

OC-20: Ultrabright Sonoluminescence of Uranyl Ions in Aqueous Solutions

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We have observed for the first time ultrabright sonoluminescence (SL) of uranyl ions in aqueous solutions. The intensity of UO_2^{2+} SL is strongly influenced by the presence of complexing agents, like phosphate ions, and by the ultrasonic frequency. The mechanism of UO_2^{2+} SL seems to vary with uranium concentration: sonophotoluminescence dominates in diluted solutions, and collisional excitation would add its contribution at higher UO_2^{2+} concentrations. This study highlights the importance of quenching processes by the products of solvent sonolysis. In light of these findings, sonoluminescence of UO_2^{2+} ions exhibits a behaviour combining the properties typical for both photoluminescence and radioluminescence.

Introduction

Excited uranyl ion (UO_2^{2+})* is a strong oxidant ($E_0 = 2.6$ V vs. NHE) and can readily react with a variety of organic and inorganic substrates [Denning]. Therefore, search for new approaches of uranyl ion excitation is of interest for developing advanced actinide separation processes and radioactive waste management. The violent implosion of gas/vapor filled microbubbles in liquids submitted to ultrasonic irradiation produces chemically active species as well as light emission, known as sonoluminescence (SL) [Suslick]. Recently, the SL of lanthanide ions was reported in concentrated (0.5-1.0 M) lanthanide salt aqueous solutions under the effect of 20 kHz ultrasound [Sharipov]. It was suggested that the SL of lanthanides would be governed by two major processes: (i) sonophotoluminescence and (ii) collisional excitation of Ln(III) ions by radicals or excited molecules at the bubble/solution interface. Herein, we report for the first time about uranyl ion SL, in acidic solutions of HClO_4 and H_3PO_4 under the effects of 20, 203 and 607 kHz ultrasound.

Experimental Section

The thermostated cylindrical sonoreactor is mounted on top of a high-frequency transducer (203 or 607 kHz, 25 cm², L-3 Communications ELAC Nautik). Ultrasonic irradiation with low frequency ultrasound of 20 kHz is performed with 1 cm² titanium horn (Vibra-Cell) placed reproducibly on top of the reactor. The experiments are performed at 35 W (20 kHz) and 60-80 W (203 and 607 kHz) of loaded power. Irradiated solutions (250 mL) are continuously sparged with argon. The cryostat temperature is set so as to have a steady-state temperature of 9-11°C within the sonoreactor during the ultrasonic treatment. The emission spectra are recorded in the range 230-800 nm using a spectrometer (SP 2356i, Roper Scientific; 300gr/mm blz. 300 and 150gr/mm blz. 500) coupled to a liquid-nitrogen cooled CCD camera (SPEC10-100BR with UV coating, Roper Scientific). Other experimental details have been described recently [Pflieger].

Results and Discussion

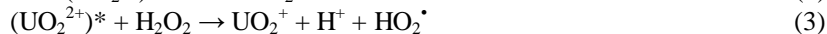
In HClO_4 solutions uranyl ions exhibit extremely weak SL. By contrast, the photoexcitation of UO_2^{2+} in HClO_4 solutions yields relatively strong uranium fluorescence in full agreement with data published elsewhere [Denning]. It can thus be concluded that the SL of UO_2^{2+} is effectively quenched in HClO_4 solutions with coordinated water molecules and with the products of solvent sonolysis.

In H_3PO_4 medium UO_2^{2+} exhibits a strong SL. However, the intensity of UO_2^{2+} SL intensity is strongly influenced by the ultrasonic frequency. As in HClO_4 solutions, the strongest intensity of UO_2^{2+} SL is observed with 203 kHz ultrasound. In a dark room the SL of UO_2^{2+} at 203 kHz can be seen by the unaided eye as a green-yellow glow. The light emission zone is layered indicating that there is a standing acoustic wave field inside the sonochemical reactor: the highest intensity of UO_2^{2+} SL is emitted from the antinodal acoustic pressure zones where the concentration of cavitation bubbles is highest.

The plot of UO_2^{2+} SL intensity (I_{SL}) measured at 516 and 539 nm (main UO_2^{2+} emission wavelengths) as a function of uranyl concentration could be subdivided into three different areas: (a) at $[\text{UO}_2^{2+}] < 1 \cdot 10^{-3}$ M the I_{SL} values decrease with decreasing uranyl concentration, (b) in the range of $1 \cdot 10^{-3} \text{ M} < [\text{UO}_2^{2+}] < 3 \cdot 10^{-2}$ M the I_{SL} is

practically independent from uranyl concentration, and (c) at $[\text{UO}_2^{2+}] > 3 \cdot 10^{-2}$ M the increase of uranyl concentration causes I_{SL} to increase. Such behavior can be understood presuming two mechanisms of UO_2^{2+} excitation with power ultrasound: sonophotoluminescence in diluted solutions and in addition to it direct collisional excitation of UO_2^{2+} at the interface of collapsing bubbles in concentrated solutions.

It is interesting that in spite of the essentially sonophotoluminescence origin of UO_2^{2+} excitation in diluted solutions there is a striking difference between sono- and photoluminescence of uranyl ions. Our study reveals that at 203 kHz ultrasound the SL intensity of UO_2^{2+} in 0.5M H_3PO_4 is increased by a factor of at least 20 compared to that in 0.2M HClO_4 solutions. At the same conditions the intensity of UO_2^{2+} photoluminescence is increased only by a factor of 6. This difference can be explained by the strong contribution of the quenching processes in UO_2^{2+} sonoluminescence compared to photoluminescence. When going from HClO_4 to H_3PO_4 the replacement of water molecules with phosphate ions in the inner coordination sphere of UO_2^{2+} reduces both the intramolecular quenching and the intermolecular quenching by chemically active species generated in situ during aqueous solution sonolysis. However, even in a strongly complexing medium some quenching of SL is clearly observed. The decrease in the presence of UO_2^{2+} of H_2 formation rate during the sonolysis of H_3PO_4 solutions can be attributed to the quenching processes expressed by equations (1-2):



Moreover, the addition of 10^{-2} M H_2O_2 to sonicated UO_2^{2+} solutions in H_3PO_4 causes a sharp drop (~40%) of I_{SL} in agreement with reaction (3). These observations represent convincing evidence that the extremely low UO_2^{2+} SL in non-complexing HClO_4 medium is related to the quenching processes.

References

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Pflieger R., Cousin V., Barré N., Moisy P., and Nikitenko S. I., 2012, *Chem. Eur. J.*, 18, 410-414.