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Near-Infrared Photoluminescence from a Plutonyl Ion

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We report the first example of photoluminescence from electronically excited states of the plutonyl ion. Discrete emission transitions were measured between 6000 and 10 200 cm^{-1} from crystalline $Cs_2U(Pu)O_2Cl_4$ cooled to 75 K following pulsed laser excitation at 628 nm. An excitation spectrum in the region of 15 000−16 500 cm^{-1} is compared with 4.2 K plane-polarized absorption spectra reported by Gorshkov and Mashirov. Analysis of excited-state lifetime data suggests multiple relaxation pathways in the electronic structure of $PuO_2Cl_4^{2-}$.

Introduction

Renewed interest in nuclear power generation and concerns about nuclear safeguards and security have increased the potential importance of methods of detection and chemical study of actinide-containing materials.[1] Photoluminescence spectroscopy has been particularly useful in a multitude of disciplines both for detection of small quantities of materials in diverse environments and for studying molecular behavior in complex, multicomponent chemical systems.[2] In particular, photoluminescence spectroscopy has long been a valuable tool for understanding fundamental photophysical properties of the uranyl ion ($U(VI)O_2^{2+}$) in the environment, aqueous solutions, and organic media.[3] Indeed, the vast majority of literature on actinide photoluminescence is confined to studies of the uranyl ion.[4]

Transuranic elements of technological importance form analogous actinyl ions, ($M(VI)O_2^{2+}$; M = Np, Pu, Am).[5] These cations also can be stable under oxidizing conditions present in the environment, and they have a functional role in nuclear process chemistry and separations strategies.[1c,6,7] Due to the presence of valence electrons in the ground states of these [Rn]-$5f^n$ ($n > 0$) electronic configurations, numbers and densities of electronic states increase from neptunium(VI) to plutonium(VI) to americium(VI).[4,5] Photoluminescence from electronically excited states of the open-shell species NpF_6 and PuF_6 has been observed in both gas-phase and matrix-isolated environments.[8] Only recently have we shown that near-infrared photoluminescence can be observed following direct excitation of NpO_2^{2+}.[9] Talbot-Eeckelaers et al. also report the photoluminescence properties of neptunyl aquo species.[10] However, the phenomenon has not been observed in transuranic plutonyl or americyl cations. We extend those results here by reporting the first observation and preliminary details of near-infrared photoluminescence from plutonyl tetrachloride.

Experimental Section

Reaction of a plutonyl (PuO_2^{2+}) stock solution with 2 equiv of CsCl in 1 mol/L HCl gave a dark-brown solution from which golden-brown blocks of $Cs_2PuO_2Cl_4$ crystallized in quantitative yield. The structure of $Cs_2PuO_2Cl_4$ is described elsewhere.[11] $Cs_2PuO_2Cl_4$ (0.003 g, 0.004 mmol) and $Cs_2UO_2Cl_4$ (0.097 g, 143 mmol) were dissolved in 2 mol/L HCl such that the neptunium to plutonium ratio in solution was 3%.[12] Light-brown needles of $Cs_2U(Pu)O_2Cl_4$ (**1**) crystallized following evaporation of the solvent at room temperature.[9b]

Needles of **1** were mounted and flame-sealed in a borosilicate capillary, and the capillary was then flame-sealed in a 5 mm borosilicate NMR tube. The doubly contained sample was suspended in the liquid nitrogen bath of a cylindrical Dewar fitted with quartz windows. For containment of contamination in the event of potential breakage of the actinide sample during cooling and subsequent heating to room temperature, the cylindrical Dewar was inserted into a container with 7/8 in. thick polyethylene walls. This container was fitted with borosilicate windows and an appropriate HEPA filter.

The excitation source was the signal beam from a tunable optical parametric oscillator (Continuum Panther) pumped by a Nd:YAG laser (Continuum Surelight II-10) operating at a 10 Hz repetition rate. The maximum laser output of the optical parametric oscillator over the 585−710 nm excitation wavelength range was <10 mJ. The beam was attenuated to <0.2 mJ and not focused prior to interaction with the sample. The spectral bandwidth of the excitation light was <6 cm^{-1}. The photoluminescence was collected at 90° to the excitation, passed through an 850 nm long-pass filter, and then dispersed using a quarter-meter spectrograph (Acton Research Corporation SpectraPro-300i) with a 600 lines/mm grating blazed at 1.0 μm. Emission intensity was detected by a 512 element InGaAs photodiode array (50×500 μm) with a detector response range of 800−1700 nm (Princeton Instruments OMA V 1.7 μm). The line positions for emission data reported here were calibrated to krypton lines reported by the National Institute of Standards and Technology.[13] Emission peak intensities were not corrected for spectrograph or detector responses. Rise times and decay

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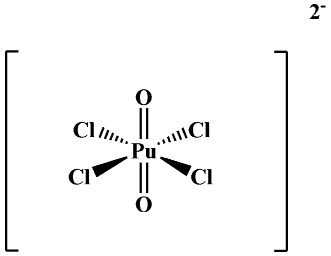
CHART 1: The Anion, $PuO_2Cl_4^{2-}$, Adopts a Pseudo-octahedral Geometry with Two Plutonyl Oxo Ligands Axially Coordinated and Four Chloride Ligands Occupying the Equatorial Plane. Charge Balance Is Maintained by Two Cesium Cations Per Tetrachlorodioxoplutonium(VI) Anion



times were measured with a liquid-nitrogen-cooled near-infrared photomultiplier tube with an InP/InGaAs photocathode (Hamamatsu R5509−72), the PMT emission signal was amplified (Stanford Research SR445), and the time-resolved photon count rates were collected using a multichannel scaler/averager (Stanford Research SR430). This combination has a response time of 5 ns. Lifetimes were determined using a commercial data analysis program and exponential model functions (Igor Pro Version 6.01). A portion of the laser output signal was monitored with a pyroelectric detector (Molectron J4−09) in order to normalize excitation spectra. Software for excitation data collection was written in house using National Instruments LabView, Version 6i. Emission and excitation spectra are reported as intensity as a function of inverse vacuum wavelength in reciprocal centimeters (cm^{-1}).

Hazards: Uranium consists primarily of the isotope uranium-238, an alpha emitter with a half-life of 4.47×10^9 years, and the plutonium used here is composed mainly of plutonium-239, an emitter with a half-life of 2.41×10^4 years. Alpha emitters are principally internal radiation hazards, and ingestion or inhalation of uranium or plutonium should be avoided. Practitioners should also adhere to their local institutional requirements for carrying out reactions and manipulations of radiological materials and for handling the radioactive waste generated from this procedure. As with all synthetic procedures involving hazardous chemicals, appropriate eye protection, gloves, and lab coats should be worn when handling these materials.

Results and Discussion

The compound $Cs_2PuO_2Cl_4$ was chosen for these photoluminescence studies for several reasons. Single-crystal X-ray diffraction analysis of $Cs_2PuO_2Cl_4$ reveals that the $PuO_2Cl_4^{2-}$ anion is isostructural with the uranium and neptunium analogues $UO_2Cl_4^{2-}$ and $NpO_2Cl_4^{2-}$ (see Chart 1).[9a,11,12] We have previously reported near-infrared photoluminescence from $NpO_2Cl_4^{2-}$ doped into a $Cs_2UO_2Cl_4$ matrix.[9b] Likewise, the plutonium compound can be doped into isostructural $Cs_2UO_2Cl_4$, diluting it to reduce potential self-quenching and taking advantage of the characteristic broad energy window below 20 000 cm^{-1} that is free of electronic transitions from the uranyl host (vide infra).[4,14] Therefore, near-infrared photoluminescence from the doped system $Cs_2U(Pu)O_2Cl_4$ is expected to arise solely from intra-5f transitions of the open-shell plutonyl ion and not from the ligand-to-metal charge-transfer bands of the host. Also, coordination of a single-atom ligand, such as chloride, to the metal is preferable to coordination of a multiple-atom ligand because the absence of intraligand vibrations eliminates a potential source of radiationless deactivation for excited-state photoluminescence.

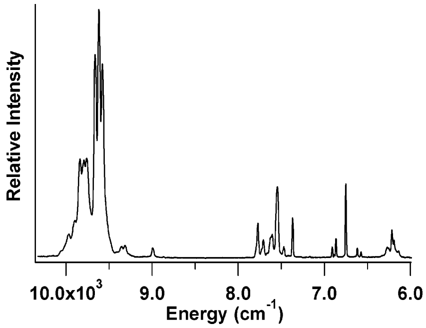


Figure 1. Photoluminescence spectrum of $Cs_2U(Pu)O_2Cl_4$ at 75 K following pulsed excitation at 628 nm.

In contrast to studies of transuranic actinyl ions, the electronic structure of the uranyl ion has been reported extensively.[4,5] The uranyl ion is conventionally understood to have a $[Rn]5f^0$ ground-state electronic configuration. The lowest-energy electronic transitions available to this closed shell are described as ligand-to-metal charge-transfer (LMCT) and lie in the green of the visible region (~20 000 cm^{-1}). Optical spectra of uranyl ions are characterized by a vibronic structure corresponding to the energy of ν_1, the symmetric O−U−O stretch, often to 5 or 6 quanta. Transuranic actinyl cations are expected to have more complex spectra because additional valence electrons in these $[Rn]5f^n$ ($n > 0$) electronic configurations yield intra-5f transitions in addition to LMCT bands, and transitions based upon this electronic structure extend from the near-infrared through the UV/vis region.[4,5,14] Because of relatively narrow energy gaps between states, nonradiative relaxation is suggested to be more likely as one moves from UO_2^{2+} to NpO_2^{+} to PuO_2^{2+}. Intra-5f bands of a centrosymmetric structure such as $MO_2Cl_4^{2-}$ (M = Np, Pu) are predicted to be weak if observed at all because ungerade → ungerade transitions are parity forbidden. However, $5f_u \rightarrow 5f_u$ bands can be allowed by magnetic dipole or electric quadrupole mechanisms, or they can be electric dipole induced by ungerade molecular vibrations. Although the vibrational energies of $Cs_2PuO_2Cl_4$ have not been reported in the literature, detailed normal-mode analyses have been carried out on $Cs_2UO_2Cl_4$ and $Cs_2NpO_2Cl_4$.[14c,15] The structure of this pseudo-D_{4h} ion is characterized by three modes resulting from vibrations of the actinyl ion itself and eight resulting from vibrations due to coordination of four chloride ligands in the equatorial plane. In particular, the five infrared-active vibrational modes are likely to induce intra-5f transitions in $PuO_2Cl_4^{2-}$, as observed with $NpO_2Cl_4^{2-}$.[14c]

Photoluminescence emission of **1** at 75 K following pulsed laser excitation at 628 nm was detected between 6000−10 200 cm^{-1}, and the spectrum is shown in Figure 1. Presumably, the relative intensities of hot bands are diminished at low temperature. It is important to note that measurable intensity toward the low end of the range was limited by the quantum efficiency of our InGaAs array detector, which drops from ~70 to <20% below 6000 cm^{-1}, and there may well be additional photoluminescence transitions from $PuO_2Cl_4^{2-}$ at lower energy. Photoluminescence emission measured between 6 000 and 10 200 cm^{-1} reveals a more complex spectrum for **1** in terms of number of transitions than that measured from $Cs_2U(Np)O_2Cl_4$, consistent with the greater number of electronic states in the plutonyl case.[9a,b,14]

Correspondence between energies and relative intensities of photoluminescence excitation lines and published absorption spectra support the attribution of the observed fluorescence to the plutonyl ion. Excitation spectra of **1** were measured by scanning the laser wavelength while monitoring emission

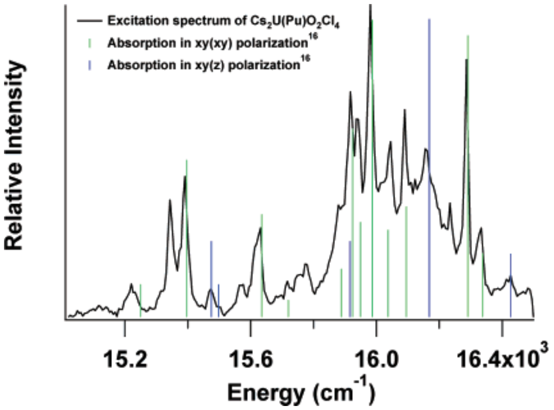


Figure 2. Photoluminescence excitation spectrum of the 7540 cm^{-1} emission line of Cs$_2$U(Pu)O$_2$Cl$_4$ at 75 K.

transitions at 9612, 7540, 6860, and 6194 cm^{-1}, and these four spectra are essentially identical. A portion of one excitation spectrum measured while monitoring 7540 cm^{-1} at 75 K is shown in Figure 2. The uncertainties in the energy positions of these peaks are determined by the calibration uncertainty of the excitation laser (±5 cm^{-1}). Superimposed on this spectrum are energies and approximate intensities of transitions from polarized absorption spectra of Cs$_2$U(Pu)O$_2$Cl$_4$ single crystals obtained at 4.2 K by Gorshkov and Mashirov.[16] Note that it is difficult to quantitatively compare the intensities of transitions from our unpolarized spectra with transitions from the separately plotted polarized spectra reported by Gorshkov and Mashirov. However, comparison of our excitation spectrum with the reported absorption spectra reveals that the number of transitions and transition energies is in close agreement. For example, the excitation transition that we measured at 15 391 cm^{-1} is comparable in energy and relative intensity to an absorption peak that Gorshkov and Mashirov measured at 15 396 cm^{-1} in the $xy(xy)$ polarization and assigned $E_{13} + S_{10}$, the excitation transition that we measured at 15 474 cm^{-1} is comparable in energy and relative intensity to an absorption peak that Gorshkov and Mashirov measured at 15 475 cm^{-1} in the $xy(z)$ polarization and assigned $E_{11} + S_3$, and so forth. Uncertainties in the energies reported by Gorshkov and Mashirov were not provided.

TABLE 1: Energies, Rise Times, and Decay Times of Photoluminescence Transitions of 1

photoluminescence transition energies (cm^{-1})	rise time (μs)	decay time (μs)
10 047(±10)	<0.1	1.2(±0.1)
9957(±5)	<0.1	1.2(±0.1)
9900(±5)	<0.1	1.2(±0.1)
9837(±5)	<0.1	1.2(±0.1)
9788(±5)	<0.1	1.2(±0.1)
9749(±5)	<0.1	1.2(±0.1)
9656(±3)	<0.1	1.2(±0.1)
9612(±3)	<0.1	1.2(±0.1)
9569(±3)	<0.1	1.2(±0.1)
9351(±5)	<0.1	1.2(±0.1)
9313(±5)	<0.1	1.2(±0.1)
8986(±3)	<0.1	1.2(±0.1)
7768(±2)	<0.1	1.2(±±0.1)
7723(±3)	<0.1	1.2(±0.1)
7702(±2)	<0.1	1.2(±0.1)
7658(±3)	<0.1	1.2(±0.1)
7617(±3)	<0.1	1.2(±0.1)
7598(±2)	<0.1	1.2(±0.1)
7540(±10)	<0.1	1.2(±0.1)
7466(±4)	<0.1	1.2(±0.1)
7363(±2)	<0.1	1.2(±0.1)
6904(±2)	0.3(±0.1)	1.7(±0.1)
6860(±2)	0.3(±0.1)	1.7(±0.1)
6746(±2)	<0.1	1.2(±0.1)
6614(±2)	0.3(±0.1)	1.7(±0.1)
6569(±2)	0.3(±0.1)	1.7(±±0.1)
6260(±10)	0.2(±0.1)	2.3(±0.1)
6212(±2)	0.2(±0.1)	2.3(±0.1)
6194(±10)	<0.1	1.6(±0.2)
6137(±10)	<0.1	1.6(±0.2)

Time-resolved photoluminescence decay waveforms were recorded while monitoring each of the emission peaks shown in Figure 1. The time dependence of the intensities were fitted to sums of exponential terms capable of accounting for both resolvable in-growth and multiple decay processes

$$I = -A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + b$$

where b is a constant background intensity, τ_1 is the time constant for the signal rise, and τ_2 is the time constant for the signal decay. The results are indicated in Table 1 as a listing of emission transitions, along with time constants for in-growth and decay. The signal decays all appear to be described by single-exponential terms. In most cases, there also appears to be a resolvable signal rise that is slower than the instrument response of approximately 10 ns. These rise times are difficult to fit accurately when they are less than 0.1 μs because they are partially obscured by early time noise in our electronics; therefore, we simply report an upper limit in those cases. When they are greater than 0.1 μs, we are able to report a best-fit value. Temporal similarity between two given emission lines suggests that either the two transitions measured originate from one common excited state or that the two transitions measured originate from two different excited states that are each populated by a common, relatively longer-lived excited state. While we cannot yet explain the complex decay kinetics that we have observed, we note that similar behavior was seen from the PuF$_6$ system.[8b]

Conclusions

This work represents the first observation of photoluminescence emission from the plutonyl ion. Spectra reveal rich electronic structure and relaxation pathways which may enable fundamental photophysical data useful for calculating electronic structures of actinide open-shell [Rn]5f^n (n > 0) electronic configurations, characterizing plutonyl speciation, and developing new diagnostics for measuring plutonyl reaction dynamics. Theoretical calculations of excited-state energies and assignments are in progress, and research on room-temperature photoluminescence from PuO$_2$Cl$_4$$^{2-}$ is ongoing.

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