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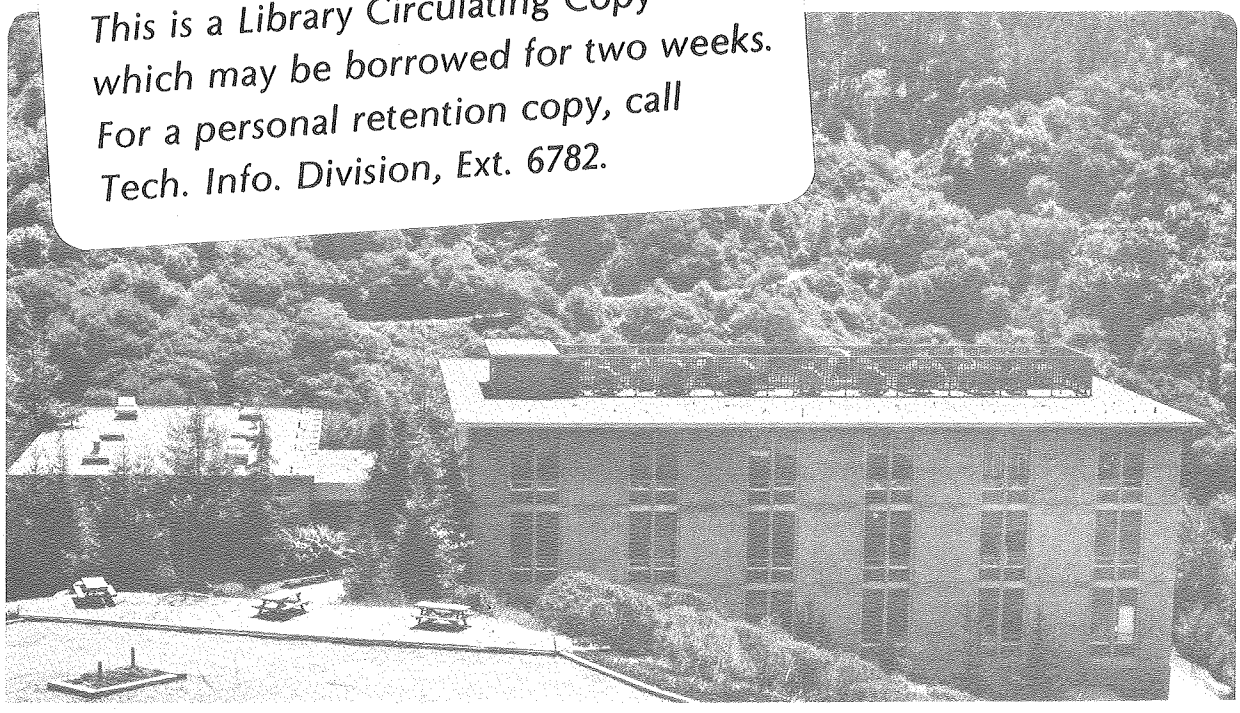

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SPECTRUM AND ENERGY LEVELS OF Pr^{3+} IN $ThBr_4$

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The strong features in the absorption spectrum and the laser excited fluorescence spectrum have been interpreted as arising from levels of Pr^{3+} in the D_{2d} symmetry site of $ThBr_4$. 43 energy levels have been fitted to the parameters with an RMS deviation of 61 cm^{-1}. The values of the crystal field parameters are $B_0^2 = 260.0$ cm^{-1}, $B_0^4 = -644.2$ cm^{-1}, $B_4^4 = 929.2$ cm^{-1}, $B_0^6 = 1089.0$ cm^{-1} and $B_4^6 = 240.6$ cm^{-1}. The presence of other crystal symmetry sites is observed.

I - INTRODUCTION

Thorium tetrabromide is of interest as a matrix for tetravalent ions of the actinide elements because it can be prepared in large, optically clear crystals[1,2]. At room temperature, $ThBr_4$ is tetragonal and isostructural with UCl_4, the thorium ion is at a site of D_{2d} symmetry. In an attempt to find a simpler and better understood system to confirm $U^{4+}(5f^2)$ work, we have studied Pr^{3+} $(4f^2)$ diluted in $ThBr_4$. We assume the Pr^{3+} substitutes into the crystal at Th^{4+} sites and therefore the most important symmetry seen by the Pr^{3+} is D_{2d}. The fact that it is a 3^+ ion in a tetravalent matrix presents some complications which are overcome because the Pr^{3+} system is so well known.

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II - EXPERIMENTAL PROCEDURES

The crystals were prepared varying in size from 6 mm in diameter to 40mm in diameter and using approximately 1% by weight $PrBr_3$ or Pr_6O_{11} as starting materials. The larger crystals yielded pieces 10 x 10 x 5mm that were optically clear and the optical axis could be easily found and positioned for the spectral studies. The spectra obtained from the two different Pr compounds were identical.

The absorption spectra were recorded in both Orsay and Berkeley. In Orsay, we used a 1 meter Jobin-Yvon "HR1000" spectrophotometer with a 1200lines/mm grating. The Berkeley work was done with a 0.75 meter photographic instrument. Polarized spectra were recorded between 4000 Å and 2 μm at room temperature, 77 K and 4.2 K. Spectra were also recorded on a Cary 17 at 77 K and 4.2 K in the wavelength region from 4000 Å to 2.5 μm.

Fluorescence of the crystals was excited with a nitrogen laser and with a nitrogen pumped dye laser. The dye laser produces a wavelength about 1 Å FWHM and was varied in 1 Å steps. The fluorescence spectra were recorded photographically with exposure times of 15 minutes.

III - RESULTS

The spectra contained many more lines than can be explained by electric dipole transitions between allowed levels in D_{2d} symmetry. The extra lines become sharper at low temperature and are found within less than 50 cm^{-1} on both sides of the strong lines. Over all, the strong lines resemble the expected Pr^{3+} spectrum and it is these that were used in the analysis of the data. In table 1 the absorption lines obtained at 4.2 K are listed.

The $^3P_0$ contains only a Γ_1 state and according to the D_{2d} selection rules[3,4,5] gives a π line for a transition with the Γ_4 state of the $^3H_4$ ground multiplet or a σ line when the transition is to a Γ_5 state. In our experiment the $^3P_0$ line was very clearly polarized σ, thus supports a Γ_5 to Γ_1 transition. Fig. 1 shows the structure around the $^3P_0$ at 77 K in both the π and σ

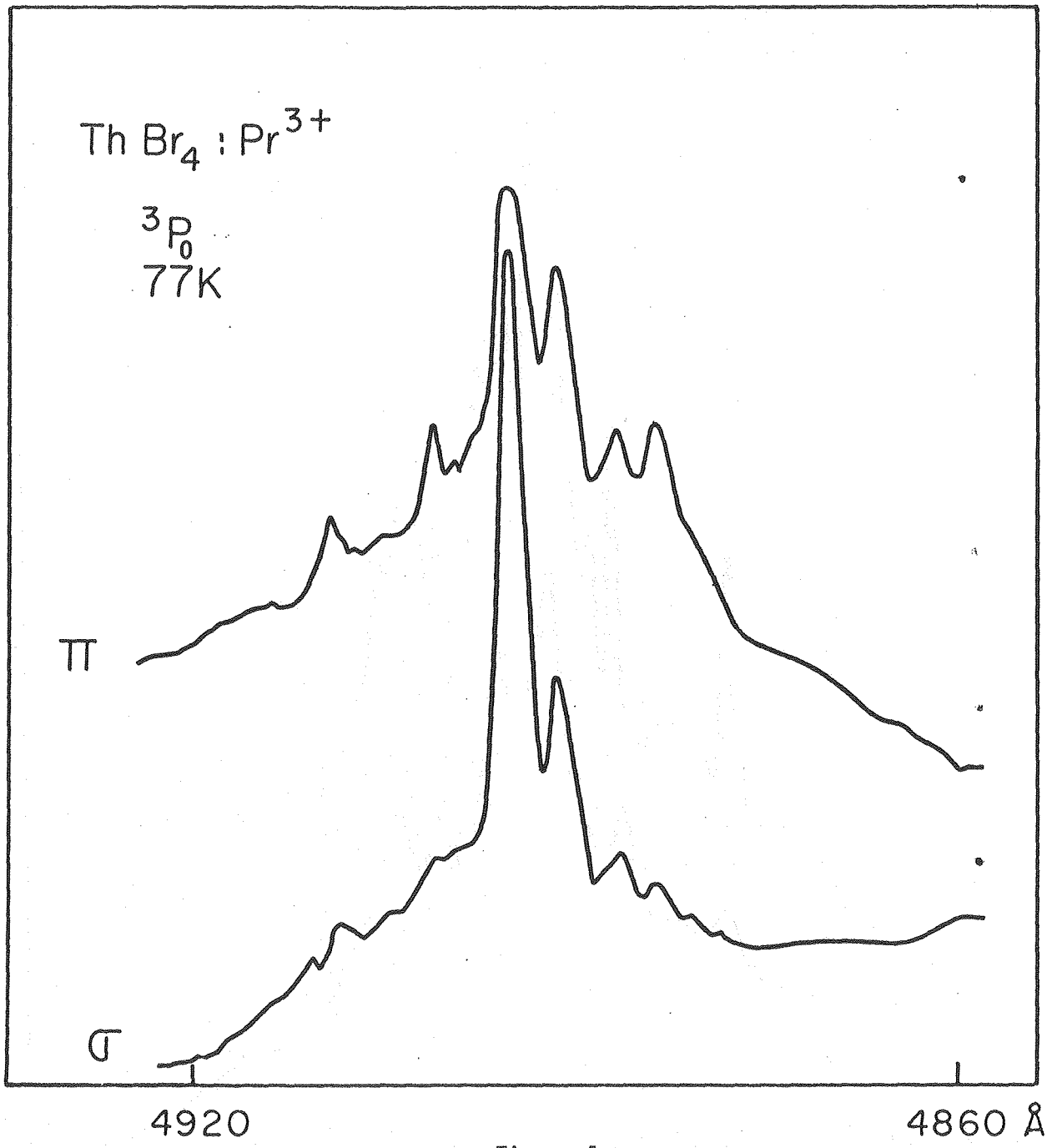

Figure 1

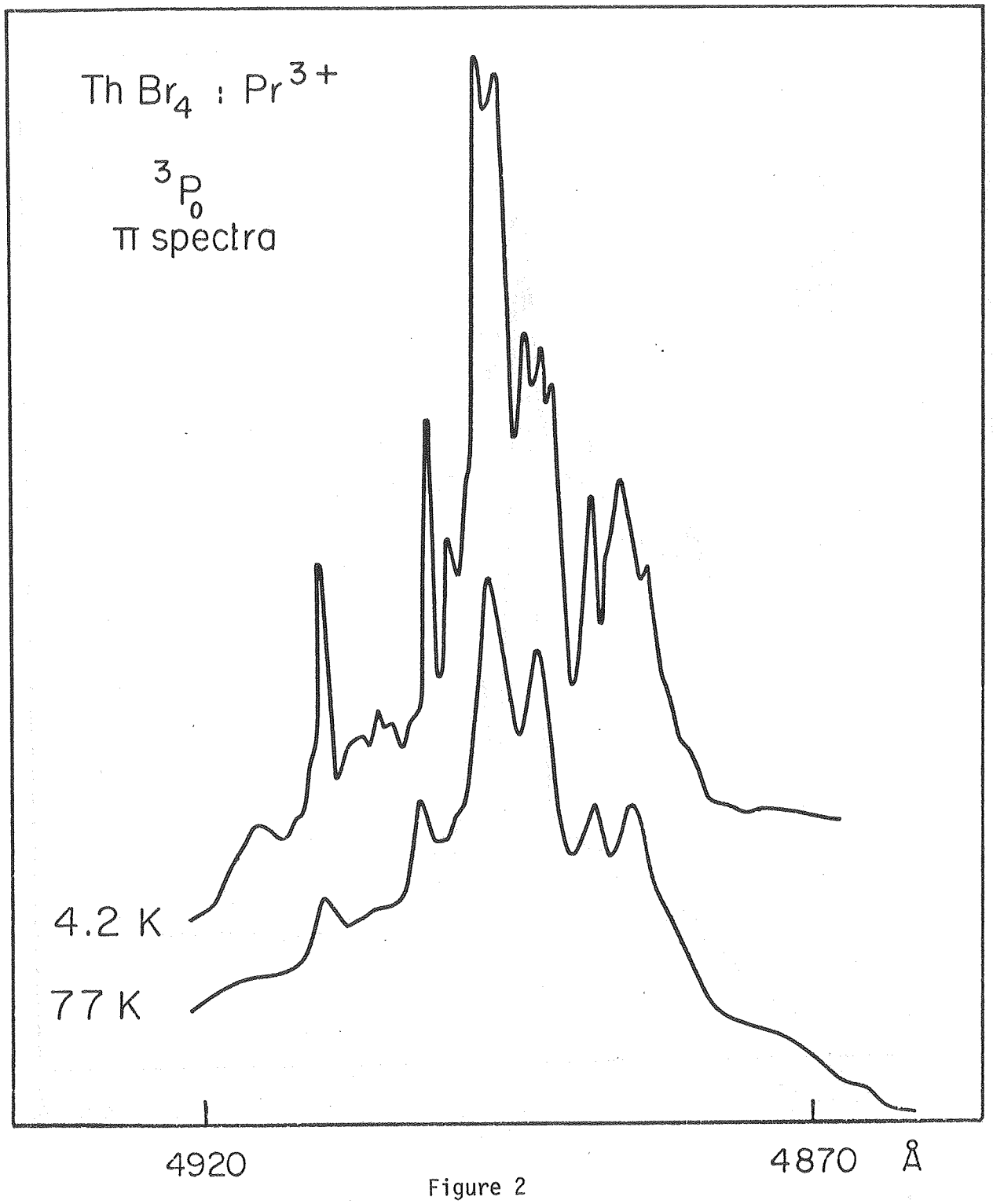

Figure 2

polarization and Fig. 2 shows the change in structure of the π polarization with the change of the temperature from 77 to 4.2 K.

The absorption spectrum at room temperature has a line at 304 cm^{-1} to the low energy side of the $^3P_0$. This was observed in a crystal perpendicular to the c-axis but was not polarized. Since this agrees with a laser fluorescence line and the only other line possible is to the Γ_4 level, it is taken as the Γ_4 to Γ_1 transition.

This assignment is supported by the transitions to the $^1D_2$. We see four lines : 3σ lines and a π line which is the case only for a Γ_5 ground state. A Γ_1, Γ_2 or Γ_4 ground state would allow only two lines, a π and a σ, and a Γ_3 ground state permits only one σ line. None of these ground states would allow transitions to the $^3P_0$.

The absorption lines were then used as data in a fitting program which adjusted the various parameters. At first the electrostatic parameters, F^2, F^4, F^6, the spin orbit parameter ξ, and the configuration interaction parameters α,β,γ were fixed at the values for aqueous ion[6]. The crystal field parameters, B_0^2, B_0^4, B_4^4, B_0^6 and B_4^6 were varied starting with the values for Pr^{3+} in Li YF_4. The ground state is different for the two matrices but otherwise the order of magnitude was correct. Once reasonable B^K values were obtained they were fixed and the $F^{K'}$s and ξ were varied. At this point, the calculated values were compared to the lines determined from the laser fluorescence experiments. These lines were not polarized, and because the levels have some vibronic components, all possible lines appeared. Thus all 7 possible lines from the $^3P_0$ to the $^3H_4$ were seen regardless of selection rules. All 10 lines from the $^3H_6$ and 4 lines from the $^3F_2$ are also seen (Table 2). These fluorescence levels were then assigned in the order derived from the fit. The $B^{K'}$s were then varied, fixing the $F^{K'}$s, ξ ; then the $F^{K'}$s varied with the $B^{K'}$s fixed and finally the $B^{K'}$s were varied again. The final parameter values are listed in table 3. Table 4 gives the values of the experimental and calculated energies together with the irreducible representations and the L-S states.

IV - CONCLUSIONS

The strong lines in the spectrum of Pr^{3+} in $ThBr_4$ resemble the structure of Pr^{3+} ion in other situations such as the aqueous solution. The data have been successfully fitted to the symmetry of the $ThBr_4$, D_{2d}.

However it should be mentionned that the Pr^{3+} ion in $ThBr_4$ is not that simple and there are many processes going on that we cannot explain and probably some of which we are not aware. A few examples should be mentioned. The $^3P_0$ shows vibronic structrure with several satellite lines on both sides of the main line. In crystals which were not as optically good as those used there was a satellite line at 89 cm^{-1} to the low energy side of this line which varied in intensity in different parts of the crystal and in different crystals. When this line was excited by the laser, it gave a very complicated spectrum in the region of the strong $^3F_2$ and $^3H_6$ transitions. Therefore it was due to Pr^{3+} but of a very different nature from the stronger $^3P_0$ line. Also, as the laser excitation wavelength was varied over the $^3P_0$ absorption peak, we saw four strong lines to the $^3F_2$ levels but a change of 2 Å to higher energy produced a doubling of each of the four lines separated by about 5 cm^{-1}. The $^3H_6$ lines were broader and did not show this splitting. We interprete this as two different sites of the same symmetry. As we scanned further from the peak the four lines faded and as many as eight other weaker lines appeared, probably due to Pr^{3+} ion in other symmetries. The $^3H_6$ showed this fading of the original lines into a complex pattern of many lines. Excitation into the absorption peaks of the $^3P_1$ and $^3P_2$ yielded the same fluorescence as the $^3P_0$, four strong lines. This is a radiationless transition from the upper levels to the lower $^3P_0$. We did not look for fluorescence from the $^1D_2$ as it would be too far in the red to be easily observed.

There is a moderately intense line at 4525 Å which is unpolarized and does not fit into D_{2d} system. One possible explanation is that it is a $^3P_2$ line of a different symmetry and is the only such line seen because of the great intensity of the $^3H_4$ - $^3P_2$ transition.

It appears that in addition to the strong features which can be interpreted as belonging to the D_{2d} symmetry site of $ThBr_4$, there is another D_{2d} site and at least two other symmetries exist in this crystal. There is also an unexplained feature due to Pr^{3+} which depends on the perfection of the quality of the crystal.

Moreover we have not been able to index the vibronic structure of the $^3P_{0,1,2}$ lines even though vibronic frequencies are known for both infrared and Raman active vibrations[7].

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Table I

Absorption wavelengthsof Pr^{3+} in $ThBr_4$ at 4.2 K

L-S state	Wavelength (Å)	Wavenumber (cm^{-1})	Intensity	Polarization
$^3F_2$	19947	5011	7	σ
	19664	5084	9	σ
	19453	5139	10	σ
$^3F_3$	15553	6427	4	π
	15471	6462	4	σ
	15377	6501	4	π
	15640	6392	2	σ
$^3F_4$	weak used fluorescence			
$^1G_4$	9932	10066	1bd	π
$^1D_2$	6003	16652	3	σ
	5987	16698	5	σ
	5864	17047	5	-
	5859	17063	5	π
$^3P_0$	4894	20428	10	σ
$^3P_1$	4739	21098	2	π
	4718	21188	9	σ
$^1I_6$	4760	21002	1	σ
	4670	21405	2	σ
	4647	21509	4	σ
$^3P_2$	4498	22226	6	σ
	4470	22362	6	σ
	4463	22398	6	σ

Table 2

Laser induced fluorescence of Pr^{3+} in $ThBr_4$ at 77 K. The excitation is into the $^3P_0$ level 20473 cm^{-1} a)

Wavelength Å	Wavenumber cm^{-1}	Level cm^{-1}	Assignment
7461.2	13399.0	7074	$^3F_4$
7442.9	13432.0	7041	"
7418.8	13475.6	6997	"
7399.5	13510.6	6962	"
7387.0	13533.6	6939	"
7379.3	13547.7	6925	"
7364.9	13574.3	6899	"
6518.0	15337.0	5136 abs	$^3F_2$
6509.0	15360.0	5113	"
6496.0	15390.0	5083 abs	"
6467.0	15459.0	5014 abs	"
6389.0	15647.0	4826	$^3H_6$
6356.0	15729.0	4744	"
6309.0	15845.0	4628	"
6280.0	15919.0	4554	"
6272.0	15941.0	4532	"
6263.0	15963.0	4510	"
6237.0	16028.0	4445	"
6206.0	16108.0	4365	"
6195.0	16138.0	4335	"
6168.0	16207.0	4266	"

a) The three absorption lines were used to find the value of the level from which fluorescence originated : the difference between the levels in absorption and fluorescence is between 1 and 3 cm^{-1}. The origin of fluorescence is 45cm^{-1} higher than the absorption value. However, there is a very weak satellite line at 4882 Å which is probably the origin of the fluorescence.

Table 3

Table of parametersobtained from fitting Pr^{3+} in $ThBr_4$

F^2	68354	
F^4	50310	
F^6	33799	
F^0	11558	
ξ	738.8	
α	21.26	fixed [a]
$\beta/12$	-66.67	fixed [a]
γ	1342.9	fixed [a]
B_0^2	260.0	
B_0^4	-644.2	
B_4^4	929.2	
B_0^6	1089.0	
B_4^6	240.6	

42 levels

$RMS^{(c)} = 61\ cm^{-1}$,

a) fixed at the aqueous values, ref. 6.

b) $RMS = \left(\frac{\Sigma(E_c-E_o)^2}{\text{number of levels-number of parameters}}\right)^{\frac{1}{2}}$

c) final fit had 42 levels and 6 parameters $B^{K'}s$, F^0

Table 4

Energy levels of Pr^{3+} in $ThBr_4$

L-S state	Levels obs_i (cm^{-1})	Levels $Calc_i^{a)}$ (cm^{-1})	Irreducible Representation
$^3H_4$	0.0	49	5
	188	200	
	300	203	4
	345	266	
	377	358	
	499	391	5
	543	496	
$^3H_5$		2170	
		2210	
		2265	5
		2298	
		2327	5
		2431	
		2471	5
		2539	
$^3H_6$	4266	4259	5
	4335	4337	
	4365	4439	
	4445	4449	5
	4510	4483	
	4532	4549	
	4554	4553	
	4628	4624	
	4744	4706	5
	4826	4732	

Table 4 (continued)

$^3F_2$	5113	5143	5
	5011	5149	
	5084	5159	
	5139	5212	
$^3F_3$		6463	5
		6520	
	6501	6557	5
		6565	
		6571	
$^3F_4$	6899	6834	
	6925	6904	5
	6935	6945	
	6962	7015	
	6997	7029	
	7041	7081	5
	7074	7112	
$^1G_4$		9581	
		9792	5
		9816	
		9830	
		9921	
	10066	10067	5
		10221	
$^1D_2$	16652	16715	
	16697	16741	
	17063	16933	5
	17047	17099	
$^3P_0$	20428	20447	
$^3P_1$	21098	21037	5
	21188	21120	

Table 4 (continued)

$^1I_6$		21136	
		21145	
		21295	5
		21315	
	21405	21326	
		21517	5
	21509	21560	
		21728	
		21739	5
		21766	
$^3P_2$	22226	22236	
		22291	5
	22362	22323	
	22398	22410	
$^1S_0$		47068	

a) The calculated values are obtained by diagonalizing the matrices using the parameters listed in Table 3.