

Crystal structure and spectroscopic measurements of room temperature intra-5f fluorescence of $\text{Cs}_2\text{Np}(\text{VI})\text{O}_2\text{Cl}_4$

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Abstract

Intra-5f fluorescence from crystalline needles of $\text{Cs}_2\text{Np}(\text{VI})\text{O}_2\text{Cl}_4$ has been observed in the near-infrared at room temperature following continuous wave excitation at 633 nm. Characterization of the molecular structure of $\text{Cs}_2\text{Np}(\text{VI})\text{O}_2\text{Cl}_4$ by single-crystal X-ray diffraction analysis is reported. The observed emission originates from an excited state approximately 6889 cm^{-1} above the ground state. The vibronic structure in the emission spectrum is assigned based on comparison with the analyses of liquid helium absorption spectra of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ published by Denning et al. and room temperature fluorescence data of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ reported by Wilkerson et al. The room temperature fluorescence lifetime of the observed origin of $\text{Cs}_2\text{Np}(\text{VI})\text{O}_2\text{Cl}_4$ is compared with lifetime data from the doped system, $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$.

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1. Introduction

To date, most efforts at rigorously describing the electronic structures of actinyl ions have focused on uranyl ($\text{U}(\text{VI})\text{O}_2^{2+}$), which is a specific case that has no valence electrons in the 5f shell of the ground state [1–5]. The lowest-energy electronic transitions to occur in this system are ligand-to-metal charge-transfer (LMCT), in which an electron is promoted between a state of primarily oxygen 2p character and a state of principally uranium 5f character. These transitions are associated with vibronic bands with an energy spacing corresponding to the energy of the symmetric stretch of the uranyl ion. In contrast to uranyl most other chemically stable actinide species contain at least one electron in the 5f valence shell of the ground state. There are two types of transitions in the spectra of $5f^n$ ($n > 0$) molecules; LMCT's and transitions that correspond to promotion of an electron from one state of predominantly 5f

orbital character to another state of primarily 5f orbital character. The intensities of $5f_u \rightarrow 5f_u$ transitions are expected to be weak, if present at all, because they are parity forbidden. For centrosymmetric structures, these transitions may be allowed through magnetic dipole or electric quadrupole mechanisms, and they can be electric dipole induced by ungerade molecular vibrations. The orbitals of neptunyl ions have been investigated through computational studies and absorption spectroscopy, but fluorescence from lower energy $5f_u \rightarrow 5f_u$ transitions of neptunyl is less explored [6–9]. Actinide species with a single electron in the 5f shell are good candidates for study because the excited states are well-separated, making the spectra easier to assign and the excited state populations less susceptible to nonradiative decay [6,9].

We have recently demonstrated that transdioxo forms of actinides with partially filled 5f shells may produce detectable fluorescence upon photoexcitation [7,8]. In particular, we have reported that a simple $5f^1$ system, the neptunyl ion, luminesces with relatively high resolution and vibronic structure in the near-infrared at 77 K, and more notably, it luminesces strongly at room temperature [8]. In this study, dilution of the luminescent analyte into host crystals was employed in order to study neptunyl fluorescence in the absence of potential self-quenching

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while offering some degree of control over the local environment. In particular, neptunyl tetrachloride ($\text{Np(VI)O}_2\text{Cl}_4^{2-}$) was doped into slightly larger isostructural uranyl tetrachloride ($\text{U(VI)O}_2\text{Cl}_4^{2-}$) crystals [8]. This matrix offers a large optical window throughout the near-infrared because the lowest energy electronic transitions of uranyl tetrachloride are $\sim 20095\text{ cm}^{-1}$ [1].

We report here the observation of near-infrared fluorescence from crystalline needles of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ following excitation at 633 nm. This report is the first example of fluorescence from neat crystalline material of the neptunyl ion. We will compare the vibronic assignments from our room temperature spectrum with Denning's liquid helium polarized absorption spectra [9] and our room temperature luminescence spectrum of $\text{Cs}_2\text{U(Np)O}_2\text{Cl}_4$ [8]. We also will compare the luminescence lifetime of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ at room temperature with the lifetime of $\text{Cs}_2\text{U(Np)O}_2\text{Cl}_4$ measured at 295 K [8].

2. Experimental

2.1. General

The synthesis of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ was carried out in a well-ventilated and radiation monitored fume hood. Neptunium-237 is an α emitter with a half-life of 2.14×10^6 years. As such, it is principally an internal radiation hazard, and ingestion or inhalation of neptunium-237 should be avoided. As with all synthetic procedures involving hazardous chemicals, appropriate eye protection, gloves and lab coats should be worn when handling this material. Practitioners should also adhere to their local institutional requirements for handling resultant radioactive waste that is generated from this procedure.

2.2. Materials

CsCl and concentrated HCl were purchased from Aldrich Chemical Company. Neptunyl stock solution was prepared by literature methods [10].

2.3. Synthesis and characterization of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ (**1**)

Cesium chloride (0.29 g, 1.7 mmol) was dissolved in 6 M HCl (10 mL), and this solution was added to a stock solution of 0.43 M NpO_2^{2+} in 1 M HCl (1.5 mL, 0.65 mmol) [10]. The vial containing the solution was gently stirred for ~ 5 min, then covered loosely with parafilm, and allowed to stand for two weeks at room temperature, yielding dark-green blocks in quantitative yield. The dark-green blocks were redissolved in 1 M HCl, and allowed to stand for two weeks, yielding dark-green needles. IR (Nujol): 920 s cm^{-1} . Raman (neat crystals): $802\text{ s}, 253\text{ m}, 226\text{ w}, 189\text{ m}, 131\text{ m cm}^{-1}$.

2.4. Crystallographic measurements and structure solutions of **1**

Details of data collection and structure refinement are given in Table 1. Samples of **1** were prepared for single-crystal X-ray diffraction analysis in a radiation monitored glove box. A dark-green block of $0.25\text{ mm} \times 0.15\text{ mm} \times 0.15\text{ mm}$ was cut from a larger crystal, thinly coated with epoxy and placed in a quartz capillary. The capillary was then coated with a thin film of acrylic dissolved in ethyl acetate. (Note: this triple containment was necessitated by the health hazards of transuranic materials.) The sample was placed under the -70°C liquid N_2 vapor coldstream on a Bruker P4/PC diffractometer and irradiated with a sealed Mo $\text{K}\alpha$ X-ray source ($\lambda = 0.71073\text{ \AA}$). Data were collected using a SMART 1k CCD detector. A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software [11]. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT software [12]. The data were

Table 1
Crystal data and structure refinement for $\text{Cs}_2\text{NpO}_2\text{Cl}_4$

Identification code	ccd538a
Empirical formula	$\text{Cl}_4\text{Cs}_2\text{NpO}_2$
Formula weight	676.62
Temperature	-70°C
Wavelength	0.71073 \AA
Crystal system	Monoclinic
Space group	$C 2/m$
Unit cell dimensions	$a = 11.828(4)\text{ \AA}; b = 7.659(2)\text{ \AA}; c = 5.7679(17)\text{ \AA}; \beta = 99.386(7)^\circ$
Volume	$515.6(3)\text{ \AA}^3$
Z	2
Density (calculated)	4.359 Mg/m^3
Absorption coefficient	18.014 mm^{-1}
$F(0\ 0\ 0)$	574
Crystal size	$0.16\text{ mm} \times 0.29\text{ mm} \times 1.2\text{ mm}$
Theta range for data collection	$3.18\text{--}28.25^\circ$
Index ranges	$-15 \leq h \leq 15, -8 \leq k \leq 8, -7 \leq l \leq 7$
Reflections collected	1935
Independent reflections	590 [$R(\text{int}) = 0.0713$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	590/0/26
Goodness-of-fit on F^2	1.493
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0957, wR2 = 0.2735$
R indices (all data)	$R1 = 0.0964, wR2 = 0.2756$
Largest diff. peak and hole	12.088 and $-10.442\text{ e \AA}^{-3}$ [near Np]

$$R1 = \sigma|F_0| - |F_c|/|\sigma|F_0|; wR2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}, \text{ and } w = 1/[\sigma^2(F_0^2) + (0.093P)^2].$$

corrected for absorption using the SADABS program [13]. Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL [14]. Refinement by full-matrix least-squares techniques on F^2 converged with $R1 = 0.0957$, and $wR2 = 0.2735$. Structural analysis of the dark-green needles of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ reveals a crystal structure that is identical to that of the dark-green blocks.

2.5. Spectroscopy of **1**

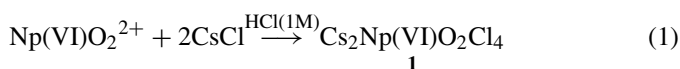
Infrared spectra of samples in Nujol mulls were measured between 400 and 4000 cm^{-1} on a Magna-IR System 750 spectrometer. Raman samples were sealed in 5 mm glass NMR tubes, and Raman spectra were recorded on a Nicolet Model 960 FT-Raman spectrometer attached to a Nicolet model 560 Magna-IR instruments. The excitation source is the 1064 nm light from a CW Nd:VO₄ laser. The interferograms were detected with an InGaAs detector operated at room temperature. An average of 256 scans at 4 cm^{-1} resolution was collected for each spectrum.

For the fluorescence measurements, crystalline needles of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ were mounted and then sealed in a borosilicate capillary, which was then sealed in a 5 mm borosilicate NMR tube. A pulsed excitation source was used for emission spectra and lifetime measurements of $\text{Cs}_2\text{U(Np)O}_2\text{Cl}_4$. The source is the output from a tunable Nd:YAG (Continuum Powerlite 8000) pumped optical parametric oscillator (Continuum Mirage 500) operating at a 10 Hz repetition rate. Pulse energies for experiments using the OPO are 1–2 mJ in 5 ns pulses with a spectral bandwidth of $\sim 0.2\text{ cm}^{-1}$. Fluorescence emission spectra of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ were collected following continuous wave excitation from a Helium-neon laser (Melles Griot 05-LHP-111) with an output wavelength of 633 nm and power of 1 mW. Lifetime measurements of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ were collected following excitation from the OPO laser. The luminescence was collected at 90° to the excitation, passed through a 695 nm long pass filter, and then dispersed using a 300 mm focal length spectrograph (Acton Research Corporation SpectraPro-300i) with a 600 lines/mm grating blazed at $1.0\text{ }\mu\text{m}$. The emission intensity

was measured using a liquid nitrogen cooled near-infrared photomultiplier tube with an InP/InGaAs photocathode (Hamamatsu R5509-72) or using a 1064 element InGaAs photodiode array (Princeton Instruments OMA V:InGaAs). Time-resolved data were collected using a multichannel scaler/averager (Stanford Research SR430). The line positions for emission data reported here have been calibrated to krypton lines reported by the National Institute of Standards and Technology, but the intensities have not been corrected for spectrograph or detector responses. Lifetimes were determined using a commercial data analysis program and a single exponential model function (Igor Pro Version 5.04B).

3. Results and discussion

The compound $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ has proven to be a useful molecule for probing near-infrared intra-5f electronic structure [7–9], and it is readily prepared in aqueous media. The reaction of neptunyl (NpO_2^{2+}) stock solution with two equivalents of CsCl in 1 M HCl gives an olive-green colored solution from which large dark-green blocks of **1** are crystallized in quantitative yield (Eq. (1)) [10].



An incomplete X-ray crystal diffraction analysis of **1** was reported by Weigel et al. [15], and we present here a complete structural analysis of dark-green blocks of **1** that is consistent with Weigel's analysis. Single-crystal X-ray diffraction analysis of dark needles of **1** obtained from recrystallization of the dark-green blocks in 1 M HCl yields an identical result. The molecular structure and atom-labeling scheme of **1** is shown in Fig. 1, and bond lengths and angles are given in Table 2. Compound **1** is isostructural with the uranium analogue $\text{Cs}_2\text{UO}_2\text{Cl}_4$, which crystallizes in the monoclinic space group $C_{2/m}$ [16,17].

The neptunium atom of **1** is coordinated in a pseudo-octahedral fashion by two oxo groups and four chloride ligands. The oxo groups of the neptunyl moiety lie *trans* to one another with a bond angle of $\text{O}(1)\text{--Np}(1)\text{--O}(2)$ of $180.0(8)^\circ$. This angle lies within the range reported for the limited number of neptunyl structures published (range $176.5(19)\text{--}180.0^\circ$) [18–32]. The $\text{Np}\text{--O}(\text{oxo})$ distances of **1** are $1.775(17)$ Å, a value within range of $\text{Np}\text{--O}(\text{oxo})$ bond lengths reported for six-coordinate neptunyl chloride compounds $\text{NpO}_2\text{Cl}_2(\text{Ph}_3\text{PO})_2$ ($1.751(18)$, $1.721(16)$ Å) and $[\text{NBu}_4]_2[\text{NpO}_2\text{Cl}_4]$ ($1.733(5)$, $1.740(6)$ Å) [18,32]. The chloride ligands lie in the equatorial plane of the

Table 2
Selected bond lengths (Å) and bond angles ($^\circ$) for $\text{Cs}_2\text{NpO}_2\text{Cl}_4$

Atoms	Distance (Å)
$\text{Np}(1)\text{--O}(1)$	1.775(17)
$\text{Np}(1)\text{--O}(2)$	1.775(17)
$\text{Np}(1)\text{--Cl}(1)$	2.653(3)
$\text{Np}(1)\text{--Cl}(2)$	2.653(3)
$\text{Np}(1)\text{--Cl}(3)$	2.653(3)
$\text{Np}(1)\text{--Cl}(4)$	2.653(3)
Atoms	Angle ($^\circ$)
$\text{O}(1)\text{--Np}(1)\text{--O}(2)$	180.0(8)
$\text{O}(1)\text{--Np}(1)\text{--Cl}(3)$	88.8(3)
$\text{O}(1)\text{--Np}(1)\text{--Cl}(1)$	91.2(3)
$\text{O}(1)\text{--Np}(1)\text{--Cl}(2)$	88.8(3)
$\text{O}(1)\text{--Np}(1)\text{--Cl}(4)$	91.2(3)
$\text{O}(2)\text{--Np}(1)\text{--Cl}(1)$	88.8(3)
$\text{O}(2)\text{--Np}(1)\text{--Cl}(2)$	91.2(3)
$\text{O}(2)\text{--Np}(1)\text{--Cl}(3)$	91.2(3)
$\text{O}(2)\text{--Np}(1)\text{--Cl}(4)$	88.8(3)
$\text{Cl}(1)\text{--Np}(1)\text{--Cl}(2)$	180.0
$\text{Cl}(1)\text{--Np}(1)\text{--Cl}(3)$	87.25(11)
$\text{Cl}(1)\text{--Np}(1)\text{--Cl}(4)$	92.75(11)
$\text{Cl}(2)\text{--Np}(1)\text{--Cl}(3)$	92.75(11)
$\text{Cl}(2)\text{--Np}(1)\text{--Cl}(4)$	87.25(11)
$\text{Cl}(3)\text{--Np}(1)\text{--Cl}(4)$	180.00(10)

neptunyl ion, and the $\text{Np}\text{--Cl}$ bond distances are $2.653(3)$ Å. These values are similar to other $\text{Np}\text{--Cl}$ bond lengths reported for other six-coordinate neptunyl structures $\text{NpO}_2\text{Cl}_2(\text{Ph}_3\text{PO})_2$ ($2.622(14)$, $2.645(13)$ Å) and $[\text{NBu}_4]_2[\text{NpO}_2\text{Cl}_4]$ ($2.637(2)$, $2.649(2)$, $2.661(2)$, $2.676(2)$ Å) [18,32].

Single-crystal X-ray diffraction analysis of data collected from **1** at liquid nitrogen temperature reveals that the ground state of the $\text{Np(VI)O}_2\text{Cl}_4^{2-}$ ion has pseudo- D_{4h} symmetry, which is characterized by four ground state $\text{O}\text{--Np}\text{--O}$ vibrational modes, of which two are Raman active and two are infrared active, and seven $\text{Np}\text{--Cl}$ modes, of which three are Raman active and four are infrared active [9]. The vibrational energies reported for $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ are listed on Table 3. The vibrational energies that we were able to measure are within range of the reported vibrational energies.

The electronic structure of the $\text{NpO}_2\text{Cl}_4^{2-}$ ion has been investigated theoretically and experimentally by several authors [6–9,33–37]. In particular, analyses of optical absorption spectra of oriented single crystals of $\text{Cs}_2\text{U(Np)O}_2\text{Cl}_4$ at liquid helium temperature reveal $5f_u \rightarrow 5f_u$ and LMCT vibronic transitions [9,33]. Assignment of electronic transitions may be identified by the presence of hot bands near the origin and the absence of a progression in the Np(VI)O_2^{2+} symmetric stretching mode, ν_1 . We have adopted Denning's labeling method in which the ground state is labeled **0**, and each excited state is identified by a Roman numeral, beginning with **I** for the first excited state, **II** for the second excited state, etc. In particular, Denning assigned three $5f\text{--}5f$ electronic origins in the near-infrared, and he directly observed the magnetic dipole allowed electronic transition, **II** \leftarrow **0**, at 6880.4 cm^{-1} [9]. Vibronic assignments corresponding to **II** + $\nu_{10} \leftarrow$ **0**, **II** + $\nu_9 \leftarrow$ **0**, **II** + $\nu_6 \leftarrow$ **0**, **II** + $\nu_3 \leftarrow$ **0**, and

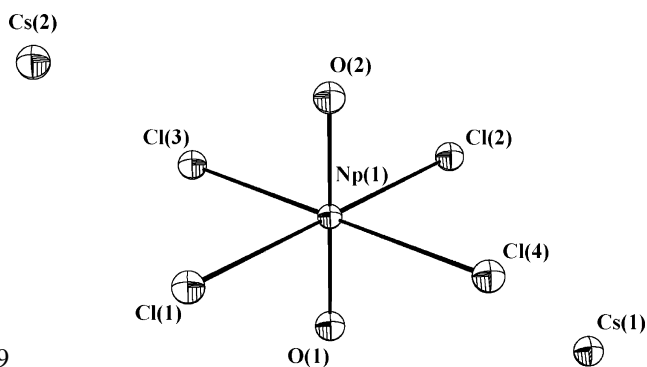


Fig. 1. Thermal ellipsoid drawing of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ showing the atom-labeling scheme used in the tables (50% probability ellipsoids).

Table 3

Vibrational modes, symmetries, description of vibration, and ground state vibrational energy (cm^{-1}) of $\text{NpO}_2\text{Cl}_4^{2-}$ [9]

Mode	Symmetry in D_{4h}	Type of vibration	Vibrational energy
ν_1	A_{1g}	O–Np–O symmetric stretch (Raman)	802
ν_2	A_{2u}	O–Np–O asymmetric stretch (Infrared)	919
ν_3	E_u	O–Np–O bend (Infrared)	267
ν_4	A_{1g}	Np–Cl symmetric stretch (Raman)	257
ν_5	B_{2g}	Np–Cl stretch (Raman)	230
ν_6	E_u	Np–Cl stretch (Infrared)	244
ν_7	B_{1g}	Np–Cl in plane bend (Raman)	133
ν_8	E_u	Np–Cl in plane bend (Infrared)	117
ν_9	A_{2u}	Np–Cl out of plane bend (Infrared)	117
ν_{10}	B_{1u}	Np–Cl out of plane bend (Raman, infrared inactive)	
ν_{11}	E_g	O–M–O rock (Raman)	185

$\text{II} + \nu_2 \leftarrow \mathbf{0}$ were reported based upon ground state vibrational mode frequencies [9]. We observed the electronic origin $\text{II} \rightarrow \mathbf{0}$ at 6889 cm^{-1} in the fluorescence spectra of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at room temperature, and this spectrum is shown in Fig. 2B [8]. The assignment of this electronic origin was supported by the presence of thermally accessible hot bands in the room temperature spectrum at 7010 and 7180 cm^{-1} . These transitions are higher in energy than the origin by approximately the energies of IR active modes ν_8 , ν_9 , ν_{10} and ν_3 , respectively, and we assigned these bands as $\text{II} + \nu_8 \rightarrow \mathbf{0}$, $\text{II} + \nu_9 \rightarrow \mathbf{0}$, $\text{II} + \nu_{10} \rightarrow \mathbf{0}$, and $\text{II} + \nu_3 \rightarrow \mathbf{0}$.

The room temperature fluorescence spectrum of neat crystalline needles of **1** is presented in Fig. 2A. Like the room

temperature spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$, the electronic and vibronic transitions observed in the room temperature spectrum of **1** are broader than those of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ measured at liquid nitrogen temperature. The energy at $\sim 6889 \text{ cm}^{-1}$ of the electronic transition corresponding to the $\text{II} \rightarrow \mathbf{0}$ origin in the room temperature spectra of both **1** and $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ is blue-shifted from that measured from $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at liquid nitrogen temperature. Likewise, the assignment of the electronic origin from **1** is supported by the presence of broad hot bands at 7010 and 7180 cm^{-1} , which lie higher in energy than the origin by approximately the energies of IR active modes ν_8 , ν_9 , ν_{10} , and ν_3 . These bands are assigned as $\text{II} + \nu_{8,9,10} \rightarrow \mathbf{0}$, and $\text{II} + \nu_3 \rightarrow \mathbf{0}$. The relative intensities between the transitions assigned to the origin and to the hot bands from **1** is comparable to the those measured in the corresponding spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$. The room temperature luminescence decay curve for origin $\text{II} \rightarrow \mathbf{0}$ of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ is compared with that of the doped system $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ in Fig. 3. The room temperature decay of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ is single exponential, yielding a lifetime of $2 \mu\text{s}$, in comparison to the $20 \mu\text{s}$ single exponential lifetime measured for the neptunyl ion in the doped uranyl system at room temperature [8]. Assuming that the Einstein A coefficients for the $\text{II} \rightarrow \mathbf{0}$ luminescence are similar in magnitude in the neat and doped systems, the decreased lifetime in neat $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ indicates an increased nonradiative coupling of the second excited state.

The vibronic assignments in the spectrum of **1** are labeled in the upper graph (A) of Fig. 2. These were determined by comparison of the energy differences between the origin and each vibronic transition with the frequencies of the ground state vibrational modes (Table 1). These assignments are supported by comparison of the transition energies with the vibronic transitions energies of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ [8]. The broad vibronic

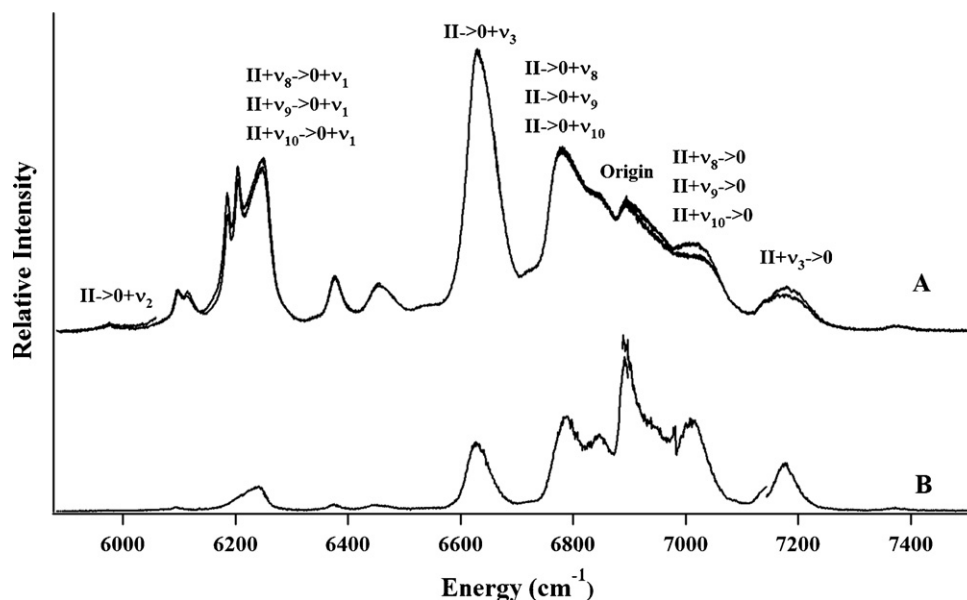


Fig. 2. (A) Luminescence spectrum of **1** at room temperature using a photodiode array following excitation at 633 nm . The spectrograph slit was $100 \mu\text{m}$ wide. (B) Luminescence spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at room temperature using a photomultiplier tube following excitation at 628.3 nm . The photon counts were collected over a $40 \mu\text{s}$ gate width following at $5 \mu\text{s}$ gate delay. Background photon counts collected over a $40 \mu\text{s}$ gate width following a $500 \mu\text{s}$ gate delay were subtracted. Spectrograph and detector slits were $100 \mu\text{m}$ wide.

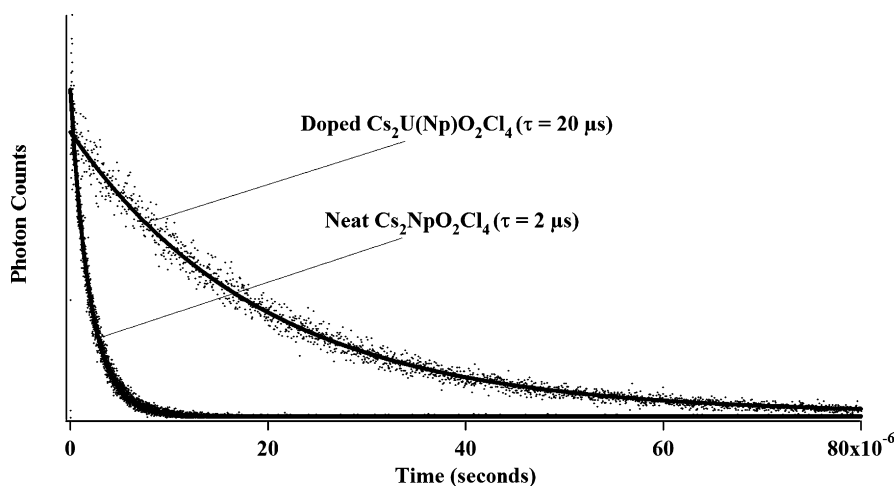


Fig. 3. Luminescence decay curves of the origin $\text{II} \rightarrow \mathbf{0}$ of $\mathbf{1}$ ($\lambda_{\text{exc}} = 590 \text{ nm}$) and of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ ($\lambda_{\text{exc}} = 628.3 \text{ nm}$). Fluorescence was collected using a photomultiplier tube following pulsed excitation.

structure of the room temperature spectrum makes some of the assignments speculative. For example, the broad peak centered at 6785 cm^{-1} is assigned here as $\text{II} \rightarrow \mathbf{0} + \nu_{8,9,10}$. The most intense band centered at 6625 cm^{-1} is broadened over $6560\text{--}6700 \text{ cm}^{-1}$, and it is assigned to $\text{II} \rightarrow \mathbf{0} + \nu_3$, and likely contains $\text{II} \rightarrow \mathbf{0} + \nu_6$. The energy of a broad peak between 6145 and 6285 cm^{-1} implies a hot band based upon ν_8 , ν_9 , and ν_{10} , and this transition is assignable to $\text{II} + \nu_{8,9,10} \rightarrow \mathbf{0} + \nu_1$. We note that, in contrast to the spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$, the intensities of these vibronic transitions are greater than the relative intensity of the origin. Another vibronic transition is observed in these data that is 919 cm^{-1} lower in energy than the origin, which is assigned to $\text{II} \rightarrow \mathbf{0} + \nu_2$.

We also observe the presence of four relatively narrow transitions at 6210 , 6190 , 6615 , and 6095 cm^{-1} and two broader transitions at 6375 and 6555 cm^{-1} . Currently, additional spectroscopic probes of crystalline $\text{Np}(\text{VI})\text{O}_2\text{Cl}_4^{2-}$ are being performed to determine the nature of these additional transitions.

4. Conclusions

We report the first example of fluorescence from neat crystals containing the neptunyl ion. It is predicted that the spectrum of a $5f^1$ system is characterized by a relatively lower number of electronic states than a $5f^n$ ($n > 1$) system because the number of optically accessible states increases with a greater number of valence electrons. Indeed, the energy region probed between 5900 and 7500 cm^{-1} contains a single electronic origin at 6889 cm^{-1} , which we assign to the $\text{II} \rightarrow \mathbf{0}$ electronic origin, based upon comparison with published absorption data and our own fluorescence data of the doped system, $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$. The room temperature decay is single exponential, yielding a decay of $2 \mu\text{s}$. Vibronic structure assignments are consistent with the energies of the ungerade vibrational modes ν_2 , ν_3 , ν_6 , ν_8 , ν_9 , and ν_{10} and the gerade mode, ν_1 .

We had initially chosen to study systems in which potential self-quenching of the analyte can be controlled by dilution of the analyte into a host lacking high frequency vibrational modes that

could serve as acceptors for radiationless deactivation. However, we present here measurements of near-infrared $5f\text{--}5f$ fluorescence from neat crystalline $\text{NpO}_2\text{Cl}_4^{2-}$ ions. We now hope to extend this work to other neptunyl systems characterized by a variety of symmetries and ligand sets.

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