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Photoluminescence and photoejection of hydrated electrons in $SnCl_3^-$ in aqueous solution induced by 266 nm laser flash photolysis

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Abstract

Aqueous solutions of $SnCl_2$ in 5 M NaCl, in which the primary Sn(II) species is $SnCl_3^-$, photoeject hydrated electrons biphotonically, with a quantum yield ranging from 0 to 0.12, when irradiated by a 7 ns, 266 nm laser pulse. Two luminescent excited states are also seen in time-resolved luminescence measurements: one at 490 nm with a lifetime of 10 ns and quantum yield of 0.0032, and the other at 740 nm with a lifetime of 314 ns and quantum yield of 0.0041, the latter of which exhibits an absorption band at 370 nm. These two excited states are formed monophotonically, indicating that they are not the source of the hydrated electrons. A mechanism involving a Sn(III) intermediate can be used to rationalize this behavior.

Keywords: Photoluminescence; Photoejection; Hydrated electrons; Laser flash photolysis

1. Introduction

Many coordination complexes of transition metals in their lower oxidation states, such as Cu(I) and Fe(II), undergo photooxidation processes when excited by UV light into charge-transfer bands that are, in nature, primarly, d → s, d → p, or d → solvent [1]. In the absence of oxidizing agents, these species may eject solvated electrons when photolyzed, as in the reaction [2–4],

$$CuCl_3^{2-} + h\nu \rightarrow CuCl_3^- + e_{aq}^- \qquad (1)$$

Such reactions often occur with high quantum yields, a behavior that may be enhanced by the existence of stable, adjacent oxidation states. On the other hand, photoejection of electrons by lower oxidation states of main group metals, such as Sn(II), Sb(III), Tl(I), and Pb(II), would have to involve the formation of an unstable oxidation state intermediate between the two stable ones, and possibly because of this, there have been no reports of this process until very recently [5], in this case from $Sn(OH)_3^-$. Other reports have shown that when $SnCl_2$ is irradiated with UV light in anaerobic hydrochloric acid solution, the following reactions occur [6,7]

$$\mathrm{Sn(II)} + \mathrm{H}^+ \xrightarrow{h\nu} \mathrm{Sn(III)} + \mathrm{H} \qquad (2a)$$

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H_2} \qquad (2b)$$

where the Sn(III) is an unstable intermediate that disproportionates. Since the concentration of chloride ion in the solutions studied was 1 M, it can be deduced from the known stability constants of the chloro complexes [8,9] of Sn(II) that the system consists of about equal parts of $SnCl_3^-$ and $SnCl_2$, with very small amounts of $SnCl^+$ and Sn^{2+}. The ability of $SnCl_3^-$ to photoreduce hydronium ion suggested that hydrated electrons may be formed in the primary photochemical process, as in Eq. (1).

In addition to photoredox behavior, $SnCl_3^-$ exhibits photoluminescence in solution. More than 50 years ago, Pringsheim and Vogels [10] observed a green luminescence in aqueous solutions of $SnCl_2$ saturated with KCl when irradiated in the UV region (270 nm). More recently, Vogler's group has reported on the photoluminescence of $SnCl_3^-$ in acetonitrile solution and characterized the absorption and emission bands [11]. The absorption spectrum exhibits three bands in the UV labeled as A, B, and C of increasing energy and absorption coefficient, and corresponding to the transitions, $^1S_0 \rightarrow {}^3P_1$, $^1S_0 \rightarrow {}^3P_2$, and $^1S_0 \rightarrow {}^1P_1$, respectively.

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The emission, occurring at $\lambda_{max} = 510$ nm, was attributed to the transition, $^3P_1 \rightarrow ^1 S_0$.

In this work, our goal was to determine if the photoredox behavior of Sn(II) could be attributed to the formation of hydrated electrons, and to try to relate the observed photoluminescence to the photoredox behavior.

2. Experimental section

Aqueous solutions containing $SnCl_3^-$ were prepared by dissolving reagent grade $SnCl_2$ in Ar-bubbled 5 M NaCl. In some experiments in which $[Cl^-]$ was varied, the ionic strength was held constant at 5 M by the addition of reagent grade $NaClO_4$. From published stability constants of the various chloro complexes of tin(II) in aqueous solution [8,9] (See Fig. 6, below) it is clear that the most ubiquitous tin(II) complexes in 5 M NaCl are $SnCl_3^-$ and $SnCl_2$ in a 4 : 1 molar ratio. In these high ionic strength solutions, there was no problem with precipitation of tin oxides or hydroxides as long as the tin concentration remained less than 0.001 M.

UV-Visible absorption spectra were obtained on Ar-bubbled samples using an HP8451 and HP8453 spectrophotometers, and stationary-state luminescence spectra were taken at room temperature on a Shimadzu RF-540 spectrofluorometer. The quantum yield of the emission band at 490 nm was estimated by measuring the ratio of the integrated (over wavenumber) emission intensity to that of quinine bisulfate in 1 N H_2SO_4, both of which were excited at 266 nm where their optical densities were fixed at 0.52. The quinine bisulfate quantum yield was taken to be 0.51 [12] for this calculation.

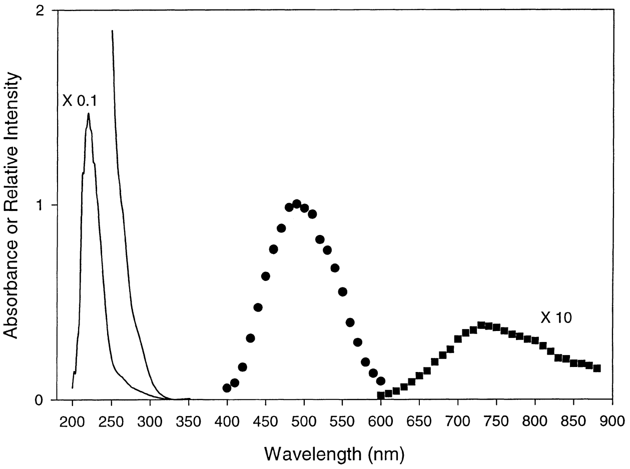

Fig. 1. (——)Absorption spectrum of 0.001 M $SnCl_2$ in 5 M NaCl in a 1 cm cuvette, along with spectrum of solution diluted 1 : 10. (●) Normalized (to 1) time-resolved emission spectrum, taken at 2 ns delay time, of same solution in 1 cm cuvette. (■) Normalized (to 0.038 of the previous emission spectrum) time-resolved emission spectrum, taken at 200 ns delay time, of same solution in 1 cm cuvette. Excitation wavelength is 266 nm for both emission spectra.

Flash photolysis experiments were carried out at room temperature in a 1 cm cuvette, in most cases a flow-through type, using as the irradiating source the 266 nm output of a Surelite Nd-YAG laser of 7 ns nominal pulsewidth. For transient absorbance measurements, the light monitoring system consisted of a 75 W Xe arclamp (PTI), pulsed by a laser diode driver (Analog Modules), with the beam traversing the cuvette collinearly with that of the exciting 266 nm beam. Light from the monitoring lamp or from the photoluminescence of the sample was admitted to the entrance slit of a monochromater (PTI), equipped with a Hammamatsu R936 photomultiplier at the exit slit. The photomultiplier signal was captured and processed by a Hewlett-Packard 54510 oscilloscope and stored on computer disk via National Instruments' LabWindow software for later processing. Time-resolved spectra were obtained by capturing single-shot signals at a series of wavelengths and storing and processing the absorbance or luminescence intensities at predetermined delay times after the flash. For monitoring the electron decays, a 6 mW, 675 nm diode laser (Oriel) was substituted for the arclamp in order to obtain signals with high STN ratio. Time-resolved luminescence spectra were measured by holding the photomultiplier voltage constant during the wavelength scan of the monochromator, and correcting for differences in wavelength sensitivity. The photomultiplier was calibrated for this purpose by scanning through the wavelengths produced by the Xe arclamp, determining at each wavelength the photomultiplier output (at constant dynode voltage), and comparing to the output of a calibrated Thorlabs S20MM silicon power meter (traceable to NIST) placed at the exit slit of the monochromator. Power studies at various wavelengths were accomplished by measuring sample transient signals at a variety of laser power supply voltages and comparing their amplitudes to the maximum 700 nm absorbance (i.e. that of the hydrated electron) in 0.001 M $Na_4Fe(CN)_6$, which photoejects hydrated electrons monophotonically at 266 nm with a known quantum yield of 0.52 [13]. The power study for electron photoejection was determined by using the 675 nm diode laser source to monitor both the Sn(II) transient absorption and that of the ferrocyanide actinometer. Transient signals for kinetic analysis were in most cases obtained by taking the average of three shots.

3. Results

Fig. 1 shows the absorbance and time-resolved emission spectra ($\lambda_{exc} = 266$ nm) of the 0.001 M $SnCl_2$ solution in 5 M. The absorbance spectrum just barely shows two shoulders, one at 266 and the other at about 290 nm, which are undoubtedly the B and A bands observed in the acetonitrile solutions of $SnCl_3^-$ [5,11]. The C band, obtained for a 10-fold diluted solution, shows a complex structure with a peak at 220 nm, in reasonable agreement with the observations in acetonitrile solution [11]. Two emission bands are observed: the first with a peak at 490 nm, and a second, 20-fold less intense one, with a peak at 740 nm. While the first band can be seen in steady-state luminescence spectra, the second, weaker band cannot be seen above the background noise, probably because of its lower intensity and the insensitivity of the spectrofluorimeter's photomultiplier at these longer wavelengths. Excitation of the 490 nm band occurs at all the UV wavelengths beginning with the onset of absorbance at 320 nm, but a meaningful excitation spectrum cannot be obtained in these solutions due to the very high absorbance at shorter wavelengths.

The lifetimes of the two emission bands are considerably different: 10 ns and 314 ns, for the 490 nm and 740 nm bands, respectively, whereas the ratio of the initial intensities of the transient luminescence signals are 1 : 0.038, respectively. From the fact that the quantum yield of emission is proportional to the intensity of a transient signal at $t = 0$, to its lifetime, and to its wavelength, the ratio of the quantum yield of the 490 nm emission to that of the 740 nm emission was estimated to be about 0.77. Comparison of the 490 nm band to the quinine bisulfate standard results in a quantum yield of 0.0032, and from the ratio, above, the quantum yield for the 740 nm emission is 0.0041.

A transient absorption band with a peak at 370 nm, shown in the time-resolved spectra of Fig. 2, forms immediately following the absorption of the 266 nm pulse, and the first-order lifetime of this transient is virtually identical to that of the 740 nm emission.

Electron ejection also results from the 266 nm excitation of the system, as confirmed by the time-resolved absorption spectra of Fig. 3, which compares the published spectrum of the hydrated electron [14,15] (solid curve) to our observations at a variety of delay times.

Fig. 4 shows the results of the power studies for the emission at 475 nm (●)and at 740 nm (▼), and for the transient absorption at 370 nm (○) and at 675 nm (■), i.e. that of the electron. It is clear that for the electron, the process is biphotonic, whereas the other three processes are monophotonic. Thus, the quantum yield of the electron is proportional to light intensity, and this relationship is shown in Fig. 5, which indicates quantum yields for electron ejection ranging as high as 0.12.

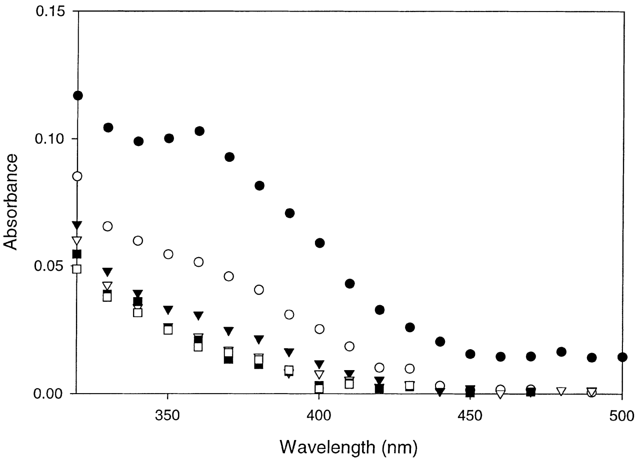

Fig. 2. Time-resolved absorption spectra in short-wavelength region of same solution as Fig. 1, taken at delay times of (●) 100, (○) 400, (▼) 800, (▽) 2000, (■) 3000, and (□) 4000 ns after excitation by 266 nm laser pulse.

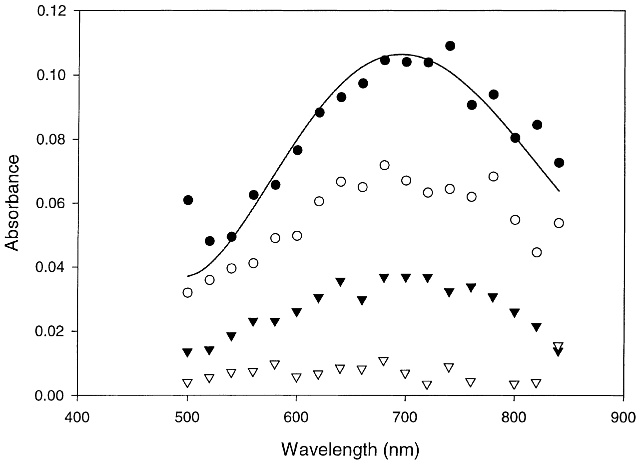

Fig. 3. Time-resolved absorption spectra in long-wavelength region of same solution as Fig. 1, taken at delay times of (●) 20, (○) 50, (▼) 100, and (▽) 200 ns, excited by 266 nm laser pulse. Solid curve shows published spectrum of hydrated electron from [13].

In order to identify which tin complexes are responsible for the two luminescence bands of Fig. 1, a series of laser-induced luminescence transients at 475 and 740 nm were measured in a series of solutions in which the added sodium chloride concentration was varied from 0 to 5 M at a constant ionic strength of 5 M (sodium perchlorate medium). The absorbance of an equilibrated mixture of

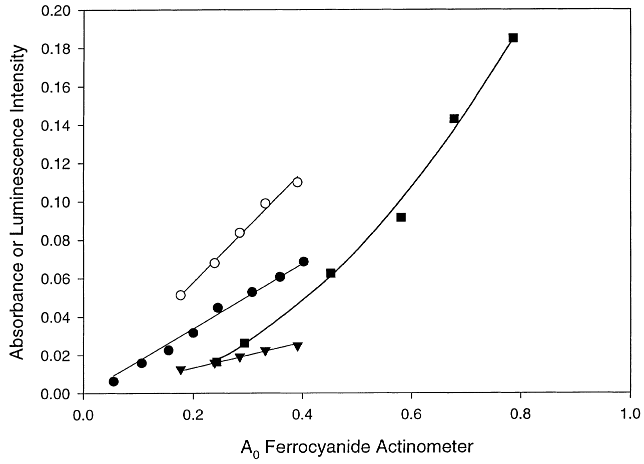

Fig. 4. Power study of 0.001 M $SnCl_2$ in 5 M NaCl, irradiated with 266 nm laser pulse. Initial values (at $t = 0$) of (○) absorbance at 370 nm, (●) luminescence intensity at 475 nm (pm voltage = 540 V), (■) luminescence intensity at 740 nm (pm voltage = 800 V), and (■) absorbance at 675 nm vs. initial absorbance at 675 nm of 0.001 M $Na_4Fe(CN)_6$ actinometer in 1 cm cuvette.

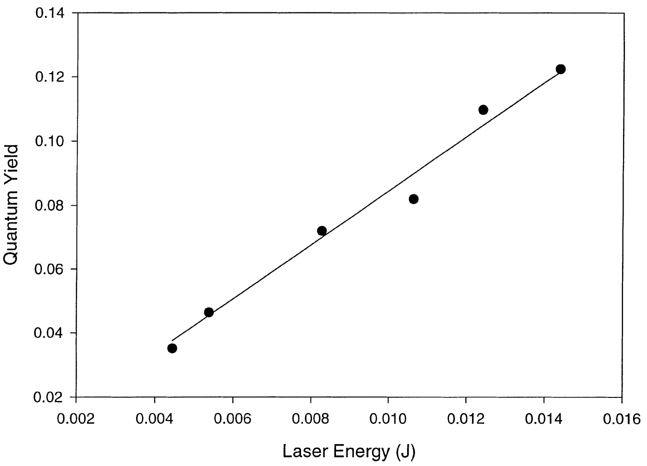

Fig. 5. Quantum yield of hydrated electron as a function of 266 nm laser pulse energy for same solution as in Fig. 1.

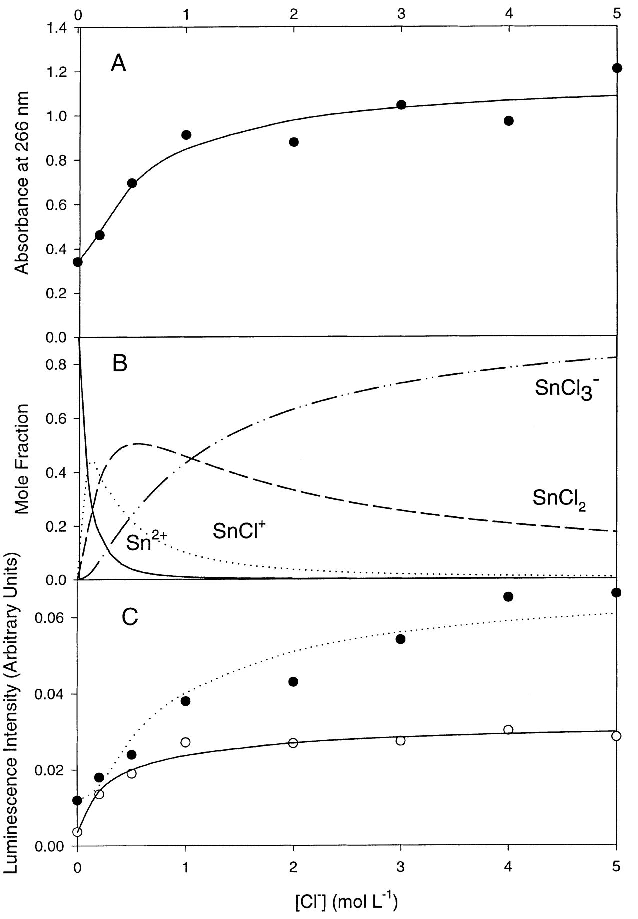

Fig. 6. (A) (•) Absorbance at 266 nm of 0.001 M $SnCl_2$ solutions in 5 M ionic strength solutions of varying concentration of NaCl. (-) Curve fit to data by Eq. (3). (B) Mole fraction distribution of Sn(II) complexes at 3 M ionic strength, using stability constants from [9]. (C) Luminescence intensity at (●) 475 nm with curve fit (—) to Eq. (4)), and at (○) 740 nm with curve fit (· · ·) to Eq. (4).

monomeric Sn(II) complexes in a 1 cm cuvette is given by,

$$A = c\frac{\sum_{i=0}^{4}\varepsilon_i\beta_i x^i}{\sum_{i=0}^{4}\beta_i x^i} \qquad (3)$$

where c is the total concentration of the four tin(II) species, Sn^{2+}, $SnCl^+$, $SnCl_2$, and $SnCl_3^-$, ε_i the molar extinction coefficient of the tin complex coordinated to i chloride ions, β_i the corresponding cumulative stability constant of the complex, and x the chloride ion concentration. Fig. 6(A) shows the absorbances measured at 266 nm along with a curve fit to Eq. (3) using the stability constants for the published 3 M ionic strength system [9], $\beta_0 = 1$, $\beta_1 = 15.12\ M^{-1}$, $\beta_2 = 54.9\ M^{-2}$, and $\beta_3 = 47.3\ M^{-3}$, yielding extinction coefficients, $\varepsilon_0 = 340$, $\varepsilon_1 = 240$, $\varepsilon_2 = 740$, and $\varepsilon_3 = 1175\ M^{-1}\ cm^{-1}$. Using the stability constants, the distribution of the four tin(II) species was calculated as a function of chloride ion concentration and these are shown in Fig. 6(B). The relative luminescence emission intensities at the two wavelengths, 475 and 740 nm, and determined from the initial intensity of a luminescence decay transient, are shown in Fig. 6(C) for comparison, suggesting that the species, $SnCl_2$ and $SnCl_3^-$, are primarily responsible for the emission at these two wavelengths. The contribution of each tin species to either emission can be estimated by considering that the observed emission intensity is given by,

$$I = I_0(1 - 10^{-A})\frac{\sum_{i=0}^{4}\phi_i\varepsilon_i\beta_i x^i}{\sum_{i=0}^{4}\varepsilon_i\beta_i x^i} \qquad (4)$$

where I_0 is the incident light intensity, and ϕ_i the quantum yield of luminescence for the tin complex with coordination number i. Since our interest was in determining, at this point, only the relative values of quantum yield, the products, $I_0\phi_i$, were obtained from a curve fit of Eq. (4) to the data of Fig. 6(C), using the values of β and ε determined earlier. This results in relative quantum yields for ϕ_0, ϕ_1, ϕ_2, and ϕ_3, respectively, which are 0.175, 0.084, 3.7×10^{-9}, and 1 for the 475 nm emission, and 0.11, 4.6×10^{-9}, 0.38, and 1 for the 740 nm emission. From these results, one must conclude that at 5 M chloride ion concentration virtually all of the 475 nm emission is produced by excitation of the $SnCl_3^-$ ion only, whereas excitation of both $SnCl_2$ and $SnCl_3^-$ produce emission at 740 nm in a ratio of about 1 : 3 for the two species.

4. Discussion

The emission band at 490 nm is undoubtedly the same one ascribed to the transition, $^3P_1 \rightarrow {}^1S_0$, by Vogler et al. [11], which they observed in acetonitrile solution, although the lifetime and quantum yield are considerably smaller, 10 ns and 0.0032 vs. 1600 ns [16] and 0.068 [11], while the Stokes shift[2] is not significantly different, 16 000 cm^{-1} vs.

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[2] The Stokes shift was calculated by taking the difference between the average energy of the 266 and 290 nm shoulders and subtracting the energy of the 490 nm band, the same method used in [9], so that a meaningful comparison could be made

15 900 cm^{-1} [11]. Since the observed emission lifetime is given by

$$T = \frac{1}{(k_{\mathrm{lum}} + k_{\mathrm{NR}})} \tag{5}$$

where k_{lum} is the luminescence decay constant and k_{NR} the net constant for all the other non-radiative decay processes, and since k_{lum} is affected essentially by the transition probability and therefore would not vary with solvent, it follows that k_{NR} and hence the luminescence quenching ability is much greater in water than in acetonitrile, a not too surprising result considering the higher tendency of water to enter the solvation sphere of the excited state ion and collisionally deactivate it. This is evident also from the smaller quantum yield, since the luminescence quantum yield is given by

$$\phi_{\mathrm{lum}} = \frac{\phi_{\mathrm{ex}} k_{\mathrm{lum}}}{(k_{\mathrm{lum}} + k_{\mathrm{NR}})} \tag{6}$$

where ϕ_{ex} is the quantum yield of population of the excited state. The ratio of the values of ϕ_{ex} for water and acetonitrile can be obtained from the ratio of ϕ_{lum}/T in water from this work to that in acetonitrile obtained from Vogler's work [16,11], resulting in a value of 7.5, indicating that the luminescent excited state is more accessible in water than in acetonitrile, perhaps due to solvent purturbations in the excited state potential wells. This emission band was described by Vogler [11] as arising from an essentially trigonal planar excited state, compared to the trigonal pyramid ground state, accounting for the large Stokes shift and lifetime.

The 740 nm emission band is somewhat more problematic because it is accessible by excitation of two complexes of rather different geometry, $SnCl_2$ and $SnCl_3^-$. It was observed that the 740 nm decay is not biexponential and that there was no shift in the 740 nm band as chloride ion concentration was varied, and thus we are left with the idea that the emission stems from a single species accessible from the excited states of either $SnCl_2$ or $SnCl_3^-$. This is possible, for example, if the excited state is a triplet state of $SnCl_2$, formed either by photoexcitation of $SnCl_2$, or by the prompt (i.e. within the laser pulsewidth) ejection of a chloro ligand from an excited state of $SnCl_3^-$.

It is clear from Fig. 4 that the two luminescent excited states are formed monophotonically, whereas the electron is ejected biphotonically. Such biphotonic processes occur when there is an intermediate excited state that absorbs a second photon leading to the observed products. The most likely intermediate, in this case, is a tin(III) species, which would be produced by excitation of a charge-transfer state of Sn(II), similarly to the process in Eq. (1). The spectrum of Sn(III) species, which has been observed in flash photolysis of $SnCl_2$ in 1 M HCl [6,7], shows a strong absorbance maximum at almost precisely the laser wavelength, 266 nm. However, in the neutral solutions used in this study, there are very few hydrogen ions to scavenge the electrons produced, such that there would likely be a very fast back-reaction yielding few hydrated electrons, as in the reaction

$$\mathrm{Sn(II)} \overset{h\nu}{\rightleftarrows} \mathrm{Sn(III)} + e^-_{\mathrm{aq}} \tag{7}$$

If the back-reaction is sufficiently slow to allow a small buildup of Sn(III) to a steady-state, a second photochemical reaction

$$\mathrm{Sn(III)} \xrightarrow{h\nu} \mathrm{Sn(IV)} + e^-_{\mathrm{aq}} \tag{8}$$

would result in hydrated electrons being ejected into the bulk of the solution and readily identified by their absorbance. Thus, such a mechanism would result in the biphotonic electron ejection process.

Acknowledgements

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