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Author(s):

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A Spectroscopic Investigation of the Electronic Structure of Neptunyl Ions

Marianne P. Wilkerson¹, James E. Barefield¹, John M. Berg², Harry J. DEWEY¹⁺, and Todd A. Hopkins²

¹Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

²Nuclear Materials and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Emission spectra of $\text{NpO}_2\text{Cl}_4^{2-}$ doped in a Cs_2ZrCl_6 matrix have been measured between 6000 and 7200 cm^{-1} . An $f\text{-}f$ transition has been assigned, and vibronic structure on this origin is reported. These electronic and vibrational energies are compared with previous studies including the theoretical work of Pitzer and co-workers, and the spectroscopic work of Denning and co-workers.

KEYWORDS: *electronic structure, emission, fluorescence spectroscopy, neptunyl, vibrational modes*

I. Introduction

The inherently stable bonding of actinyl ions (MO_2^{2+} , $\text{M}=\text{U}$, Np , Pu) is unique among metal dioxo species¹. This robust character is most influential on the molecular structure and chemical behavior of actinyl compounds², and considerable effort has been directed toward the identification of valence orbitals and electronic transitions involved in this bonding. Such information is also essential for solution speciation analysis³, and comparison of spectra obtained from molecules containing more complex ligand environments⁴.

Optical spectroscopy is a key technique that has been employed to interrogate the electronic structure of the uranyl ion, a closed shell system in which electronic transitions are ligand-to-metal charge transfer (an electron originally in an orbital of substantial oxygen character is transferred to a metal orbital)⁵. Spectroscopic investigations of other actinyl systems that contain additional electrons in the valence f shell are not similarly complete. In these systems, there should be additional transitions corresponding to transfer of an electron from an f orbital to another f orbital.

The electronic structure of neptunyl has been studied by other research groups, as well. For example, Pitzer and co-workers calculated eleven excited state energies for the neptunyl ion doped in $\text{Cs}_2\text{UO}_2\text{Cl}_4$ using a layered-cluster computational method⁶. These energies were compared with the polarized, single-crystal absorption spectra of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at 4.2 K reported by Denning and co-workers⁷. In this latter study, ten excited states were identified.

One study of neptunyl luminescence, which included emission spectra of $\text{NpO}_2\text{Cl}_4^{2-}$ doped in $\text{Cs}_2\text{UO}_2\text{Cl}_4$, has been reported⁸. Although some of the excited state energies of neptunyl were determined in this study, the identification of others is complicated by overlap of the $f\text{-}f$ excited state bands with vibrational structure on the ground state origin.

Experimentally, measurements of $f\text{-}f$ transitions are difficult to obtain because the excited states lie in the near-infrared region where previous detector technology has been limited.

With technical improvements in near infrared detectors, we have begun studies on actinyl luminescence. The principal goal of this study is to identify the $f\text{-}f$ excited state bands of f^1 neptunyl ions using state-of-the-art high resolution emission spectroscopy in order to have a more complete understanding of the electronic structure of f orbital occupied actinyl systems. Cesium hexachlorozirconate (Cs_2ZrCl_6) has been chosen as the matrix material for neptunyl because it lacks any high frequency vibrational modes that could serve as acceptors for radiationless deactivation, and it has sites of appropriate size for accommodation of actinyl tetrachloride ions⁹. In addition, highly resolved emission at 77K of a comparable system, $\text{Cs}_2\text{ZrCl}_6:\text{UO}_2\text{Cl}_4^{2-}$, has been reported¹⁰. In this paper, we present our initial studies on the emission of $\text{NpO}_2\text{Cl}_4^{2-}$ doped into a Cs_2ZrCl_6 matrix at liquid nitrogen temperature.

II. Experimental

Materials. $\text{Cs}_2\text{NpO}_2\text{Cl}_4$. A stock solution of 0.4 M NpO_2^{2+} (2 mL, 0.8 mmol) was added to a solution of CsCl (0.28 g, 1.6 mmol) in 6M HCl (~ 3 mL). The solution was diluted with distilled water (~ 3 mL) and stirred for ~ 10 minutes. Large dark yellow blocks and needles precipitated from the solution (0.51 g, 0.76 mmol, 94%) over several weeks.

Cs_2ZrCl_6 . CsCl (2.89 g, 17.2 mmol) was added to a boiling solution of ZrCl_4 (2.00 g, 8.58 mmol) in concentrated HCl (~ 40 mL). The mixture was stirred under reflux for ~ 10 minutes and then filtered through a medium glass frit under a flow of nitrogen. The material was dried under vacuum. The material was then triply sublimed under vacuum at 850°C (2.4 g, 4.3 mmol, 50%).

⁺ Corresponding author, Tel. 505-667-4686, Fax 505-665-4631
E-mail: hd@lanl.gov

Crystallographic Measurement. Crystal data for $\text{Cs}_2\text{NpO}_2\text{Cl}_4$: $M_r = 676.6$, monoclinic space group $C2/m$, $a = 11.828(4)$ Å, $b = 7.659(2)$ Å, $c = 5.7679(17)$ Å, $\beta = 99.386(7)^\circ$, $V = 515.6(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 4.359$ g cm⁻³, $F(000) = 574$, $\lambda = 0.71073$ Å, $T = -70^\circ$ C, $\mu(\text{Mo K}\alpha) = 18.014$ mm⁻¹. Refinement of 390 reflections gave $R1 = 0.096$.

Emission Measurements. Samples were contained in sealed quartz capillary tubes that were placed inside of quartz 5 mm NMR tubes. The excitation source was either an argon-ion (Spectra Physics 2045) or a Nd:YAG (Continuum Powerlite 8000) laser pumping a tunable optical parametric oscillator (Continuum Mirage 500) operating at a 10 Hz repetition rate. Pulse energies for experiments using the OPO were typically 4-9 mJ over the 400-600 nm excitation wavelength range. The luminescence was collected at a 90° angle to the excitation, and then dispersed using a quarter-meter spectrograph (Acton Research Corporation SpectraPro-300i). The emission intensity was measured using a 512 element InGaAs photodiode array (Princeton Instruments). Luminescence data were obtained by suspending the sample tubes in a liquid nitrogen immersion Dewar fitted with collection optics. The emission data have not been corrected for monochromator or detector response.

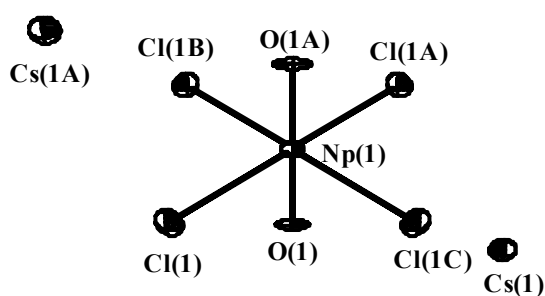


Figure 1 Thermal ellipsoid drawing of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ (50% probability ellipsoids).

III. Results and Discussion

Dilution of $\text{NpO}_2\text{Cl}_4^{2-}$ into host crystals affords the opportunity to study $f \rightarrow f$ transitions in the absence of self-quenching. For reasons stated in the Introduction, Cs_2ZrCl_6 is a favorable matrix material for our studies. The crystal structure of Cs_2ZrCl_6 is cubic, space group $Fm\bar{3}m$, and there are four ZrCl_6^{2-} ions per unit cell⁽¹¹⁾. Conflicting information has appeared in the literature regarding the synthesis of this compound. Several research groups have reported that the material can be prepared from dissolution of ZrCl_4 and two equivalents of CsCl in concentrated HCl solution^(10b,12). Others suggest that the hygroscopic nature of Cs_2ZrCl_6 precludes the synthesis of pure material in the presence of water^(9,10a). Our analysis of material isolated from concentrated HCl solution at room temperature confirms that there is a minor amount of Cs_2ZrCl_6 in the bulk material, as inferred from a comparison of the powder X-ray diffraction pattern with the calculated 2θ from the single-crystal structure determination. It was not possible to identify other

constituents from these data. Other reports suggest that Cs_2ZrCl_6 decomposes to ZrOCl_2 in HCl at temperatures below $50\text{--}60^\circ\text{C}$ ⁽¹³⁾. We determined that, while filtration of Cs_2ZrCl_6 from refluxing HCl_{conc} under a flow of nitrogen allows for the isolation of cleaner material, sublimation was required for complete purification.

Crystals of $\text{Cs}_2\text{ZrCl}_6\text{:NpO}_2\text{Cl}_4^{2-}$ can be grown from a melt of Cs_2ZrCl_6 and $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ (2 molar %). A full crystallographic analysis of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ has been made, and the crystal structure is monoclinic, space group $C2/m$ (14). This molecule, shown in Figure 1, is isostructural with $\text{Cs}_2\text{UO}_2\text{Cl}_4$ (15). The site symmetry of the neptunium atom is $C2h$, and $\text{NpO}_2\text{Cl}_4^{2-}$ units have approximate $D4h$ symmetry. We assume that each $\text{NpO}_2\text{Cl}_4^{2-}$ unit occupies a ZrCl_6^{2-} site, and that each neptunyl ion may be randomly oriented along one of the three crystallographic ZrCl_6^{2-} axes.

A preliminary emission spectrum of $\text{Cs}_2\text{ZrCl}_6\text{:NpO}_2\text{Cl}_4^{2-}$ using 488 nm (CW Ar⁺ laser) excitation is shown in Figure 2. The emission spectrum of $\text{Cs}_2\text{ZrCl}_6\text{:NpO}_2\text{Cl}_4^{2-}$ excited at 588 nm (Nd:YAG pumped OPO), shown in Figure 3, has a similar profile. Each of these spectra is well-resolved, and the most intense line (6934.3 and 6939.6 cm⁻¹, respectively) is assigned to the 0-0 band, in good agreement with results from other studies. The origin of the second excited state was calculated by Pitzer's group to be 5775 cm⁻¹(6), and Denning and co-workers reported the second excited state of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at 6880 cm⁻¹(7a).

Vibronic structure is also apparent in Figures 2 and 3, and these features are labeled according to their displacements from the electronic origin. As a benchmark, the normal modes, symmetry in $D4h$, and ground state vibrational frequencies in cm⁻¹ of crystalline $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ are listed in Table 17a). Comparison of our experimental values (Fig. 1: 109, 129, 256, 278 cm⁻¹; Fig. 2: 111, 131, 259, 284 cm⁻¹) with equivalent ground state vibrational frequencies in crystalline $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ (\square_3 , \square_6 , \square_9 , and \square_{10}) show reasonable agreement.

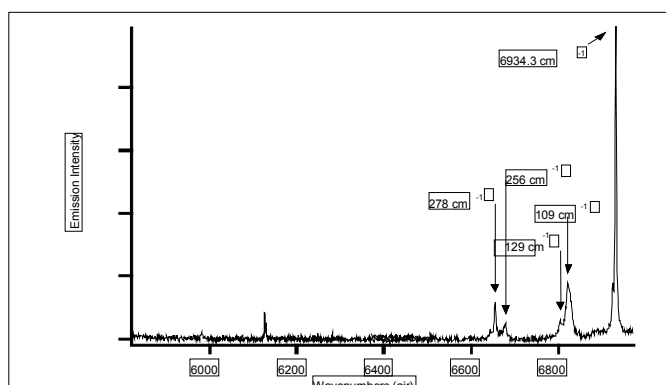


Figure 2 Emission spectrum of $\text{Cs}_2\text{ZrCl}_6\text{:NpO}_2\text{Cl}_4^{2-}$ excited at 488 nm.

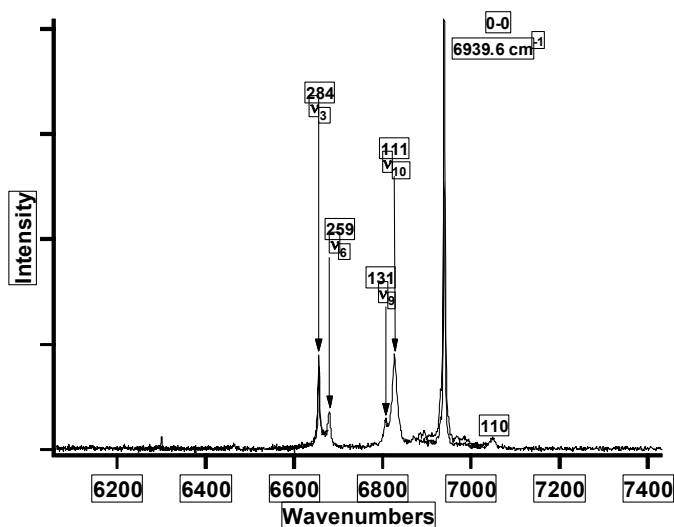


Figure 3 Emission spectrum of $\text{Cs}_2\text{ZrCl}_6\text{:NpO}_2\text{Cl}_4^{2-}$ excited at 588 nm.

Table 1 Normal modes, symmetry, and ground state vibrational frequencies of crystalline $\text{Cs}_2\text{NpO}_2\text{Cl}_4$.

mode	symmetry (D_{4h})	$\text{Cs}_2\text{NpO}_2\text{Cl}_4$
ν_1	A_{1g}	802
ν_2	A_{2u}	919
ν_3	E_u	267
ν_4	A_{1g}	257
ν_5	B_{2g}	230
ν_6	E_u	244
ν_7	B_{1g}	133
ν_8	E_u	117
ν_9	A_{2u}	117
ν_{10}	B_{1u}	
ν_{11}	E_g	185,190

V. Conclusion

While this experiment will provide the opportunity to determine the energies of the $f \rightarrow f$ transitions of neptunyl doped into a Cs_2ZrCl_6 matrix, refinement of the experimental apparatus will allow for analysis of a variety of other

neptunyl doped systems using other crystalline matrices or room-temperature ionic liquids. Additionally, we plan to characterize the electronic properties of the more complex but less studied plutonyl ion, which has two f electrons in the ground state.

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