



Visible and near-infrared excitation spectra from the neptunyl ion doped into a uranyl tetrachloride lattice



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ABSTRACT

Visible and near-infrared illumination induces 5f-5f and ligand-to-metal charge-transfer (LMCT) transitions of the neptunyl tetrachloride anion in polycrystalline $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$, and results in near-infrared luminescence from the second electronically excited state to the ground state. This photoluminescence is used as a detection method to collect excitation spectra throughout the near-infrared and visible regions. The excitation spectra of LMCT transitions in excitation spectra were identified in previous work. Here the measurement and analysis is extended to include both LMCT and intra-5f transitions. The results manifest variation in structural properties of the neptunium-oxo bond among the low-lying electronic states. Vibronic intensity patterns and energy spacings are used to compare bond lengths and vibrational frequencies in the excited states, confirming significant characteristic differences between those excited by 5f-5f transitions from those due to LMCT transitions. Results are compared with recently published RASPT2/SO calculations of $[\text{NpO}_2\text{Cl}_4]^{2-}$.

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1. Introduction

Electronic structure modeling of open-shell actinyl ions has been hindered by the high number and density of valence states characteristic of these systems and by the relative paucity of experimental data for validation of theoretical results [1–11]. Typically, transitions between these electronic states span a broad energy range from the near-infrared to the ultraviolet. The transitions are described as either 5f-5f or ligand-to-metal charge-transfer (LMCT). Optical studies have been conducted on $5f^1$ uranium(V) dioxo molecules, which contain the simplest open-shell ground state electronic configuration, $[\text{Rn}]5f^1$, but stable U(V) compounds are limited in number due to disproportionation of U(V) to U(IV) and U(VI) [12,13]. The neptunyl ion, $\text{Np}(\text{VI})\text{O}_2^{2+}$, is perhaps a more attractive member of the open-shell family for spectroscopic analyses because it can form stable compounds that are isostructural with those of the well-studied, closed-shell uranyl ion $\text{U}(\text{VI})\text{O}_2^{2+}$. This latter property enables $\text{Np}(\text{VI})\text{O}_2^{2+}$ to be doped into stable chemical environments of uranyl compounds and studied as a dilute component in a host that is optically transparent

in the near-infrared [14–23]. The neptunyl tetrachloride ion $[\text{NpO}_2\text{Cl}_4]^{2-}$ doped into a $\text{Cs}_2\text{UO}_2\text{Cl}_4$ host has been the subject of several studies largely for these reasons, and because the chloride ligands introduce no internal ligand vibrations to complicate spectral interpretation.

Near-infrared absorption spectra were first reported by Stafsudd in 1969, and later by Gorshkov [14,15]. Subsequently, Denning and co-workers recorded polarized absorption spectra at 4.2 K [18,19], as well as magnetic circular dichroism spectra, and Zeeman effect measurements, and then used parameterized ligand field theory to assign ten electronically excited transitions and associated vibronic structure in the region between 600 and 22,000 cm^{-1} . In this work, we adhere to Denning's convention of labeling excited electronic states as Roman numerals **I** through **X** and the ground electronic state as **0**.

In principle, photoluminescence excitation and absorption spectra measure similar information concerning electronic structure, but luminescence spectroscopy allows signals from impurities to be excluded more effectively and is easier to employ on small, irregularly shaped crystals. Dilution of the $[\text{NpO}_2\text{Cl}_4]^{2-}$ dianion into a $\text{Cs}_2\text{UO}_2\text{Cl}_4$ host inhibits potential self-quenching of the lower energy photoemission [21,22]. Near-infrared photoluminescence of $[\text{NpO}_2\text{Cl}_4]^{2-}$ from the electronic state **II** to the ground state **0** was first reported by Wilkerson and Berg using $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ crystals

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cooled to 75 K [21]. This study revealed the feasibility of using luminescence to detect valence electronic transitions of open-shell actinide molecules in the solid state. Later, Wilkerson and Berg used photoluminescence from **II** → **0** to record an excitation spectrum of Cs₂U(Np)O₂Cl₄ between 13,200 and 21,275 cm⁻¹ [23]. Transitions **0** → **IV** through **VII**, **IX** and **X**, each characterized by Denning as LMCT, were identified in this spectral region, and the vibronic transitions in the emission and excitation spectra were assigned with the aid of Denning's absorption data [18,19].

This paper presents a comprehensive report of photoluminescence excitation spectra of transitions over a broader range and of higher quality from the ground electronic state to excited electronic states throughout the near-infrared and visible spectral regions (6585–24,000 cm⁻¹) using the near-infrared photoluminescence from state **II** to the ground state **0** as a sensitive means of detection. We discuss the significance of observed vibronic progressions in the neptunyl symmetric stretch, and present several low-intensity previously unobserved features belonging to states **II** and **III** that suggest new information concerning the nature of the neptunium-oxo bond. We apply a standard approach to modeling the intensity of vibronic progressions in the neptunyl symmetric stretch in both 5f-5f and LMCT transitions to derive neptunium-oxo bond length changes upon excitation into excited electronic states. We compare these results with RASPT2/SO (restricted-active-space perturbation theory with spin-orbit coupling) calculations reported in the literature [10,24].

2. Experimental

The synthesis and structural characterization of Cs₂NpO₂Cl₄, and preparation of Cs₂U(Np)O₂Cl₄ crystals are described elsewhere [21–23]. The ratio of Np:U is ~3%, based upon the relative concentrations of Np and U dissolved in the parent solution. The polycrystalline needles are ~5 mm long and ~1–2 mm wide.

The excitation source used for this study is a tunable optical parametric oscillator (Continuum Panther) pumped by a pulsed Nd:YAG laser (Continuum Surelight II-10) operating at 10 Hz. The OPO has a spectral bandwidth of ~5 cm⁻¹. The laser beam was attenuated to <5 mJ and not focused prior to interaction with the sample. A portion of the laser output signal was monitored with a pyroelectric detector (Molelectron J4-09) in order to normalize the intensity of the excitation spectra to the intensity of the laser. Excitation spectra were calibrated by dispersing scattered laser light through a calibrated monochromator. The monochromator itself was calibrated using the atomic emission lines from a Kr lamp [25]. Photoluminescence from the sample was collected at 90° from the excitation laser and dispersed using a 300 mm focal length spectrograph (Acton Research Corporation SpectraPro-300i) with a 600 line/mm grating blazed at 1.0 μm. For excitation spectra, a slit width of 0.15 mm was used, and the resolution of emission was ~5 cm⁻¹. Photoluminescence was detected using a photomultiplier tube (PMT) (Hamamatsu R5509-72). The error in the reported peak positions from the excitation spectrum is ±5 cm⁻¹.

3. Results and discussion

The [NpO₂Cl₄]²⁻ anion is centrosymmetric with pseudo-D_{4h} symmetry [18,19,22]. Electric dipole transitions between 5f and low-lying LMCT electronic states are parity forbidden in D_{4h}, but may be allowed through magnetic dipole or electric quadrupole mechanisms, or can be electric dipole allowed if coupled with excitation or de-excitation of ungerade molecular vibrations. The combination of electric-dipole forbidden pure electronic transitions and vibronic coupling to ungerade modes can result in stronger vibronic sidebands. The [NpO₂Cl₄]²⁻ anion has eleven

vibrational modes, including a symmetric neptunyl stretch (ν₁), an asymmetric neptunyl stretch (ν₂), the neptunyl bend (ν₃), and four asymmetric Np–Cl stretches and bends. In particular, the totally symmetric stretching mode (ν₁) has a significant role in spectroscopic analysis if the metal–oxygen bond distance changes upon excitation. The reported symmetries and energies of these modes in the ground electronic state are listed in Table 1. Identification of vibronic transitions involving these modes in the excited states is greatly aided by the reasonable assumption that the frequencies will be similar to those in the ground state.

In this paper we retain the labeling scheme previously used by Denning to identify the electronic states [18,19]. Each electronic state is identified by a Roman numeral stated in bold, starting with **0** for the ground state, **I** for the first excited state, **II** for the second excited state, etc. Table 2 shows the states, the type of states (5f-5f or LMCT), and a summary for the experimentally derived energy and the ν₁ vibrational frequency for each electronic state versus the results from the RASPT2/SO calculations [10,18,19]. Table 3 shows energies and vibrational frequencies of ν₁ and ν₂ for states **II**–**VI** which were derived from our excitation spectrum. The average energy of ν₁ for the LMCT states is ~709 cm⁻¹, and the average energy of ν₁ for the 5f δ and φ states (**0** to **III**) is measurably higher at ~807 cm⁻¹.

The excitation spectrum of Cs₂U(Np)O₂Cl₄ crystals cooled to 75 K is shown in Fig. 1. The region between 7460 and 24,000 cm⁻¹ was collected by monitoring the intensity of **II** → **0** at 6880 cm⁻¹ while scanning the excitation laser. The features between 6585–7460 cm⁻¹ were collected by placing a 1500 nm (6667 cm⁻¹) long-pass filter in front of the monochromator with the diffraction grating in its zeroth-order position, excluding the **II** → **0** origin at 6880 cm⁻¹ but allowing light from vibronic emission transitions with wavelengths longer than 1500 nm to reach the PMT.

Overall, the number of peaks, the peak energies and relative intensities in the excitation spectrum are in reasonable agreement with those in the absorption spectra reported by Denning from crystals cooled to 4.2 K, but new vibronic assignments are made involving the ν₁ mode for transitions to states **II** and **III** [18,19]. In comparison with solution spectra of U(V)O₂²⁺ compounds, the intra-5f transitions of the more oxidizing NpO₂²⁺ are predictably lower in energy as a result of the higher positive charge on Np(VI) [12,13]. A superscript following the symbol ν signifies the electronic state to which the vibronic peak is associated.

The portion of the excitation spectrum between 6585 and 10,000 cm⁻¹ is shown in Fig. 2, and peak assignments and energies of each transition identified in our excitation spectrum are provided in Table 4. Features in this region involve **0** → **II** and **0** → **III** electronic transitions. The intense and narrow transition at 6880 cm⁻¹ is assigned as **0** → **II** origin, in agreement with Denning's reported value of 6880.4 cm⁻¹. The assignment of this

Table 1
Vibrational modes, symmetries in D_{4h}, and ground state vibrational frequencies of Cs₂NpO₂Cl₄ [18].

Mode	Symmetry in D _{4h}	Vibrational energy (cm ⁻¹)
ν ₁ ⁰	A _{1g}	802
ν ₂ ⁰	A _{2u}	919
ν ₃ ⁰	E _u	267
ν ₄ ⁰	A _{1g}	257
ν ₅ ⁰	B _{2g}	230
ν ₆ ⁰	E _u	244
ν ₇ ⁰	B _{1g}	133
ν ₈ ⁰	E _u	117
ν ₉ ⁰	A _{2u}	117
ν ₁₀ ⁰	B _{1u}	Raman, infrared inactive
ν ₁₁ ⁰	E _g	185/190

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