

First observation of intra- $5f$ fluorescence from an actinyl center: Np(VI) near-IR emission in $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$

Marianne P. Wilkerson^{a,*}, John M. Berg^b, Todd A. Hopkins^b, Harry J. Dewey^a

^aChemistry Division, Los Alamos National Laboratory, Post Office Box 1663 Mail Stop J565, Los Alamos, NM 87545-1663, USA

^bNuclear Materials and Technology Division, Los Alamos National Laboratory, Los Alamos, NM, USA

Received 5 May 2004; received in revised form 2 July 2004; accepted 28 July 2004

Available online 22 September 2004

Abstract

Fluorescence from an excited $5f$ state of Np(VI) has been observed in the doped impurity system $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$. This is the first intra- $5f$ fluorescence transition that has been detected at room temperature in a condensed-phase system with an actinyl ($An(\text{VI})\text{O}_2^{2+}$) core, and it is a rare example of fluorescence of any kind from non-uranyl ions of this type. The emission originates from an excited state approximately 6890 cm^{-1} above the ground state. Its emission spectrum and fluorescence lifetime at 295 K will be discussed. Vibronic structure in the emission spectrum is assigned based on comparison with the detailed analysis of the absorption spectra published by Denning et al.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Neptunyl; Neptunyl lifetime; Neptunyl luminescence; Neptunyl tetrachloride; Near-infrared luminescence; $5f$ – $5f$

1. Introduction

The chemistry of actinyl species ($An(\text{VI})\text{O}_2^{2+}$; $An = \text{U}, \text{Np}, \text{Pu}, \text{Am}$) is intriguing due to the structural simplicity and stability of these fascinating cations [1]. Much of our understanding of the chemistry of actinyl ions is based upon studies of compounds prepared from acidic and near-neutral solutions [2]. These investigations report that the electronic structures of actinyl molecules can be quite complex. The numbers of orbitals and electrons available to actinide elements generate an abundance of optically accessible states and intricate signatures [3]. Furthermore, the density and strong spin–orbit coupling of states may easily confound attempts to describe actinide species in terms of spatial parameters related to coordination environments.

Most spectroscopic studies of actinyl molecules have focused on the simplest electronic system, the uranyl ion

($\text{U}(\text{VI})\text{O}_2^{2+}$) which has no valence electrons in the $5f$ shell [4]. The electronic transitions that are available to uranyl species can be described as ligand-to-metal charge-transfer (LMCT), in which an electron is promoted from an orbital of primarily oxo ligand character to another orbital of predominantly metal character. The lowest energies of these LMCT transitions are generally $\sim 20,000\text{ cm}^{-1}$, and the electronic signatures are characterized by a series of vibronic bands with a spacing corresponding to the energy of ν_1 , the symmetric stretch of the linear uranyl ion. The excited states are known to luminesce with lifetimes on the order of milliseconds and with quantum yields that can approach unity. Indeed, investigations of luminescence from uranyl molecules have clearly demonstrated its potential utility as an analytical diagnostic of chemical speciation [5].

However, this $5f^0$ electronic configuration is not typical of transuranic actinide species, most of which contain one or more electrons in the $5f$ valence shell [3]. There are two classes of transitions available in the spectra of $5f^n$ ($n > 0$) molecules: LMCT and $5f$ – $5f$

*Corresponding author. Fax: +1-505-665-4631.

E-mail addresses: mpw@lanl.gov (M.P. Wilkerson),
jberg@lanl.gov (J.M. Berg), hd@lanl.gov (H.J. Dewey).

transitions that correspond to promotion of an electron from one orbital of primarily $5f$ metal character to another orbital of predominantly $5f$ metal character. Of the transuranic actinyl dications, neptunyl has the simplest $5f$ ground state electronic configuration of $[\text{Rn}]5f^4$. Studies of an actinide-containing compound with a single electron in the valence $5f$ shell could provide a unique opportunity to explore $5f$ electronic structures of actinide species without introducing some of the complicating factors that can result from more than one electron in the valence shell, such as a relatively high density of states.

Several experimental and theoretical investigations of the $5f$ – $5f$ transitions in neptunyl compounds have been reported. Denning published polarized absorption spectra of $\text{Np}(\text{VI})\text{O}_2\text{Cl}_4^{2-}$ and $\text{Np}(\text{VI})\text{O}_2(\text{NO}_3)_3^-$, both of which were obtained at liquid helium temperature [6]. These data reveal well-defined $5f$ – $5f$ vibronic structures in the near-infrared region. Matsika and Pitzer calculated the ground and excited state energies of neptunyl tetrachloride in a crystalline matrix using cluster-layered methods and quantum chemical theory, and the results are in general agreement with experimentally measured energies [7].

We have recently detected near-infrared luminescence at 75 K from centrosymmetric $\text{NpO}_2\text{Cl}_4^{2-}$ doped into $\text{Cs}_2\text{UO}_2\text{Cl}_4$ [8]. This is the first example of $5f$ – $5f$ luminescence in such a system. In the present study, we report that the neptunyl tetrachloride ion luminesces in the near-infrared region not only at liquid nitrogen temperature, but also at 295 K. We will compare the vibronic assignments from our room temperature spectrum with Denning's liquid helium polarized absorption spectra and our low temperature luminescence spectra of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ [6a,8]. We also will compare the luminescence lifetime of a $5f$ – $5f$ origin at room temperature with that measured at 75 K [8].

2. Experimental

The synthesis and structural characterization of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ and the preparation of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ have been described elsewhere [6a,8a].

The crystalline needles of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ were mounted and then sealed in a borosilicate capillary, which was then sealed in a 5 mm borosilicate NMR tube. The low temperature spectra were collected from a sample, which was immersed in a liquid N_2 bath of a cylindrical dewar fitted with quartz windows.

The excitation source is either the signal from a tunable optical parametric oscillator (Continuum Mirage 500) operating at a 10 Hz repetition rate pumped by a Nd:YAG laser (Continuum Powerlite 8000) or the signal from a continuous wave Helium-neon laser (Melles Griot 05-LHP-111). Pulse energies for experi-

ments using the OPO are 1–2 mJ with a bandwidth of $\sim 0.2 \text{ cm}^{-1}$ over the 585–700 nm excitation wavelength range. The luminescence was collected at 90° to the excitation, passed through a 695 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 $1.0 \mu\text{m}$. 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 $2.2 \mu\text{m}$). The amplified signal from the PMT detector was measured using a photon counter (Stanford Research SR400). A portion of the laser output signal was monitored with a pyroelectric detector (Moletron J4-09) connected to a boxcar averager and gated integrator (Stanford Research SR250) for normalization of the signals from the PMT detector. Time-resolved data were collected using a multichannel scaler/averager (Stanford Research SR430). Emission luminescence spectra were collected in 0.2 nm increments and converted to energy units in order to clearly portray energy shifts. Software for data collection from the PMT was written in house using National Instruments LabView, Version 6i. 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 4.09).

3. Results and discussion

We have initiated our spectroscopic studies of $5f$ – $5f$ electronic structures with $\text{Cs}_2\text{Np}(\text{VI})\text{O}_2\text{Cl}_4$ because it has many favorable properties. This relatively simple molecule consists of a neptunium atom coordinated in a pseudooctahedral fashion by two apical oxo groups and four equatorial chloride ligands such that the $\text{NpO}_2\text{Cl}_4^{2-}$ anion is centrosymmetric and has approximate D_{4h} symmetry [8a,9]. The charge of the dianion is balanced by two cesium cations. The electronic configuration of $\text{NpO}_2\text{Cl}_4^{2-}$ is $[\text{Rn}]5f^4$. $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ is readily doped into isostructural $\text{Cs}_2\text{UO}_2\text{Cl}_4$, a compound which offers a large window for observing dopant spectra throughout the near-infrared region because its lowest energy electronic transition is $20,095.7 \text{ cm}^{-1}$ [4,10]. Furthermore, the $\text{Cs}_2\text{UO}_2\text{Cl}_4$ molecule itself lacks any high frequency vibrational modes that could serve as acceptors for radiationless deactivation [6a].

Spectroscopically, the intensities of $5f_u \rightarrow 5f_u$ electronic bands are expected to be weak because the transitions are parity forbidden [11]. For centrosymmetric

structures such as $\text{Cs}_2\text{NpO}_2\text{Cl}_4$, they can be allowed by magnetic dipole or electric quadrupole mechanisms, or they can be electric dipole induced by ungerade molecular vibrations [6]. Denning reported the vibrational normal mode energies of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$, which are listed in Table 1. The linear neptunyl ion itself has a Raman active symmetric stretch and two infrared active modes, an asymmetric stretch and a bend. Additional vibrations result from coordination of four chloride ligands in the equatorial plane of the $\text{NpO}_2\text{Cl}_4^{2-}$ ion. Four are Raman active, and three are infrared active. For the centrosymmetric structure of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$, the five infrared active vibrational modes could be expected to induce $5f-5f$ transitions.

Polarized absorption spectra of oriented single crystals of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at liquid helium temperature have been reported, and they have well-defined structures assignable to $5f-5f$ and LMCT transitions.[6] The energies of the excited states within these manifolds are shown in Fig. 1. We have adopted Denning's labeling method in which each state is identified by a Roman numeral, beginning with **I** for the first excited state, **II** for the second excited state, etc. We have labeled the ground state as **0**. In particular, Denning assigned three $5f-5f$ electronic origins in the near-infrared, and he directly observed the magnetic dipole allowed electronic transition, $\text{II} \leftarrow \mathbf{0}$, at 6880.4 cm^{-1} [6a]. Vibronic assignments corresponding to $\text{II} + \nu_{10} \leftarrow \mathbf{0}$, $\text{II} + \nu_9 \leftarrow \mathbf{0}$, $\text{II} + \nu_6 \leftarrow \mathbf{0}$, $\text{II} + \nu_3 \leftarrow \mathbf{0}$, and $\text{II} + \nu_2 \leftarrow \mathbf{0}$ were reported based upon ground state vibrational mode frequencies. In a separate study of the vibronic spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at liquid helium temperature, a slightly higher energy, 6890 cm^{-1} , was reported for the $\text{II} \leftarrow \mathbf{0}$ electronic origin [12].

We have recently demonstrated that the $\text{NpO}_2\text{Cl}_4^{2-}$ ion luminesces in the near-infrared with relatively well-defined vibronic structure following visible photoexcitation at 75 K. Here, we report that near-infrared luminescence from this ion is observed at 295 K as well.

Two examples of the room temperature luminescence obtained with different excitation sources and detectors are shown in Fig. 2.

In order to assign the room temperature luminescence spectrum of the $\text{NpO}_2\text{Cl}_4^{2-}$ ion, it is helpful to consider the luminescence spectrum at 75 K, as well as the reported absorption and vibrational data [6a,8]. At 75 K, the narrow, intense luminescence peak at $6880.6(2)\text{ cm}^{-1}$ has been assigned as the $\text{II} \rightarrow \mathbf{0}$ electronic origin [8]. This assignment is supported by the observed agreement between its excitation spectrum and absorption data of Denning et al. over the range $15,700-16,000\text{ cm}^{-1}$ [6b,8]. Assignment of the vibronic transitions observed in the 75 K luminescence is aided by the close correspondence between the excited state and ground state vibronic structure observed in absorption and luminescence, respectively [6a]. The vibronic transitions in luminescence at liquid nitrogen temperature are assigned to $\text{II} \rightarrow \mathbf{0} + \nu_2$, $\text{II} \rightarrow \mathbf{0} + \nu_3$, $\text{II} \rightarrow \mathbf{0} + \nu_6$, $\text{II} \rightarrow \mathbf{0} + \nu_8$, $\text{II} \rightarrow \mathbf{0} + \nu_9$, and $\text{II} \rightarrow \mathbf{0} + \nu_{10}$. The differences in energy between the origin and each of these vibronic bands are included in Table 1.

The most intense peak in the room temperature luminescence is also assigned to the $\text{II} \rightarrow \mathbf{0}$ electronic origin (Fig. 2). It is considerably broader than the corresponding peaks in the luminescence spectrum at 75 K and in the absorption spectrum at 4.2 K, and it is also blue-shifted to 6889 cm^{-1} [6a,8]. The assignment of the electronic origin is supported by the presence of broad hot bands at 7010 and 7180 cm^{-1} . These transitions lie higher in energy than the origin by approximately the energies of IR active modes ν_8 , ν_9 , ν_{10} , and ν_3 , respectively. Therefore, we interpret the assignment of these thermally accessible hot 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 luminescence decay curve for origin **II** of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ is compared with 75 K decay in Fig. 3. The room temperature decay is single exponential, yielding a lifetime of $20\text{ }\mu\text{s}$, while a longer

Table 1

Vibrational modes, symmetries, and ground state vibrational frequencies of $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ [6a] (the gerade vibrational modes are Raman active, and the ungerade vibrational modes are infrared active)

| Mode | Symmetry in D_{4h} | Type of vibration | Vibrational energy (cm^{-1}) | E_{0-0} vibronic transition (cm^{-1}), 75 K | E_{0-0} vibronic transition (cm^{-1}), 295 K |
|------------|----------------------|--------------------------|---|--|---|
| ν_1 | A_{1g} | O–M–O symmetric stretch | 802 | 793 | 794 |
| ν_2 | A_{2u} | O–M–O asymmetric stretch | 919 | 913 | 914 |
| ν_3 | E_u | O–M–O bend | 267 | 272 | 264 |
| ν_4 | A_{1g} | M–Cl symmetric stretch | 257 | | |
| ν_5 | B_{2g} | M–Cl stretch | 230 | | |
| ν_6 | E_u | M–Cl stretch | 244 | 247 | |
| ν_7 | B_{1g} | M–Cl in plane bend | 133 | | |
| ν_8 | E_u | M–Cl in plane bend | 117 | 118 | 104 |
| ν_9 | A_{2u} | M–Cl out of plane bend | 117 | 118 | 104 |
| ν_{10} | B_{1u} | M–Cl out of plane bend | Raman, IR Inactive | 109 | 104 |
| ν_{11} | E_g | M–Cl out of plane bend | 185 | | |

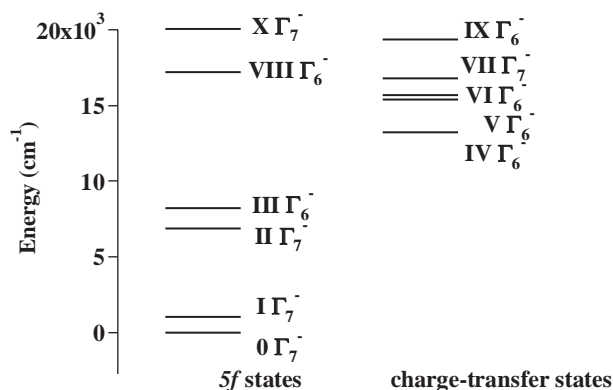


Fig. 1. Excited state energies of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ measured using polarized absorption spectroscopy at liquid helium temperature. State assignments were based upon a D_{4h}^* symmetry [6].

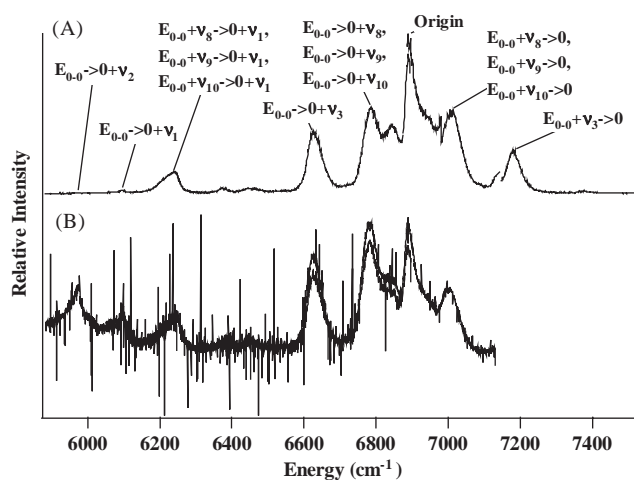


Fig. 2. (A) Luminescence spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at room temperature using a photomultiplier tube following excitation at 628.3 nm. The photon counts were collected over a 40 μs gate width following a 5 μs delay. Background photon counts collected over a 40 μs gate width following a 500 μs gate delay were subtracted. Spectrograph and detector slits were 100 μm wide. (B) Luminescence spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at room temperature using array detection following excitation from a continuous wave excitation source (633 nm).

lifetime of 71 μs was measured at liquid nitrogen temperature [8].

The vibronic assignments in the spectrum of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ 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). For example, the broad peak centered at 6785 cm^{-1} is assigned as possibly containing $\text{II} \rightarrow \mathbf{0} + \nu_8$, $\text{II} \rightarrow \mathbf{0} + \nu_9$, and $\text{II} \rightarrow \mathbf{0} + \nu_{10}$. Another band centered at 6625 cm^{-1} is broadened over 6560 to 6690 cm^{-1} , and it is assigned to $\text{II} \rightarrow \mathbf{0} + \nu_3$, but may also contain $\text{II} \rightarrow \mathbf{0} + \nu_6$. Because the photomulti-

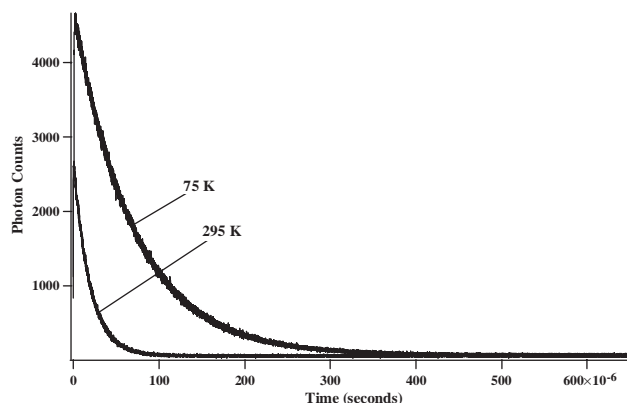


Fig. 3. Luminescence decay curves of the origin $\text{II} \rightarrow \mathbf{0}$ of $\text{Cs}_2\text{U}(\text{Np})\text{O}_2\text{Cl}_4$ at liquid nitrogen temperature and room temperature.

plier tube employed for these measurements has a rapid drop off in quantum efficiency at wavelengths $> 1.6 \mu\text{m}$, a more responsive albeit noisy detector was employed in order to observe the weak transitions at the lower energy region. These data are shown in the lower spectrum (B) of Fig. 2. An additional vibronic transition is observed in these data which is 914 cm^{-1} lower in energy than the origin. This band is assigned to $\text{II} \rightarrow \mathbf{0} + \nu_2$.

An additional pair of transitions is apparent in both of the spectra represented in Fig. 2. A relatively weak band at 6095 is coincident with $\text{II} \rightarrow \mathbf{0} + \nu_1$. However, the symmetric stretch of $\text{NpO}_2\text{Cl}_4^{2-}$ is gerade, and it is not expected that vibronic transitions involving gerade modes would be as intense as the origin. Denning noted that a vibronic mode based upon ν_1 is not featured in the near-infrared 4.2 K absorption spectra [6]. Comparison of the room temperature spectrum with that at 75 K reveals the appearance at 295 K of a broad hot band that is characterized by an asymmetric shape suggestive of overlapping transitions. The energy of this peak (6145–6285 cm^{-1}) implies a hot band based upon ν_8 , ν_9 , and ν_{10} , and this transition is assignable to $\text{II} + \nu_8 \rightarrow \mathbf{0} + \nu_1$, $\text{II} + \nu_9 \rightarrow \mathbf{0} + \nu_1$, and $\text{II} + \nu_{10} \rightarrow \mathbf{0} + \nu_1$.

4. Conclusions

In summary, we have demonstrated that the neptunyl tetrachloride ion exhibits luminescence at room temperature from a low-lying 5f state to the 5f ground state. We assign a strong, narrow transition at 6889 cm^{-1} to the $\text{II} \rightarrow \mathbf{0}$ electronic origin, which correlates well with published absorption data. The lifetime of this transition is 20 μs . 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 .

It remains to be seen how structural variation from other ligand sets will influence efficiencies and energies of the neptunyl luminescence, effects which have been

studied extensively in uranyl species. By correlating spectroscopic measurements from simple electronic systems having a variety of molecular symmetries and/or ligand sets, however, we hope to characterize simple electronic structures as a function of molecular environments in a predictable, meaningful fashion.

Acknowledgments

This research at Los Alamos National Laboratory was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, and by the Laboratory Directed Research and Development Program. Los Alamos National Laboratory is operated by the University of California for the US. Department of Energy under Contract W-7405-ENG-36.

References

- [1] (a) A.F. Wells, *Structural Inorganic Chemistry*, Oxford, Clarendon Press, 1995 (Chapter 28);
(b) J.H. Burns, in: J.J. Katz, G.T. Seaborg, L.R. Morss (Eds.), *The Chemistry of the Actinide Elements*, vol. 2, Chapman & Hall, New York, 1986.
- [2] F. Weigel, in: J.J. Katz, G.T. Seaborg, L.R. Morss (Eds.), *The Chemistry of the Actinide Elements*, vol. 1, Chapman & Hall, New York, 1986.
- [3] W.T. Carnall, H.M. Crosswhite, in: J.J. Katz, G.T. Seaborg, L.R. Morss (Eds.), *The Chemistry of the Actinide Elements*, vol. 2, Chapman & Hall, New York, 1986.
- [4] (a) R.G. Denning, *Struct. Bonding (Berlin)* 79 (1992) 215;
(b) S.P. McGlynn, J.K. Smith, *J. Mol. Spectrosc.* 6 (1961) 164.
- [5] I. Billard, E. Ansoborlo, K. Apperson, S. Arpigny, M.E. Azenha, D. Birch, P. Bros, H.D. Burrows, G. Choppin, L. Couston, V. Dubois, T. Fanghänel, G. Geipel, S. Hubert, J.I. Kim, T. Kimura, R. Klenze, A. Kronenberg, M. Kumke, G. Lagarde, G. Lamarque, S. Lis, C. Madic, G. Meinrath, C. Moulin, R. Nagaishi, D. Parker, G. Planque, F. Scherbaum, E. Simoni, S. Sinkov, C. Viallesoubranne, *Appl. Spectrosc.* 57 (2003) 1027.
- [6] (a) R.G. Denning, J.O.W. Norris, B. Brown, *Mol. Phys.* 46 (1982) 287;
(b) R.G. Denning, J.O.W. Norris, D. Brown, *Mol. Phys.* 46 (1982) 325.
- [7] S. Matsika, R.M. Pitzer, *J. Phys. Chem. A* 105 (2001) 637.
- [8] (a) M.P. Wilkerson, J.M. Berg, H.J. Dewey, T.A. Hopkins. Manuscript in preparation;
(b) M.P. Wilkerson, J.E. Barefield, J.M. Berg, H.J. Dewey, T.A. Hopkins, In: *Proceedings of Actinide 2001 International Conference*; *J. Nucl. Sci. Technol.* 2002, Suppl. 3, 129.
- [9] F. Weigel, G.D. Werner, Ch. Kalus, *Physica* 102B (1980) 308.
- [10] (a) D.J. Watkin, R.G. Denning, K. Prout, *Acta Crystallogr. C* 47 (1991) 2517;
(b) D. Hall, A.D. Rae, T.N. Waters, *Acta Crystallogr.* 20 (1966) 160.
- [11] G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand Reinhold Company, New York, 1966.
- [12] N.G. Gorshkov, L.G. Mashirov, *Radiokhimiya (Translated)* 26 (1984) 514.