

Lawrence Berkeley National Laboratory

Recent Work

Title

The 5f $\rightarrow$ 6d Absorption Spectrum of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

Permalink

<https://escholarship.org/uc/item/81v2k735>

Journal

Journal of Chemical Physics, 96(1)

Authors

Edelstein, N.

Kot, W.K.

Krupa, J.-C.

Publication Date

1991-08-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Journal of Chemical Physics

The $5f \rightarrow 6d$ Absorption Spectrum of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

N. Edelstein, W.K. Kot, and J.-C. Krupa

August 1991



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

1 LOAN COPY 1
1 Circulates 1
1 for 4 weeks 1 Bldg. 50 Library.
Copy 2

LBL-31108

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

The $5f \rightarrow 6d$ Absorption Spectrum of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

N. Edelstein and Wing K. Kot

Chemical Sciences Division

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

and

J.-C. Krupa

Laboratoire de Radiochimie, Institut de Physique Nucleaire

Universite de Paris-Sud, B.P. 1

91406 Orsay Cedex, France

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

The $5f \rightarrow 6d$ Absorption Spectrum of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

N. Edelstein and Wing K. Kot
Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

and

J.-C. Krupa
Laboratoire de Radiochimie, Institut de Physique Nucleaire
Universite de Paris-Sud, B.P. 1
91406 Orsay Cedex, France

Abstract

The $5f^1 \rightarrow 6d^1$ absorption spectrum of $^{231}\text{Pa}^{4+}$ diluted in a single crystal of Cs_2ZrCl_6 has been measured at 4.2K. Three bands corresponding to the $6d(\Gamma_{8g}, \Gamma_{7g}, \text{ and } \Gamma_{8g}')$ levels are assigned. Extensive vibronic structure has been observed for the lowest $5f \rightarrow 6d$ transition and this structure is compared to that recently reported for the $6d^1 \rightarrow 5f^1$ emission spectra in the same system.

Introduction

The $5f^1$ configuration is the ground electronic configuration of the Pa^{4+} free ion and the $6d^1$ is the first excited configuration at $\sim 50000 \text{ cm}^{-1}$. In the solid state the relative splittings between these two configurations are greatly reduced.¹ Axe and coworkers measured the optical spectrum of the $\text{Pa}^{4+} 5f^1$ configuration as the PaCl_6^{2-} complex diluted in single crystals of Cs_2ZrCl_6 and recorded the EPR (electron paramagnetic resonance) of its Γ_7 ground crystal field state.² Edelstein, et al. have reported the room temperature $5f \rightarrow 6d$ absorption spectra of solutions of the hexachloro and hexabromo salts of PaCl_6^{2-} and PaBr_6^{2-} .¹ Recently the high resolution $6d \rightarrow 5f$ fluorescence spectra of PaCl_6^{2-} in a single crystal of Cs_2ZrCl_6 were obtained and analyzed.³

The emission spectra showed highly structured vibronic sidebands for four of the five electronic transitions. The major feature in this structure was a vibronic progression for the totally symmetric (ν_1, a_{1g}) stretch of the PaCl_6^{2-} complex. Superimposed on these progressions were other vibronic peaks which corresponded for the most part to even parity vibrations of the PaCl_6^{2-} complex or of the host lattice. These spectra were assigned to transitions from the lowest vibrational state of the $6d(\Gamma_{8g})$ electronic level to all the $5f$ electronic (and vibrational) states. Since the $6d(\Gamma_{8g})$ level is electronically degenerate, estimates of dynamic Jahn-Teller distortion energies for this state were obtained.³

Complementary information on the excited vibronic structure of $6d(\Gamma_{8g})$ state can be obtained by high-resolution absorption spectra from the ground $5f \Gamma_{7u}$ state to the $6d$ configuration. In this paper we report the absorption spectra of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ in the visible and ultra-violet regions.

Experimental

The sample used in this experiment was obtained from the crystal batch whose growth was described earlier.³ A thin slice was taken, polished, and sealed in a quartz tube with 300 Torr of gaseous helium.

The absorption spectra were obtained by immersing the quartz tube containing the crystal directly into a liquid He bath. A tungsten lamp was used to illuminate the sample and the visible spectra were recorded with a 1 meter Jobin Yvon monochromator equipped with a photomultiplier on the exit slit and associated electronics. The ultraviolet absorption spectra were obtained with a 200 watt Xe source. The data were obtained on chart paper and the peaks were measured from these records. For illustrative purposes and for the integrations, the spectra were digitized and the wavelength axis converted from nanometers to wavenumbers (in vacuum). It was assumed the y ordinate was at ~ 100% transmission before the absorption took place and the maximum absorption corresponded to approximately 10% transmission. The y axis was converted to a number proportional to absorbance. After conversion the spectral regions were then integrated to obtain the relative areas under each of the vibronic progressions. No corrections were made for the variation of the tungsten lamp intensity as a function of wavelength.

Results

A visible absorption spectrum taken at 4.2K is shown in Fig. 1a. Two bands are observed; the lowest energy band is assigned as the $5f\Gamma_{7u} \rightarrow 6d\Gamma_{8g}$ electronic transition and shows extensive vibronic structure, the higher energy band is assigned to the $5f\Gamma_{7u} \rightarrow 6d\Gamma_{7g}$ transition and shows no structure. Both bands arise primarily from the spin-orbit splitting of the t_{2g} crystal field level in O_h symmetry as expected for a heavy ion such as Pa^{4+} . The ultra-violet spectrum of this crystal is also shown in Fig. 1b. This spectrum consists of a relatively sharp cutoff with a small dip at approximately 42000 cm^{-1} . We assign this spectrum as the sum of the $5f\Gamma_{7u} \rightarrow 6d\Gamma_{8g}'$ transition plus the cutoff of the host crystal. These assignments, including the tentative Γ_{8g}' one, are shown in Table 1. A high resolution spectrum of the $5f\Gamma_{7u} \rightarrow 6d\Gamma_{8g}$ transition is shown in Fig. 2 where it is replotted as the difference between the zero-phonon line and the other features, along with the green ($6d\Gamma_{8g} \rightarrow 5f\Gamma_{7u}$) and yellow ($6d\Gamma_{8g} \rightarrow 5f\Gamma_{8u}$) emission lines of the fluorescence

spectrum plotted in a similar way. A comparison of the measured peaks is given in Table II for the absorption spectrum and the two transitions from the emission spectrum.

There are a number of similarities and differences in the absorption and emission spectra. First of all both types of spectra show a progression based on the ν_1 (a_{1g}) mode although the frequency appears slightly diminished in the absorption spectrum. The vibronic patterns based on the zero-phonon line are the most similar for the two types of spectra. Here the most prominent feature is the zero phonon line followed by an intense band at $\sim 46 \text{ cm}^{-1}$. Both spectra have a weaker band at $\sim 170 \text{ cm}^{-1}$. Two weak sharp lines assigned to the ν_2 (e_g) and ν_5 (t_{2g}) vibrations at 253 cm^{-1} and 126 cm^{-1} , respectively, of PaCl_6^{2-} in the emission spectra are missing from the absorption band. In the absorption band two relatively weak bands are observed at $\sim 100 \text{ cm}^{-1}$ (which is sometimes observed in the emission spectra) and at $\sim 215 \text{ cm}^{-1}$.

A comparison of the vibronic patterns based on the first progression of the ν_1 stretch begins to show major differences between the absorption and emission spectra. In the absorption spectrum, the vibronic features in the first progression are broader than found for the features based on the zero-phonon band. In addition the intensities of the features around $170\text{-}200 \text{ cm}^{-1}$ have increased in intensity relative to the features at $0 \sim 60 \text{ cm}^{-1}$ (in the first progression). By contrast the vibronic features for the first progression in the emission spectra retain approximately the widths and relative intensities found in the zero phonon band. These trends continue so that in the fourth progression of the absorption spectrum the first two bands between $0\text{-}60 \text{ cm}^{-1}$ have merged and become almost lost in the background while the $170\text{-}200 \text{ cm}^{-1}$ bands, although broadened, are quite distinct. In the emission spectra the bands remain relatively narrow and lose intensity only in the higher progressions.

Theory

The intensity of an electronic transition from initial state i to the final state f may be written in the adiabatic approximation (which assumes the electronic part of the wavefunction is independent of the vibrational coordinates) as

$$I \propto |\langle i | \mathbf{er} | f \rangle \langle l | m \rangle|^2 \quad (1)$$

where I is the intensity, $\mathbf{er}$ the electric dipole operator, and l and m are the initial and final vibrational states, respectively. If it is further assumed that the electronic-vibrational coupling is linear (i.e., the vibrational frequencies in the ground and excited states are equal), then for the case where only the lowest electronic energy level is populated, the intensity

$$I_n \propto e^{-S} \left(\frac{S^n}{n!} \right) \quad (2)$$

where S is the Huang-Rhys parameter and n is the vibrational quantum number of the terminal state.^{4,5}

With the assumptions made in deriving the above equations, the value of S should be the same for both the emission and absorption spectra. Examination of Table II and of Fig. 2 show that the value of frequency of the ν_1 mode from the absorption spectrum $302 \pm 4 \text{ cm}^{-1}$ is a few percent smaller than the frequency of 310 cm^{-1} obtained from the emission spectrum. Nevertheless, we assume the model holds. The integrals of each progression shown in Fig. 2 have been obtained and normalized to the integral of the second progression. The data for the absorption spectrum and one of the emission lines are shown in Fig. 3 along with the calculated relative intensities for $S = 1.84$ and $S = 2.0$. A value of $S = 1.9 \pm 0.15$ fits both sets of data quite satisfactorily.

Discussion

Two major differences are observed between the emission spectra and the absorption spectrum. The first is the absence of features in the absorption spectrum which

can be attributed to e_{2g} and t_{2g} vibrations, and the second is the broadening and relative increase in intensity of the vibronic features at $\sim 170\text{-}200\text{ cm}^{-1}$ compared to the bands at $0 \sim 60\text{ cm}^{-1}$ in the higher progressions of the absorption spectrum. In the emission spectrum these vibronic features in the higher progressions decrease in intensity (relative to each other) without noticeable broadening.

The first observation can be attributed to the fact that the initial state in the absorption spectrum at 4K is the $5f^1 \Gamma_{7u}$ ground state which is not electronically degenerate and thus cannot undergo a Jahn-Teller distortion. Therefore during the electronic transition only vibrational features that have a non-zero Franck-Condon factor are observed, which exclude the e_{2g} and t_{2g} distortions of the $6d(\Gamma_{8g})$ level. In the emission spectra, the initial state is the $6d(\Gamma_{8g})$ state which can undergo e_{2g} and t_{2g} distortions by the dynamic Jahn-Teller effect. Since the electronic transition takes place adiabatically, the final state $5f^1(\Gamma_{7u}, \Gamma_{8u}, \text{ or } \Gamma_{6u})$ will have the same geometrical distortion as the initial state and these transitions have been observed. The second observation is again due to different Franck-Condon factors in the absorption and emission processes. The absorption spectrum probes the excited $6d$ potential energy surface which, for the higher-lying states, is expected to be quite different than the excited $5f$ potential energy surface involved in the emission spectra.

Schatz, et al. have reported the $4f^1 \rightarrow 5d^1$ MCD and absorption spectra (at $\sim 6\text{K}$) of Ce^{3+} diluted in $\text{Cs}_2\text{NaYCl}_6$.⁶ Their high-resolution absorption spectrum is very similar to the Pa^{4+} spectrum reported in this paper (except for the energy difference between the $5d(\Gamma_{8g})$ and $5d(\Gamma_{7g})$ states due to the smaller spin-orbit coupling in Ce^{3+}) which is not surprising since the nearest-neighbor ions and geometry are similar in the two crystals. There also appears to be a relative increase in the intensities of the higher energy vibronic features relative to the $0 - 60\text{ cm}^{-1}$ features in the higher order progressions. However in the Ce^{3+} case it is not as evident due to the start of the $5d(\Gamma_{7g})$ absorption. The expectation is that the value of $10 Dq$ for $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ should be greater than for $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$, however the value reported here of $\sim 18,600\text{ cm}^{-1}$ for PaCl_6^{2-} is smaller than the lower

energy limit of $20,000\text{ cm}^{-1}$ given by Schatz, et al. The value of $\zeta_{6d} \approx 1860\text{ cm}^{-1}$ for Pa^{4+} found empirically is about 0.6 of the free ion value of 3095 cm^{-1} obtained from a relativistic Hartree-Fock calculation.¹

Acknowledgement.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. N. Edelstein, J.C. Krupa, R.C. Naik, K. Rajnak, B. Whittaker, and D. Brown, *Inorg. Chem.* 27, 3186 (1988).
2. J.D. Axe, H.J. Stapleton, and C.D. Jeffries, *Phys. Rev.* 121, 1630 (1961).
3. D. Piehler, W.K. Kot, and N. Edelstein, *J. Chem. Phys.* 94, 942 (1991).
4. R.G. Denning, in "Vibronic Processes in Inorganic Chemistry," C.D. Flint, Ed. NATO ASI Series C: Vol. 288, Kluwer, Dordrecht, 1989, p. 111.
5. B. Henderson and G.F. Imbusch, "Optical Spectroscopy of Inorganic Solids," Oxford University Press, Oxford, 1989.
6. R.W. Schwartz and P.N. Schatz, *Phys. Rev. B* 8, 3229 (1973).

Table 1. Experimental and calculated energy levels
for the 6d configuration

Transition	Energy of 6d level (cm ⁻¹)	Calculated Energy ^a (cm ⁻¹)
5f Γ_{7u} $\rightarrow$ 6d Γ_{8g}	19954	19954
5f Γ_{7u} $\rightarrow$ 6d Γ_{7g}	23000	23000
5f Γ_{7u} $\rightarrow$ 6d Γ_{8g}'	40000	40000

^aParameters: $E_{Ave}^{(6d)} = 28582 \text{ cm}^{-1}$, $\zeta(6d) = 1856.5 \text{ cm}^{-1}$, $B_0^4 = 39050 \text{ cm}^{-1}$ (or $10 Dq =$

18600 cm^{-1}). See Ref. 1 for the definition of the parameters.

Table 2. Measured vibronic peaks and assignments.

phonons involved	$6d\Gamma_{8g} \rightarrow {}^2F_{5/2}(\Gamma_{7u})$ line position (cm ⁻¹) ^a	$6d\Gamma_{8g} \rightarrow {}^2F_{5/2}(\Gamma_{8u})$ line position (cm ⁻¹) ^a	${}^2F_{5/2}(\Gamma_{7u}) \rightarrow 6d(\Gamma_{8g})$ line position (cm ⁻¹) ^b
zero phonon line	19954	17847	19947
ν_{L1}		37	
ν_{L2}	48	48	45
ν_{100}			97
ν_5	126	123	
ν_{170}	174	180	165 216
ν_2	253	256	
ν_1	310	310	(1) 308
$\nu_1 + \nu_{L1}$	310 + 34	310 + 36	
$\nu_1 + \nu_{L2}$	310 + 48	310 + 49	49
$\nu_1 + \nu_{100}$			102
$\nu_1 + \nu_5$	310 + 126	310 + 123	
$\nu_1 + \nu_{170}$	310 + 175	310 + 170	163 201
$\nu_1 + \nu_2$	310 + 253	310 + 251	
$2\nu_1$	2(310)	2(310)	(2) 604
$2\nu_1 + \nu_{L1}$	2(310) + 36	2(310) + 36	
$2\nu_1 + \nu_{L2}$	2(310) + 46	2(310) + 45	50
$2\nu_1 + \nu_{100}$	2(310) + 105	2(310) + 91	
$2\nu_1 + \nu_5$	2(310) + 125	2(310) + 126	
$2\nu_1 + \nu_{170}$	2(310) + 174		170 202
$2\nu_1 + \nu_2$	2(310) + 253		
$3\nu_1$	3(310)	3(310)	(3) 908
$3\nu_1 + \nu_{L1}$		3(310) + 41	
$3\nu_1 + \nu_{L2}$	3(310) + 47		33
$3\nu_1 + \nu_{100}$		3(310) + 113	
$3\nu_1 + \nu_5$	3(310) + 125		
$3\nu_1 + \nu_{170}$	3(310) + 168		170 208
$3\nu_1 + \nu_2$	3(310) + 254		
$4\nu_1$	4(310)	4(310)	(4) 1207
$4\nu_1 + \nu_{L1}$	4(310) + 32		
$4\nu_1 + \nu_{100}$		4(310) + 114	
$4\nu_1 + \nu_{170}$			165 193
$5\nu_1$		5(310)	

Table 2 (continued)

^aExcept for the zero-phonon line, the column represents the difference between the zero-phonon line and the vibronic peaks (From Ref. 3).

^bEstimated absolute accuracy $\pm 5 \text{ cm}^{-1}$. Except for the zero-phonon line, each of the vibronic lines assigned solely to a ν_1 progression is given as the difference between the vibronic peak and the zero-phonon line. For other vibronic lines assigned to a particular ν_1 progression plus another vibration, the energies listed are the differences between the vibronic line and that particular ν_1 vibration.

Figures

- Figure 1. Absorption spectra of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ at 4.2K; a - the visible region, b - the ultra violet region.
- Figure 2. Comparison of the vibronic structure observed in the absorption spectrum with the vibronic structure in two emission bands, the yellow band (zero phonon line at 17847 cm^{-1}) and the green band (zero phonon line at 19954 cm^{-1}). The abscissa for the absorption data represents the differences between the vibronic data and the zero phonon line; the abscissa for the emission data represents the differences between the respective zero phonon lines and the vibronic data.
- Figure 3. Comparison of the relative intensities of the n th harmonics of the ν_1 vibration in the absorption spectrum of $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ with that obtained from the yellow emission band. Two calculated lines are also shown for $S = 1.84$ and $S = 2.0$.

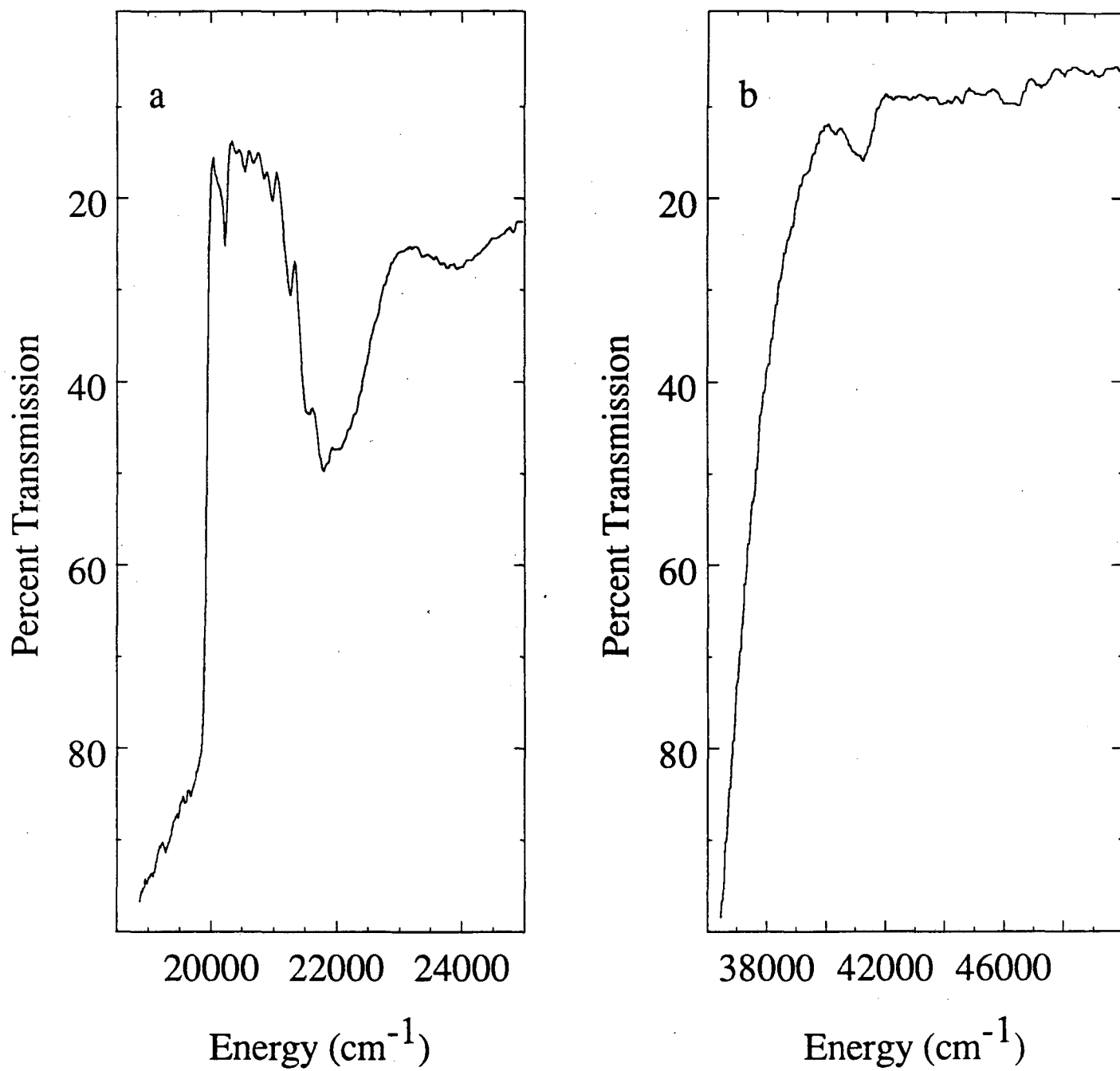


Figure 1

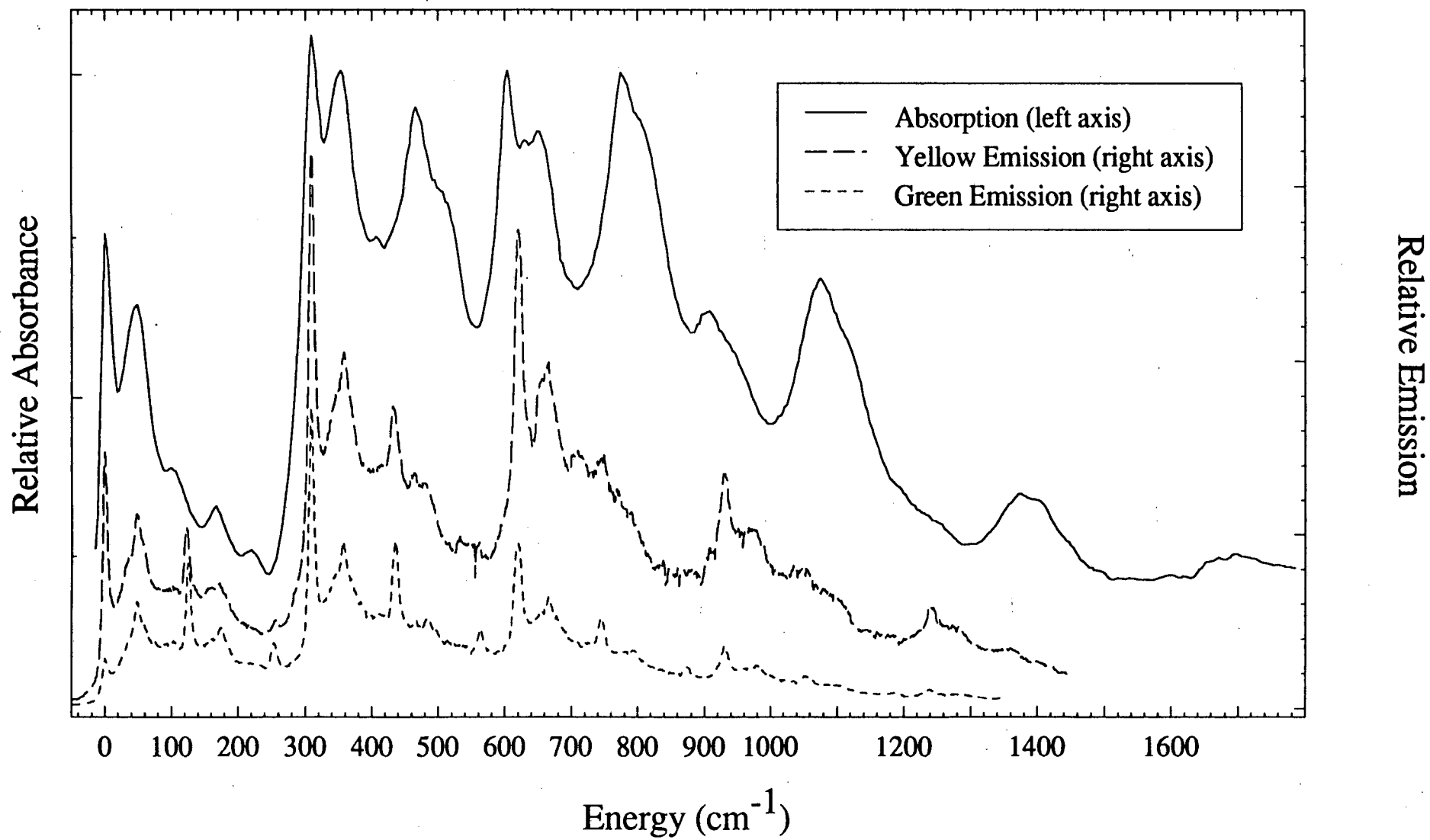


Figure 2

Huang-Rhys Parameter $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

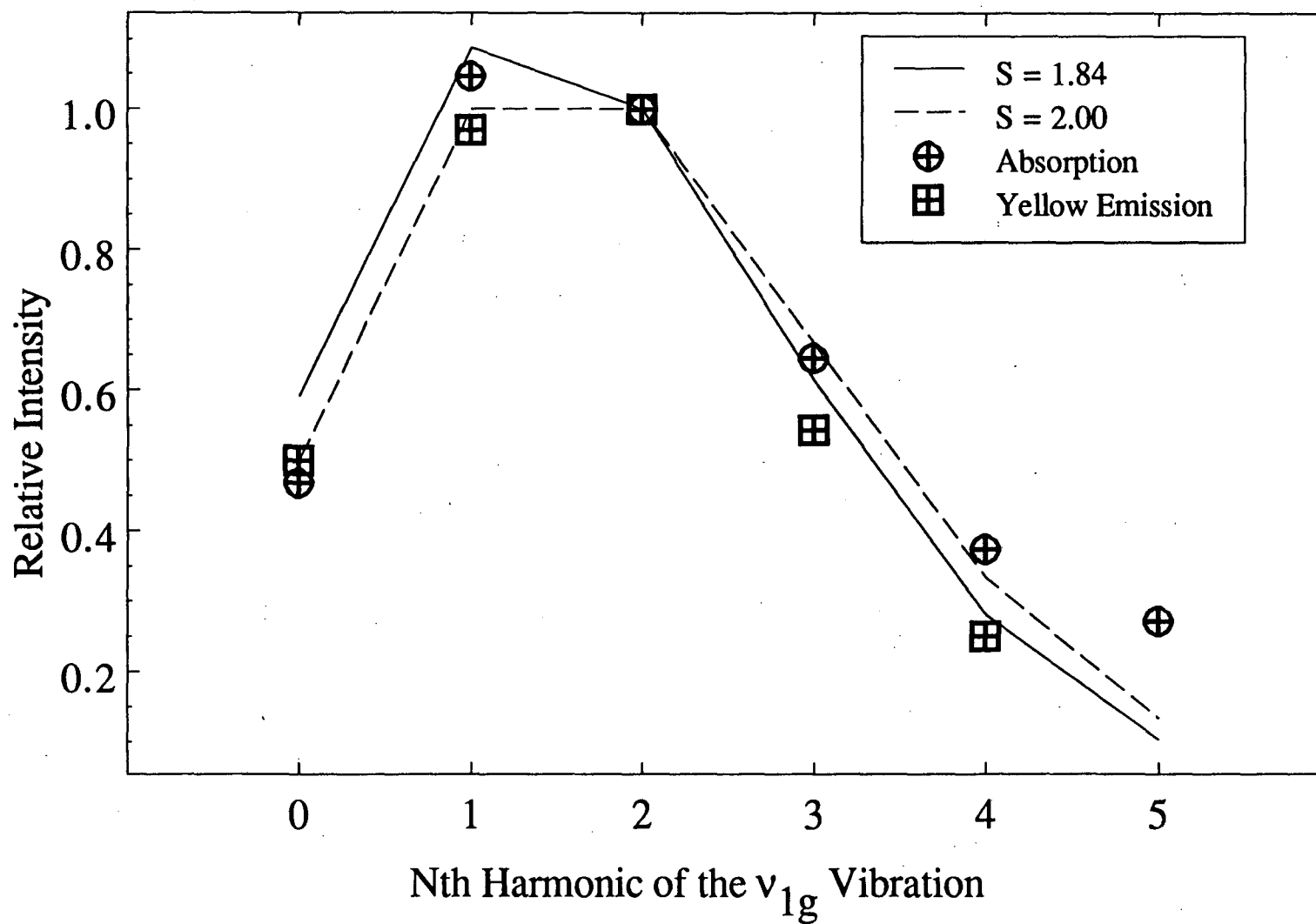


Figure 3

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720