# Low temperature absorption spectra and ground state electronic structure of tetrakis(2,6-di-tert-butylphenoxide)uranium(IV)

## John M. Berg

*Nuclear Materials Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)*

## Abstract

We present low temperature visible and near-IR intra-$5f^2$ electronic absorption spectra of $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$, a compound of near-$T_d$ point group symmetry about the uranium. The ground state is tentatively assigned as having E symmetry in $T_d$, because the number of symmetry-allowed transitions is close to the number which we observed. Transitions out of an excited state 90 cm$^{-1}$ above the ground state were also observed. This state is assigned to $A_1$ symmetry, again based on counting transitions. These assignments are consistent with magnetic susceptibility measurements.

## 1. Introduction

Optical spectroscopy of the homoleptic U(IV) aryloxide compound $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ could give a unique insight into actinide electronic structure, because the complex exhibits an unusually high degree of symmetry. Its synthesis and characterization were described in a recent paper [1]. The characterization included the presentation of several optical spectra in solution, accompanied by a brief, qualitative discussion of the molecular properties that give rise to the observed features. In this paper, we present optical absorption data on microcrystalline solid samples at low temperature. Our discussion of these data focuses generally on the effect of the ligands in the $5f^2$ electronic configuration of the central U(IV) ion and, specifically, on the properties of the ground state and the lowest lying electronic state.

Analyses of the complicated $5f^n$ electronic configurations of actinide ions in coordination complexes challenge both spectroscopic assignment methods and the best current ligand field models. In complexes with high degrees of symmetry, degeneracies in the $5f^n$ configuration are split less extensively than in complexes with low degrees of symmetry, so producing simpler spectra. The observed degeneracies also place a number of constraints on the parameters that models produce to describe the energy levels. As a result, the best fit parameters are easier to determine and more reliable than those derived for more complex systems. Because $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ exhibits very close to tetrahedral symmetry about the uranium ion, we expect its absorption spectrum to reflect one of the simplest manifolds of $5f^2$ energy levels among the known U(IV) compounds.

As discussed in ref. 1, the single-crystal X-ray structure obtained at $-145$ °C (128 K) showed that the crystallographic symmetry is $S_4$. This means that all four ligands are equivalent. The symmetry of the $UO_4$ central group of atoms is only slightly distorted from $T_d$ to $D_{2d}$. Variable temperature $^1$H NMR (nuclear magnetic resonance) spectra in benzene-$d_6$ suggested that the solid state $S_4$ symmetry is preserved in solution at low temperatures but, with warming, the protons on opposites sides of the aromatic ring of the ligand become equivalent, indicating that the ligands are rotating rapidly on the NMR time-scale. The time-averaged symmetry is probably $T_d$ at room temperature, and we make the initial simplifying assumption that the optical spectra can be analyzed in this point group. We will discuss the effects of the slight distortions from this idealized symmetry after our initial analysis.

## 2. Experimental details and results

Samples of microcrystalline $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ were ground, mixed with KBr and pressed into pellets under a dry, oxygen-free argon atmosphere in a glovebox. The pellets were mounted on the cold finger of an optical cryostat and cooled with a closed-cycle helium refrigerator. The temperature was measured with a thermocouple located on the sample holder near the edge of the sample. Because of its poor thermal conductivity, the region of the sample probed by the optical beam was probably at a higher temperature than that
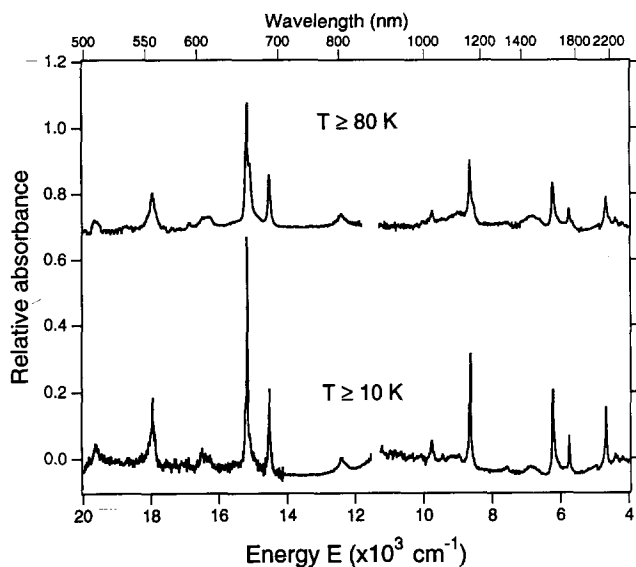
Fig. 1. Absorption spectra of microcrystalline U($O$-2,6-$t$-Bu₂C₆H₃)₄ in a KBr pellet at low temperature. A baseline linear in energy has been subtracted from each spectrum prior to plotting them in order to correct for increasing light scattering by the KBr pellet at shorter wavelengths. Temperatures are reported as measured at the sample holder. We believe the actual sample temperatures are higher.

which we measured at the holder. Since we do not have a reliable measurement of this difference, we simply report the measured temperature of the sample holder. The spectra were obtained with a PE330 grating spectrometer operating in transmition mode. Light scattering from the optically cloudy sample pellets increased nearly linearly with increasing photon energy. We compensated for this by subtracting a linear function of the photon energy from the acquired spectra, to make the base-line flat over the visible and near-IR regions.

We collected spectra from samples held at temperatures from 8 K up to room temperature. Two of these spectra, after base-line subtraction, are shown in Fig. 1. These spectra show considerable sharpening of the 5f–5f transitions compared with the room temperature spectra. All the major sharp features match closely those observed in toluene glass at 75 K [1] but there are small differences in some of the weaker peaks.

## 3. Discussion

In a field of $T_d$ symmetry, the $5f^2$ configuration splits into 40 electronic states. Transitions from the ground electronic state to approximately 30 of these should fall within the energy window 4500–20 000 cm⁻¹, which we were able to scan in the KBr matrix. The number of states that we observe in our spectra is expected to be somewhat less than this, because, for a ground state of any possible symmetry representation, symmetry se-

lection rules forbid transitions to a specific subset of the excited states. The number of forbidden transitions depends upon the symmetry transformation properties of the ground state. Here, the four symmetry possibilities for the ground state are $A_1$, E, $T_1$ and $T_2$. There should be one electronic state of each of these symmetries in the lowest energy group of states. The number of forbidden transitions is greatest for an $A_1$ ground state and decreases progressively through E, $T_1$ and $T_2$. More than two-thirds of the possible transitions are forbidden for an $A_1$ ground state, while only about one-tenth are forbidden for a $T_2$ ground state.

Counting the peaks in the lowest temperature spectrum in Fig. 1 gives a lower limit for the number of allowed transitions. We observe 19 distinct peaks between 4500 and 20000 cm⁻¹. Several of the peaks in this list are broad enough that they may consist of two or more unresolved transitions, so the actual number of allowed transitions may be slightly higher. This peak count is more than twice the number of peaks allowed in $T_d$ if the ground state transforms as $A_1$. It also exceeds the number of peaks expected for an E ground state, though only by about 20%. For a $T_1$ or $T_2$ ground state, the number of observed peaks is about 20% less than the expected number of symmetry-allowed transitions. Thus, the peak count supports the assignment of the ground state as either $T_1$ or $T_2$, and is marginal for a ground state of E symmetry. It argues strongly against the assignment of the ground state as $A_1$.

As the temperature is increased, several new absorption bands grow into the spectrum. All these thermally activated transitions — or hot bands — appear 90 cm⁻¹ lower in energy than one of the low temperature absorption bands. No hot bands are observed elsewhere in the spectrum. Also, hot bands do not grow adjacent to all the low temperature absorption bands. These observations indicate that there is an excited electronic state 90 cm⁻¹ in energy above the ground electronic state.

We do not believe that the observed hot bands can be assigned to transitions originating from a vibronic level of the ground electronic state, primarily because no excited-state vibronic levels appear in our spectra. Since the excited states and the ground state all originate from the $5f^2$ configuration, a large effect of vibronic interactions on the transition probabilities should not be unique to the ground state. Also, unlike the case of complexes of $O_h$ symmetry, $T_d$ complexes have no inversion center, so do not require vibronic interactions to make electric dipole transitions parity allowed.

Because only some of the states accessible from the ground state via the absorption of a single optical photon appear to be accessible from the thermally populated state and no additional excited states are accessible, the thermally populated state must be of a

symmetry from which transitions are allowed only to a subset of the states which are accessible from the ground state. Since there are hot bands associated with six of the eight transitions out of the ground state which are strong and narrow enough to be observed, we have a very rough measure of the ratio of the allowed transitions out of the ground and 90 cm$^{-1}$ states. This ratio is consistent with the ground state–excited state combinations T$_2$–E, T$_1$–E and E–A$_1$, each of which should result in more than half of the transitions out of the ground state being allowed out of the excited state. It argues moderately against T$_1$–A$_1$ and T$_1$–A$_1$ combinations, because less than half as many states should be accessible out of the A$_1$ state. It also argues strongly against E–T$_1$, E–T$_2$ or an A$_1$ ground state in combination with any excited-state symmetry, because these possibilities would all produce more allowed transitions out of the excited state than out of the ground state.

The magnetic susceptibility of this compound has been measured recently [2, 3] and it is currently being modeled [3]. It shows clear evidence of a temperature-independent paramagnetic behavior below about 30 K. This is not consistent with a T$_1$ or T$_2$ ground state, but it is consistent with either an E or A$_1$ ground state.

Taken together, the evidence from our preliminary analysis suggests an E ground state and an A$_1$ excited state, because these assignments predict more transitions out of the ground state than out of the excited state, and they predict a temperature-independent paramagnetic behavior at low temperatures. However, we count slightly more peaks in our absorption spectra than should be allowed by symmetry out of an E ground state. It is possible that additional transitions become allowed through the slight distortion of the complex from T$_d$ symmetry to the actual S$_4$ symmetry shown in the X-ray structure.

We are currently modeling the magnetic susceptibility to determine if it can be reproduced using this lower symmetry crystal field. We are also hopeful that synthetic efforts now under way will produce isostructural analoges with slightly different distortions from effective T$_d$ symmetry, so that we can quantify the effects on the energies of the ligand field levels.

## Acknowledgments

## References

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