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Journal
Journal of Chemical Physics, 96(1)

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Publication Date
1991-08-01
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August 1991
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The 5f $\rightarrow$ 6d Absorption Spectrum of Pa$^{4+}$/Cs$_2$ZrCl$_6$

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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 $^{231}\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

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Abstract

The $5f^1 \rightarrow 6d^1$ absorption spectrum of $^{231}\text{Pa}^{4+}$ diluted in a single crystal of $\text{Cs}_2\text{ZrCl}_6$ has been measured at 4.2K. Three bands corresponding to the $6d(\Gamma_{8g}, \Gamma_{7g}$, 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 ~ 50000 cm$^{-1}$. In the solid state the relative splittings between these two configurations are greatly reduced. Axe and coworkers measured the optical spectrum of the Pa$^{4+}$ 5f$^1$ configuration as the PaCl$_6^{2-}$ complex diluted in single crystals of Cs$_2$ZrCl$_6$ and recorded the EPR (electron paramagnetic resonance) of its $\Gamma_7$ ground crystal field state. 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$_6^{2-}$. Recently the high resolution 6d $\rightarrow$ 5f fluorescence spectra of PaCl$_6^{2-}$ in a single crystal of Cs$_2$ZrCl$_6$ were obtained and analyzed.

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 ($v_1$, $a_{1g}$) 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.

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 Pa$^{4+}$/Cs$_2$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. 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 \(\Gamma_{8g}^{1}\) 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 $v_1$ ($a_{1g}$) 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 $\sim 46$ cm$^{-1}$. Both spectra have a weaker band at $\sim 170$ cm$^{-1}$. Two weak sharp lines assigned to the $v_2$ ($e_g$) and $v_5$ ($t_{2g}$) vibrations at 253 cm$^{-1}$ and 126 cm$^{-1}$, respectively, of $\text{PaCl}_6^-$ in the emission spectra are missing from the absorption band. In the absorption band two relatively weak bands are observed at $\sim 100$ cm$^{-1}$ (which is sometimes observed in the emission spectra) and at $\sim 215$ cm$^{-1}$.

A comparison of the vibronic patterns based on the first progression of the $v_1$ 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 170-200 cm$^{-1}$ have increased in intensity relative to the features at 0 $\sim$ 60 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 0-60 cm$^{-1}$ have merged and become almost lost in the background while the 170-200 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

$$I \propto |\langle i | r | f \rangle |^2$$

where $I$ is the intensity, $r$ the electric dipole operator, and $i$ and $f$ 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

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

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 $v_1$ mode from the absorption spectrum $302 \pm 4 \text{ cm}^{-1}$ is a few percent smaller than the frequency of $310 \text{ cm}^{-1}$ 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 $\sim 170$-$200$ cm$^{-1}$ compared to the bands at $0$-$60$ 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 $\sim 6$K) of Ce$^{3+}$ diluted in Cs$_2$NaYCl$_6$. 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 $0$-$60$ 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 Pa$^{4+}$/Cs$_2$ZrCl$_6$ should be greater than for Ce$^{3+}$/Cs$_2$NaYCl$_6$, however the value reported here of $\sim 18,600$ cm$^{-1}$ for PaCl$_6^{2-}$ is smaller than the lower
energy limit of 20,000 cm\(^{-1}\) given by Schatz, et al. The value of \(\zeta_{6d} \approx 1860\) 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


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

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy of 6d level (cm⁻¹)</th>
<th>Calculated Energyᵃ (cm⁻¹)</th>
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<tr>
<td>5fΓ₇ᵤ → 6dΓ₈ᵍ</td>
<td>19954</td>
<td>19954</td>
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<tr>
<td>5fΓ₇ᵤ → 6dΓ₇ᵍ</td>
<td>23000</td>
<td>23000</td>
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<tr>
<td>5fΓ₇ᵤ → 6dΓ¹</td>
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<td>40000</td>
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</table>

ᵃParameters: $E^{(6d)}_{Ave} = 28582$ cm⁻¹, $\xi(6d) = 1856.5$ cm⁻¹, $B^{4}_{0} = 39050$ cm⁻¹ (or 10 Dq = 18600 cm⁻¹). See Ref. 1 for the definition of the parameters.
Table 2. Measured vibronic peaks and assignments.

<table>
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<tr>
<th>phonons involved</th>
<th>6dΓ₈g → ²F₅/₂(T₇u)</th>
<th>6dΓ₈g → ²F₅/₂(T₈u)</th>
<th>²F₅/₂(T₇u) → 6dΓ₈g</th>
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<tr>
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<td>line position (cm⁻¹)ᵇ</td>
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<td>ν₈L₁</td>
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<td>19947</td>
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<td>2(310)</td>
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<td>193</td>
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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 ± 5 cm⁻¹. Except for the zero-phonon line, each of the vibronic lines assigned solely to a $v_1$ progression is given as the difference between the vibronic peak and the zero-phonon line. For other vibronic lines assigned to a particular $v_1$ progression plus another vibration, the energies listed are the differences between the vibronic line and that particular $v_1$ vibration.
Figures

Figure 1. Absorption spectra of Pa$^{4+}$/Cs$_2$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 $\nu_1$ vibration in the absorption spectrum of Pa$^{4+}$/Cs$_2$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

Absorption (left axis)
Yellow Emission (right axis)
Green Emission (right axis)
Huang-Rhys Parameter $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$

Figure 3

- $S = 1.84$
- $S = 2.00$
- Absorption
- Yellow Emission

Relative Intensity vs. Nth Harmonic of the $v_{1g}$ Vibration