $UO_2F_4^{2-}$ at 1 M fluoride (if Fig. 4b represents their work) agree with the 6250 s^{-1} decay rate reported by Billing and coworkers[6] for uranyl in 0.5 M NaF at pH = 7.4 (attributed by them to $UO_2F_4^{2-}$).

The much longer luminescence lifetimes observed in the present work and also reported by Moulin and coworkers in 0.67 M HF[7], in comparison with those reported by Moriyasu and coworkers [5] and Billing and coworkers[6], can be understood in terms of uranyl fluoride equilibria that are influenced by whether or not such complexes are electronically excited. If we assume that equilibrium occurs, on the time scale of the observed luminescence, among UO_2F^+, UO_2F_2, $UO_2F_3^-$, and $UO_2F_4^{2-}$ and F^-, <u>for electronically excited uranyl species</u> (denoted by an asterisk in equilibrium reactions), we can model the observed data shown in Fig. 3. From a recent NMR study [17], the fluoride ion exchange rate for <u>ground state</u> uranyl fluorides is slower their luminescence decay rates. However, several luminescence studies, including work on uranyl sulfate [18] and nitrate [19] complexes, have concluded that ligand exchange rates for complexes of electronically excited uranyl can be so rapid that equilibrium is achieved on the luminescence time scale. Fixing the luminescence decay rate of UO_2F^+ at 13333 s^{-1} [5] and that of $UO_2F_4^{2-}$ at 6250 s^{-1} [6] and carrying out nonlinear least squares adjustment, gives the solid line shown in Fig. 3 for fit values of 8044 M^{-1} for the equilibrium constant for formation of UO_2F_2* via $UO_2F^{+*} + F^- \rightarrow UO_2F_2^*$, of 0.7868 M^{-1} for formation of $UO_2F_3^{-*}$ via $UO_2F_2^* + F^- \rightarrow UO_2F_3^{-}$ *, of 1.053x10^{-4} M^{-1} for formation of $UO_2F_4^{2-*}$ via $UO_2F_3^{-*} + F^- \rightarrow UO_2F_4^{2-*}$ and of 3799 s^{-1} and 11850 s^{-1} as the luminescence decay rates of UO_2F_2 and $UO_2F_3^-$, respectively. Free fluoride ion concentration, $[F^-]$ (see Fig. 3), was calculated using the stability constants of Ahrland and Kullberg[10] without correction for changes in ionic strength. Due to low total uranyl concentration, there is negligible change in $[F^-]$ due to speciation changes resulting from electronic excitation of uranyl fluorides. For the stated model parameters, the calculated decay rate for trace level uranyl in 0.67 M HF at 299 K is 3972 s^{-1}, which differs little from the 293 K value of 3333 s^{-1} that was reported by Moulin and coworkers with no error limit stated [7]. Similarly, the calculated decay rate of dilute uranyl in 0.5 M added NaF and 299 K is 6041 s^{-1}, which differs little from the 6250 s^{-1} value assumed for $UO_2F_4^{2-}$, based on the work of Billing and coworkers at "room temperature" [6]. The calculated decay rate in 1 M HF + 1 M $HClO_4$ at 299 K is 4774 s^{-1}. As expected, the calculated decay rate for uranyl fluorides at very low $[F^-]$ is 13333 s^{-1}, i.e., the reported value for UO_2F^+ [5]. Our model also provides a rationale for the similarity, noted above, of the reported emission spectra of uranyl in weakly to strongly acid solutions that contain fluoride. Our model predicts that emission from UO_2F_2 accounts for 71%, 91%, and 94% of the emitted photons from uranyl fluorides at 299 K in, respectively, 1 M HF + 1 M $HClO_4$, 0.5 M NaF at pH 2, and 0.67 M HF following 337 nm excitation.

What is not immediately evident is the reason why Moriyasu and coworkers found no decay rate slower than 6667 s^{-1}. If we assume that Fig. 4b represents their work, then only their reported lifetime data points from 0.03 M to 0.011 M fluoride are significantly different than those that we calculate using our fitted equilibrium constants and luminescence decay rates and $[F^-]$ as calculated for Fig. 4b. The calculated HF concentration for Fig. 4b rises rapidly to its maximum value (0.089 M) over the range of 0.03 M to 0.15 M added NaF. Due to the presumably long (but unstated) time necessary for Moriyasu and coworkers[5] to acquire a luminescence decay curve using a pulsed discharge in N_2 gas as the light source, it may be that HF attack on their sample cell was significant and altered solution pH sufficiently to suppress the otherwise expected dominance of UO_2F_2 and $UO_2F_3^-$ in the range of 0.03 M to 0.11 M added NaF. In addition, the possibility of self-quenching of uranyl luminescence in the work of Moriyasu and coworkers can not be ruled out due to the relatively high uranyl concentration that they used. Finally, basic impurities in NaF (such as those reported by Ahrland and Kullberg in their work [10]), if present, would have converted uranyl to $UO_2F_4^{2-}$ more rapidly over the concentration range in question and so rendered observation of the slow luminescence decay of UO_2F_2 more difficult in the work of Moriyasu and coworkers [5].

The relatively weak quenching of uranyl fluoride luminescence by nitrate and tungstate ions found in the present work suggests that high sensitivity determination of the UF_6 content of WF_6 gas should be feasible via luminescence determination of uranyl following hydrolysis of impure WF_6 gas in dilute nitric acid solution. Even higher sensitivity would be expected if dilute perchloric acid is used for hydrolysis of WF_6 gas. Determination of trace level uranium in Zr metal has been demonstrated using uranyl luminescence following dissolution of the metal in 0.67 M HF + 0.11 M HNO_3 [7].

4. Conclusions

Long lived, temperature dependent, single exponential luminescence decay of uranyl in 1 M HF + 1 M $HClO_4$ has been observed and is attributed to emission predominantly from UO_2F_2 based on uranyl speciation calculations and a luminescence dynamics model that assumes that electronically excited uranyl fluorides are in equilibrium with each other and free F^- ion on the luminescence decay time scale. The model accounts for the observed luminescence dynamics and spectra of uranyl fluorides in aqueous solution following near ultraviolet excitation of acidic solutions containing significant amounts of fluoride. Relatively weak quenching of uranyl fluoride luminescence by tungstate and nitrate ions suggests that high sensitivity determination of the UF_6 content of WF_6 gas should be feasible via uranyl luminescence analysis of hydrolyzed gas samples of impure WF_6.

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Figure Captions

Fig. 1. Emission spectra of 1.3×10^{-5} M uranyl in 1 M HF + 1 M $HClO_4$ at 301 K (320 μs wide analyzer gate, opened 2.6 μs before each 337 nm excitation pulse). Curve **a**, shown with linear and logarithmic axes, was recorded prior to addition of any $LiNO_3$. Curve **b**, scaled in intensity so that its most prominent peak has the same peak-to-valley ratio as the corresponding peak of curve **a**, was recorded after addition of 0.98 M $LiNO_3$. Curve **c** is the result of subtracting curve a from curve **b**.

Fig. 2. The observed luminescence decay of 1.3×10^{-5} M uranyl ion in 1 M HF + 1 M $HClO_4$ at 296 K, following 337 nm excitation, is shown as symbols (every 20th datum shown) along with the best fit single exponential decay curve (solid line, $k_1 = 3718\ s^{-1}$).

Fig. 3. Observed luminescence decay rate versus concentration of added NaF for a solution at 299 K that initially contained 3×10^{-6} M uranyl in 0.1 M $HClO_4$ (symbols) and the best fit curve (solid line) for a model, described in the text, that assumes equilibrium among electronically excited uranyl fluorides and free fluoride ion. Also shown is the free fluoride ion concentration resulting from addition of NaF that was calculated using the stability constants of Ahrland and Kullberg [10].

Fig. 4. Calculated concentration of uranyl species (0.01 M total uranyl) as a function of total fluoride ion concentration in pH =1, ionic strength = 1 solutions at 298 K. (panel **a**). Calculated concentration of uranyl species as a function of added NaF for a solution initially 0.01 M in uranyl, pH = 1, and ionic strength = 1 at 298 K (panel **b**).

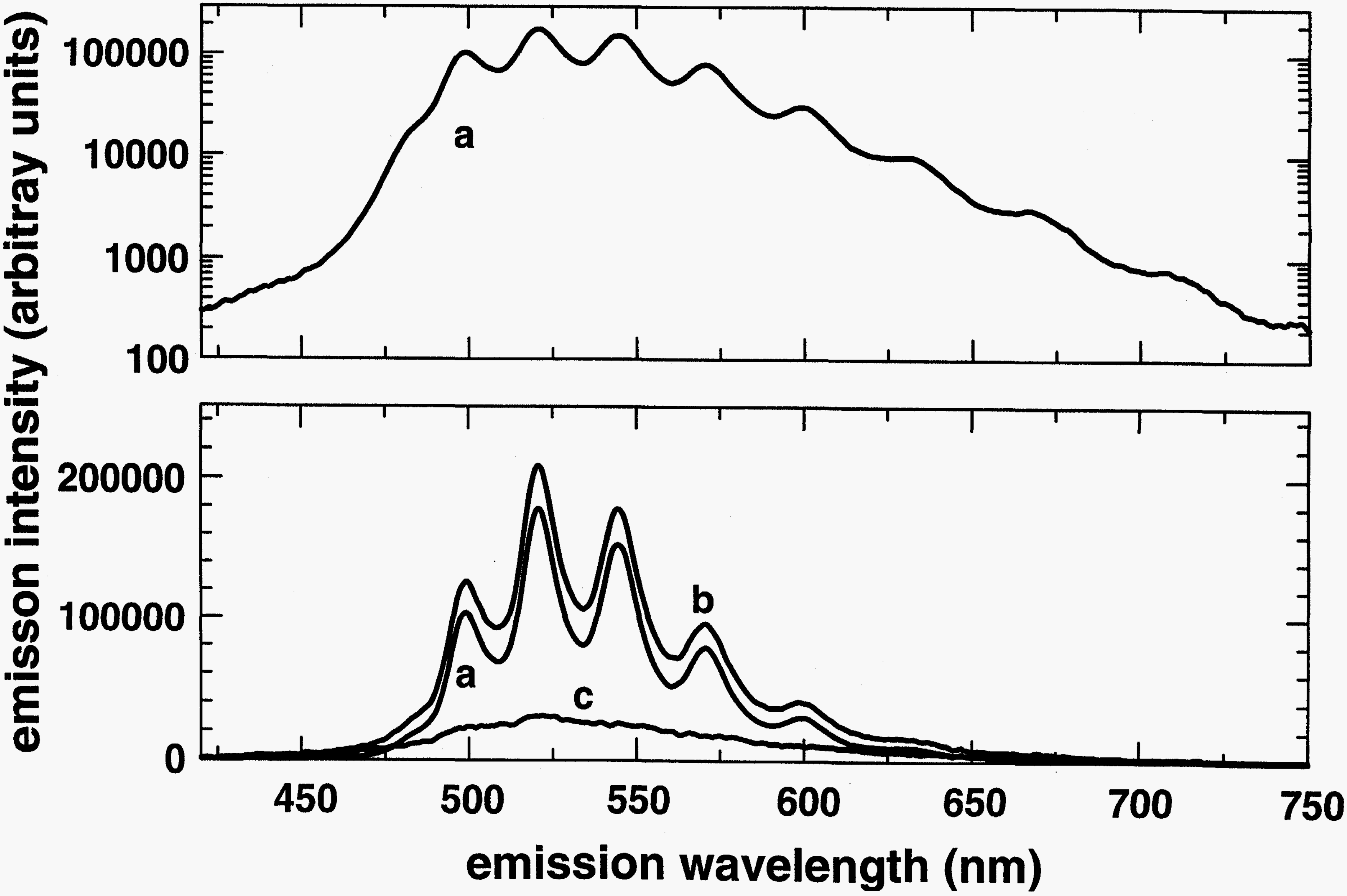
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Fig 1

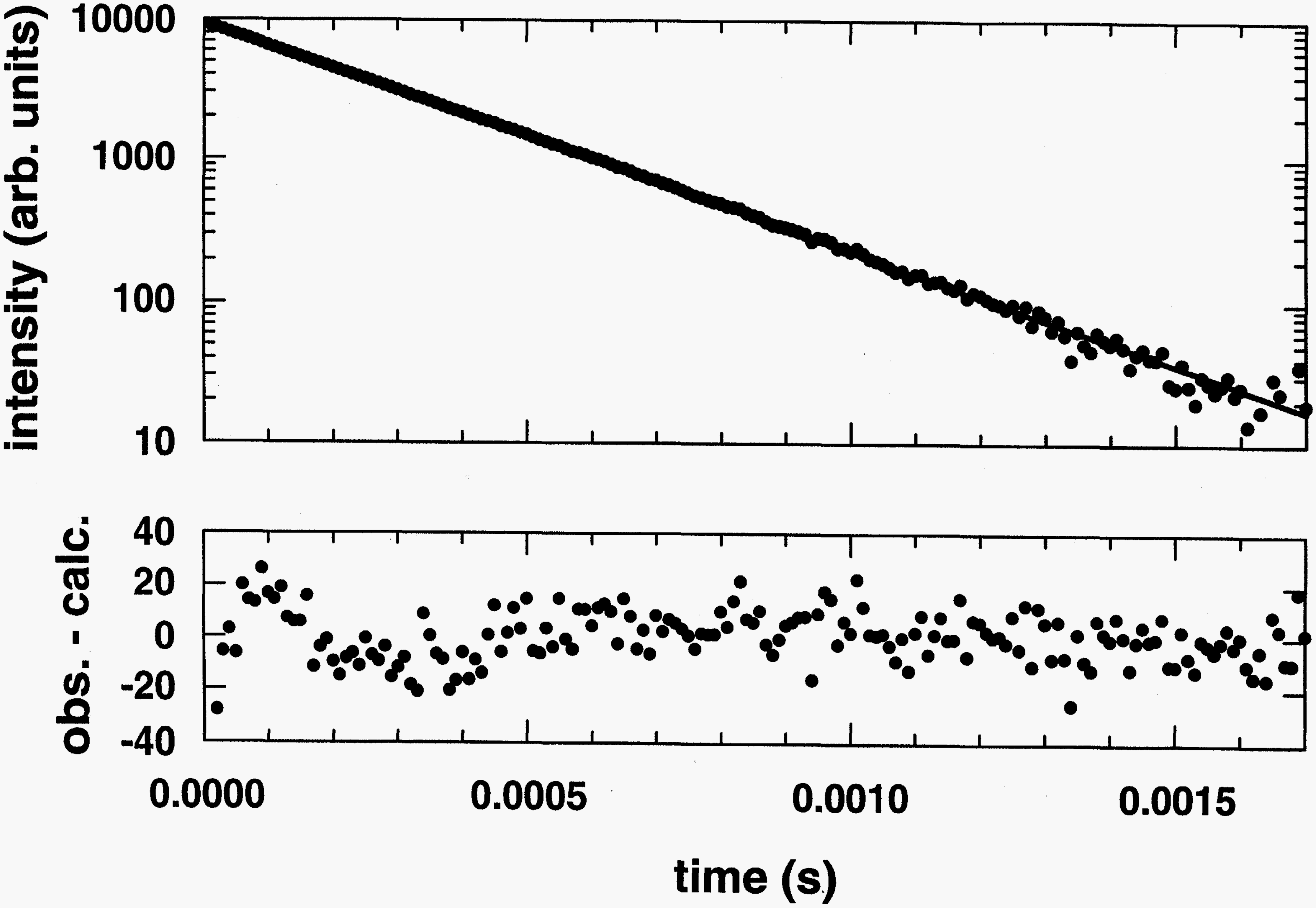
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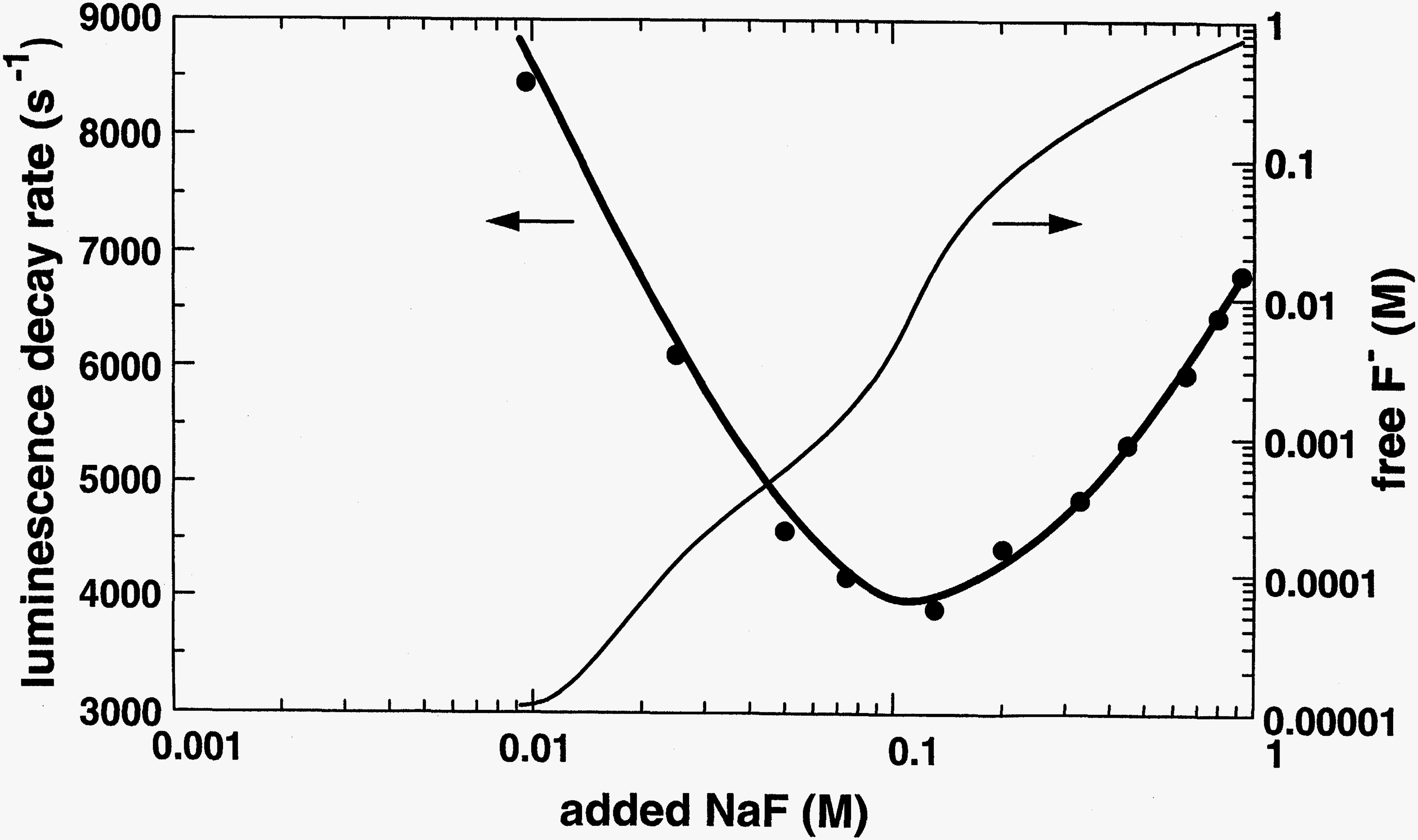
Fig 2


luminescence decay rate (s⁻¹)
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8000
7000
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5000
4000
3000
0.001
0.01
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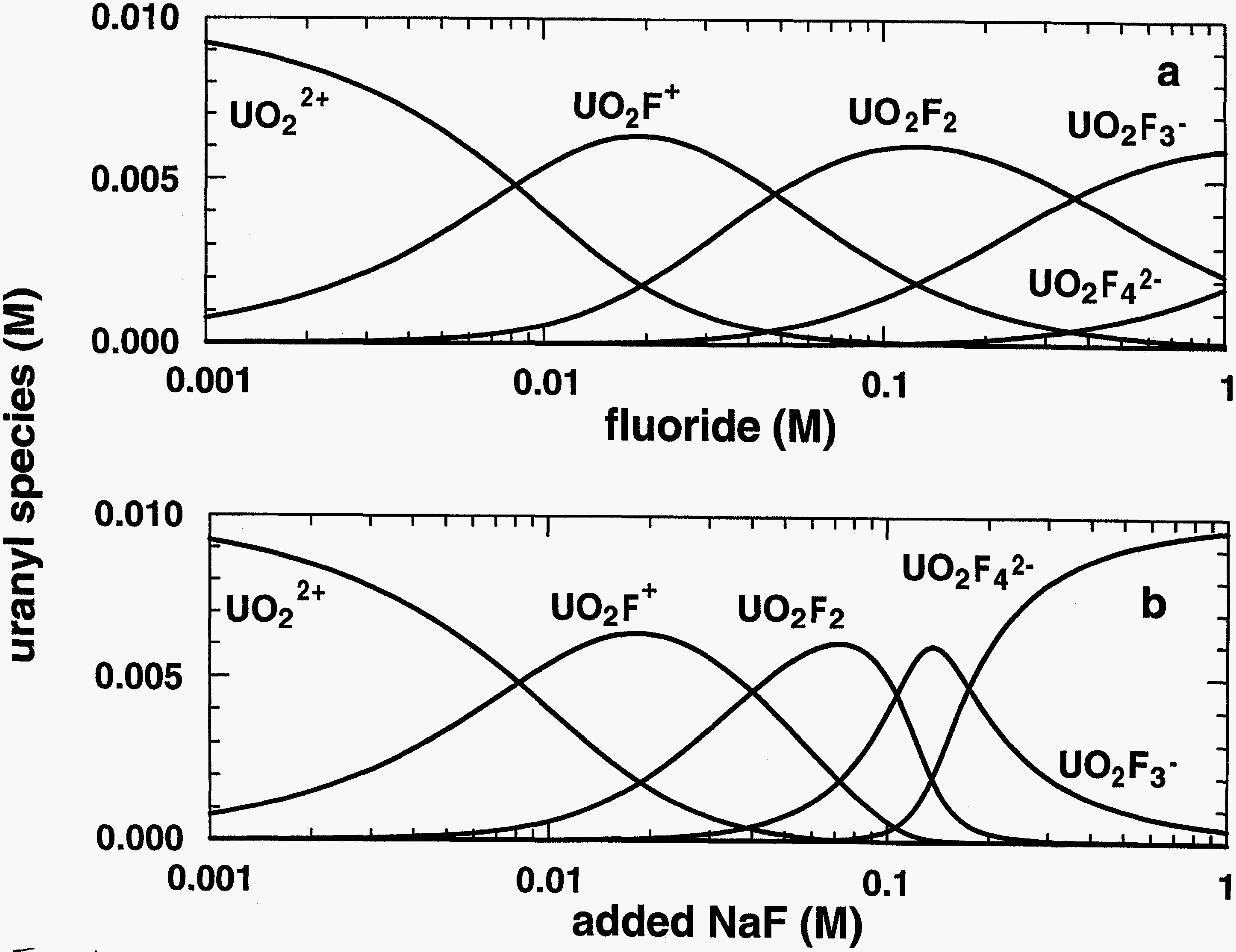
added NaF (M)
free F⁻ (M)
1
0.1
0.01
0.001
0.0001
0.00001

Fig 3


uranyl species (M)
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fluoride (M)
a
UO_2^{2+}
UO_2F^+
UO_2F_2
$UO_2F_3^-$
$UO_2F_4^{2-}$
0.010
0.005
0.000
0.001
0.01
0.1
1
added NaF (M)
b
UO_2^{2+}
UO_2F^+
UO_2F_2
$UO_2F_4^{2-}$
$UO_2F_3^-$

Fig 4