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Analysis of the $5f^1 \rightarrow 6d^1$ Transitions
in PaX_6^{2-} (X=Cl, Br) and $\text{Pa}^{4+}/\text{ThBr}_4$

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Abstract

The optical spectra of $\text{Pa}^{4+}/\text{ThBr}_4$ and M_2PaX_6 ($\text{M}=\text{Cs}$, $\text{X}=\text{Cl}$; $\text{M}=\text{NEt}_4$, $\text{X}=\text{Cl}$, Br) in the visible and ultra-violet ranges have been obtained and are analyzed in terms of a Hamiltonian including the crystal field and spin-orbit interactions for the $6d^1$ configuration. A lower limit of $\sim 13800 \text{ cm}^{-1}$ is obtained for the total crystal field splitting of PaX_6^{2-} . Spin-orbit coupling constants of $\zeta_{6d} = 2050 \text{ cm}^{-1}$ (PaX_6^{2-}) and $\zeta_{6d} = 1570 \text{ cm}^{-1}$ ($\text{Pa}^{4+}/\text{ThBr}_4$) are obtained. Relative shifts of 5f-6d configuration centroids in crystals are compared to the free-ion values.

Introduction

The $5f^1$ configuration is an attractive system to study because of the simplicity of its electronic spectrum. For the ion Pa^{4+} , relatively few data have been reported. Axe was the first to report and analyze intraconfigurational $f \rightarrow f$ transitions in the system $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$.¹ This work was followed by optical studies on other Pa^{4+} hexahalo-compounds^{2,3} and on Pa^{4+} diluted in single crystals of ThBr_4 and ThCl_4 .⁴

Strong absorption bands in the visible range were first observed by Axe in $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$ but were not conclusively assigned.¹ Recently, Naik and Krupa have reported absorption and fluorescence spectra in $\text{Pa}^{4+}/\text{ThBr}_4$ which have been assigned to transitions between the ground $5f^1$ and the excited $6d^1$ configurations.⁵ We report herein more detailed absorption and fluorescence spectra of $\text{Pa}^{4+}/\text{ThBr}_4$ and solution absorption spectra of M_2PaX_6 ($\text{M}=\text{Cs}$, $\text{X}=\text{Cl}$; $\text{M}=\text{NEt}_4$, $\text{X}=\text{Cl}$, Br). The observed bands are assigned and the data analyzed in terms of a Hamiltonian containing spin-orbit and crystal field interactions.

Experimental

Absorption spectra of $\text{Pa}^{4+}/\text{ThBr}_4$ were obtained at 300 and 77K in the visible and ultra-violet ranges with a Cary 17, a Spex Model 1403 spectrophotometer using a tungsten lamp as a source, and photographically with a Jarrell-Ash F-6 spectrograph. For the absorption studies, the $\text{Pa}^{4+}/\text{ThBr}_4$ crystal was oriented such that the $\vec{c}$ axis was either parallel to the direction of propagation of the light (α spectrum which corresponds to σ polarization) or perpendicular to this direction ($\sigma + \pi$ spectrum) (see Figure 1). Conventional polarized σ and π spectra were also obtained with the $\vec{c}$ axis perpendicular to the direction of the propagation of light by use of polarizing filters. No differences in the fluorescence spectra were observed with conventional polarization measurements. The dependence on excitation frequency was obtained in the fluorescence spectra by pumping into the different absorption bands (Figure 2). Various argon ion laser lines, a N_2 pumped dye laser, and the filtered 2537Å Hg line were used for excitation. Solution spectra (under an atmosphere of Ar) of Cs_2PaCl_6 , $(\text{NEt}_4)_2\text{PaCl}_6$ and $(\text{NEt}_4)_2\text{PaBr}_6$ dissolved in CH_3CN were obtained at room temperature on a Cary 14 spectrophotometer. A solution spectrum of $(\text{Et}_4\text{N})_2\text{PaBr}_6$ is shown in Figure 3.

Theory and Assignments

The Hamiltonian for a one electron configuration outside a closed shell may be written as the sum of three terms:

$$H = H_{\text{so}} + H_{\text{CF}} + E_{\text{Ave}}$$

where

$$H_{so} = \zeta_{nl} \vec{l} \cdot \vec{s} \quad (nl = 5f, 6d)$$

and for D_{2d} symmetry

$$H_{CF} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_4^4 [C_{-4}^4 + C_4^4] + B_0^6 C_0^6 + B_4^6 [C_{-4}^6 + C_4^6].$$

E_{Ave} is defined as the center of gravity of the $5f^1$ or $6d^1$ configuration. Sixth order terms in H_{CF} occur only for the f^1 configuration. In the case of O_h symmetry, $B_0^2 = 0$, $B_4^4 = (\frac{5}{14})^{1/2} B_0^4$, and $B_4^6 = -(\frac{7}{2})^{1/2} B_0^6$.

A number of absorption bands were observed for $Pa^{4+}/ThBr_4$ in the wavelength range of 5000-3000Å (see Figure 1). The three highest energy bands were measured as shoulders on the broad background of the charge-transfer transition observed in pure $ThBr_4$. Since only five $f \rightarrow d$ transitions are allowed, the highest energy band was assigned to a charge-transfer transition in $Pa^{4+}/ThBr_4$.

The ground state for the $5f^1$ configuration of $Pa^{4+}/ThBr_4$ is of Γ_6 symmetry.⁴ In accord with the electric dipole selection rules for D_{2d} symmetry ($\Gamma_6 \leftrightarrow \Gamma_7$ ($\vec{E} \parallel \vec{c}$) Π polarization; Γ_6 or $\Gamma_7 \leftrightarrow \Gamma_6$ or Γ_7 ($\vec{E} \perp \vec{c}$) σ polarization) bands which appeared to be relatively less intense in the α spectra (which corresponds to σ polarization) than in the σ and π spectra were assigned to the Γ_6 excited states. These assignments are shown in Table 1. Conventional polarized absorption spectra showed no extinctions, only relative intensity changes in the bands similar to

those shown in Fig. 1 (α spectrum similar to σ spectrum; π spectrum similar to π and σ spectrum).

The spin-orbit and crystal field parameters obtained by fitting the calculated energies to the experimental values are given in Table 2. Because there are four parameters (besides E_{Ave} the center of gravity of the configuration) and four energy differences, the calculated and experimental energies agree. Calculated relative intensities based on the wavefunctions obtained from these assignments, are also given in Table 1.

Fluorescence bands from the 6d levels to the ground $5f^1$ states of $Pa^{4+}/ThBr_4$ were obtained by selective excitation into the various 6d absorption bands. Excitation at any wavelength into the lowest energy 6d band (A in Figure 1) gave rise to two pairs of emission bands, I and II as shown in Figure 2. These emission bands are assigned as transitions from the lowest 6d crystal field level to the two spin-orbit split multiplets, $^2F_{5/2}(I)$ and $^2F_{7/2}(II)$ as shown in Figure 4. Selective excitation in the second absorption band (B in Figure 1) resulted in the addition of a new feature (III in Figure 2) which is assigned to transitions from the B level to the $^2F_{7/2}$ multiplet (Figure 4). When Hg emission lines were used for excitation, the new fluorescent bands IV and V appeared and were assigned as transitions from the B and C levels to the ground $^2F_{5/2}$ multiplet.

For the octahedral anion PaX_6^{2-} , the crystal field splits the $6d^1$ configuration into a t_{2g} lower state and a higher e_g state. Spin-orbit coupling will split the lower t_{2g} state into a Γ_6 and a Γ_8 state with the splitting $\sim 3/2 \zeta_d$ where ζ_d is the 6d spin-orbit coupling constant.

From the spectrum (and similar spectra for the other PaX_6^{2-} complexes) shown in Figure 3, we obtain $\zeta_d \approx 2000 \text{ cm}^{-1}$. The e_g state is obscured in the ultra-violet by a broad continuum at $\sim 3000\text{\AA}$. There is some indication of a level just before this broad band which we have tentatively assigned to the $5f^1(\Gamma_6) \rightarrow 5d^1(e_g)$ transitions (see Table 3). With this assignment the parameters given in Table 4 were obtained. This assignment represents a lower limit to the crystal field splitting. Again the experimental and calculated energies agree because of the equal number of levels and energy differences. Calculated relative intensities are given in Table 3.

Discussion

The $5f^1$ and $6d^1$ parameters (Table 5) for octahedral PaX_6^{2-} have the same signs. In a point charge model (which is known to be incorrect but is used here qualitatively), the cubic parameter B_0^4 scales as the ratio of $\frac{\langle r^4 \rangle_{6d}}{\langle r^4 \rangle_{5f}}$. Values of the energies of the $5f^1$ and $6d^1$ configurations, spin-orbit coupling constants, and various radial averages calculated from the Cowan HF code with a relativistic correction (HFR)⁶ are given in Table 5. The experimental data do not follow these ratios. The spin-orbit coupling constant for the $6d^1$ configuration is $\sim .6$ of the calculated free ion value.

For the tetragonal crystal ThBr_4 , the sign of B_0^2 for the $6d^1$ configuration is opposite that of the $5f^1$ configuration and $B_0^4(6d^1)$ is less than three times the value for $B_0^4(5f^1)$. However $B_4^4(6d^1)$ is ~ 5 times greater. Interestingly, the signs and relative magnitudes of the

crystal field parameters for the $\text{Pa}^{4+}/\text{ThBr}_4(6d^1)$ are similar to those found for $\text{Ce}^{3+}/\text{LuPO}_4(5d^1)$ which also has D_{2d} symmetry at the metal ion site.⁷ The signs of the crystal field parameters for $\text{Pa}^{4+}/\text{ThBr}_4(5f^1)$ are the same as found for $\text{Ce}^{3+}/\text{LuPO}_4(4f^1)$ except for B_0^2 which is large and negative for Pa^{4+} and is very small and positive for Ce^{3+} .^{4,7}

The total crystal field splitting of the $6d^1$ configuration for the octahedral anion PaCl_6^{2-} is on the order of $13,800 \text{ cm}^{-1}$. This value seems rather low when compared with the reported weak d-d bands of the six coordinate $\text{NbCl}_6^{2-}(4d^1)$ and $\text{TaCl}_6^{2-}(5d^1)$ of $\sim 20,000 \text{ cm}^{-1}$,⁸ and the lower limit found for CeCl_6^{3-} of $15,000 \text{ cm}^{-1}$.⁹ Because of the uncertainty in the assignment of the highest energy band in PaX_6^{2-} ($\text{X}=\text{Cl}, \text{Br}$), and the expectation that the total crystal field splitting for a $6d^1$ configuration should be greater than for a $4d^1$ or $5d^1$ configuration with the same ligand and geometry, it is best to regard the value of $\sim 13,800 \text{ cm}^{-1}$ as a lower limit. Nevertheless, the spin-orbit coupling constant of $\zeta_{6d} \sim 2,050 \text{ cm}^{-1}$ compared to the free ion calculation of $\sim 3,000 \text{ cm}^{-1}$ suggests that covalent effects are quite important in the $6d^1$ configuration.

In $\text{Pa}^{4+}/\text{ThBr}_4$, $\zeta_{6d} \sim 1,570 \text{ cm}^{-1}$, an even lower value than found for the PaBr_6^{2-} ion. In addition, the total crystal field splitting is only about $\sim 10,000 \text{ cm}^{-1}$. In octahedral symmetry the Pa-Br bond length is shorter than found in $\text{Pa}^{4+}/\text{ThBr}_4$ which should result in a stronger crystal field. The Pa^{4+} ion in a D_{2d} site may be considered to be at the center of two tetrahedra, with the tetrahedron with the shortest bond distance giving the largest contribution to the crystal field. However this contribution (in a point charge model) would be only 4/9

that of octahedral coordination at the same bond distance. Thus the smaller crystal field splitting for the $6d^1$ configuration in D_{2d} symmetry than in octahedral symmetry is qualitatively consistent with the point-charge model.

The Auzel parameter, $N_{\sqrt{4\pi}}$, can be used as a measure of the crystal field strength for f^n ions. The values for the $5f^1$ configuration are given in Tables 2 and 4 for PaX_6^{2-} and $\text{Pa}^{4+}/\text{ThBr}_4$. By this measure, the $5f^1$ crystal field strength is greater for Pa^{4+} in octahedral symmetry than for Pa^{4+} in dodecahedral symmetry which again qualitatively agrees with the results for the $6d^1$ configuration.

Data are available for the $4f^1 \rightarrow 5d^1$ transitions of Ce^{3+} diluted in LuPO_4 .⁷ This ion is also at a site of D_{2d} symmetry. The total $5d^1$ crystal field splitting is on the order of $\sim 20000 \text{ cm}^{-1}$ and the spin-orbit coupling constant is approximately the same as the free ion value, $\zeta_{5d} \sim 1000 \text{ cm}^{-1}$. Since the crystal field splitting for a $6d$ configuration should be greater than for a $5d$ configuration in the same host, these data suggest the LuPO_4 host has a considerably larger crystal field than ThBr_4 .

From the HFR calculations shown in Table 5, the difference in the centers of gravity (E_{Ave}) between the $5f^1$ and $6d^1$ configurations is $\approx 45,000 \text{ cm}^{-1}$. Fitting the free ion data for the isoelectronic series Ra^{1+} , Ac^{2+} , Th^{3+} , and U^{5+} gives a value of approximately $50,000 \text{ cm}^{-1}$ for the Pa^{4+} free ion.¹⁰⁻¹² Tables 2 and 4 show this difference to be $\approx 22,000 \text{ cm}^{-1}$ for the Pa^{4+} complexes. This difference in the corresponding configurations in $\text{Ce}^{3+}/\text{LuPO}_4$ ($5d^1$ and $4f^1$) is $\approx 40,000 \text{ cm}^{-1}$.⁷ For the Ce^{3+} free ion, this energy difference is $49,943 \text{ cm}^{-1}$.¹³

while the HFR calculations give $45,366 \text{ cm}^{-1}$. Thus the 6d configuration is affected more strongly by the crystal field than the 5d configuration (relative to the 5f and 4f configurations, respectively).

In the crystal field model, the energy difference between the centers of gravity of configurations is determined by the differences in the spherically symmetric terms (i.e., $B_0^0(6d) - B_0^0(5f)$ for Pa^{4+} ; $B_0^0(5d) - B_0^0(4f)$ for Ce^{3+}) of the crystal field Hamiltonians. The various interactions which contribute to these parameters have recently been discussed.¹⁴

CONCLUSION

Crystal field analyses of the spectra of the $6d^1$ configuration of $\text{Pa}^{4+}/\text{ThBr}_4$ and PaX_6^{2-} ($X=\text{Cl}, \text{Br}$) have shown that both the crystal field and spin-orbit coupling parameters are much smaller than might have been expected by extrapolation from Ce^{3+} or consideration of ions such as NbCl_6^{2-} and TaCl_6^{2-} . The differences in the total crystal field splittings for Pa^{4+} in the two different crystal symmetries agree qualitatively with a point-charge model. The difference between the centers of gravity of the $6d^1$ and $5f^1$ configurations decreases markedly for Pa^{4+} in the crystal when compared to the free ion. Such a dramatic effect is not found for the differences of the centers of gravity between the $5d^1$ and $4f^1$ configurations for $\text{Ce}^{3+}/\text{LuPO}_4$ and Ce^{3+} free ion.

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Table 1
 $\text{Pa}^{4+}/\text{ThBr}_4$ Energy Levels for the $6d^1$ Configuration

Assign. ^a	Energy (cm^{-1})	Calc. Rel. Intens. ^b		
		σ polar.	π polar.	Unpol.
Γ_7	20710	.2	1.0	.6
Γ_6	23600	1.18	0	.59
Γ_7	26310	.122	.124	.123
Γ_6	28160	.24	0	.12
Γ_7	30110	.19	.82	.51

^aAssignment

^bCalculated Relative Intensities

Table 2
 Parameter Values for $\text{Pa}^{4+}/\text{ThBr}_4$

	$5f^1$	$6d^1$
E_{Ave}	3496	25778
ζ	1533	1567
B_0^2	-1047	1629
B_0^4	1366	3038
B_0^6	-1162	-
B_4^4	-1990	-10430
B_4^6	623	-
$\frac{N_V}{\sqrt{4\pi}}$	1212.5	

Table 3

PaX_6^{2-} Assignments from CH_3CN Solutions

Assign. ^a				Cal. Rel. Intens. ^b
	Cs_2PaCl_6	$(\text{NEt}_4)_2\text{PaCl}_6$	$(\text{NEt}_4)_2\text{PaBr}_6$	(unpolarized)
Γ_8	20780	20860	19280	1
Γ_6	24340	24550	22770	.1
Γ'_8	32780 ^c	33350 ^c	33180 ^c	.6

^aAssignment

^bCalculated Relative Intensities

^cTentative Assignment

Table 4
Parameter Values for PaX_6^{2-} (X=Cl, Br)

	Cs_2PaCl_6		$(\text{NEt}_2)_4\text{PaCl}_6$		$(\text{NEt}_2)_4\text{PaBr}_6$	
	$5f^1$	$6d^1$	$5f^1$	$6d^1$	$5f^1$	$6d^1$
E_{Ave}	4245	26289	4441	26591	4237	25539
ζ	1490	2021	1523	2092	1535	2023
B_0^4	7104	20831	6665	21720	5413	25146
B_0^6	670	-	394	-	-68	-
$\frac{N_v}{\sqrt{4\pi}}$	3145		2925		2363	

Table 5
HFR Values for Pa⁴⁺ Free Ion

	E_{Ave} (cm ⁻¹)	ζ_{nl} (cm ⁻¹)	$\langle r^2 \rangle^a$	$\langle r^4 \rangle^a$	$\langle r^6 \rangle^a$
5f ¹	0	1834	2.222	9.025	61.10
6d ¹	45075	3095	6.209	56.33	705.6

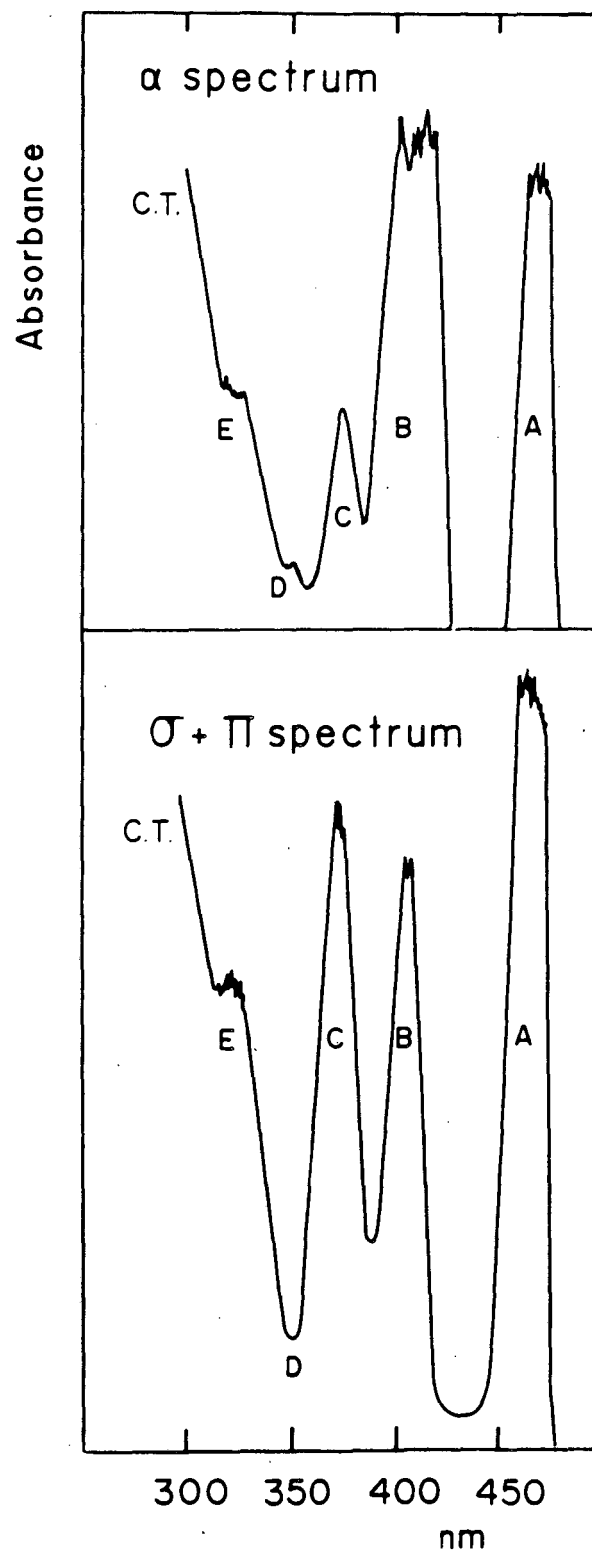
^a atomic units

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Figure Captions

- Figure 1. Optical spectra of $\text{Pa}^{4+}/\text{ThBr}_4$ at 77°K a) α spectrum, b) unpolarized spectrum, C.T. is the charge transfer band.
- Figure 2. Fluorescence spectra with various excitation frequencies.
- Figure 3. Room temperature optical spectrum of $(\text{NEt}_4)_2\text{PaBr}_6$ in CH_3CN solution.
- Figure 4. Assignments of the fluorescence bands obtained by selective excitation.



XBL 883-852

Figure 1

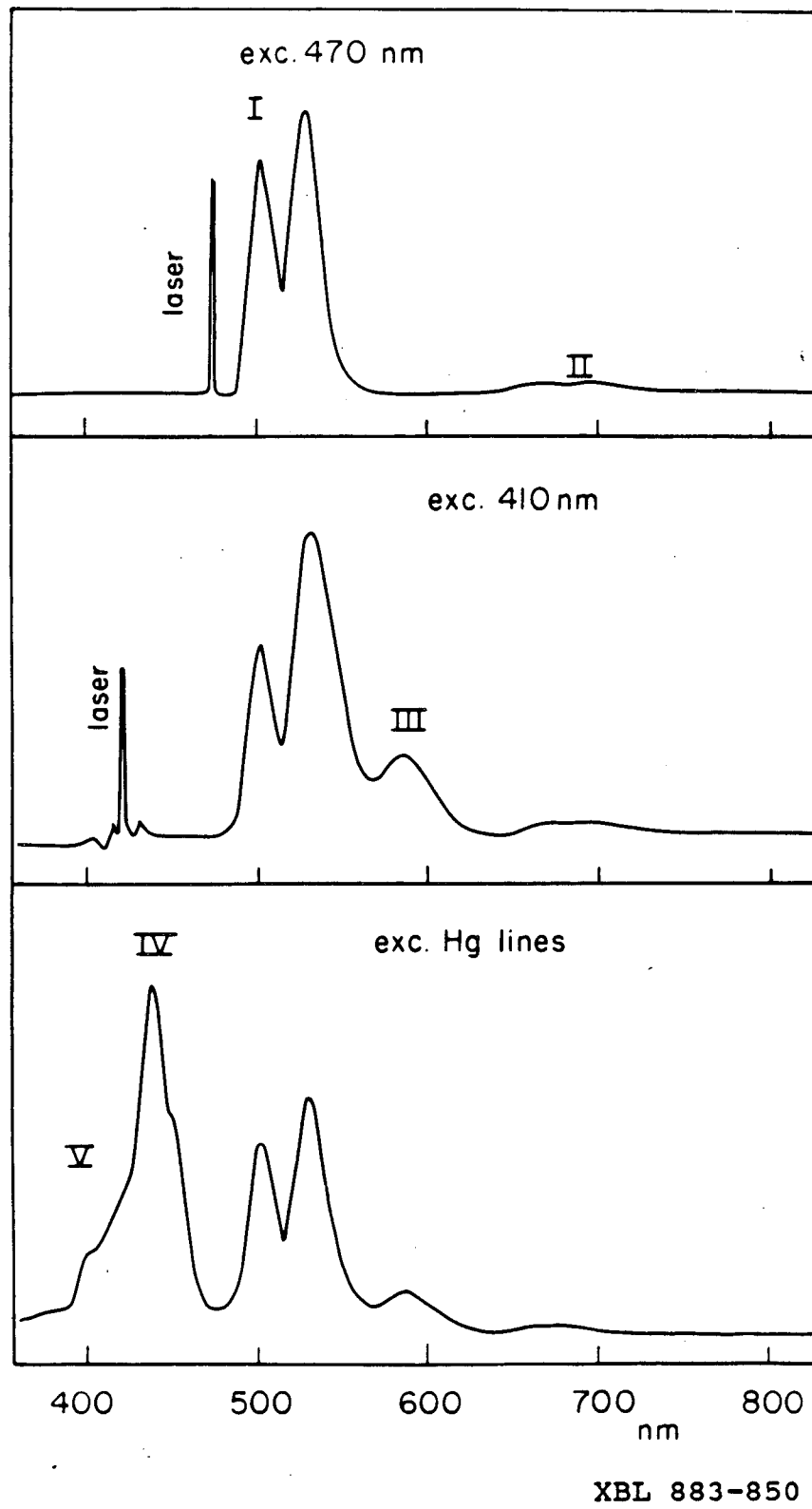
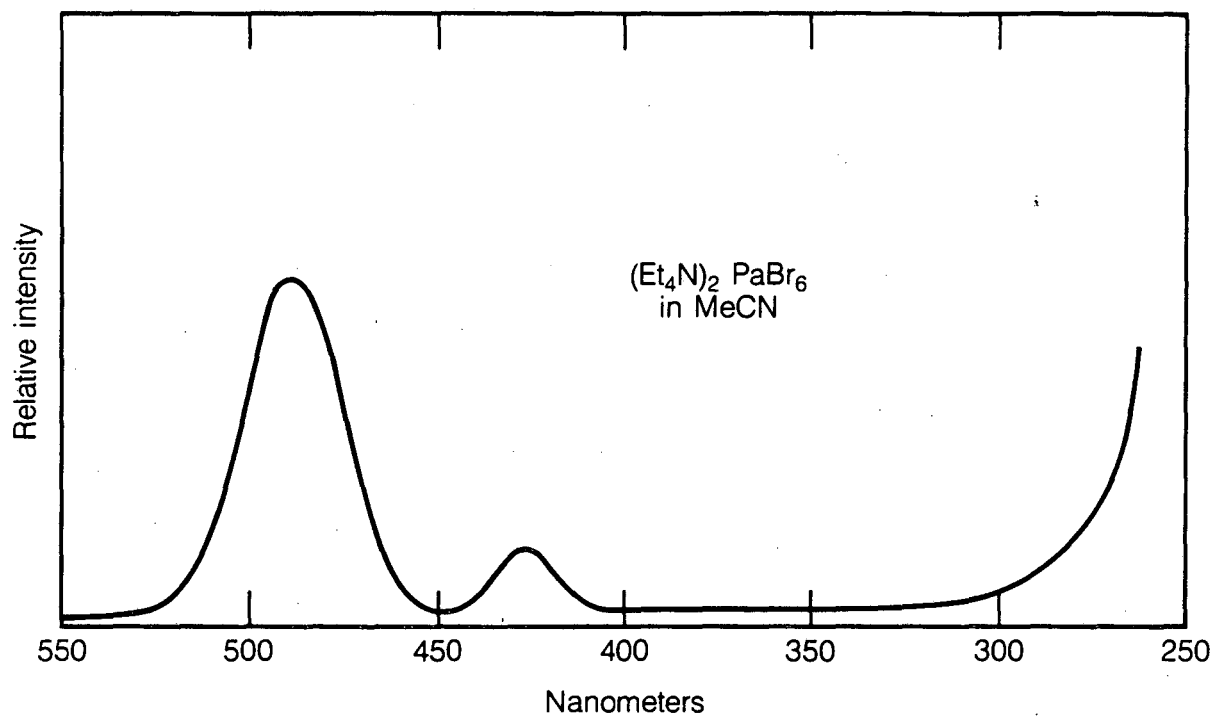
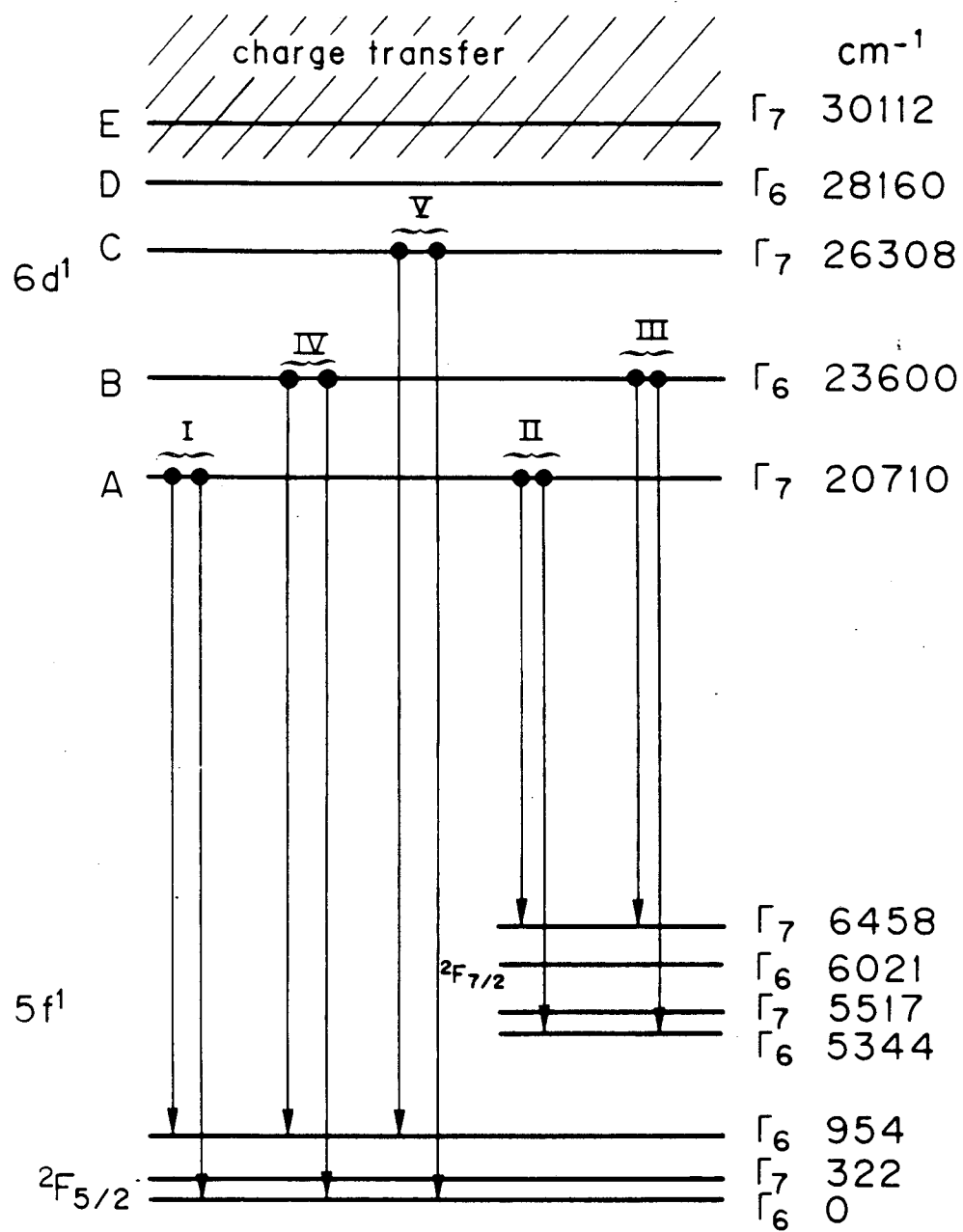


Figure 2



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Figure 3



$\text{Pa}^{4+} : \text{ThBr}_4$

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Figure 4

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