Radioactive Origin of Emissions Observed from Uranium Compounds and Their Silica Cells

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Introduction

A visible emission has been reported[1,2] for ^{233}U samples that also contain traces of its ^{229m}Th α decay daughter; this emission has been ascribed[1] to an electronic bridge mechanism coupling thorium's nucleus and electrons. We have recorded spontaneous (i.e., radioactivity-induced) and stimulated emission from uranium compounds and demonstrate that the 520 nm visible emission can actually be assigned to luminescence from the uranyl ion, the primary sample constituent.

One normally considers that ultraviolet or visible light emission originates from electronic transitions of atoms or molecules. Recently there has been a great deal of interest in the fascinating possibility that, for a certain actinide nucleus, ^{229m}Th, near UV and visible radiation might be observed. There have been two similar reports describing such a spontaneous emission related to the radioactive ^{233}U/^{229}Th decay chain for $^{233}UO_4 \cdot 2H_2O$ powder[1] and $^{233}UO_2(NO_3)_2$ solution[2] samples. It was suggested[1] that the UV portion of this emission might be the isomeric transition from the decay of the metastable nuclear state of the ^{229}Th daughter that is expected to lie 3.5 ± 1.0 eV above the ground state.[3] We have previously shown that the UV emission reported in both studies is from N_2 gas that is present in the air around the samples; the N_2 emission was electronically excited by the nuclear activity of the samples.[4] Utter et al. also speculated[5] that N_2 might be the origin of the UV emission, but did not confirm this spectrally. Both earlier reports[1,2] also discuss a broad visible emission at 2.4 eV.

We have suspected that the visible emission reported[1,2] is at least partly due to uranyl ion fluorescence, excited by the sample radioactivity. Control experiments to excite uranyl ion fluorescence using UV light and γ (^{60}Co) excitation sources were attempted by Irwin and Kim[1] unsuccessfully. No indication of the isotopic purity of the uranium in that study was given. Frequently ^{232}U is an impurity in ^{233}U; ^{232}U has a 70 year half-life, compared to the 10^5 year ^{233}U half-life. The activity of even a few parts per million of ^{232}U impurity in ^{233}U will dominate the sample radioactivity of a several year old mixture of the two isotopes. In the Richardson et al. study,[2] it was reported that the ^{233}U sample was 6 years old, but the isotopic purity was not reported. They prepared $^{238}UO_2(NO_3)_2$ "blank" solutions that were radioactively balanced by adding ^{232}U to yield a sample α activity comparable to that of their ^{233}U sample. The reported emission spectrum, produced by subtraction of a blank spectrum 20 times as intense as the sample spectrum, appeared similar to that of ref 1, but the effective measurement time was much longer.

Experimental Section

Samples. We prepared two test solutions to determine whether nuclear radiation could induce fluorescence in uranyl nitrate solutions. The first was a uranyl nitrate solution in 8 M HNO_3 that contained 350 mg of ^{233}U/mL known to have a 6 ppm ^{232}U impurity. The second was a 600 μL solution containing 300 mg of ^{238}U/mL as uranyl nitrate (depleted uranium abundance) and 50 μCi of ^{225}actinium nitrate in 6 M HNO_3. At equilibrium the latter solution yields α radiation activity equivalent to that of the former solution. We measured emission spectra for 80 μL samples of both solutions in sealed fused silica tubes. The radioactive samples used in these experiments were handled in a manner consistent with safe health physics operating guidelines.

Spectral Studies. The spectral studies were carried out in the manner described in our $^{233}U/N_2$ study.[4] The sealed sample tubes were imaged onto the slit of a 0.46 m focal length f/5.3 spectrograph (Model HR460, Spex Industries, Edison, NJ) containing a 150 line/mm diffraction grating. The spectrograph was fitted with a liquid-nitrogen-cooled 1024 × 256 pixel charge-coupled device (CCD) image plane detector (Model CCD15-11-1-226, EEV, Inc., Elmsford, NY). Emission spectral images of many hour duration were recorded as single integrations over a 400 nm wavelength range, using a 0.5 mm slit (7 nm spectral resolution). It should be noted that the pixel amplitude bias for the CCD camera is approximately 830 counts for each pixel for no light with a day-to-day variability of ±50 counts. Thus, the *Y*-axis origin for the image-based data plots shown is typically 2.15×10^5 (e.g., 830 counts × 256 pixels/column = 212 500). The liquid-nitrogen-cooled camera dark current is specified as <1 count/pixel/h. Laser-induced luminescence spectra were acquired using a substantially shorter acquisition time (few seconds) and were recorded using a different data acquisition routine that resulted in a lower apparent baseline. The spectra have not been corrected for the wavelength-dependent response of the CCD camera. The peak quantum efficiency occurs at 700 nm and is approximately 3-fold higher than the ultraviolet response.

Wavelength calibration was accomplished using a mercury discharge lamp, and spectral data were extracted from the images as described previously.[4] The He−Cd laser used in these studies (Model 4680/20 NF, Liconix, Santa Clara, CA) is a class 3b device, and safe operation procedures consistent with this classification were followed.

Results and Discussion

The emission spectrum obtained from the $^{233/232}$uranyl nitrate solution is shown in Figure 1a. No external excitation source was utilized, and the sample was maintained in a dark environment. The visible spectrum is broad with a maximum at approximately 530 nm. The CCD integration time was 22 h to yield Figure 1a. The optically excited luminescence of the uranyl ion is well-known,[6] and the spectrum of Figure 1a resembles it closely. The wavelength maximum of uranyl luminescence in nitric acid is nitrate ion concentration dependent,[6] and the observed 530 nm corresponds to our highly acidic solution.

We also observed a weak and broad, three-band emission from pure ^{233}U (<0.1 ppm ^{232}U) compounds, $^{233}UO_4 \cdot 2H_2O$ or

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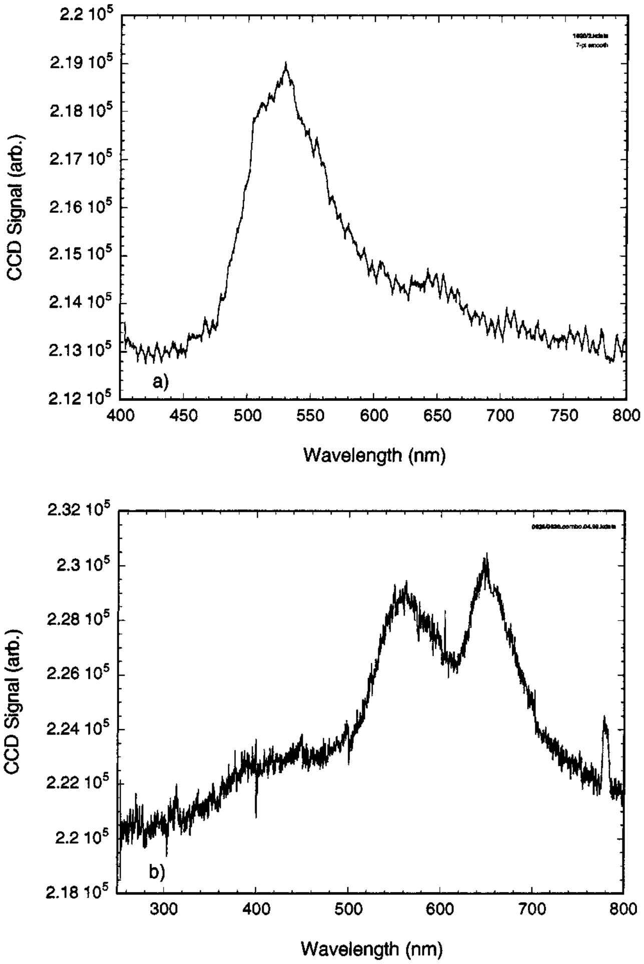

Figure 1. (a) Emission from a $^{233/232}$uranyl nitrate solution excited by the sample radioactivity (22 h signal integration). (b) Emission from a silica sample tube excited by the radioactivity of a $^{233}UO_4 \cdot 2H_2O$ sample (43 h signal integration).

$^{233}UO_3$, contained in sealed silica tubes. That spectrum is shown in Figure 1b and exhibits wavelength maxima around 415, 565, and 650 nm. Spectral image integration periods of approximately 43 h are required to observe this weak emission. The energy positions of the three bands of this spectrum correspond to the three bands reported for the cathodoluminescence of silica.[7] It is of interest to note that the relative intensities of our emission components are not as reported, but are consistent with the view that they do come from silica; the relative intensities vary with the composition of the silica and the type of excitation source.[8] Further studies of this emission are underway. The instrumentally limited line at 778 nm in Figure 1b is assigned to atomic oxygen. A companion line at 845 nm has also been recorded in other data sets extending to longer wavelengths. It is interesting to note that unlike radioactivity-excited N_2 that yields molecular and ionic emission (the 391.3 nm line we reported[4] is most likely due to N_2 molecular ion[9]), this oxygen luminescence is atomic in origin.

The lowest energy (650 nm) band of the silica emission spectrum can be noted on the uranyl ion fluorescence envelope of Figure 1a. For radioactive samples, one can indeed identify the source of different emissions. We therefore take issue with the generalization made in an earlier report[5] that longer measurement times than those used in that study would not improve the ability to observe and identify weak emissions from radioactive samples. This perhaps was true for their particular case, but it is not true for a dispersive optical arrangement in image mode where both wavelength and spatial separation are achieved.

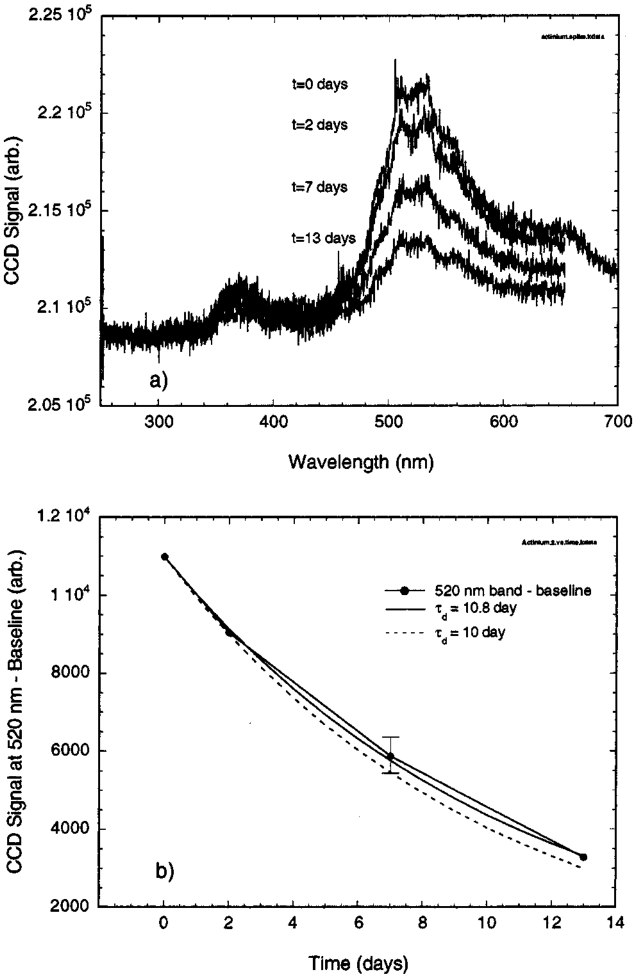

Figure 2. (a) Emission spectra from a $^{238}UO_2(NO3)_2$ solution, spiked with 50 μCi of $^{225}Ac(NO_3)_4$ as a function of time (the signal integration time for each spectrum was 47 h). (b) Fit of the emission intensity at 520 nm of the spectra in (a) to an exponential function. The optimum fitting coefficient found was 10.8 days.

A time series of emission spectra of the ^{225}Ac-doped $^{238}UO_2(NO_3)_2$ solution is shown in Figure 2a. The broad emission maximum is near 520 nm, and the overall spectrum resembles the uranyl ion luminescence. Note in Figure 2a that the fluorescence intensity of the uranyl ion decreases rapidly with time. The fluorescence intensity at 520 nm vs time is plotted as Figure 2b and fitted to an exponential decay function. The error bar shown indicates an estimate of the intensity imprecision due to the noise amplitude and our ability to accurately gauge the true baseline location. A fitting coefficient 10.8 day half-life was determined, in good agreement with the ^{225}Ac 10.0 day half-life,[10] indicating that the excitation mechanism for the uranyl ion luminescence is associated with the actinium decay. The overall actinium decay chain comprises seven daughters, five of which are α active; however, all of the daughters possess much shorter half-lives than the parent. Thus, the decay of the overall sample activity should follow the actinium half-life. The

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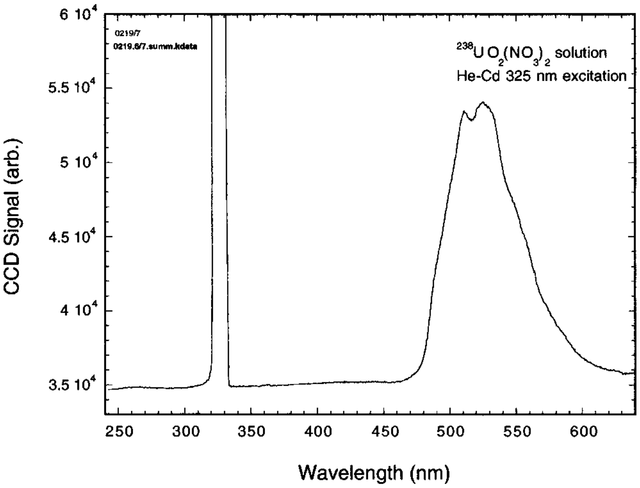

Figure 3. He−Cd laser-excited emission spectrum of a ^{225}Ac-spiked $^{238}UO_2(NO_3)_2$ solution (5 s signal integration). The emission was filtered using a 335 nm cutoff interference filter.

lowest energy (650 nm) band of the silica emission spectrum can again be observed in the emission spectrum that extends to that wavelength range.

We have also excited the 520 nm luminescence band of the uranyl ion in the ^{225}Ac−$^{238}UO_2(NO_3)_2$ solution using 0.5 mW of the 325 nm line of a He−Cd laser. This emission spectrum is shown in Figure 3. The luminescence was obviously visible to the eye and could be recorded in seconds rather than the days required for the radioactivity-induced effect.

Notice the similarity of the 520 nm region of the spectrum shown in Figure 3 with that shown in Figure 2a. Note also the additional 370 nm emission in the radioactivity-excited spectrum. The identification of this emission is under study. The broad bandwidth indicates a molecular entity. Its intensity also decreases with the 10 day ^{225}Ac half-life. Particularly in strong acid, it is unlikely to be related to any oxy-ionic species of the progeny of ^{225}Ac. It would seem more likely to be associated with either some radiolytically generated species in the solution, e.g., nitrate and/or water decomposition products, or some different uranyl ion de-excitation path due to the radioactive excitation process.

The results shown in Figures 1a and 2a demonstrate that uranyl ion luminescence in uranyl nitrate solutions can be excited by radioactivity. The source is ^{232}U in the former case and ^{225}Ac in the latter case. The excitation mechanism is similiar to that utilized in radiochemical scintillation counting where energetic radioactive emissions are detected optically as the result of their interaction with and energy transfer to an organic fluorophore.[11] In the present case, the uranyl ion has replaced the more typical organic dye fluorophore.

In a separate study, we have recorded uranyl ion fluorescence from our sample of pure $^{233}UO_4{\cdot}2H_2O$ by excitation with the 325 nm line of a He−Cd laser; the spectrum peaks around 520 nm. Similar uranyl fluorescence from UO_4 would be expected in Figure 1b, but is probably overshadowed by the silica luminescence. The uranyl ion has been identified in infrared spectral studies of various UO_4 preparations.[12] Therefore, it would seem that Irwin and Kim[1] should have recorded uranyl ion fluorescence for their UO_4 sample if UV excitation of the proper wavelength were employed.

Conclusions

We believe that the green emission described in the former reports of ^{233}U sample emission spectra[1,2] is at least in part due to uranyl ion fluorescence excited by radioactivity. The results shown in Figures 1a and 2a demonstrate such an excitation of uranyl ion luminescence. The source is ^{232}U in the former case and ^{225}Ac in the latter case.

Uranium, not thorium, is the major component in these samples; it is imperative to be able to delineate the emission due to a major sample component from that of a low concentration of a γ-active daughter, ^{229}Th. One must consider and account for a radioactivity-excitation scenario in any investigation of emission from radioactive samples.

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