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Title:	Near-infrared Photoluminescence of Neptunyl and Plutonyl Ions
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Form 836 (7/06)

Near-infrared Photoluminescence of Neptunyl and Plutonyl Ions

Marianne Wilkerson[1], Beau J. Barker[2], and John M. Berg[1]

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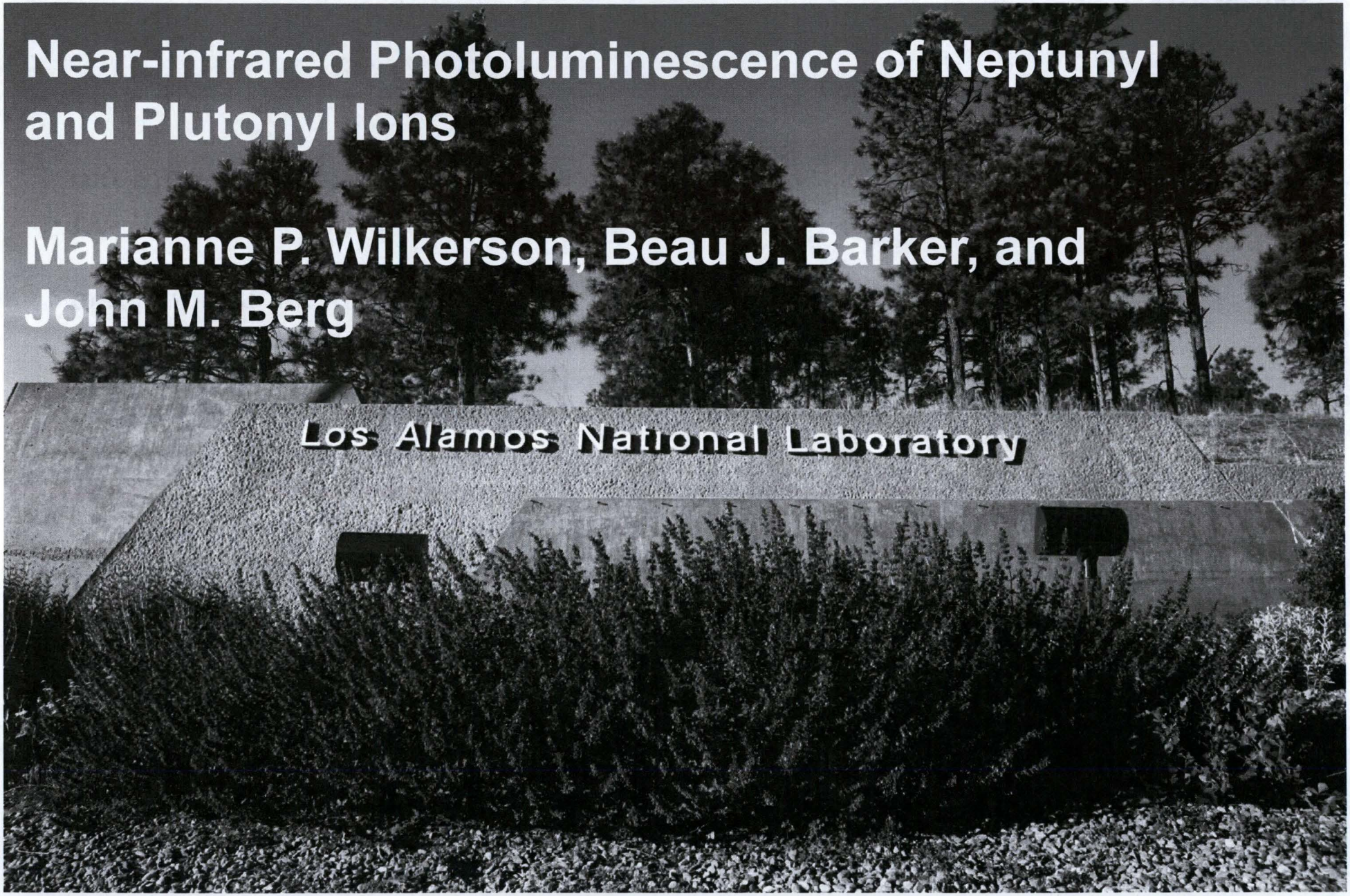
The actinyl ions, AnO_2^{2+} (An = U, Np, Pu, and Am), are a series of linear dioxo dications that dominate the chemistry of the light actinides in their higher oxidation states. Theoretical and experimental studies have been reported on the nature of the bonding in this structural motif. We will discuss photoluminescence emission measurements between 6000 and 10,200 cm^{-1} from crystalline $Cs_2U(Pu)O_2Cl_4$ both at room temperature and cooled to 75 K. Pulsed laser excitation between 625-1200 nm produces rich emission spectra that are more complex than the electronically simpler $5f^1$ $Cs_2U(Np)O_2Cl_4$ system, as one would expect. Photoluminescence decay dynamics, and excitation energy dependence indicate multiple emitting states and complex decay pathways.

LA-UR 11-05998

Near-infrared Photoluminescence of Neptunyl and Plutonyl Ions

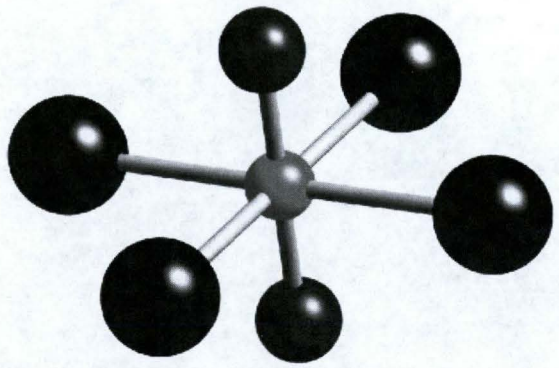
Marianne P. Wilkerson, Beau J. Barker, and John M. Berg



US DOE Office of Basic Energy Sciences, Heavy Element Chemistry Program

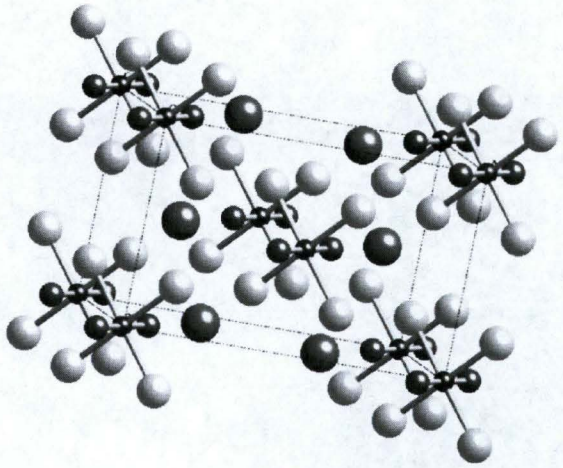
Actinyl Tetrachloride

- Benchmark system for probing electronic structure and covalency in An-oxo bonding.
- Our understanding of An-oxo bonding is historically derived from seminal studies of the uranyl ion.
- While the primary focus has been on U-oxo bonding, Cl K-edge X-ray absorption spectroscopy (XAS) facilitates a more complete picture of electronic structure.
- We have the opportunity to extend our study of actinyl to TRU ions.



$$M(VI)O_2^{2+} + 2\ CsCl \xrightarrow{2\ M\ HCl} Cs_2MO_2Cl_4$$

Quantitative yield



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We are employing a range of spectroscopic tools to explore actinide electronic structure. Why is this information interesting?

Photoluminescence

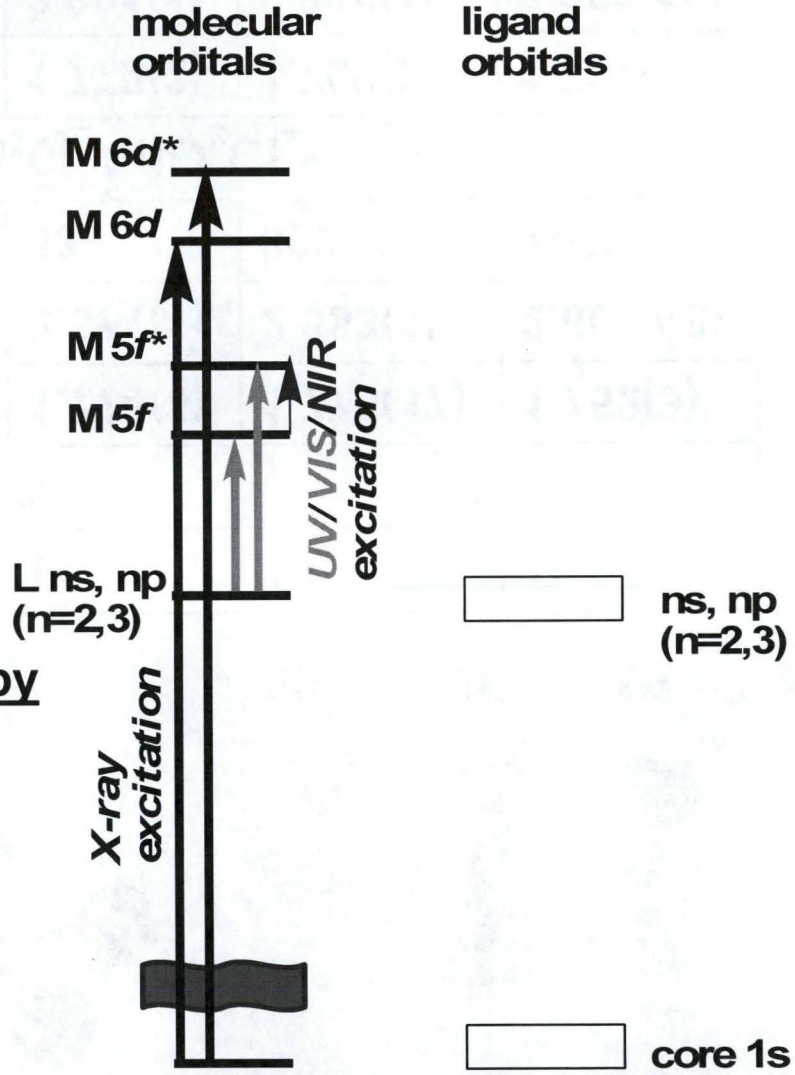
- Recent work reveals the utility for measuring valence excited state properties and local vibrational modes of transuranic molecules.

Our current focus is in probing the optical luminescence of single crystals containing neptunyl and plutonyl ions.

Ligand K-edge X-ray Absorption Spectroscopy

- Probe of relative energies and roles of 5*f* and 6*d* orbitals across the early actinide series.

- Opportunity to quantify covalency in actinide bonding



Solomon, E. I.; Hedman, B.; Hodgson, K. O.; Dey, A.; Szilagyi, R. K. *Coord. Chem. Rev.* 2005, *249*, 97.

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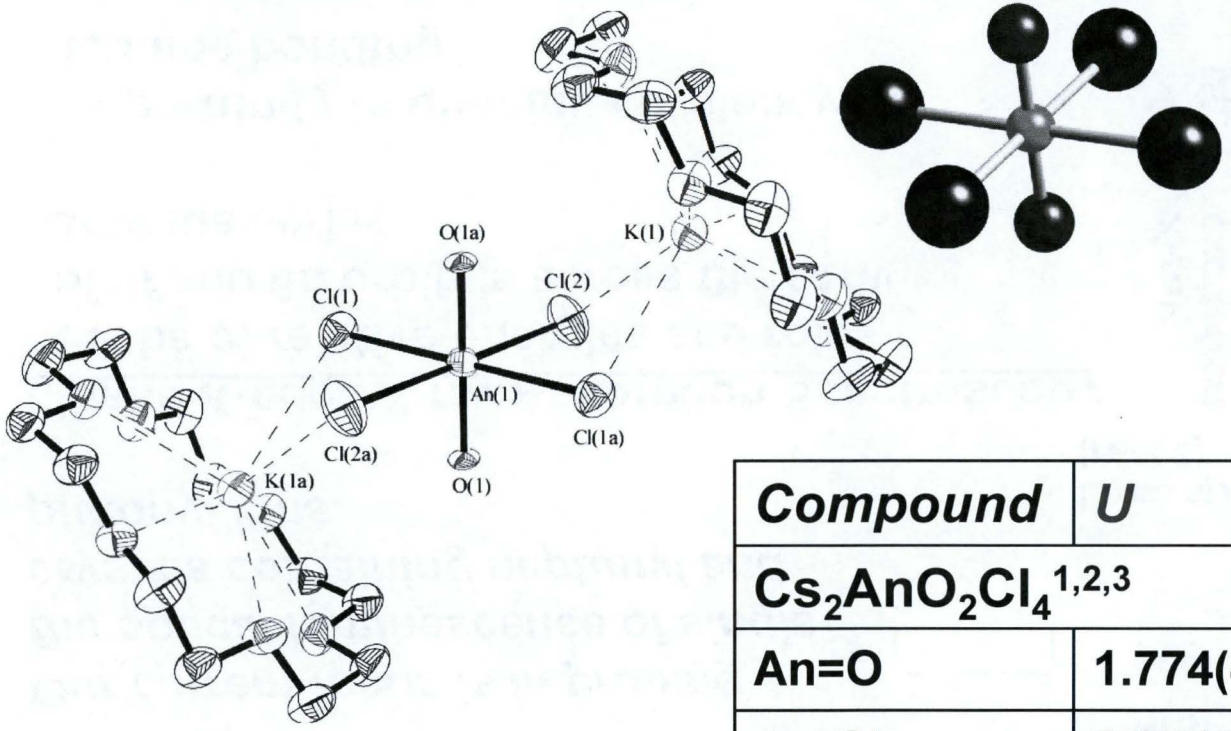
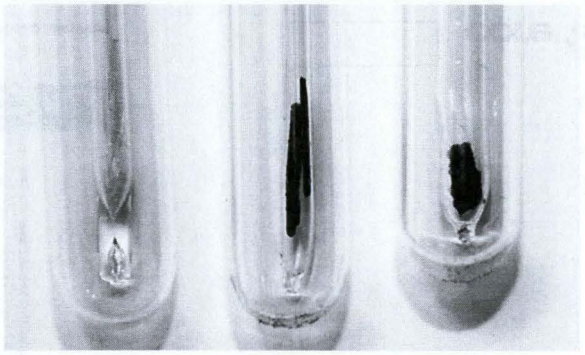
Single crystal X-ray diffraction analyses of $Cs_2AnO_2Cl_4$ reveal centrosymmetric anions isostructural with $[K\text{-}18\text{-}C\text{-}6]_2AnO2Cl4$.



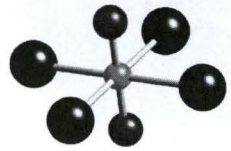


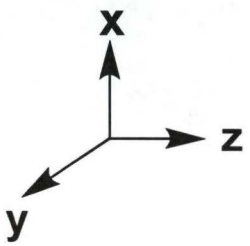
$5f^0$ $5f^1$ $5f^2$

Compound	*U*	*Np*	*Pu*
$Cs_2AnO_2Cl_4$[1,2,3]			
An=O	1.774(4)	1.775(17)	1.752(3)
An-Cl	2.671(1)	2.653(1)	2.6648(8)
ν_1 (cm^{-1})	832	802	TBD
$[K\text{-}18\text{-}Crown\text{-}6]_2AnO_2Cl_4$[4]			
An=O	1.772(2)	1.759(2)	1.737(3)
An-Cl	2.681(1)	2.665(1)	2.656(1)
ν_1 (cm^{-1})	833	793	791

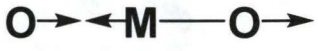
1. Watkin, D. J.; Denning, R. G.; Prout, K. *Acta Cryst.* 1991, *C47*, 2517.
2. Wilkerson, M. P.; Arrington, C. A.; Berg, J. M.; Scott, B. L. *J. Alloys Compd.* 2007, *444-445*, 634.
3. Stone, P. J. *Dissertation*, University of Oxford 1986.
4. Wilkerson, M. P.; Scott, B. L. *Acta Crystallogr.* 2008, 64(1), i5.
5. Clark, D. L., et al. *Unpublished results.*

Energies of vibrational modes of $Cs_2U(VI)O_2Cl_4$ are likely similar to those of $Cs_2Np(VI)O_2Cl_4$, $Cs_2Pu(VI)O_2Cl_4$.

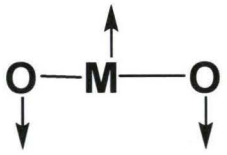




$\nu_1\ A_{1g}$

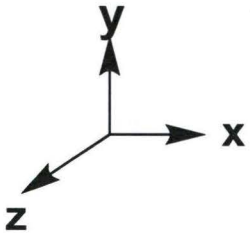


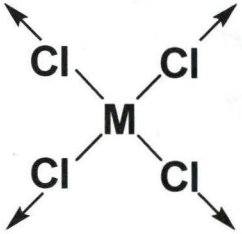
$\nu_2\ A_{2u}$



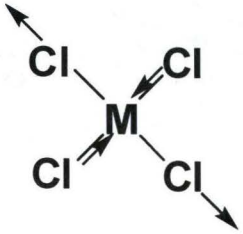
$\nu_3\ E_u$

Raman active
Infrared active
Inactive

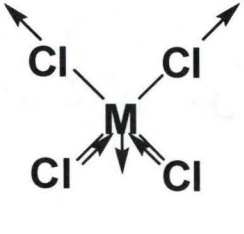




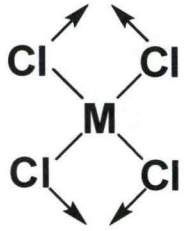
$\nu_4\ A_{1g}$



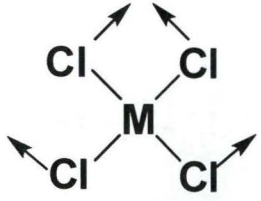
$\nu_5\ B_{2g}$



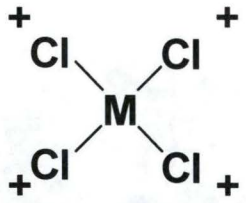
$\nu_6\ E_u$



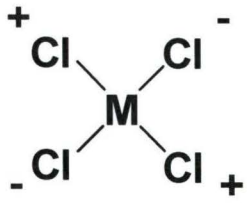
$\nu_7\ B_{1g}$



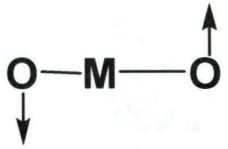
$\nu_8\ E_u$



$\nu_9\ A_{2u}$



$\nu_{10}\ B_{1u}$



$\nu_{11}\ E_g$

1. Ohwada, K. *Spectrochimica Acta* 1975, *31A*, 973.
2. Ohwada, K. *Appl. Spectrosc.* 1980, *34*, 327.
3. Denning, R. G.; Norris, J. O. W.; Brown, D. *Mol. Physics* 1982, *46*, 287.

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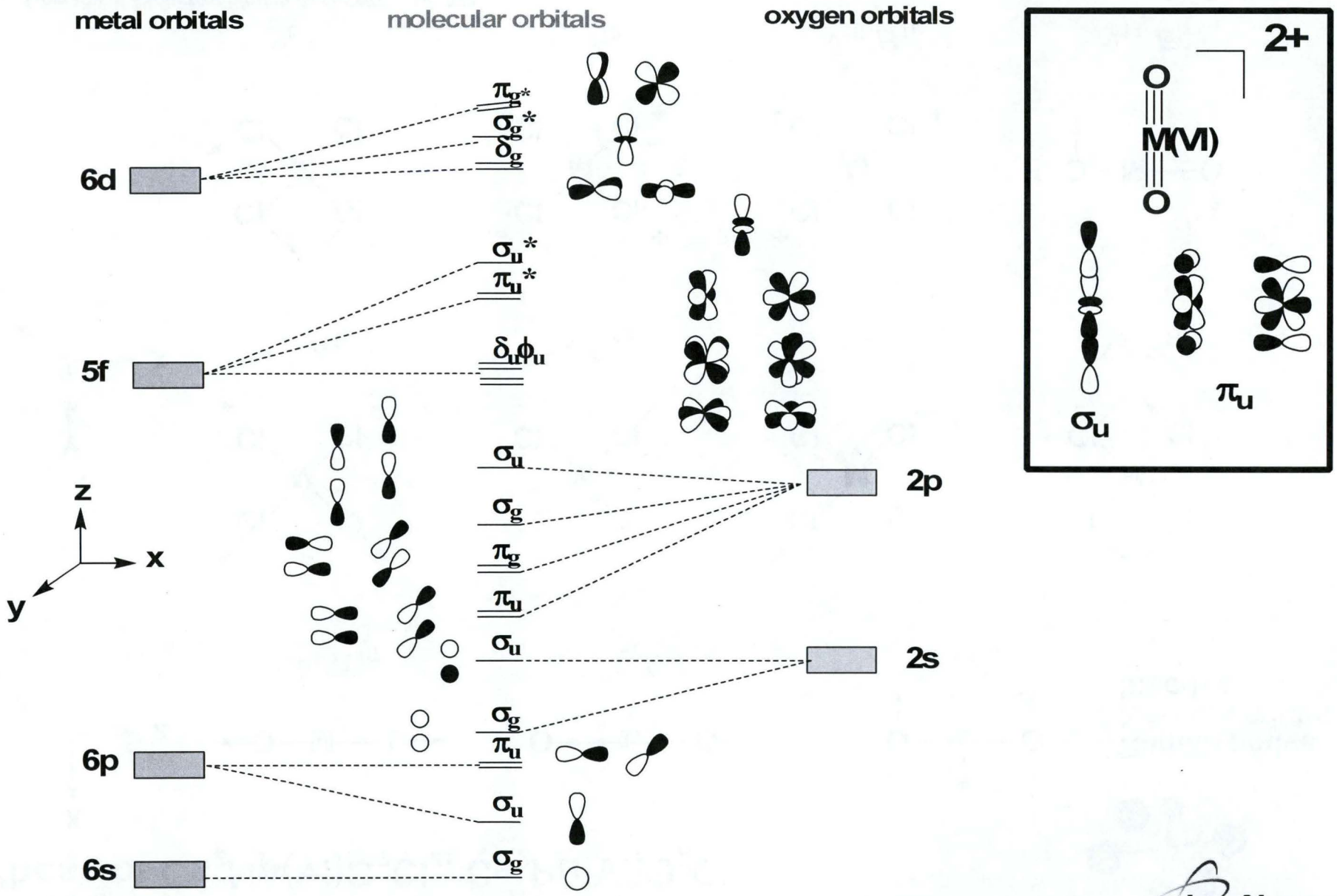
A molecular orbital diagram for $M(VI)O_2^{2+}$ under the point group $D_{\infty h}$, based upon group theory.



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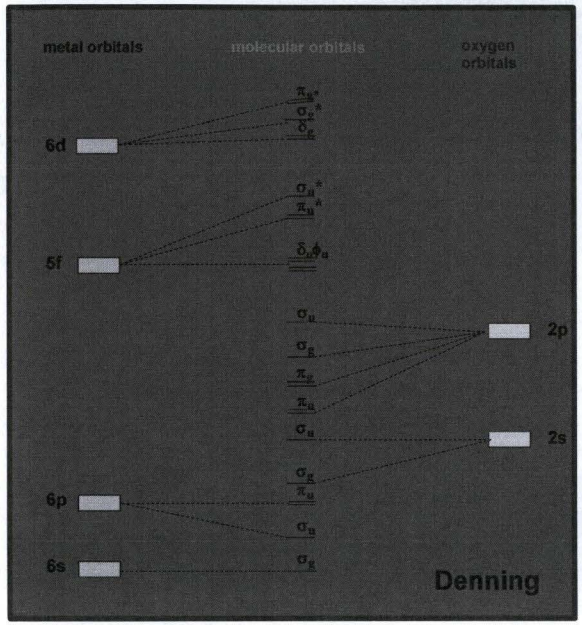
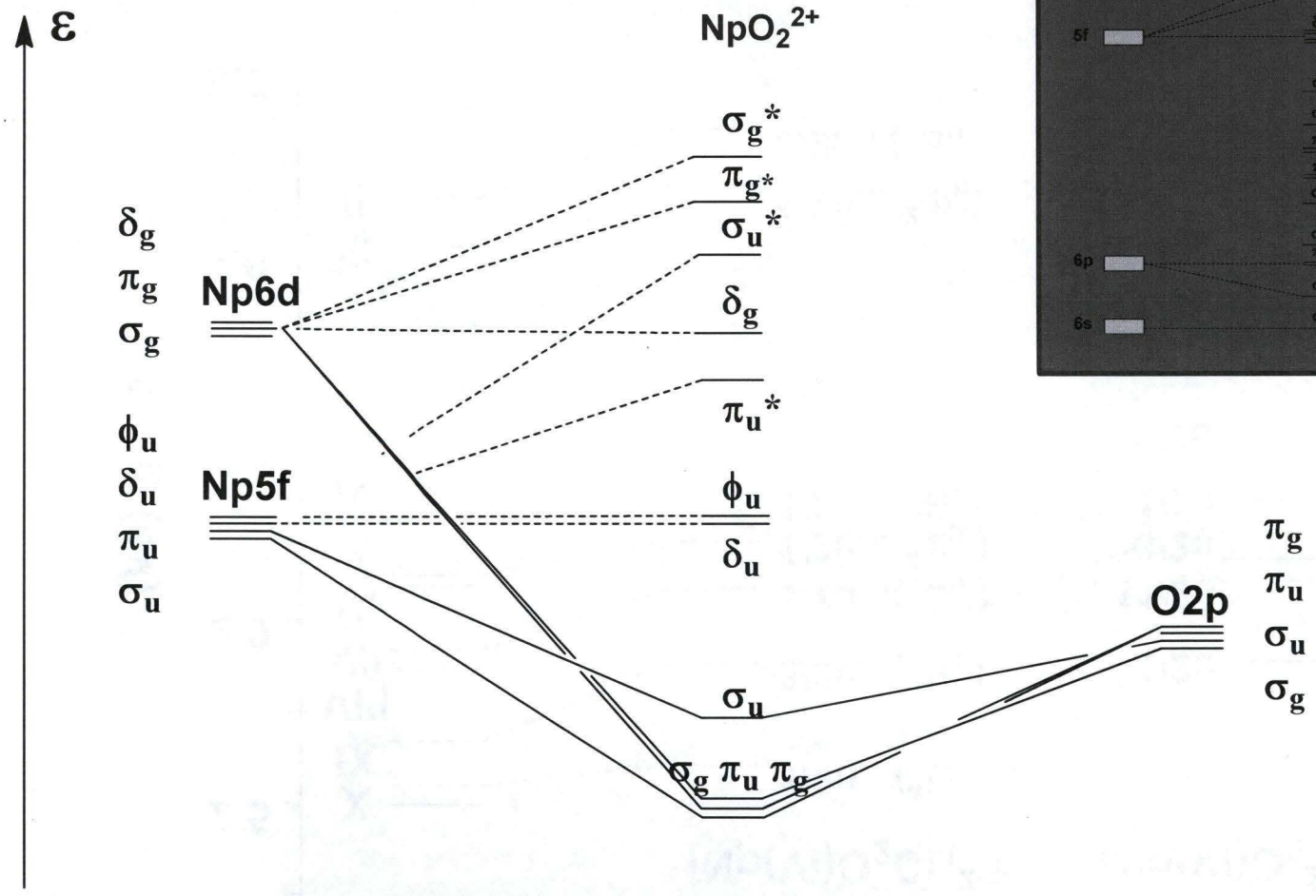
A qualitative scalar-relativistic valence orbital energy-level scheme for $Np(VI)O_2^{2+}$ under the point group $D_{\infty h}$.





Su, J.; Schwarz, W. H. E.; Li, J. *Inorg. Chem.* 2012, *51*, 3231.

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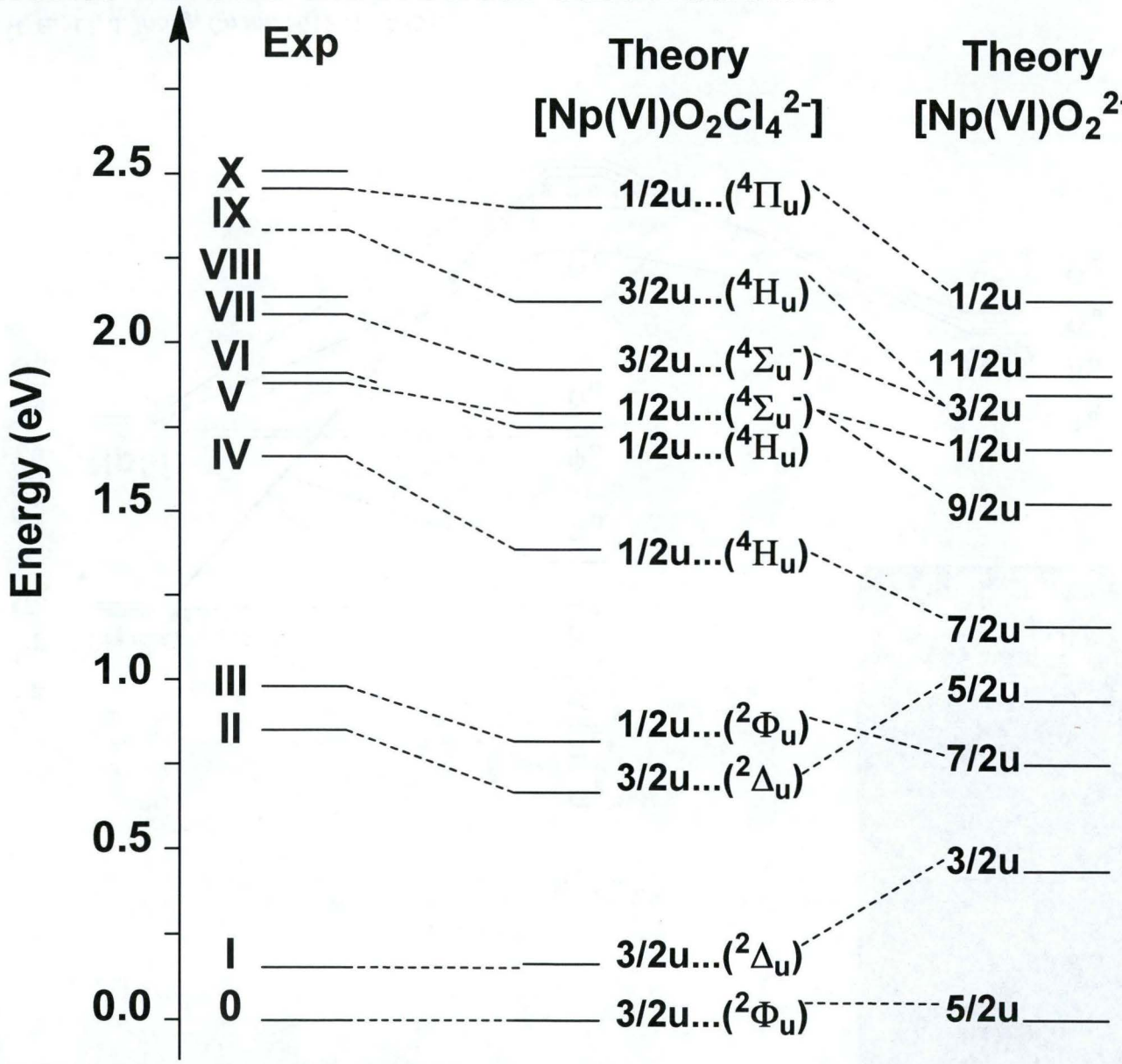
Comparison of electronic excitation energies from experimental measurements versus theoretical calculations.



Su, J.; Schwarz, W. H. E.; Li, J. *Inorg. Chem.* 2012, *51*, 3231.

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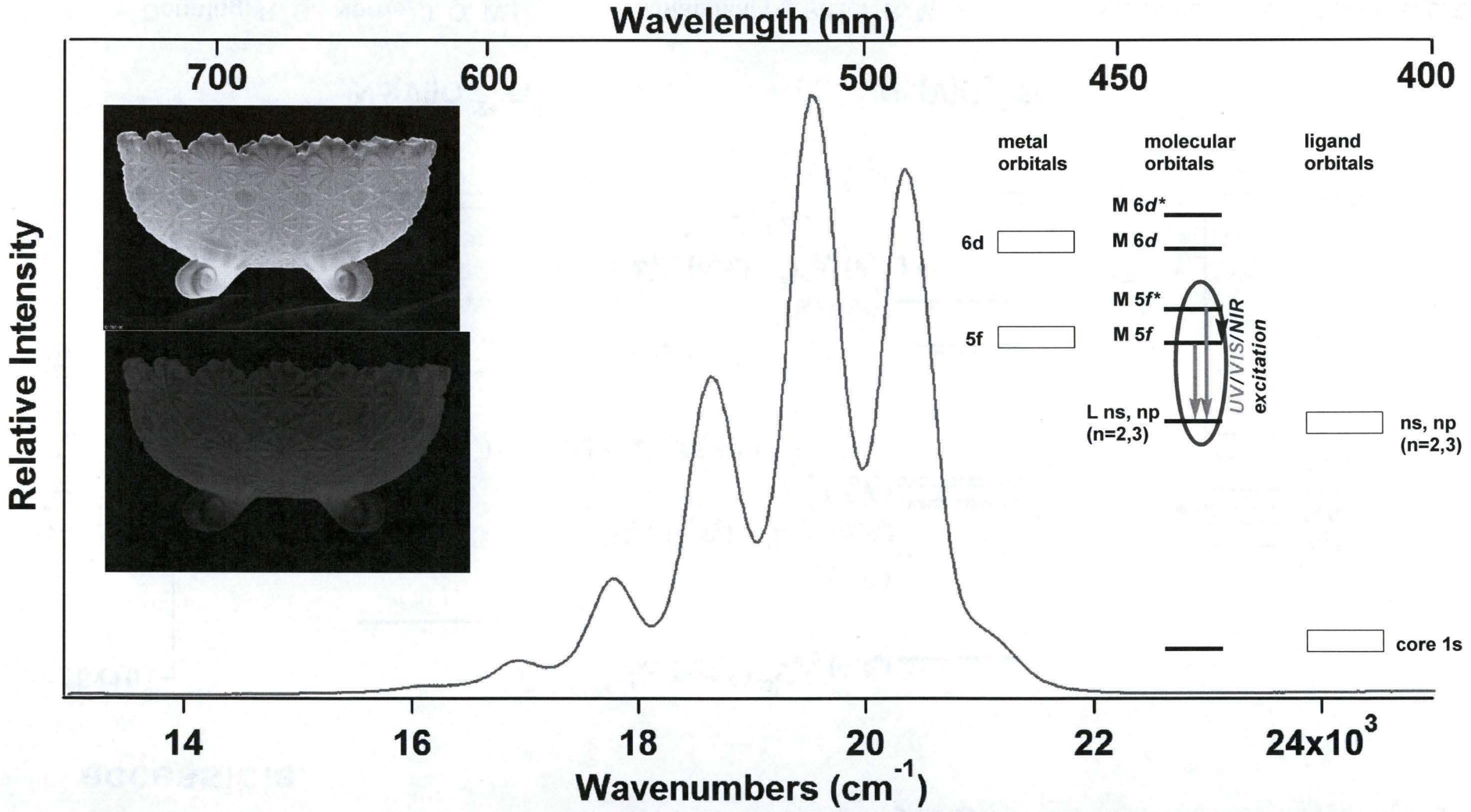
UV excitation produces visible luminescence from uranyl. The structure in the spectrum is vibronic.



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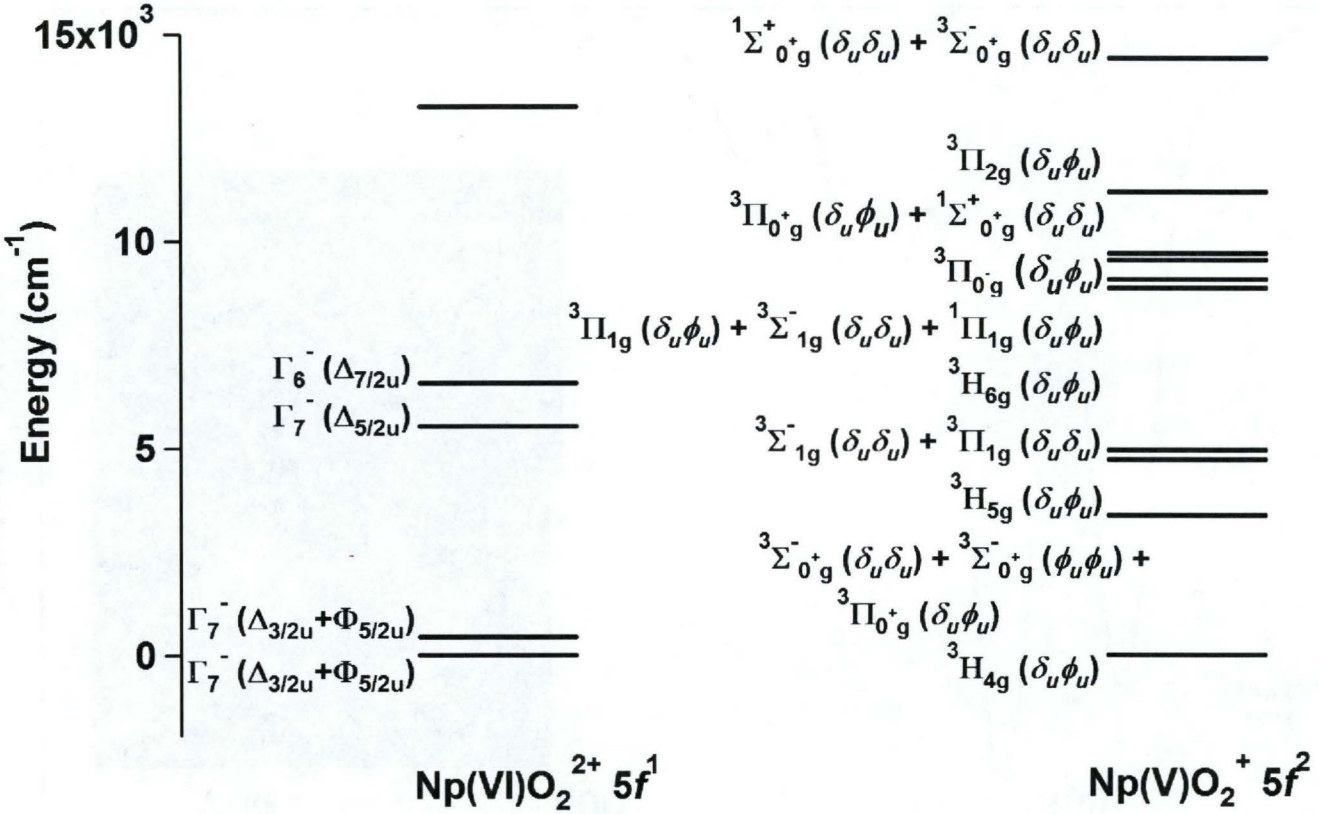
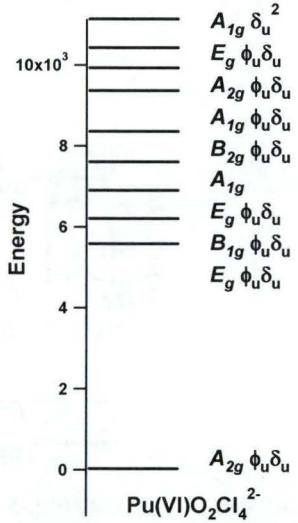
Analyses of the electronic structures of $5f^n$ (n>0) are challenging because there are an abundance of low-lying states that are optically accessible.





Denning, R. G.; Norris, J. O. W.; Brown, D. *Mol. Phys. 1982, 46,* 287.

Matsika, S.; Pitzer, R. M. *J. Phys. Chem. A* 2000, *104,* 4064.

Gorshkov, N. G.; Mashirov, L. G. *Radiokhimiya* 1985, *27(5),* 511.

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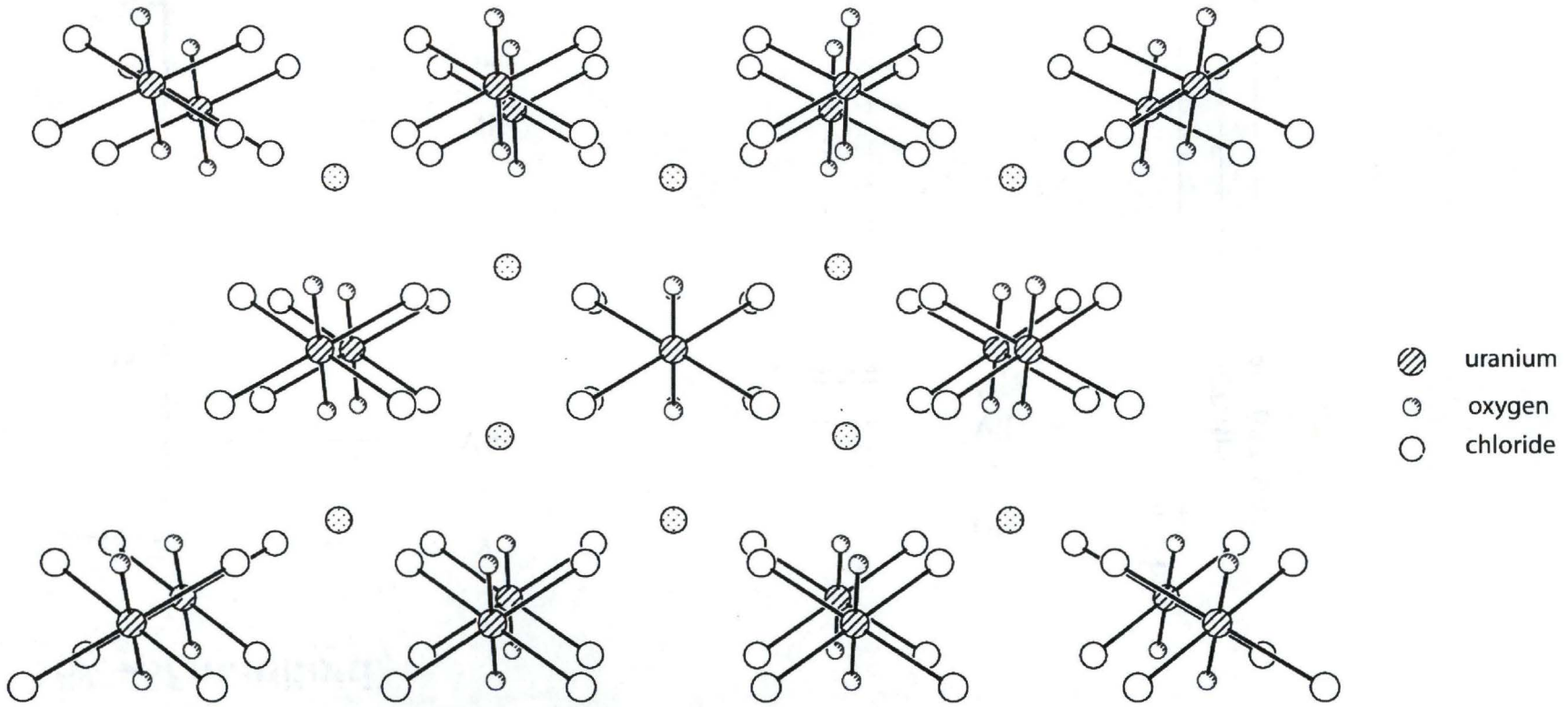
Self-quenching may be controlled by dilution of the analyte into host crystals that have sites of appropriate size for accommodation of the dopant, are chemically unreactive with the dopant, and lack high frequency vibrational modes that could serve as acceptors for radiationless deactivation.



Watkin, D. J.; Denning, R. G.; Prout, K. *Acta Crystallogr.* 1991, *C47*, 2517.

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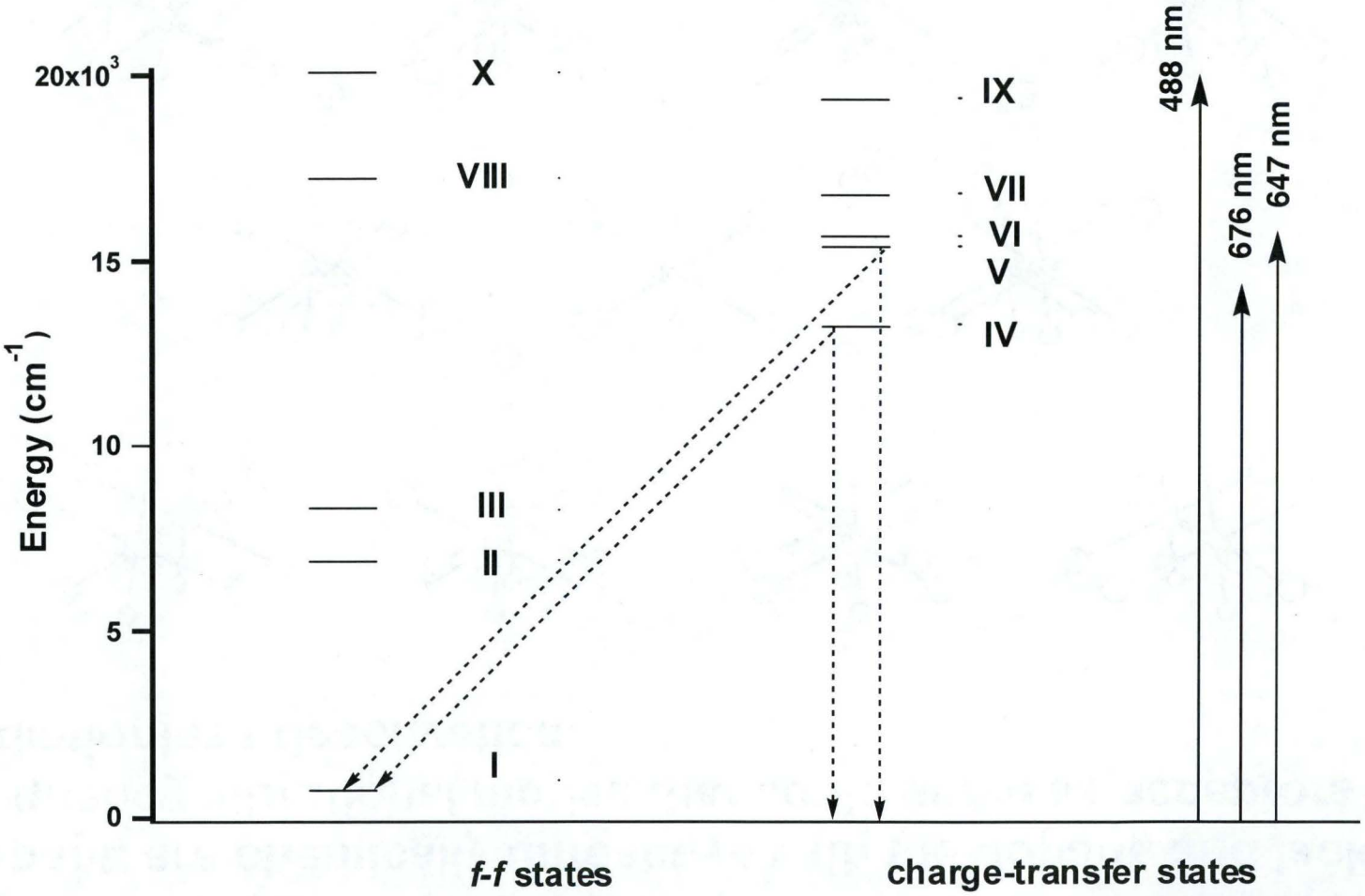
Emission spectra from Denning's group suggest that excited states in the LMCT manifold of $Cs_2NpO_2Cl_4$:$Cs_2UO_2Cl_4$ relax to both the ground state and the first excited electronic state, which lies in the *5f*→*5f* manifold.



Stone, P. J. *Dissertation*, University of Oxford 1986.

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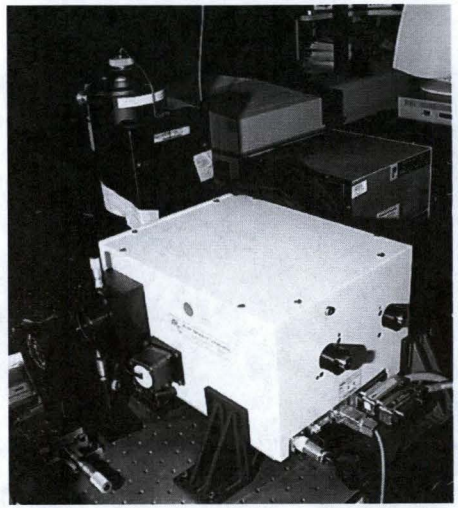
Optical layout of laser excitation and near-infrared detection



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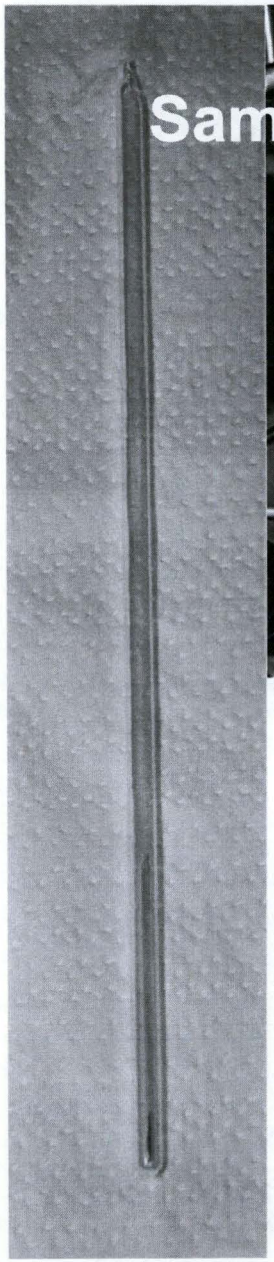
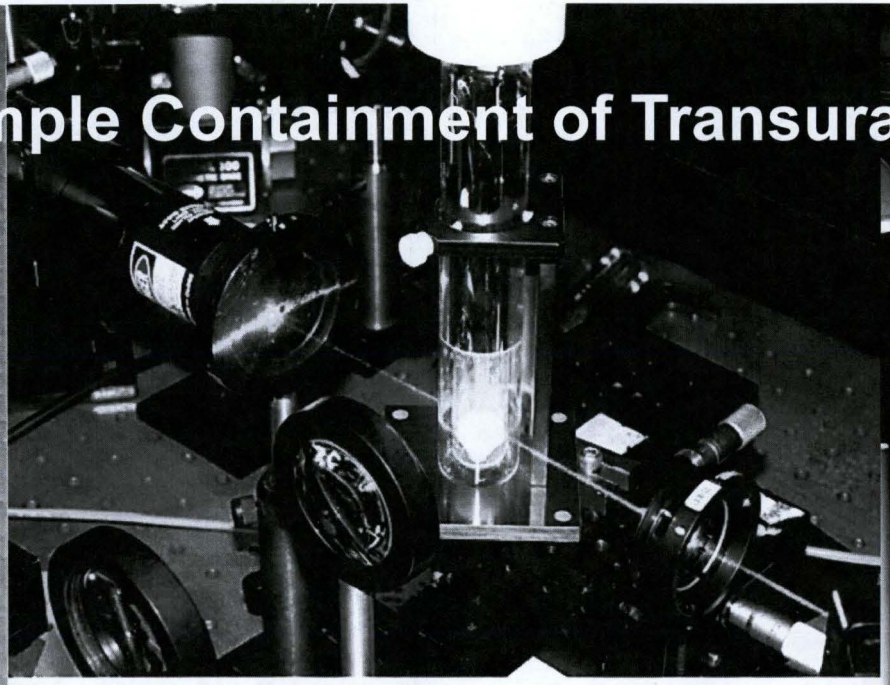
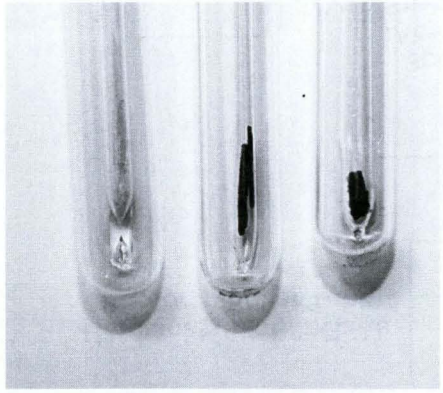
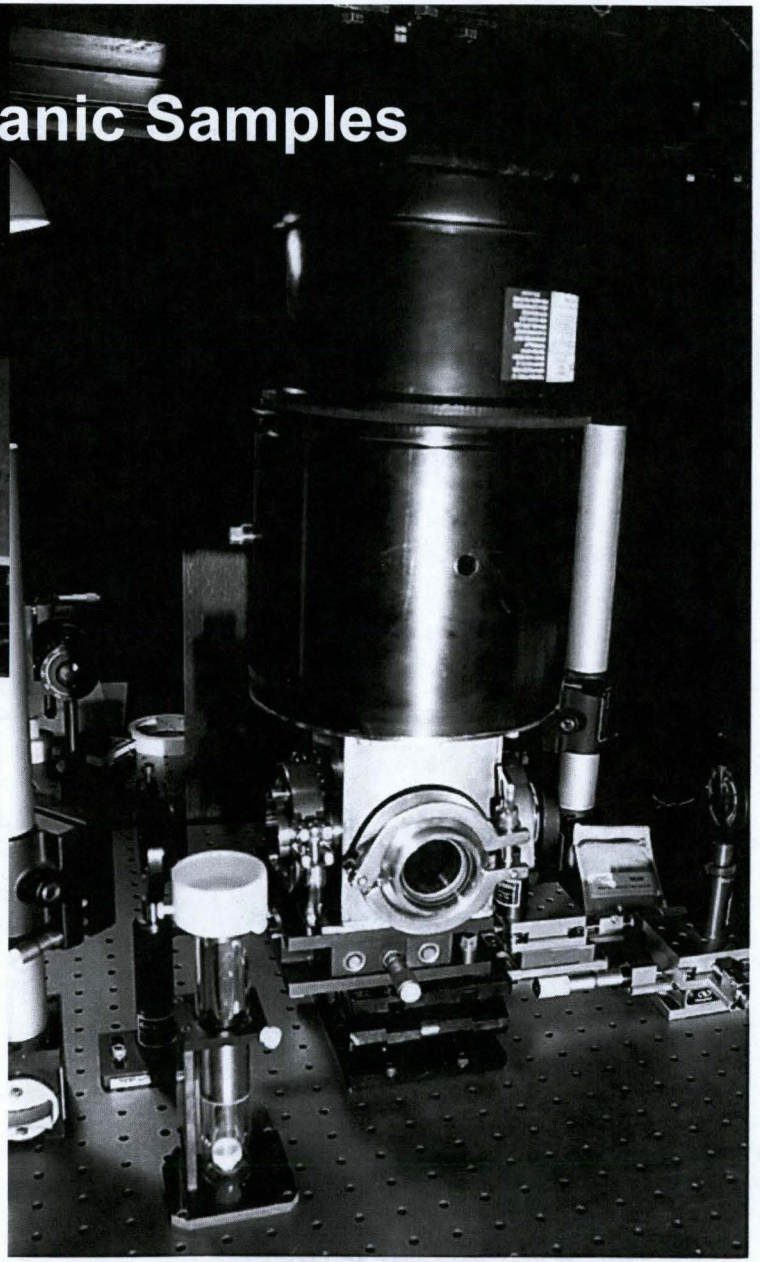
Sample Containment of Transuranic Samples

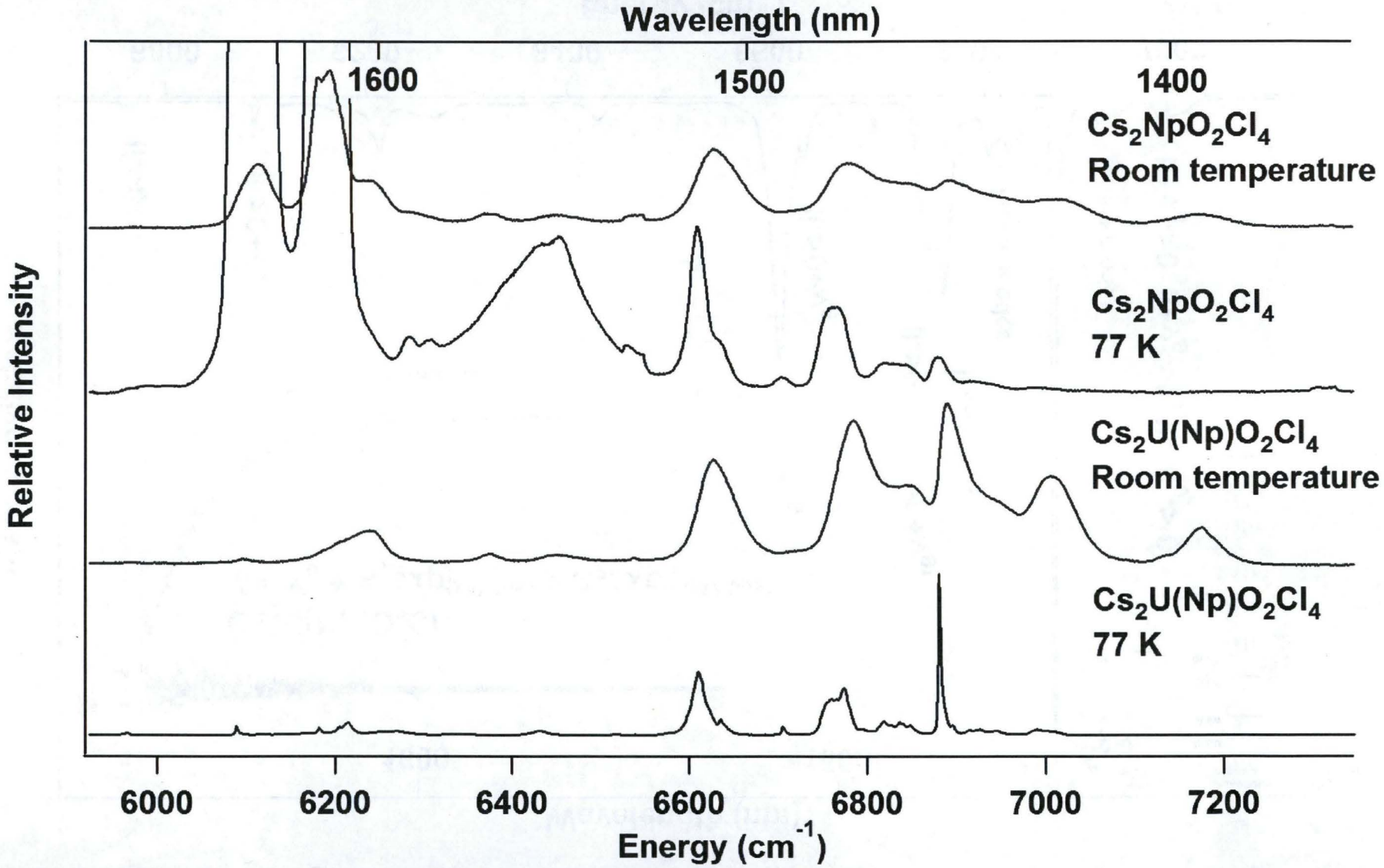








We measure photoluminescence from solid samples containing NpO_2^{2+} at room temperature and liquid nitrogen temperatures.



1. Wilkerson, M. P.; Arrington, C. A.; Berg, J. M.; Scott, B. L. *J. Alloys Compd.* 2007, *444-445*, 634.
2. Wilkerson, M. P.; Berg, J. M.; Hopkins, T. A.; Dewey, H. J. *J. Solid State Chem.* 2005, *178*, 584.

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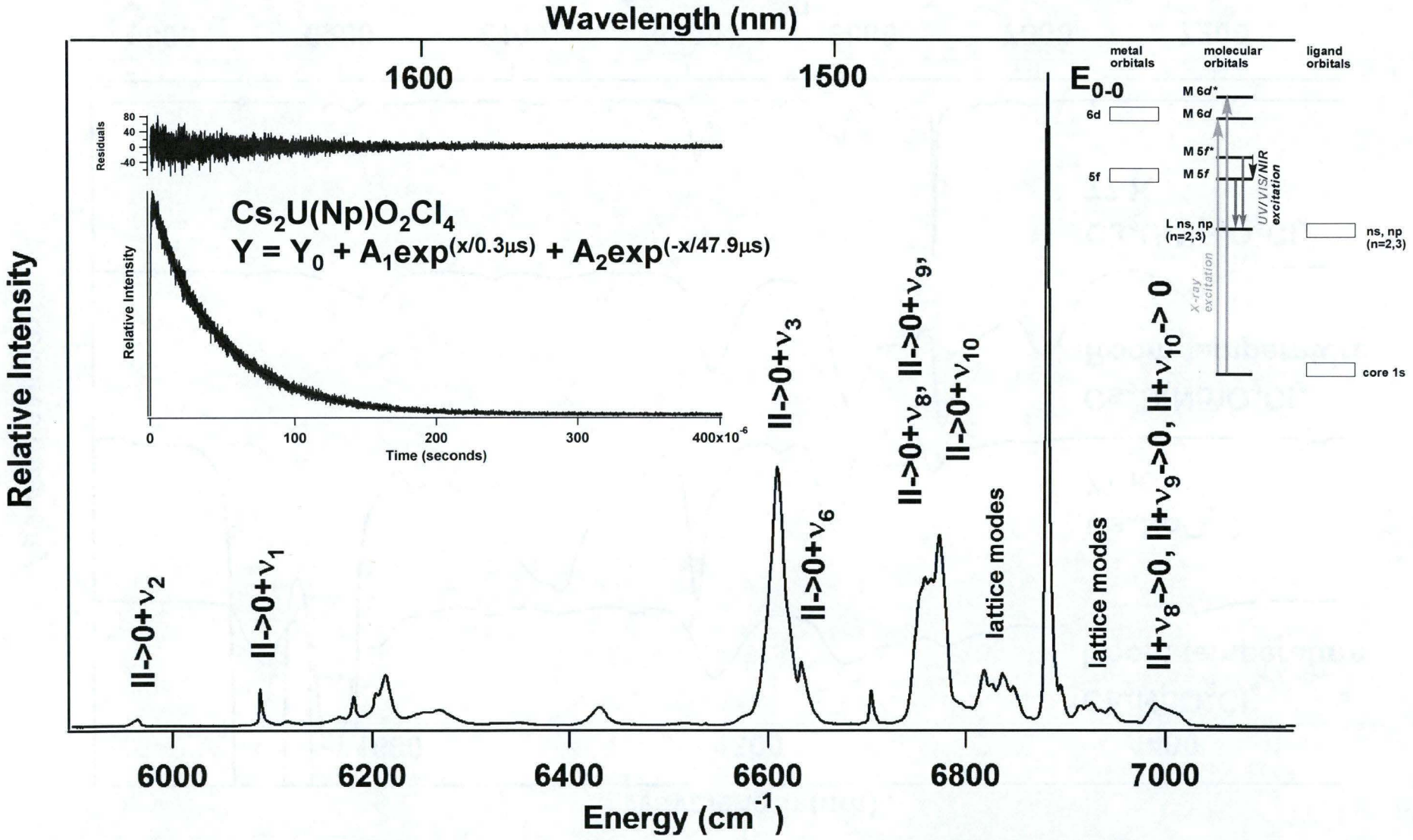
Emission spectra (λ_{exc} = 628 nm) of $Cs_2U(Np)O_2Cl_4$ at 75K reveals a well-defined origin and vibronic structure.



Wilkerson, M. P.; Berg, J. M.; Hopkins, T. A.; Dewey, H. J. *J. Solid State Chem.* 2005, *178*, 584.

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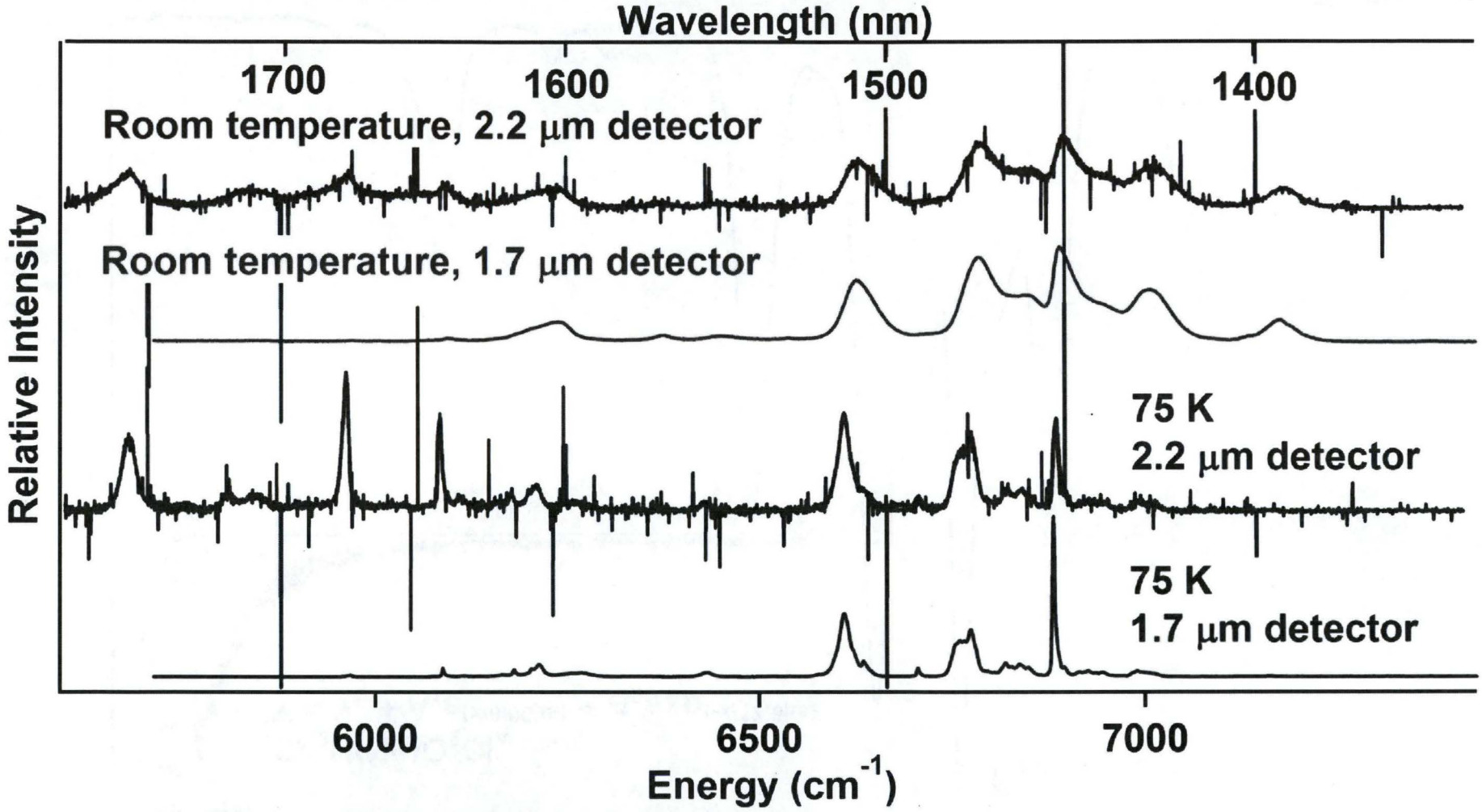
A 2.2 μm detector provide access to additional transitions.



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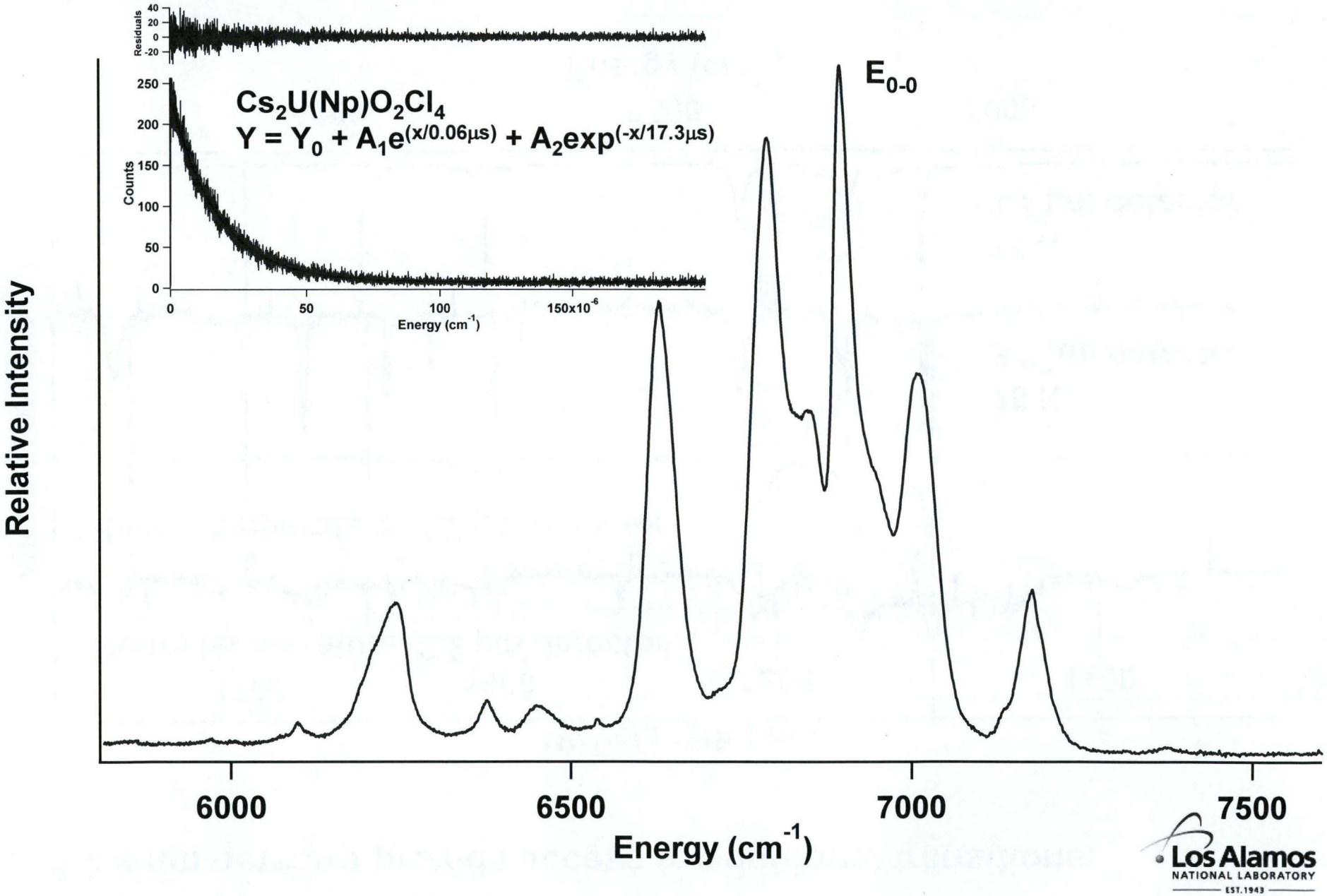
Relaxation pathways (λ_{exc} = 628 nm) of $Cs_2U(Np)O_2Cl_4$ at room temperature are competitive with nonradiative pathways.



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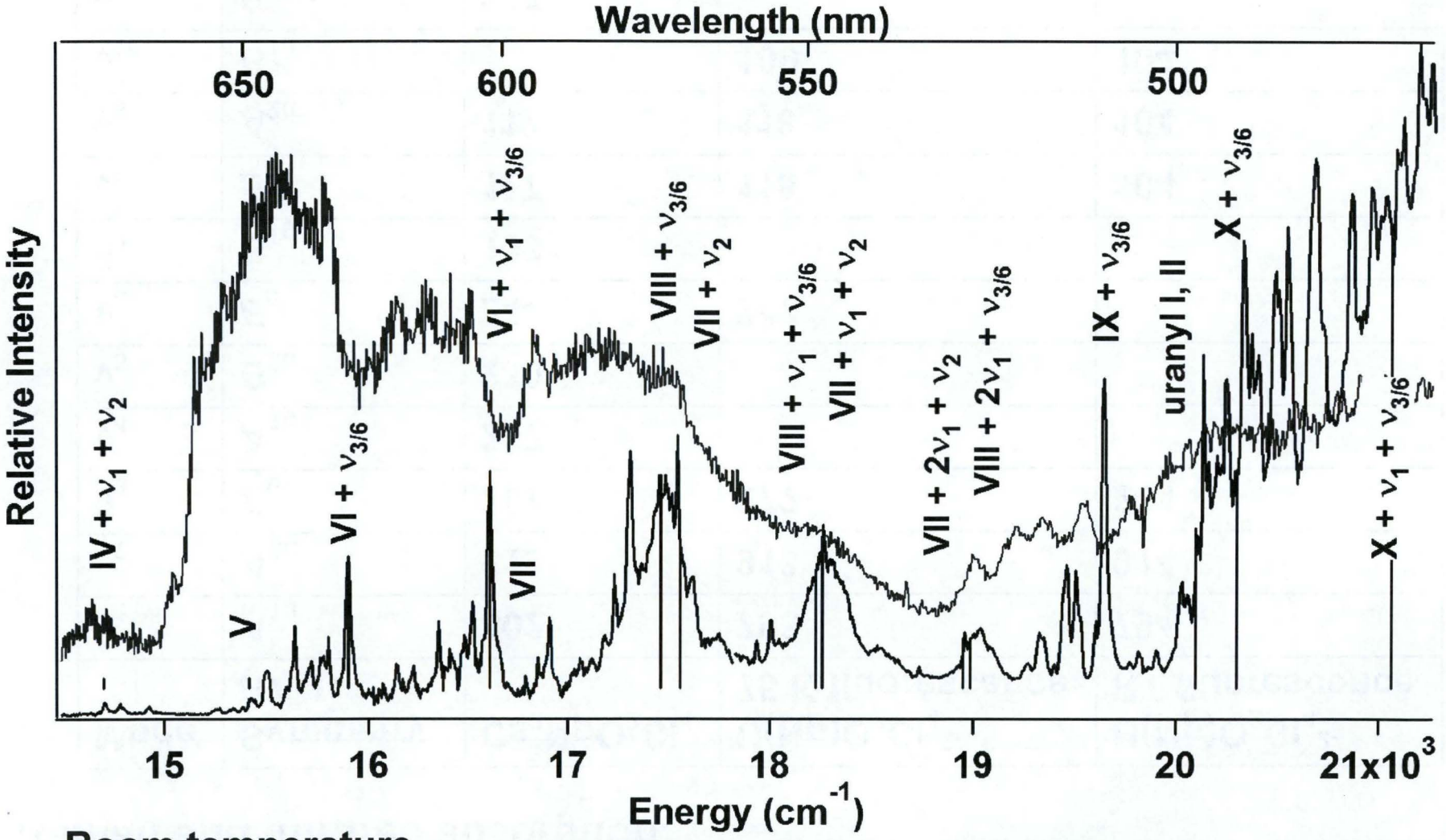
Vibrational frequencies from our emission spectra of $Cs_2U(Np)O_2Cl_4$ are comparable to the frequencies of neat $Cs_2NpO_2Cl_4$ measured by Raman and infrared absorption.

Mode	Symmetry (D_{4h})	$Cs_2NpO_2Cl_4$	$U(Np)O_2Cl_4^{2-}$ 75 K fluorescence	$U(Np)O_2Cl_4^{2-}$ RT fluorescence
ν_1	A_{1g}	802	793	794
ν_2	A_{2u}	919	913	914
ν_3	E_u	267	272	264
ν_4	A_{1g}	257		
ν_5	B_{2u}	230		
ν_6	E_u	244	247	
ν_7	B_{1g}	133		
ν_8	E_u	117	118	104
ν_9	A_{2u}	117	118	104
ν_{10}	B_{1u}		109	104
ν_{11}	E_g	185		

Denning, R. G.; Norris, J. O. W.; Brown, D. *Mol. Physics* 1982, *46*, 325.

Excitation spectra (λ_{em} = 6880.6 cm^{-1}) are consistent with $Cs_2U(Np)O_2Cl_4$ absorption spectra.



Room temperature
Liquid nitrogen

Wilkerson, M. P.; Berg, J. M. *Radiochim. Acta* 2009, *97*, 223-226.
Denning, R. G.; Norris, J. O. W.; Brown, D. *Mol. Physics* 1982, *46*, 325.

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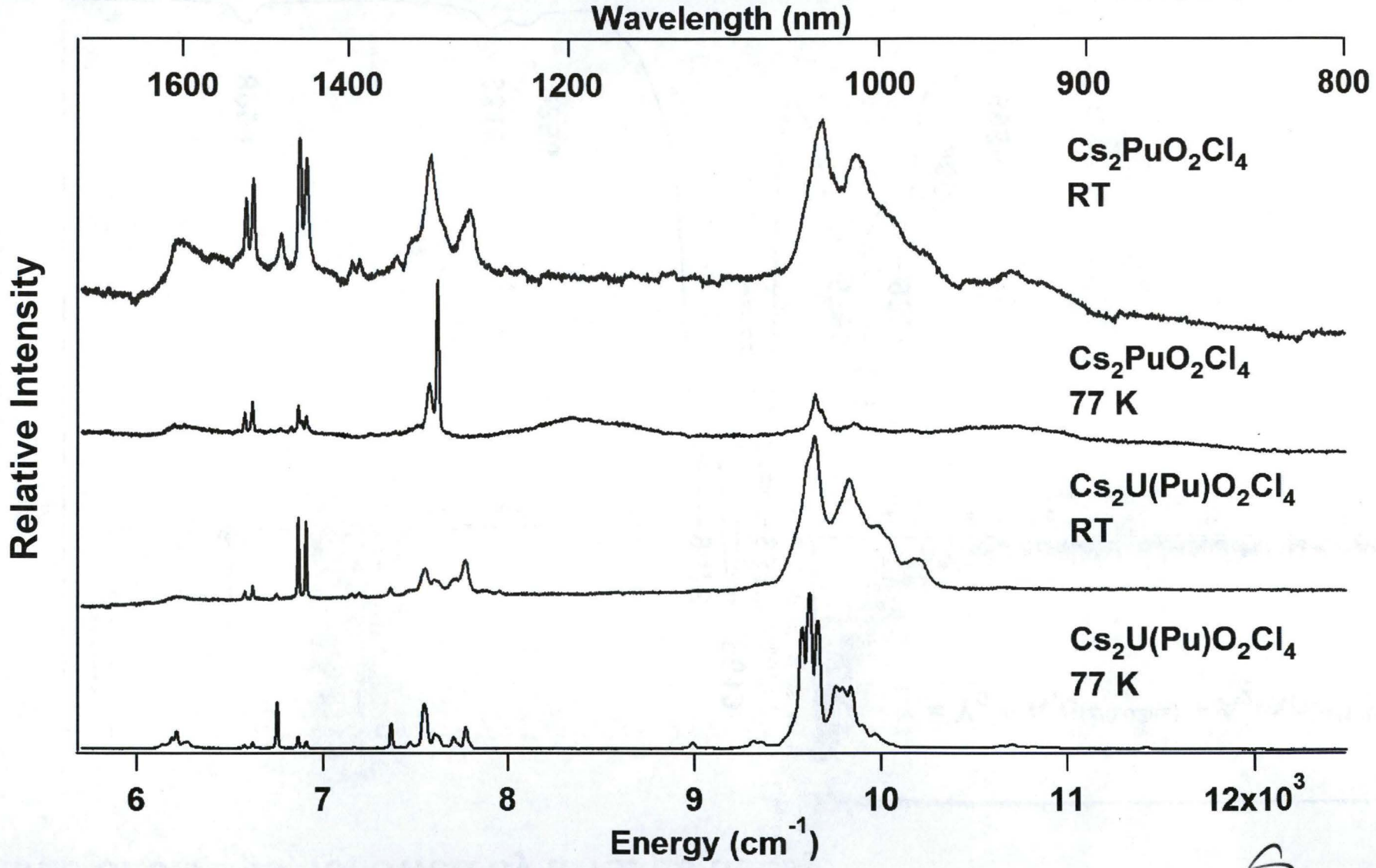
We measure photoluminescence emission from solid samples containing plutonyl at room and liquid nitrogen temperatures.



Wilkerson, M. P.; Berg, J. M. *J. Phys. Chem. A* 2008, *112(12)*, 2515.

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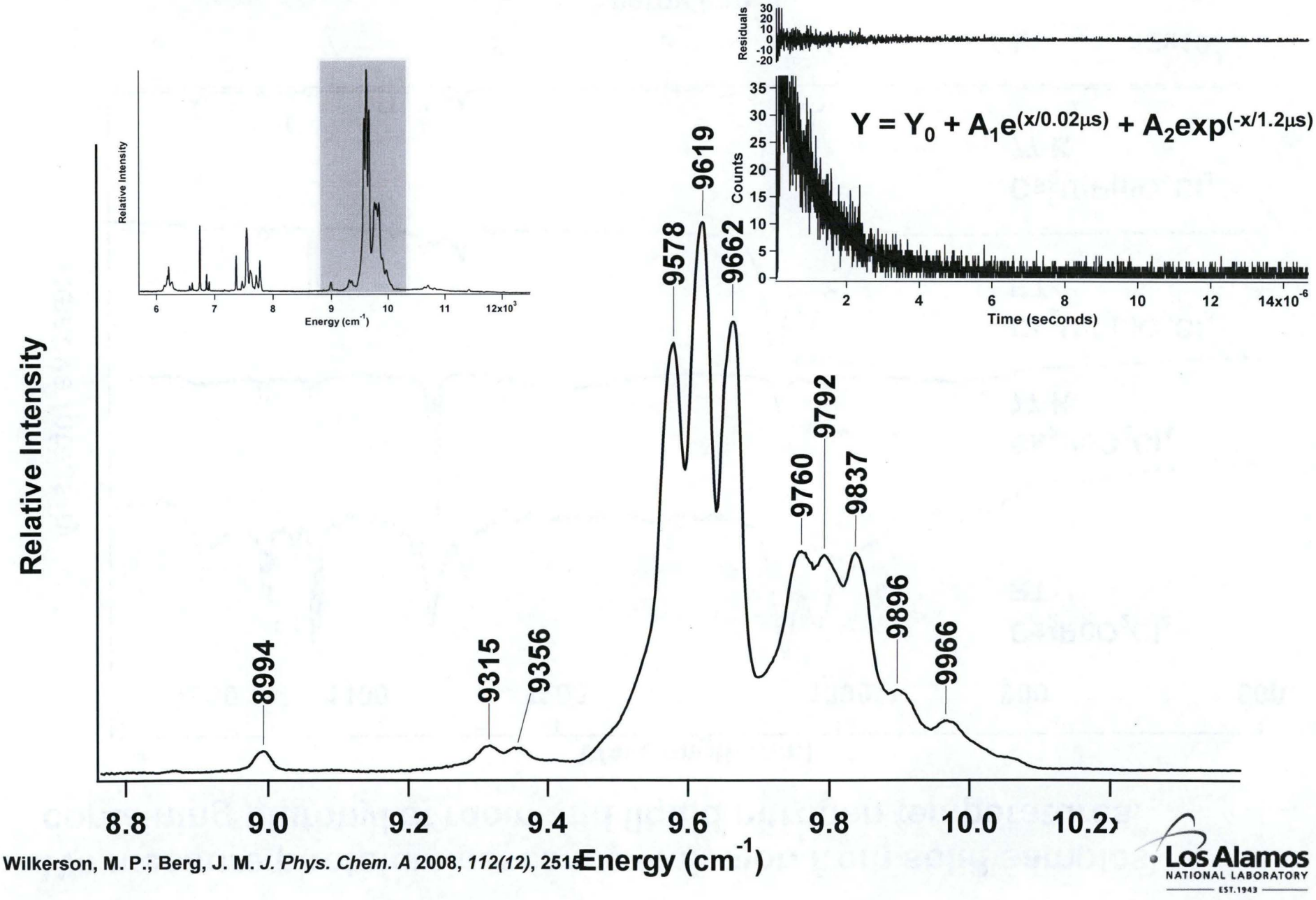
The lifetimes of peaks centered around 9619 cm^{-1} each fit to a rise time of 0.02 μs, followed by a 1.2 μs decay.



Wilkerson, M. P.; Berg, J. M. *J. Phys. Chem. A* 2008, *112(12)*, 2515

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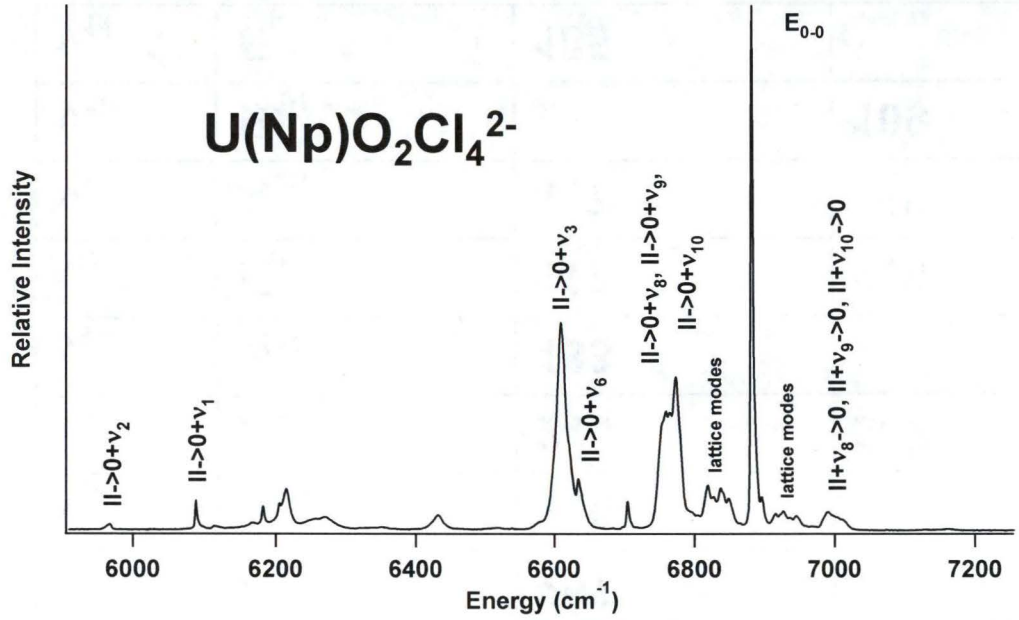
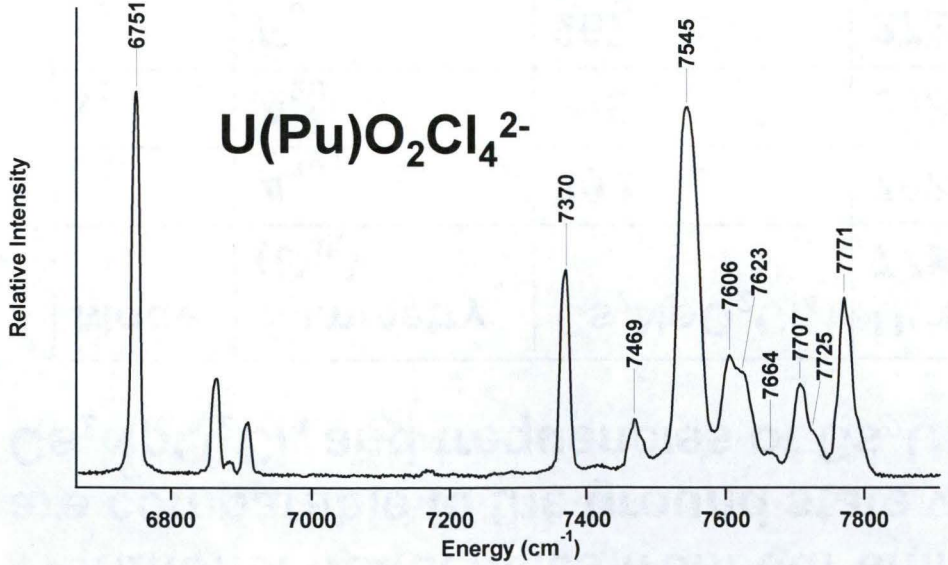
Vibronic structure around 7664 cm^{-1} is similar in profile to *5f-5f* transitions measured from $U(Np)O_2Cl_4^{2-}$ (blue).

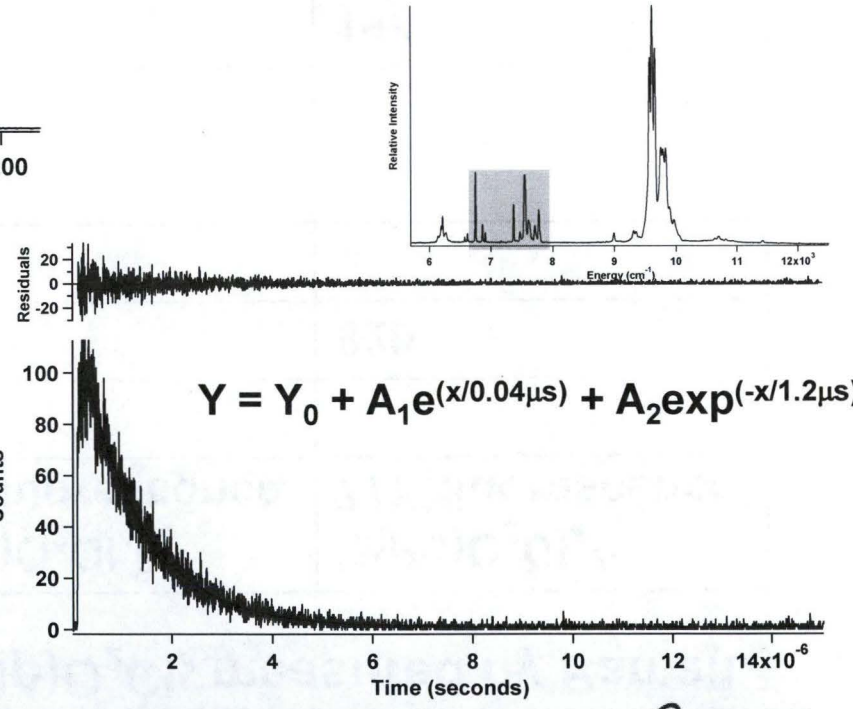


$Cs_2U(Np)O_2Cl_4$

$Y = A_1e^{-x/0.3\mu s} + A_2exp^{x/47.9\mu s}$

Wilkerson, M. P.; Berg, J. M.; et. al. *JSSC*, 2005, *178*, 584.





$Y = Y_0 + A_1e^{(x/0.04\mu s)} + A_2exp^{(-x/1.2\mu s)}$

Wilkerson, M. P.; Berg, J. M. *J. Phys. Chem. A* 2008, *112(12)*, 2515.

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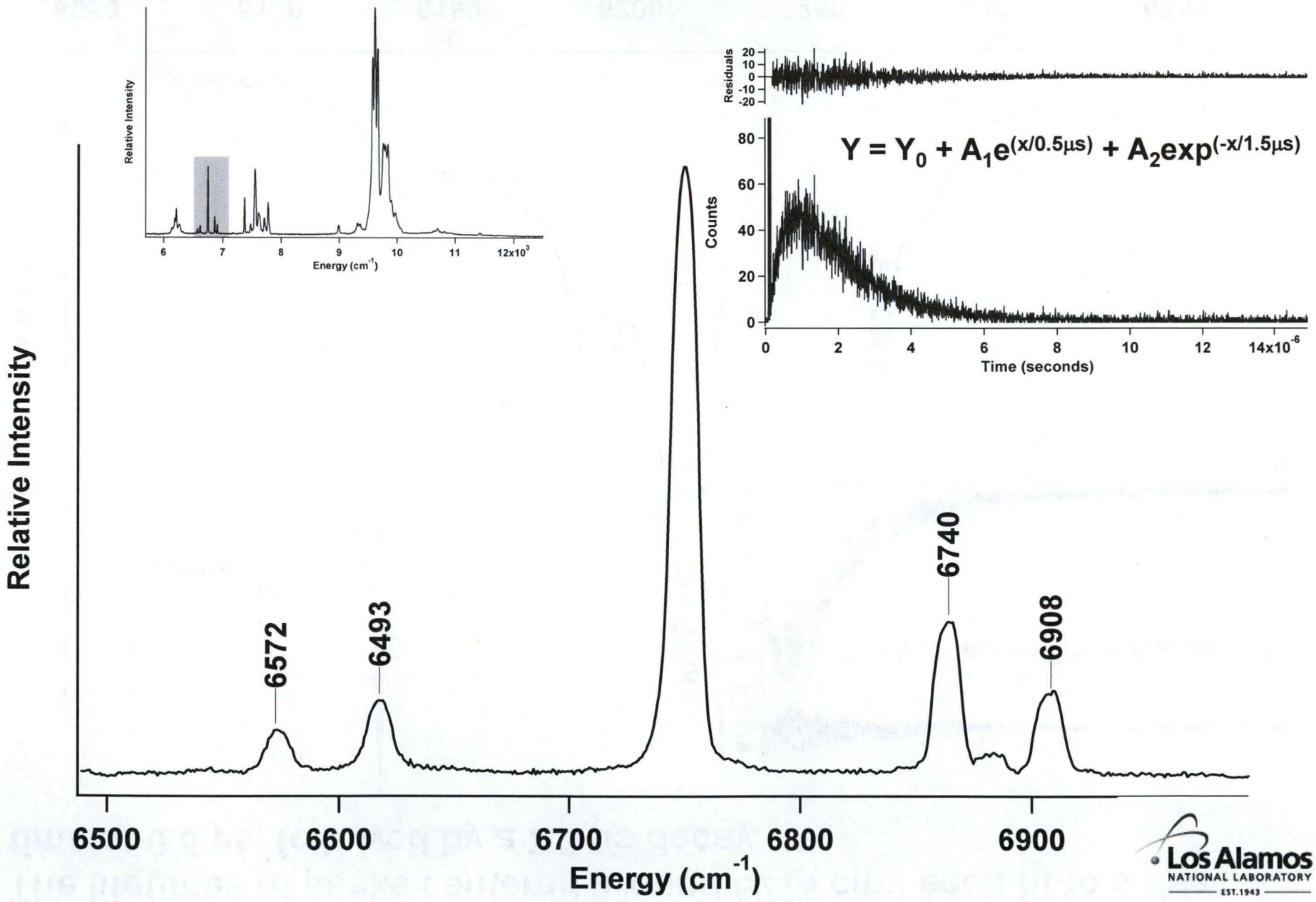
Vibrational frequencies from our emission spectra of $Cs_2U(Pu)O_2Cl_4$ are comparable to the ground state vibrational frequencies of neat $Cs_2NpO_2Cl_4$ and frequencies of $Cs_2U(Np)O_2Cl_4$ measured by Raman.

Mode	Symmetry (D_{4h})	$Cs_2NpO_2Cl_4$	$U(Np)O_2Cl_4^{2-}$ 77K fluorescence	$U(Pu)O_2Cl_4^{2-}$ 77K fluorescence
ν_1	A_{1g}	802	793	
ν_2	A_{2u}	919	913	920
ν_3	E_u	267	272	
ν_4	A_{1g}	257		
ν_5	B_{2u}	230		
ν_6	E_u	244	247	197
ν_7	B_{1g}	133		
ν_8	E_u	117	118	121
ν_9	A_{2u}	117	118	121
ν_{10}	B_{1u}		109	
ν_{11}	E_g	185		

1. Denning, R. G.; Norris, J. O. W.; Brown, D. *Mol. Physics* 1982, *46*, 325.
2. Wilkerson, M. P.; Berg, J. M.; Hopkins, T. A.; Dewey, H. J. *JSSC* 2005, *178*, 584.

The lifetimes of peaks centered around 6740 cm^{-1} each fit to a rise time of 0.5 μs, followed by a 1.5 μs decay.



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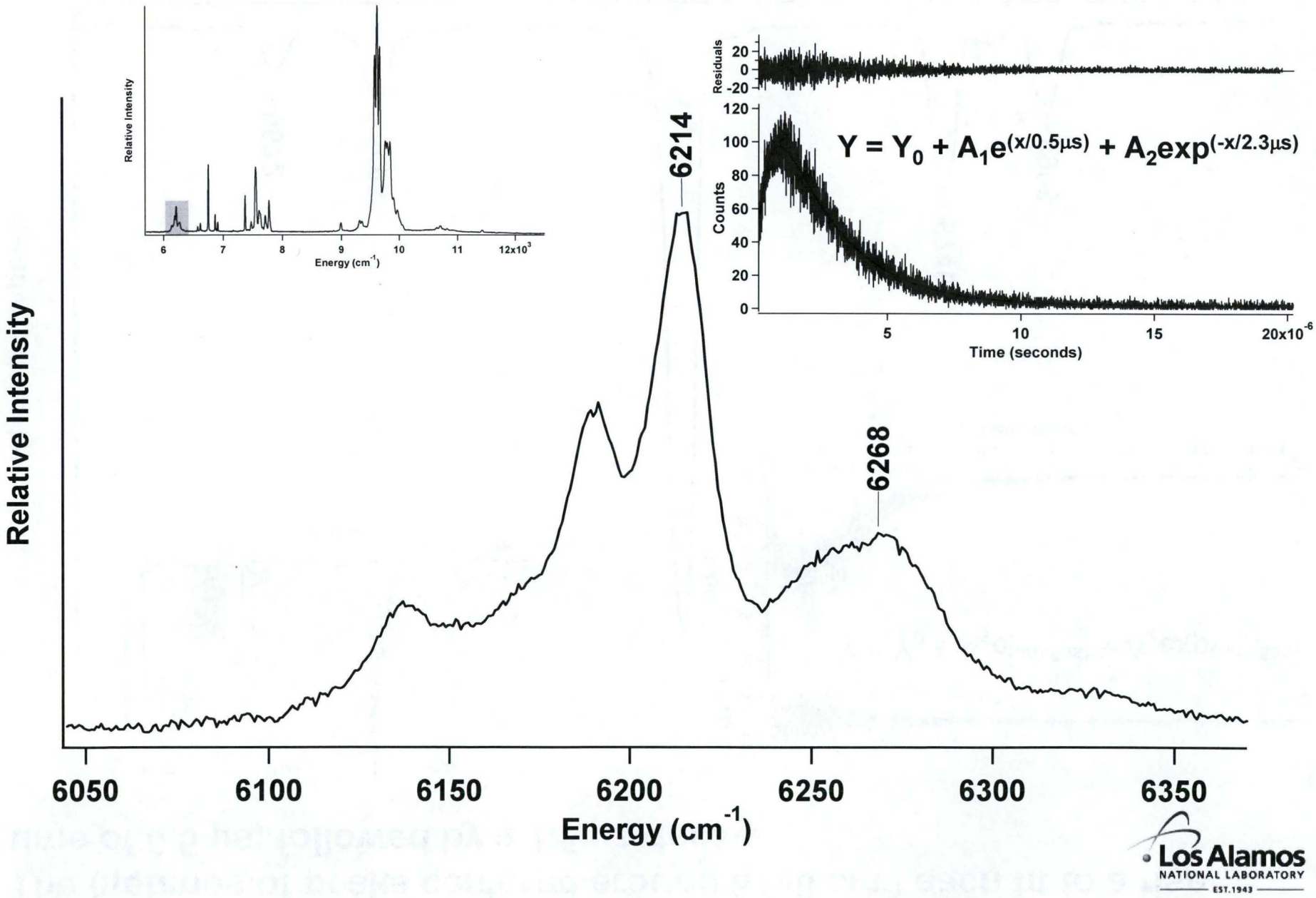
The lifetimes of peaks centered around 6214 cm^{-1} each fit to a rise time of 0.5 μs, followed by a 2.3 μs decay.



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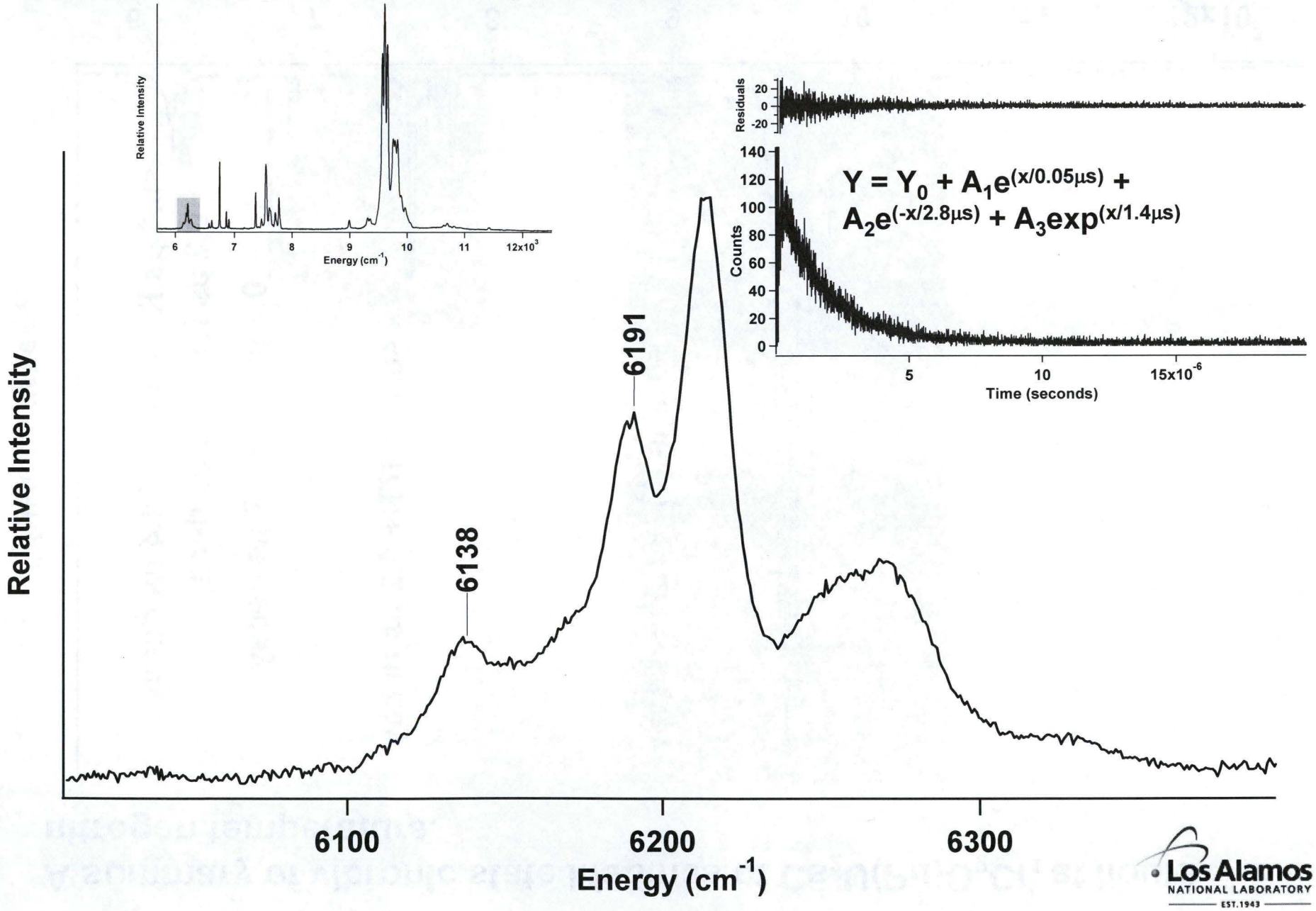
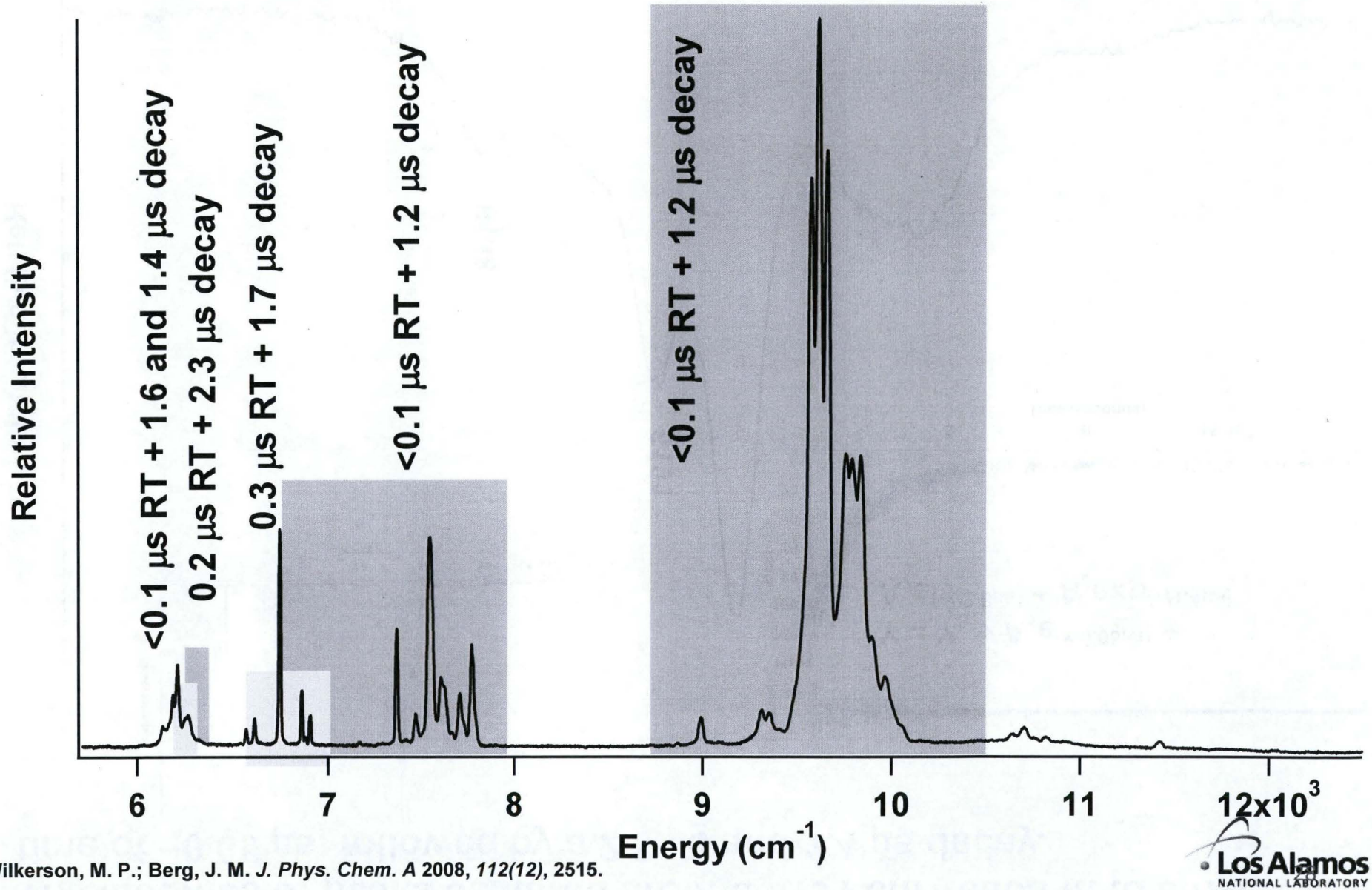
The lifetimes of peaks centered around 6191 cm^{-1} each fit to a rise time of ~0.05 μs, followed by a 2.8 μs and 1.4 μs decay.



A summary of vibronic state lifetimes of $Cs_2U(Pu)O_2Cl_4$ at liquid nitrogen temperature.



Wilkerson, M. P.; Berg, J. M. *J. Phys. Chem. A* 2008, *112(12)*, 2515.

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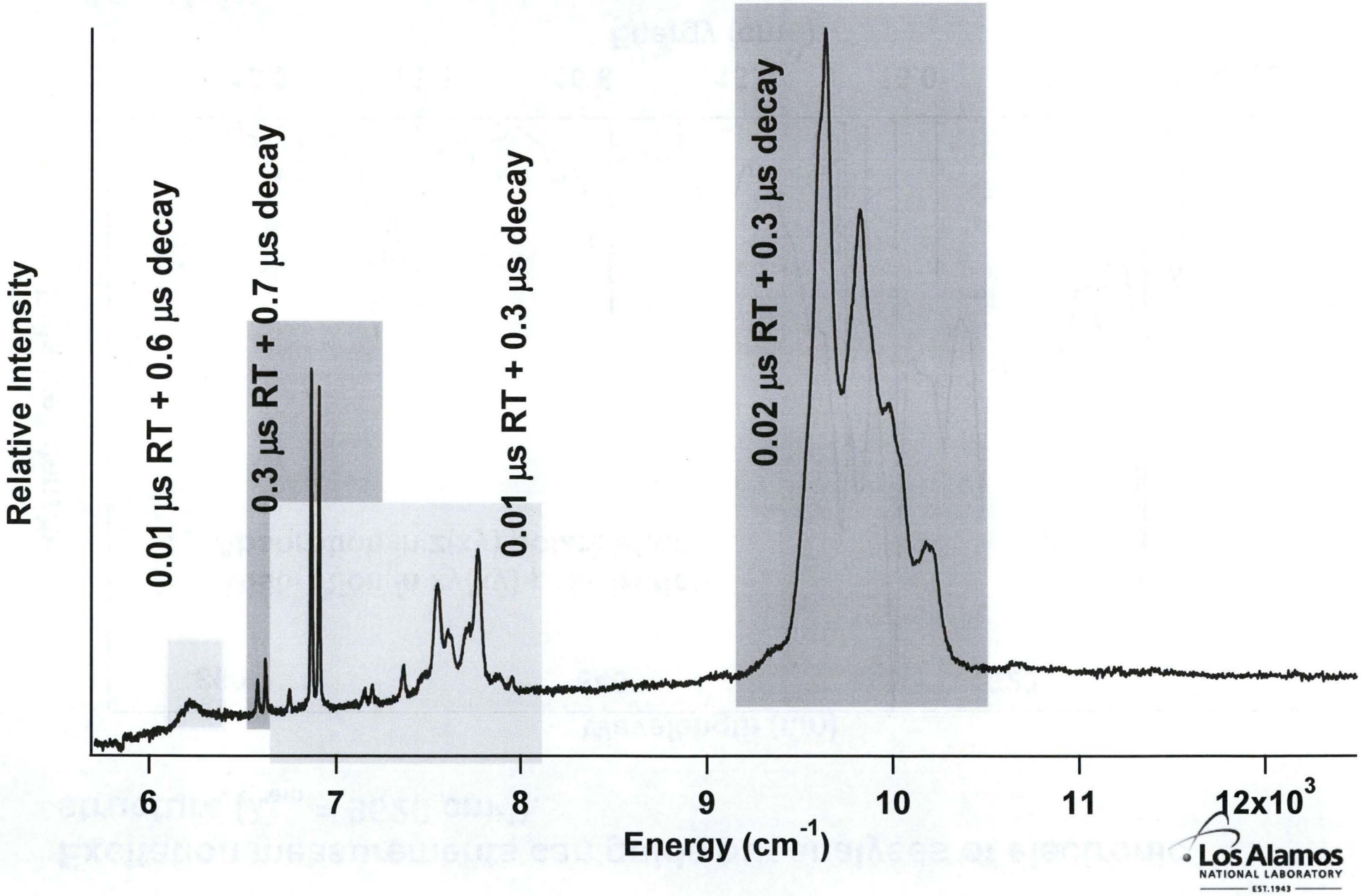
A summary of vibronic state lifetimes of $Cs_2U(Pu)O_2Cl_4$ at room temperature.



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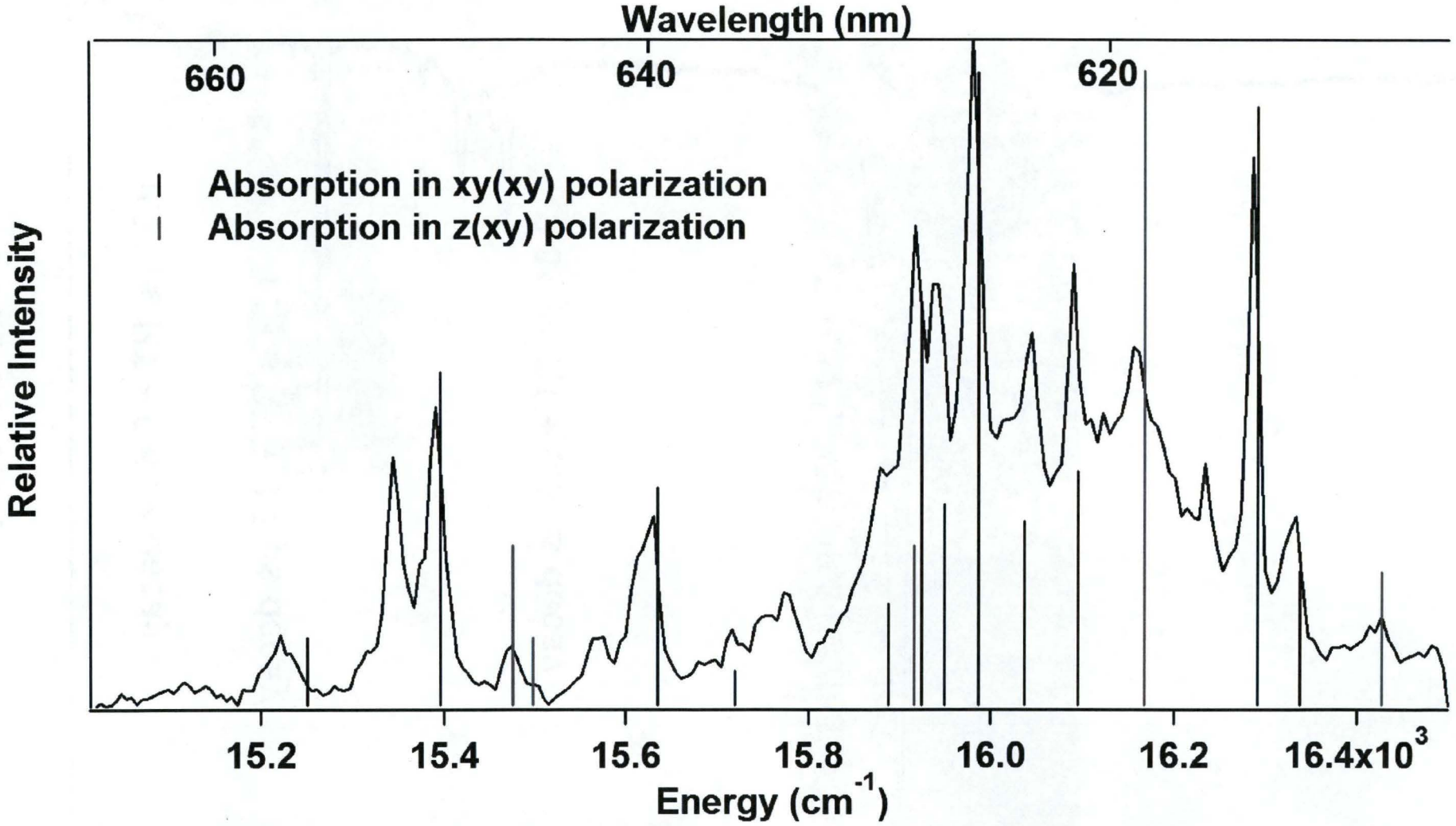
Excitation measurements can guide our analyses of electronic structure (λ_{em} = 9620 cm^{-1}).



Gorshkov, N. G.; Mashirov, L. G. *Radiokhimiya* 1985, *27(5)*. 511.
Wilkerson, M. P.; Berg, J. M. *J. Phys. Chem. A* 2008, *112(12)*, 2515.

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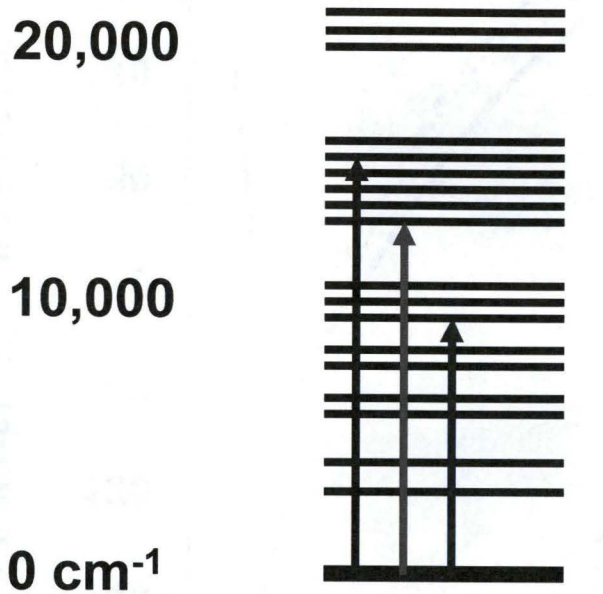
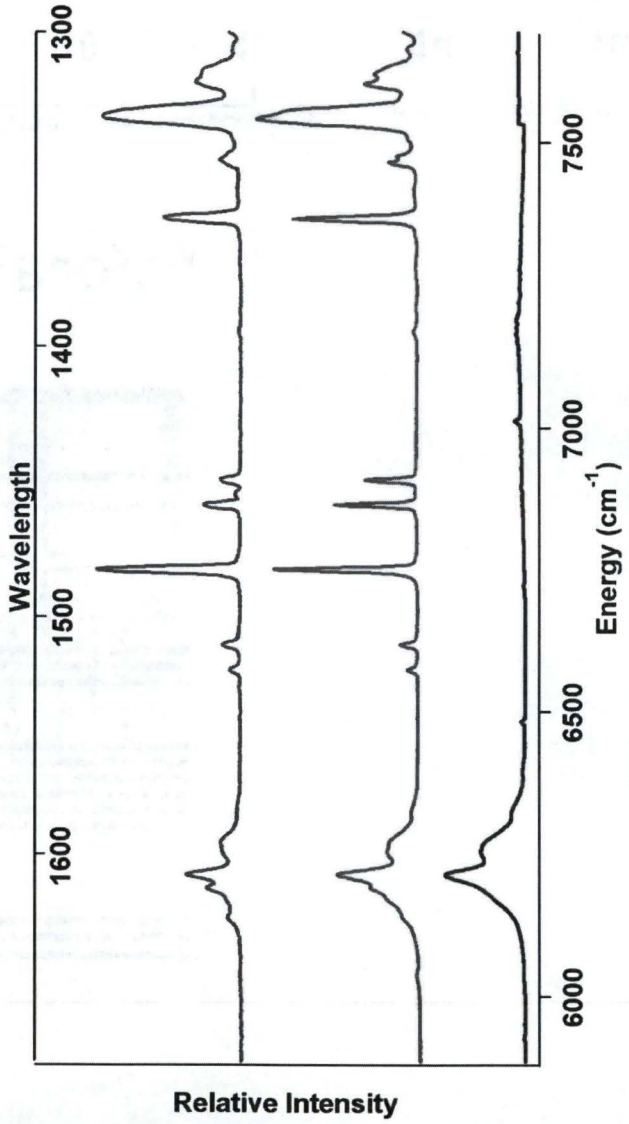
We can lower the excitation energy in order to cut off relaxation pathways.

λ_{exc} = 628 nm
λ_{exc} = 980 nm
λ_{exc} = 1170 nm



$Cs_2PuO_2Cl_4$



Berg, J. M.; Wilkerson, M. P. *Mater. Res. Soc. Symp. Proc.* 2008, 1104-NN08-08.

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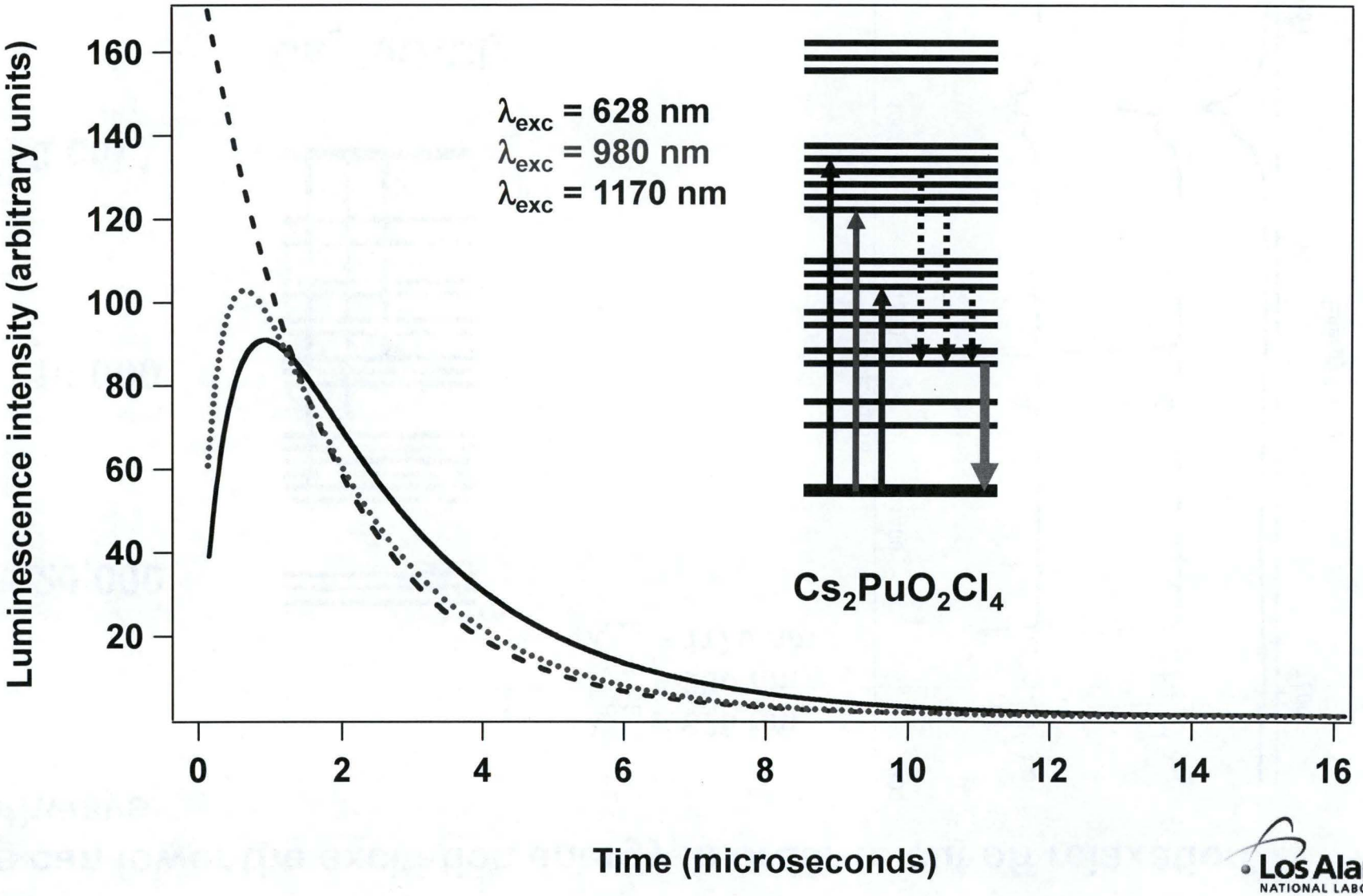
Kinetics of 6200 cm^{-1} luminescence vary with excitation energy.



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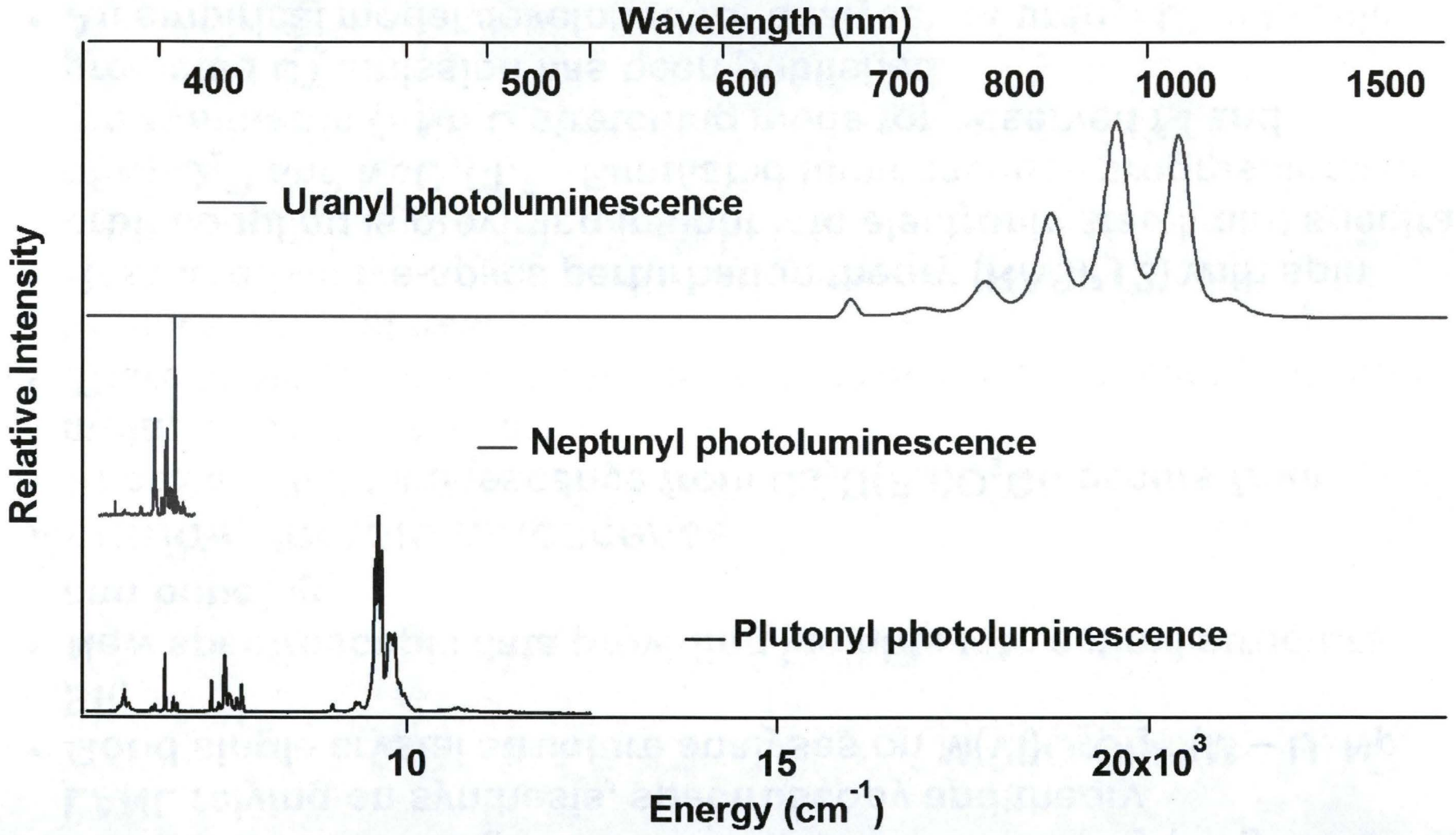
Optical spectra of UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+} are measurably different in terms of numbers of transitions and transition energies.



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Results and Conclusions

- Results from an integrated Heavy Element Chemistry program at LANL relying on synthesis, spectroscopy and theory.
- Good single crystal structure analyses on $M(VI)O_2Cl_4^{2-}$ (M – U, Np, Pu)
- New spectroscopic data providing insights into actinyl structure and bonding

Actinide Photoluminescence

- Photo-excited luminescence from $Cs_2U(Pu)O_2Cl_4$ occurs from multiple excited states.
- There is evidence for multi-step excitation decay involving several luminescence states.
- Restricted-active-space perturbation theory (RASPT2) with spin orbit coupling is providing insight into electronic states and spectra of NpO_2^{2+} and $NpO_2Cl_4^{2-}$. Simulated luminescence progressions of the symmetric O-Np-O stretching mode for observed f-f and predicted CT emission has been published.
- An empirical model developed for analyses of uranyl CT vibronic transitions is been employed to simulate excitation spectra of neptunyl compounds of different compositions and structural symmetries.

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Heavy Element Chemistry Program