Spontaneous Ultraviolet Emission from ^{233}Uranium/^{229}Thorium Samples

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The spontaneous ultraviolet luminescence reported [G. M. Irwin and K. H. Kim, Phys. Rev. Lett. **79**, 990 (1997); D. S. Richardson *et al., ibid.* **80**, 3206 (1998)] from ^{233}uranium compounds and ascribed to an ultraviolet gamma-ray emission from the metastable ^{229}thorium daughter is actually N_2 discharge emission induced in the air surrounding the sample by the sample radioactivity. The UV spectrum from high elemental and isotopic purity $^{233}UO_3$ reported here also exhibits a line at 391.3 nm that does not appear to be due to electric discharge N_2 emission. [S0031-9007(99)08412-4]

There has been a recent interest in observing an ultraviolet nuclear signature from samples containing the unique isotope ^{229}thorium. Early successes in this regard have been reported previously [1,2], but we feel they are in error. We report here results from a study employing $^{233}UO_3$ of high isotopic purity; the same ultraviolet multiplet was observed, but we feel that it is due to N_2 discharge emission in the air surrounding the sample induced by the sample radioactivity.

The ^{229}Th nuclide possesses a unique isomeric level positioned a scant 3.5 ± 1 eV above the ground nuclear level [3] and may possibly emit gamma rays in the ultraviolet [1,2]. Thorium-229 is typically generated by alpha decay of ^{233}U, wherein 2% of the thorium daughter passes through the metastable isomeric level. Irwin and Kim [1] reported spontaneous emission from two ^{233}U powder samples. The chemical compositions of these were uncertain, but one was probably $^{233}UO_4 \cdot 2H_2O$. The UV emission observed was weak, multiline, and centered at ca. 350 nm. They suggested that this emission was the 3.5 eV gamma ray, but did not offer a detailed explanation for its multiline character. In addition, they reported broad emission centered at 522 nm that they ascribed to an inelastic electronic bridge mechanism, whereby the outgoing gamma ray induced electronic excitation in the thorium atom and thus was observed at a reduced energy. This bridging mechanism has been addressed theoretically by Strizhov and Tkalya [4]. Richardson *et al.* [2] extended the experimental observations using multichannel detection and uranyl nitrate solution samples. Their interesting approach was to use a ^{232}U-containing sample as a blank; that isotope decays to ^{228}Th which lacks the low-lying isomeric nuclear state and thus should not exhibit ultraviolet emission. Subtraction of the two spectra left a residual signature indicative of the differences between the two isotopes. They reported the UV multiplet and also a broad visible band at 500 nm. Richardson *et al.* were cautious about the assignment of the UV lines, indicating that they may possibly be due to emission from daughters within

the ^{233}U decay chain (e.g., Ac or Fr) that do not occur in the ^{232}U chain.

We have local access to ^{233}U compounds of very high isotopic purity. This pure isotope is the starting material for a process leading to ^{213}Bi, a radioisotope with important medical uses [5,6]. The ^{233}U was freshly separated chemically (ca. four months) and thus the concentration of daughter isotopes was low. Additionally, the uranium isotopic purity was high. Both of these factors limit the radioactivity of the samples we utilize. Typical ^{233}U samples contain 2–10 ppm ^{232}U impurity, an isotope with more than a 2000-fold higher specific activity. Our ^{233}U contains less than 0.1 ppm ^{232}U, as estimated by radiochemical analysis. UO_3 powder was prepared by thermal decomposition of uranyl nitrate [7] and loaded into quartz sample tubes (1 mm i.d. by 25 mm long, 40 mg sample). These tubes were sealed under air and placed in an air tight sample holder with 25 mm quartz windows. The sample holder represents a double confinement, allowing us to handle the loaded samples in a conventional chemical laboratory.

The sample tube was imaged onto the slit of a 0.46 m focal length, $f/5.3$ spectrograph (model HR460, Spex Industries, Edison, New Jersey) with 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, New York). This arrangement allowed us to record image data with a 400 nm spectral range in a single integration, but limited our resolution to 7 nm FWHM due to our 0.5 mm slit width. Wavelength calibration was accomplished using a small Hg-argon discharge lamp and is thought to be ± 0.6 nm. A standard two-lens light collection arrangement was used. The laboratory was dark and great care was used to eliminate background light; the sample and collection optics were enclosed in a light tight cylinder. The CCD was operated in an image mode to assist us in discovering very weak spectral features. Integrations of up to 46 hours were logged. The cosmic ray-induced image features

(clusters of a few bright pixels that lack consistency along a wavelength column) commonplace to such long integrations were removed by replacing them using the most frequent pixel amplitude of the overall 262 144 element array. The array columns were subsequently summed to yield spectra.

Figure 1(a) shows the result of a 46 h integration of the ^{233}UO$_3$ sample. The multiplet at 350 nm is apparent and is very similar to that reported by Irwin and Kim [1] and Richardson *et al.* [2]. The arrows shown in Fig. 1 mark the lines reported in Ref. [2]. The line positions we observed were 317.7, 337.7, 356.7, 378.8, 391.3, 402.2, and 427.1 nm. The line at 391.3 nm appears to be absent in the earlier reports [1,2]. The emission from our sample was very weak. Using the manufacturer-specified CCD amplifier and analog-to-digital converter gains, we estimate that, on line center at the 356.7 nm line, the detected photon level is 3 (photons/pixel)/h. Our spectral measurement is approximately at the dark count rate [specified as <6 (photons/pixel)/h]. In a 2D image presentation, the lines are apparent as columns of bright CCD pixels, and can be clearly distinguished from random noise.

We had earlier noted the coincidental alignment of the 337 nm spectral line reported by Irwin and Kim [1] with the wavelength of the nitrogen laser and considered attempting to excite a nuclear transition using such a laser. Upon further investigation of the literature, we noted an overall match between the ^{233}U compound spectrum and the ultraviolet N$_2$ discharge spectrum [8,9].
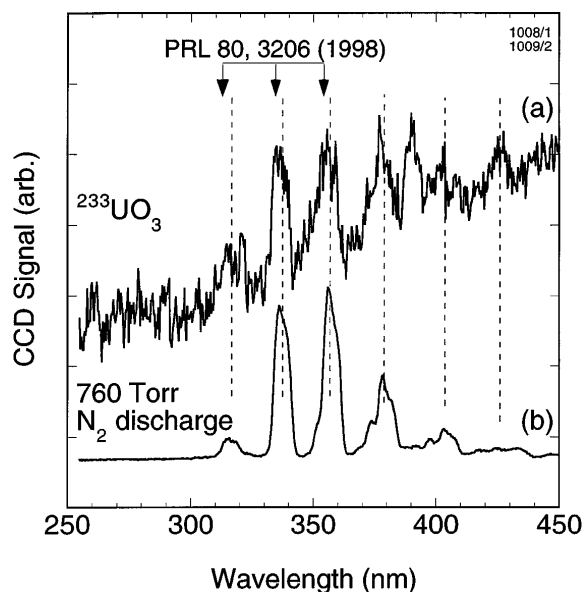

FIG. 1. (a) Spontaneous luminescence spectrum from a ^{233}UO$_3$ powder sample (46 h integration, 0.5 mm slit). (b) Emission spectrum of an atmospheric pressure N$_2$ discharge, under the conditions of (a), except for a 1 s integration time. The traces are offset vertically for clarity. The arrows mark the line positions reported in Ref. [2].

An atmospheric pressure N$_2$ discharge lamp (0.2 mm electrode gap, 3 kV applied voltage) was assembled and investigated using the spectrograph described above. Figure 1(b) represents a 1 s integration of the N$_2$ discharge. The similarity of the two traces of Fig. 1 is obvious. The traces of Fig. 1 were offset vertically for clarity; the vertical dashed lines aid in line position comparisons.

The radioactivity of the ^{233}U sample induces N$_2$ emission in the air surrounding the sample. It is well known that the air track of an alpha particle is highly ionized. This localized discharge could exhibit the same ambient gas excitation as that of an electrical discharge. We cannot be certain at this point whether the N$_2$ luminescence is induced by alpha or by other (beta or gamma) activity; we suspect alpha particles due to their short stopping distance in air.

We examined a ^{238}UO$_3$ powder sample as a blank. This "depleted" uranium oxide is predominantly the ^{238}U isotope, with less than ca. 0.3% abundance of the ^{235}U isotope. The ^{233}U concentration is expected to be in the ppm range or less. In an experiment designed to be identical to the one that produced the data of Fig. 1(a), the ^{238}U sample yielded only a noisy baseline for a 24 h integration. This less radioactive sample was not as effective at inducing N$_2$ luminescence as the ^{233}U sample.

The broad spectral feature near 500 nm reported by both Irwin and Kim [1] and by Richardson *et al.* [2] is not consistent with the N$_2$ discharge spectrum of our lamp. The N$_2$ discharge does show weak features at 539, 578, and 629 nm, but they seem to be more narrow than the reported bands (by comparison of the UV and visible bands) [1,2]. We do observe some broad spectral features in the visible region luminescence from the ^{233}UO$_3$ sample. However, they do not correspond to the reported 500 nm emission and seem to extend to longer wavelengths.

The 391.3 nm line of Fig. 1(a) that does not coincide with a feature of the N$_2$ discharge spectrum or with the luminescence of ^{233}U compounds reported earlier is obviously of interest. It falls within the tolerance of the ^{229}Th isomeric level position [3] and thus could be the ^{229}Th ultraviolet gamma ray. However, there are other candidates for its identity. It could correspond to a gaseous daughter atomic (e.g., He) or ionic emission; alternatively, there could be some minor state population discrepancies between electrically excited and decay-excited N$_2$ luminescence that result in a subtle spectral change. This line as well as the spontaneous visible luminescence are currently under further investigation.

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