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 SO-RASPT2 calculations of $[\text{NpO}_2\text{Cl}_4]^{2-}$.

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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^I uranium(V) dioxo molecules, which contain the simplest open-shell ground state electronic configuration, $[\text{Rn}]5f^I$, 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.¹⁴⁻²⁰ 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.^{19,20} Subsequently, Denning and co-workers recorded polarized absorption spectra at 4.2 K,^{14,15} 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 600-22,000 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.^{16,17} 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 cooled to 75 K.¹⁶ 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** $\rightarrow$ **0** to record an excitation spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ between 13,200 and 21,275 cm^{-1} .¹⁸ Transitions **0** $\rightarrow$ **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.^{14,15}

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 (6,585 – 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 SO-RASPT2 (restricted-active-space perturbation theory with spin-orbit coupling) calculations reported in the literature.^{10,14-23}

Experimental

The synthesis and structural characterization of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$, and preparation of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ crystals are described elsewhere.¹⁶⁻¹⁸ The ratio of Np:U is $\sim 3\%$, 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 $\sim 5\text{ cm}^{-1}$. 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.²⁴ 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 $1.0\text{ }\mu\text{m}$. For excitation spectra, a slit width of 0.15 mm was used, and the resolution of emission was $\sim 5\text{ cm}^{-1}$. Photoluminescence was detected using a photomultiplier tube (PMT) (Hamamatsu R5509-72). The error in the reported peak positions from the excitation spectrum is $\pm 5\text{ cm}^{-1}$.

Results and Discussion

The $[\text{NpO}_2\text{Cl}_4]^{2-}$ anion is centrosymmetric with pseudo- D_{4h} symmetry.^{14,15,17} 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.^{6,14,15,17} The combination of electric-dipole forbidden pure electronic transitions and vibronic coupling to ungerade modes can result in stronger vibronic sidebands. The $[\text{NpO}_2\text{Cl}_4]^{2-}$ anion has eleven vibrational modes, including a symmetric stretch (ν_1), an asymmetric O=Np=O stretch (ν_2), the neptunyl bend (ν_3), and four asymmetric Np-Cl stretches and bends. In particular, the totally symmetric O=Np=O stretching mode (ν_1) 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.^{14,15} 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 a summary

for the experimentally derived energy, the ν_1 vibrational frequency for each electronic state compared with the results from the SO-RASPT2 calculations.^{10,14,15} Table 3 shows energies and vibrational frequencies of ν_1 and ν_2 for states **II-VI** which were derived from our excitation spectrum. The average energy of ν_1 for the LMCT states is $\sim 709 \text{ cm}^{-1}$, and the average energy of ν_1 for the 5f δ and ϕ states (**0** to **III**) is measurably higher $\sim 807 \text{ cm}^{-1}$.

The excitation spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ crystals cooled to 75 K is shown in Figure 1. The region between 7,460 and 24,000 cm^{-1} was collected by monitoring the intensity of **II** $\rightarrow$ **0** at 6,880 cm^{-1} while scanning the excitation laser. The features between 6,585-7,460 cm^{-1} were collected by placing a 1,500 nm (6,667 cm^{-1}) long pass filter in front of the monochromator with the diffraction grating in its zeroth-order position, excluding the **II** $\rightarrow$ **0** origin at 6,880 cm^{-1} but allowing light from vibronic emission transitions with wavelengths longer than 1,500 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 ν_1 mode for transitions to states **II** and **III**.^{14,15} In comparison with solution spectra of $\text{U}(\text{V})\text{O}_2^+$ compounds, the intra-5f transitions of the more oxidizing NpO_2^{2+} are predictably lower in energy as a result of the higher positive charge on $\text{Np}(\text{VI})$.^{12,13} A superscript following the symbol ν signifies the electronic state to which the vibronic peak is associated.

Figure 1. Laser-induced excitation spectrum between 6,585-24,000 cm^{-1} recorded while monitoring luminescence from the **II** $\rightarrow$ **0** transition (6,880 cm^{-1}) of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at 75 K.

The portion of the excitation spectrum between 6,585 and 10,000 cm^{-1} is shown in Figure 2. Features in this region involve **0** $\rightarrow$ **II** and **0** $\rightarrow$ **III** electronic transitions. The intense and narrow transition at 6,880 cm^{-1} is assigned as **0** $\rightarrow$ **II** origin, in agreement with Denning's reported value of 6,880.4 cm^{-1} . The assignment of this electronic transition is supported by the presence of vibronic hot bands at $\sim 6,769 \text{ cm}^{-1}$ and $\sim 6,837 \text{ cm}^{-1}$. These transitions are lower in energy than the origin by approximately the energies of the infrared-active ground state neptunium-chloride modes $\nu_{8,9}^0$, ν_9^0 (100-130 cm^{-1}) and the lattice modes (0-80 cm^{-1}), and we assign these modes as **0** + $\nu_{8,9}^0 \rightarrow$ **II** and **0** + **lattice modes** $\rightarrow$ **II**, respectively. The transitions 0-80 cm^{-1} and 100-130 cm^{-1} higher in energy than origin **II** and near mirror images of the hot bands are assigned to **0** $\rightarrow$ **II** + **lattice modes** (6,923 cm^{-1}) and **0** $\rightarrow$ **II** + $\nu_{8,9}^{\text{II}}$ (7,009 cm^{-1}). The peaks

240-285 cm^{-1} above $\mathbf{0} \rightarrow \mathbf{II}$ are assigned to vibronic structure built on the neptunium-chloride stretching mode, $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}^{\mathbf{II}}_6$ (7,126 cm^{-1}), and the neptunium-oxo bending mode, $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}^{\mathbf{II}}_3$ (7,157 cm^{-1}).

The intense and sharp transition at 7,801 cm^{-1} , 921 cm^{-1} higher in energy than $\mathbf{0} \rightarrow \mathbf{II}$, could be assigned to either $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}^{\mathbf{II}}_2$ or to $\mathbf{0} \rightarrow \mathbf{III}$. To unambiguously assign this peak, we compared our excitation spectrum to an absorption spectrum reported by Stone in his Ph.D. thesis (advisor Robert Denning), which is not published in the open literature.²⁵ In this investigation, a second absorption spectrum was recorded using ^{18}O enriched NpO_2^{2+} . Isotopic substitution allows vibronic structure belonging to neptunium-oxo vibrational modes to be identified because they are shifted to lower energy while the energies of pure electronic transitions and neptunium-chloride vibronic transitions are only slightly perturbed. Stone was able to assign the peak at 7,801 cm^{-1} as $\mathbf{II} + \mathbf{v}^{\mathbf{II}}_2$ because it was blue-shifted by $\sim 44 \text{ cm}^{-1}$ after ^{18}O substitution.

A weak feature at 7,706 cm^{-1} is assigned as $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}_1$. The energy difference from the $\mathbf{0} \rightarrow \mathbf{II}$ origin to this peak gives a value of 826 cm^{-1} for $\mathbf{v}^{\mathbf{II}}_1$. This value is measurably larger than $\mathbf{v}^0_1$ in the ground electronic state. The weak but sharp peak in our excitation spectrum at 8,613 cm^{-1} is assigned as $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}^{\mathbf{II}}_2 + \mathbf{v}^{\mathbf{II}}_1$. This outcome gives a frequency of 812 cm^{-1} for $\mathbf{v}^{\mathbf{II}}_1$ from the energy gap between $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}^{\mathbf{II}}_2$ and $\mathbf{0} \rightarrow \mathbf{II} + \mathbf{v}^{\mathbf{II}}_2 + \mathbf{v}^{\mathbf{II}}_1$, and indicates that the combination band has some significant anharmonicity. The combination $\mathbf{v}^0_1 + \mathbf{v}^0_2$ band in the ground electronic state from Denning's absorption spectra shows a similar anharmonicity when compared to the sum of the energies of $\mathbf{v}^0_1$ and $\mathbf{v}^0_2$ measured directly. Neither the 7,706 cm^{-1} nor the 8,613 cm^{-1} peak appears in either the published spectra of Denning et al. or Stone's thesis. This result is not entirely surprising, however, because the peaks are quite weak and may well have been obscured by baseline noise in their absorption spectra.

The set of strong, partially resolved features at 7,989, 8,020, 8,118, and 8,143 cm^{-1} , appear both here and in Stone's spectra. These peaks shifted very little with Stone's ^{18}O substitution, and consequently they were assigned as vibronic transitions involving excitation of chlorine modes with the upper states being $\mathbf{III} + \mathbf{v}^{\mathbf{III}}_8$, $\mathbf{III} + \mathbf{v}^{\mathbf{III}}_9$, $\mathbf{III} + \mathbf{v}^{\mathbf{III}}_6$, and $\mathbf{III} + \mathbf{v}^{\mathbf{III}}_3$, respectively. No feature assignable as the $\mathbf{0} \rightarrow \mathbf{III}$ transition can be identified in our excitation spectrum (see Figure 2), nor in the absorption spectra recorded by Stone or Denning. Origin $\mathbf{III}$ energy can be estimated by assuming that the $\mathbf{v}^{\mathbf{III}}_8$, $\mathbf{v}^{\mathbf{III}}_9$, $\mathbf{v}^{\mathbf{III}}_6$, and $\mathbf{v}^{\mathbf{III}}_3$ vibronic modes have energies similar to those of the ground vibrational state. Making this assumption places origin $\mathbf{III}$ at $\sim 7,875 \text{ cm}^{-1} \pm 20 \text{ cm}^{-1}$, in agreement with Denning's estimate of 7,890 cm^{-1} .

The doublets at 8,797 and 8,830 cm^{-1} , and at 9,593 and 9,635 cm^{-1} are $\sim 800 \text{ cm}^{-1}$ apart, suggestive of progressions in $\mathbf{v}_1$. The first pair of peaks was observed but not assigned by Denning, and the second set

of higher energy peaks is outside the energy of their published spectrum. In Denning's spectra, the lower energy peaks show polarization behavior identical to other vibronic features belong to state **III** confirming that these peaks belong to state **III**. The lower energy peak in the first pair (8,797 cm⁻¹) is ~ 922 cm⁻¹ above the inferred position of the **0** → **III** origin, so it could be assigned as **0** → **III** + $\nu_{\text{III}}^{\text{III}}_2$. It is also 808 cm⁻¹ above the peak assigned as **0** → **III** + $\nu_{\text{III}}^{\text{III}}_8$ (7,989 cm⁻¹), making **0** → **III** + $\nu_{\text{III}}^{\text{III}}_8$ + $\nu_{\text{III}}^{\text{III}}_1$ a plausible assignment as well. The peak at 9,593 cm⁻¹ is 796 cm⁻¹ higher in energy, and is assigned as **0** → **III** + $\nu_{\text{III}}^{\text{III}}_8$ + $2\nu_{\text{III}}^{\text{III}}_1$ or **0** → **III** + $\nu_{\text{III}}^{\text{III}}_2$ + $\nu_{\text{III}}^{\text{III}}_1$. The feature at 8,830 cm⁻¹ is 810 cm⁻¹ above the **III** + $\nu_{\text{III}}^{\text{III}}_9$ peak and is assigned as **III** + $\nu_{\text{III}}^{\text{III}}_9$ + $\nu_{\text{III}}^{\text{III}}_1$, and the feature at 9,635 cm⁻¹ is an additional 805 cm⁻¹ higher in energy and is assigned as **III** + $\nu_{\text{III}}^{\text{III}}_9$ + $2\nu_{\text{III}}^{\text{III}}_1$. Using these assignments, the average energy for the first two quanta of the neptunium-oxo symmetric stretch in state **III** ($\nu_{\text{III}}^{\text{III}}_1$), is 805 cm⁻¹, close to the observed ν_1^0 frequency in the ground state.

Figure 2. Laser-induced excitation spectrum between 6,585-10,000 cm⁻¹ recorded while monitoring luminescence from the **II** → **0** transition of Cs₂U(Np)O₂Cl₄ at 75 K.

The region of the excitation spectrum between 12,800 and 15,000 cm⁻¹ is shown in Figure 3, and peak assignments and energies of each transition identified in our excitation spectrum are provided in Table 5. The narrow feature observed at 13,248 cm⁻¹ is assigned to the origin of **0** → **IV**. This value is somewhat lower in energy than reported by Denning (13,264.9 cm⁻¹) and Stone (13,259.0 cm⁻¹). Our assignment of **0** → **IV** is supported by the presence of vibronic hot bands at ~ 13,133 cm⁻¹ and 13,210 cm⁻¹, which are 115 cm⁻¹ and 38 cm⁻¹ lower in energy, and we assign these modes as **0** + $\nu_{\text{IV}}^0_{8/9}$ → **IV** and **0** + **lattice modes** → **IV**, respectively. The intense peaks at 13,282 and 13,352 cm⁻¹ are assigned to **0** → **IV** + **lattice modes** and **0** → **IV** + $\nu_{\text{IV}}^{\text{IV}}_{8/9}$. The peaks at 13,486 and 13,497 cm⁻¹ are ~ 240-285 cm⁻¹ higher in energy than **0** → **IV** and are assigned to **0** → **IV** + $\nu_{\text{IV}}^{\text{IV}}_6$, and **0** → **IV** + $\nu_{\text{IV}}^{\text{IV}}_3$, respectively. The transitions measured at 13,968 and 14,008 cm⁻¹ are assigned as **0** → **IV** + $\nu_{\text{IV}}^{\text{IV}}_1$ and **0** → **IV** + $\nu_{\text{IV}}^{\text{IV}}_2$, giving frequencies for $\nu_{\text{IV}}^{\text{IV}}_1$ and $\nu_{\text{IV}}^{\text{IV}}_2$ of 720 cm⁻¹ and 760 cm⁻¹, respectively. These agree with those observed in Denning's spectra. Denning reported the frequency of **IV** + $\nu_{\text{IV}}^{\text{IV}}_2$ + $\nu_{\text{IV}}^{\text{IV}}_1$ at 710.9 cm⁻¹ above the origin **IV** + $\nu_{\text{IV}}^{\text{IV}}_2$, attributing the lower $\nu_{\text{IV}}^{\text{IV}}_1$ frequency in the combination band to anharmonic coupling.¹⁵ We derive a corresponding value of 718 cm⁻¹ from the position of the assigned **0** → **IV** + $\nu_{\text{IV}}^{\text{IV}}_2$ + $\nu_{\text{IV}}^{\text{IV}}_1$ peak at 14,726 cm⁻¹. Other combination bands involving the chlorine modes, such as the peak at 14,074 cm⁻¹ assigned as **IV** + $\nu_{\text{IV}}^{\text{IV}}_{8/9}$ + $\nu_{\text{IV}}^{\text{IV}}_1$, yield values for $\nu_{\text{IV}}^{\text{IV}}_1$ that are indistinguishable from the progression built on the electronic origin. The energies of $\nu_{\text{IV}}^{\text{IV}}_1$ and $\nu_{\text{IV}}^{\text{IV}}_2$ are significantly lower than the energies of these

modes in the ground state, consistent with the charge transfer nature of $\mathbf{0} \rightarrow \mathbf{IV}$ and consequent weakening of the neptunium-oxo bonds in the excited state.

Figure 3. Laser-induced excitation spectrum between 12,800-15,000 cm^{-1} recorded while monitoring luminescence from the $\mathbf{II} \rightarrow \mathbf{0}$ transition of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at 75 K. The absence of spectral data between $\sim 14,100$ - $14,400 \text{ cm}^{-1}$ is due to very low laser power at these energies.

The third region of the excitation spectrum between 15,000-18,000 cm^{-1} is shown in Figure 4. This region contains vibronic transitions from the ground state to excited states $\mathbf{V}$ and $\mathbf{VI}$. We focus on features assigned to $\mathbf{0} \rightarrow \mathbf{V}$ and its vibronic sidebands, as excitation spectra of $\mathbf{VI-X}$ have been reported elsewhere.¹⁸ The energy of $\mathbf{0} \rightarrow \mathbf{V}$ measured at $\sim 15,402 \text{ cm}^{-1}$ agrees with the energy reported by Denning at $15,406.4 \text{ cm}^{-1}$. The assignment of this electronic origin is supported by the presence of vibronic hot bands at $15,355$ and $15,284 \text{ cm}^{-1}$ which are lower in energy than the origin by the energies of lattice modes (0 - 80 cm^{-1}), and neptunium-chloride modes $\mathbf{v}_8^0$ and $\mathbf{v}_9^0$ (100 - 130 cm^{-1}). Therefore, we assign these transitions as $\mathbf{0} + \text{lattice modes} \rightarrow \mathbf{V}$ and $\mathbf{0} + \mathbf{v}_{8,9}^0 \rightarrow \mathbf{V}$. The reader is referred to the labeling on Figure 4 and the listing in Table 6 for the other peak assignments. The weak peak at $16,116 \text{ cm}^{-1}$ is assigned to $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_1^V$, and the next prominent feature $\sim 40 \text{ cm}^{-1}$ above this transition ($16,158 \text{ cm}^{-1}$) is assigned as the $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_2^V$. The differences in energies of these vibronic bands from the energy of $\mathbf{0} \rightarrow \mathbf{V}$ provides frequencies for $\mathbf{v}_1^V = 714 \text{ cm}^{-1}$ and $\mathbf{v}_2^V = 756 \text{ cm}^{-1}$. The lowering of these frequencies from their values in the ground state is consistent with the LMCT nature of $\mathbf{0} \rightarrow \mathbf{V}$, as previously noted by Denning.¹⁵ The next sharp features at $16,237$, $16,372$, and $16,540 \text{ cm}^{-1}$ are assigned as $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_{8,9}^V + \mathbf{v}_1^V$, $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_{3/6}^V + \mathbf{v}_1^V$, and $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_3^V + \mathbf{v}_{11}^V + \mathbf{v}_1^V$ by comparison with the absorption spectrum reported by Denning.

The remaining $\mathbf{0} \rightarrow \mathbf{V}$ structure in Figure 4 from $16,800$ - $18,000 \text{ cm}^{-1}$ is more difficult to assign because vibronic transitions built on $\mathbf{0} \rightarrow \mathbf{VI}$ and $\mathbf{0} \rightarrow \mathbf{VII}$ overlap the $\mathbf{0} \rightarrow \mathbf{V}$ transitions. However, several members of progressions in $\mathbf{v}_1^V$ ($\sim 715 \text{ cm}^{-1}$) are evident. The first of these, at $16,872 \text{ cm}^{-1}$, is assigned to $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_2^V + \mathbf{v}_1^V$. Others are identified as $\mathbf{V} + \mathbf{v}_{8,9}^V + 2\mathbf{v}_1^V$ at $16,953 \text{ cm}^{-1}$ and $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_{3/6}^V + 2\mathbf{v}_1^V$ at $17,085 \text{ cm}^{-1}$. The peak at $17,246 \text{ cm}^{-1}$ was assigned by Denning to the overlapping transitions $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_3^V + \mathbf{v}_{11}^V + 2\mathbf{v}_1^V$ and $\mathbf{0} \rightarrow \mathbf{VIII}$. The peak at $17,944 \text{ cm}^{-1}$ is assigned as $\mathbf{0} \rightarrow \mathbf{V} + \mathbf{v}_3^V + \mathbf{v}_{11}^V + 3\mathbf{v}_1^V$.

Three transitions belonging $\mathbf{0} \rightarrow \mathbf{VI}$ have also been assigned to a progression in $\mathbf{v}_1^{\text{VI}}$ built upon $\mathbf{0} \rightarrow \mathbf{VI} + \mathbf{v}_{3/6}$. This progression exhibits an average value of 701 cm^{-1} for $\mathbf{v}_1^{\text{VI}}$. The region of the spectrum

above 17,600 cm⁻¹ has been discussed thoroughly in Denning’s work as well as our prior report of excitation from Cs₂U(Np)O₂Cl₄, and will not be reproduced here.^{14,15,18}

Figure 4. Laser-induced excitation spectrum between 15,000-18,000 cm⁻¹ recorded while monitoring luminescence from the **II** → **0** transition of Cs₂U(Np) O₂Cl₄ at 75 K.

Of particular interest in these spectra is the relation between vibronic peak intensities and changes in the neptunium-oxo bond distance. It is well documented that there are distinct differences expected following intra-5f versus LMCT transitions. It has been shown that the change in neptunium-oxo bond lengths can be estimated using the relative intensities of peaks in vibronic progressions in ν_1 using Equation 1:¹⁰

$$\Delta R_{NpO} \approx [2Sw^{-1}/\omega_f m_O]^{1/2} \quad (1)$$

where ΔR_{NpO} is the absolute change in the length of the neptunium-oxo bond distance, S is the Huang-Rhys factor, ω_f is frequency of ν_1 in the excited electronic state, and m_O is the mass of the oxygen atom. The quantity w is the topological factor which takes into account the effective mass in a given molecular symmetry; w is equal to 2 for linear D_{∞h} molecules such as the [O-Np-O]²⁺ moiety. The value of the Huang-Rhys factor value is estimated from the measured relative intensities of the first three members of the ν_1 vibronic progression, which should exhibit the ratios 1: S : $S^2/2$. Equation 1 assumes a harmonic approximation without Jahn—Teller distortion or Dushinsky rotations, and does not take into account anharmonicity, change in the vibrational frequency, or vibrational coupling to other modes. Su estimated that Equation 1 should accurately predict changes in bond length to within 10%.

We calculated the change in the neptunium-oxo bond lengths, ΔR_{NpO} , upon excitation into electronic states **II** - **VI** using the integrated peak intensity either from our excitation spectra or the absorption spectra of Denning to get values for S to use in Equation 1. The relative intensity of vibronic bands, Huang-Rhys factor and ΔR_{NpO} are tabulated in Table 7 along with values for ΔR_{NpO} calculated using SO-RASPT2 RASPT2 by Su.¹⁰ Uncertainties in our ΔR_{NpO} values were calculated by assuming that the Huang-Rhys factor is accurate to within 20%. Note that for excitations into state **IV**, the Huang-Rhys factors were calculated using the intensities of vibronic features in the absorption spectra recorded by Denning rather than from our excitation spectrum because the laser power dropped off rapidly to unreliably low levels when approaching the gap seen in Figure 3 from either direction. While peaks could be observed and assigned, their relative intensities do not accurately reflect the true relative transition probabilities.^{15,25} The average change in neptunium-oxo bond length induced by LMCT transitions (**IV**-**VI**) is $\Delta R_{NpO} \approx 5.4 \pm 1$ pm, which is in reasonable agreement with the results from the RASPT2 calcula-

tions ($|\Delta R| = 6.1$ pm).¹⁰ Using absorption spectra of $\text{Cs}_2\text{UO}_2\text{Cl}_4$, Denning calculated the change in the uranium-oxo bond lengths to be $\Delta R_{\text{UO}} \approx 6.5$ pm for several LMCT transitions in uranyl using a different method than that described using Equation 1.^{6,19,21,25,27} The average ν_1 energy associated with states **IV**, **V**, and **VI** is ~ 710 cm^{-1} , considerably lower than the ground state vibrational energy of ν_1^0 (802 cm^{-1}) and a weaker neptunium-oxo bond.

We used the same method to estimate the changes in the neptunium-oxo bond lengths from the intra-5f transitions. The results agree reasonably well with calculations using RASPT2 for $\mathbf{0} \rightarrow \mathbf{II}$ but not for $\mathbf{0} \rightarrow \mathbf{III}$. The average value of ν_1 for the 5f δ and ϕ states **II** and **III**, ~ 806 cm^{-1} , is closer in energy to the energy of ν_1^0 in the ground state, and thus it would be predicted that the neptunium-oxo bond length does not change from that of the ground state. The change in neptunium-oxo bond length, $|\Delta R_{\text{NpO}}|$ calculated by RASPT2, predicted that the excitations into states **II** and **III** to be 0.8 and 0.3 pm respectively, which is consistent with this prediction.¹⁰ The changes in the neptunyl bond length derived from the relative intensities of vibronic excitations into the 5f states (**II** and **III**), shown in Table 7, were calculated as well. The ΔR_{NpO} calculated from the progressions built on $\mathbf{0} \rightarrow \mathbf{II}$ and $\mathbf{0} \rightarrow \mathbf{II} + \nu_1^{\mathbf{II}}_2$ are 0.8 and 1.2 pm, in reasonable agreement with the RASPT2 results. For $\mathbf{0} \rightarrow \mathbf{III}$, however, the intensity ratios are consistent with a significantly larger bond length change, about 2.3 pm. While these values for ΔR_{NpO} are somewhat smaller than those derived from exciting states **IV**, **V** and **VI**, they are much larger than the 0.3 pm predicted by the RASPT2 calculations.¹⁰ One would expect that a ΔR_{NpO} as large as ~ 2.3 pm would be accompanied by significant change in ν_1 frequency, whereas essentially no change is observed. The ΔR_{NpO} values predicted by the RASPT2 calculations (0.3-0.8 pm) would be consistent with values for S that are smaller by a factor of 10 than those derived from the excitation spectrum; this result is well outside the estimated 20% uncertainty for the Huang-Rhys parameters derived from the data. Currently, we do not have a definitive explanation for the large ΔR_{NpO} value derived from progression intensities for $\mathbf{0} \rightarrow \mathbf{III}$.

Alternative assignments are plausible for ν_1 progressions built on $\mathbf{0} \rightarrow \mathbf{III}$ but these do not improve the agreement with the bond from the RASPT2 calculations. We might consider that the excitation features at $\sim 8,700$ and $9,700$ cm^{-1} , assigned to members of ν_1 progressions, could instead be due to the presence of an impurity, but this scenario is not likely because the impurity would have to fluoresce at an energy that is within ~ 10 cm^{-1} of the **II** $\rightarrow$ **0** transition (6880 cm^{-1}) that was monitored to collect the excitation spectrum. Another possibility is that there is significant interaction between vibronic states that are nearly degenerate, which would invalidate the approximations needed to use Eq. 1. This may warrant further investigation.

The lack of an observed $0 \rightarrow \text{III}$ origin is in agreement with ligand field calculations by Denning which predict no electric or magnetic dipole oscillator strength for the pure electronic transition between the ground electronic state 0 and state III , which is in contrast to the $0 \rightarrow \text{II}$ for which significant magnetic dipole oscillator strength is predicted.¹⁴ It is also possible that the origin band for $0 \rightarrow \text{III}$ and $0 \rightarrow \text{II} + \nu_1^{\text{II}}$ are nearly degenerate. As mentioned above, Stone does not observe the $0 \rightarrow \text{III}$ origin upon removing the potential degeneracy by substitution with ^{18}O .²⁵ However we cannot eliminate the possibility that the $0 \rightarrow \text{III}$ is buried in the low-intensity structure near the $0 \rightarrow \text{II} + \nu_1^{\text{II}}$. Both the $0 \rightarrow \text{II}$ and $0 \rightarrow \text{III}$ transitions are of the 5f-5f type and might be expected to have similar band structure.

Conclusions

We report excitation spectra of the intra-5f and LMCT transitions of the $[\text{NpO}_2\text{Cl}_4]^{2-}$ anion in $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ between 6,600 and 22,000 cm^{-1} . The excitations are tracked by detecting photoluminescence from the $\text{II} \rightarrow 0$ transition, providing high sensitivity and specificity. Nearly all of the absorption features from Denning's earlier single crystal absorption study are observed in our excitation spectrum, indicating that decay pathways from all higher-lying excited states to the ground state include the $\text{II} \rightarrow 0$ transition. The observed vibronic structure includes progressions in the ν_1 symmetric stretching mode of the 5f states II and III which were not previously reported. Analysis of all ν_1 progression intensities in these transitions as well as in the LMCT transitions produces estimates of the neptunium-oxo bond length changes that are consistent with theoretical results and prior identification of the two types of excited states.

TABLES

Table 1. Vibrational modes, symmetries in D_{4h} , and ground state vibrational frequencies of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$.¹⁴

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

Table 2. Excited state, main term, and energy for the ground state and the first 10 electronic states of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ as reported in references.^{10,14,15}

		Calculated values from reference 10			experimental values from references 14,15	
state	type	main term	energy (cm^{-1})	ν_1 (cm^{-1})	energy (cm^{-1})	ν_1 (cm^{-1})
0	5f	$^2\Phi_u$	0	786	0	802
I	5f	$^2\Delta_u$	1,055	812	~1,000	—
II	5f	$^2\Delta_u$	5,767	809	6,880.4 / 6880*	826*
III	5f	$^2\Phi_u$	6,658	800	~7,990 / 7875*	808*
IV	LMCT	$^4\text{H}_u$	11,127	664	13,264.9 / 13,248*	722 / 720*
V	LMCT	$^4\Sigma_u^-$	14,375	665	15,406.4 / 15,402*	715 / 714
VI	LMCT	$^4\text{H}_u$	14,122	663	~15,683	711
VII	LMCT	$^4\Sigma_u^-$	15,330	662	16,799.8	713
VIII	5f	—	—	—	17,241.4	—
IX	LMCT	$^4\Pi_u$	18,774	663	19,375.2	686
X	5f	—	—	—	20,080.8	—

*Values from this study

Table 3. Transition energy, type, frequencies for ν_1 and ν_2 .

transition	type	energy (cm^{-1})	ν_1 (cm^{-1})	ν_2 (cm^{-1})
II	5f	6,880	826	921
III	5f	7,875	805 (average)	922
IV	LMCT	13,248	720	760
V	LMCT	15,402	714	756
VI	LMCT		702	—

Table 4. Assignments of vibronic structure and transition energies for **II** and **III**, as well as energies relative to the electronic origin.

transition	energy (cm ⁻¹)	energy from origin (cm ⁻¹)
0 + $\nu_{8/9}^0 \rightarrow \text{II}$	6,769	-111
0 + lattice modes $\rightarrow \text{II}$	6,837	-43
0 $\rightarrow \text{II}$ (origin)	6,880	0
0 $\rightarrow \text{II}$ + lattice modes	6,923	43
0 $\rightarrow \text{II}$ + $\nu_{8/9}^{\text{II}}$	7,009	129
0 $\rightarrow \text{II}$ + ν_6^{II}	7,126	246
0 $\rightarrow \text{II}$ + ν_3^{II}	7,157	277
0 $\rightarrow \text{II}$ + ν_1^{II}	7,706	826
0 $\rightarrow \text{II}$ + ν_2^{II}	7,801	921
0 $\rightarrow \text{II}$ + ν_2^{II} + ν_1^{II}	8,613	1733
0 $\rightarrow \text{III}$ (origin)*	7,875	0
0 $\rightarrow \text{III}$ + ν_8^{III}	7,989	114
0 $\rightarrow \text{III}$ + ν_9^{III}	8,020	145
0 $\rightarrow \text{III}$ + ν_6^{III}	8,118	243
0 $\rightarrow \text{III}$ + ν_3^{III}	8,143	268
0 $\rightarrow \text{III}$ + ν_8^{III} + ν_1^{III} or 0 $\rightarrow \text{III}$ + ν_2^{III}	8,797	922
0 $\rightarrow \text{III}$ + ν_9^{III} + ν_1^{III}	8,830	955
0 $\rightarrow \text{III}$ + ν_8^{III} + $2\nu_1^{\text{III}}$ or 0 $\rightarrow \text{III}$ + ν_2^{III} + ν_1^{III}	9,593	1718
0 $\rightarrow \text{III}$ + ν_9^{III} + $2\nu_1^{\text{III}}$	9,635	1760

*Energy estimated, see text.

Table 5. Assignments of vibronic structure and transition energies for **IV**, as well as energies relative to the electronic origin.

transition	energy (cm ⁻¹)	energy from origin (cm ⁻¹)
0 + v_{8/9}⁰ → IV	13,133	-115
0 + lattice modes → IV	13,210	-38
0 → IV (origin)	13,248	0
0 → IV + lattice modes	13,282	34
0 → IV + v_{8/9}^{IV}	13,352	104
0 → IV + v₆^{IV}	13,486	238
0 → IV + v₃^{IV}	13,497	249
0 → IV + v₁^{IV}	13,968	720
0 → IV + v₂^{IV}	14,008	760
0 → IV + v_{8/9}^{IV} + v₁^{IV}	14,074	826
0 → IV + v₂^{IV} + v₁^{IV}	14,726	1478

Table 6. Assignments of vibronic structure and transition energies for **V** and **VI**, as well as energies relative to the electronic origin.

transition	energy (cm ⁻¹)	energy from origin (cm ⁻¹)
$0 + v_{8/9}^0 \rightarrow \mathbf{V}$	15,284	-118
$0 + \text{lattice modes} \rightarrow \mathbf{V}$	15,355	-47
$0 \rightarrow \mathbf{V}$ (origin)	15,402	0
$0 \rightarrow \mathbf{V} + \text{lattice modes}$	15,449	47
$0 \rightarrow \mathbf{V} + v_{8/9}^{\mathbf{V}}$	15,525	123
$0 \rightarrow \mathbf{V} + v_6^{\mathbf{V}}$	15,613	211
$0 \rightarrow \mathbf{V} + v_3^{\mathbf{V}}$	15,654	252
$0 \rightarrow \mathbf{V} + v_3^{\mathbf{V}} + v_{11}^{\mathbf{V}}$	15,822	420
$0 \rightarrow \mathbf{V} + v_1^{\mathbf{V}}$	16,116	714
$0 \rightarrow \mathbf{V} + v_2^{\mathbf{V}}$	16,158	756
$0 \rightarrow \mathbf{V} + v_{8/9}^{\mathbf{V}} + v_1^{\mathbf{V}}$	16,237	835
$0 \rightarrow \mathbf{V} + v_{3/6}^{\mathbf{V}} + v_1^{\mathbf{V}}$	16,372	970
$0 \rightarrow \mathbf{V} + v_3^{\mathbf{V}} + v_{11}^{\mathbf{V}} + v_1^{\mathbf{V}}$	16,540	1,138
$0 \rightarrow \mathbf{V} + v_2^{\mathbf{V}} + v_1^{\mathbf{V}}$	16,872	1,470
$0 \rightarrow \mathbf{V} + v_{8/9}^{\mathbf{V}} + 2v_1^{\mathbf{V}}$	16,953	1,551
$0 \rightarrow \mathbf{V} + v_{3/6}^{\mathbf{V}} + 2v_1^{\mathbf{V}}$	17,085	1,683
$0 \rightarrow \mathbf{V} + v_3^{\mathbf{V}} + v_{11}^{\mathbf{V}} + 2v_1^{\mathbf{V}}$ or $0 \rightarrow \mathbf{VIII}$ (origin)	17,246	1,844
$0 \rightarrow \mathbf{V} + v_3^{\mathbf{V}} + v_{11}^{\mathbf{V}} + 3v_1^{\mathbf{V}}$	17,944	2,542
$0 \rightarrow \mathbf{VI} + v_{3/6}^{\mathbf{V}}$	15,917	—
$0 \rightarrow \mathbf{VI} + v_{3/6}^{\mathbf{V}} + v_1^{\mathbf{V}}$	16,623	—
$0 \rightarrow \mathbf{VI} + v_{3/6}^{\mathbf{V}} + 2v_1^{\mathbf{V}}$	17,321	—

Table 7. Vibronic progressions based on ν_1 observed in the excitation spectra, the relative intensity of these bands to $x=0$, the Huang-Rhys parameter (S), and the absolute change in the neptunium-oxo bond distance (ΔR) derived from Equation 1. Units on ΔR are pm. Uncertainties are obtained assuming that the Huang-Rhys parameter is correct to within 20% of its value. The subscripts in the notation S_{0X} and ΔR_{0X} refer to the vibrational quantum numbers from which the value is derived. The value for ΔR_{ave} is simply the average value of the derived bond length change.

transition	x=0	x=1	x=2	S_{01}	S_{02}	ΔR_{01}	ΔR_{02}	ΔR_{ave}	$ \Delta R ^{10}$
$0 \rightarrow II + x\nu_1^{II}$	1.00	0.03	—	0.03	---	0.9	—	0.9(0.3)	-0.8
$0 \rightarrow II + \nu_2^{II} + x\nu_1^{II}$	1.00	0.06	—	0.06	—	1.2	—	1.2(0.3)	-0.8
$*0 \rightarrow III + \nu_8^{III} + x\nu_1^{III}$	1.00	0.17	0.03	0.17	0.2	2.1	2.5	2.3(0.6)	0.3
$*0 \rightarrow III + \nu_2^{III} + x\nu_1^{III}$	1.00	0.18	—	0.18	—	2.2	—	2.2(0.6)	0.3
$0 \rightarrow III + \nu_9^{III} + x\nu_1^{III}$	1.00	0.16	0.03	0.16	0.2	2.0	2.5	2.3(0.5)	0.3
$0 \rightarrow IV + \nu_2^{IV} + x\nu_1^{IV}$	1.00	0.83	0.40	0.83	0.9	4.9	5.1	5.0(1.0)	6.4
$0 \rightarrow IV + \nu_{8/9}^{IV} + x\nu_1^{IV}$	1.00	0.86	0.41	0.86	0.9	5.0	5.2	5.1(1.0)	6.4
$0 \rightarrow V + \nu_{8/9}^V + x\nu_1^V$	1.00	1.03	0.85	1.03	1.3	5.5	6.2	5.9(1.0)	6.3
$0 \rightarrow V + \nu_{3/6}^V + x\nu_1^V$	1.00	1.12	0.60	1.12	1.1	5.8	5.7	5.8(1.0)	6.3
$0 \rightarrow V + \nu_3^V + \nu_{11}^V + x\nu_1^V$	1.00	0.95	0.74	0.95	1.2	5.3	6.0	5.7(1.0)	6.3
$0 \rightarrow VI + \nu_{3/6}^{VI} + x\nu_1^{VI}$	1.00	0.82	0.26	0.82	0.7	4.9	4.6	4.8(1.0)	5.4

*For alternative assignments, see text.

NOTE: ΔR for $0 \rightarrow IV + \nu_2^{IV} + x\nu_1^{IV}$ and $0 \rightarrow IV + \nu_{8/9}^{IV} + x\nu_1^{IV}$ were determined using intensities from Denning's absorption spectra.¹⁵

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Notes

The authors declare no competing financial interests.

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