ELECTRONIC ABSORPTION SPECTRA OF Pr³⁺ COMPLEXES IN SOLUTION

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ABSTRACT

Electronic absorption spectra of Pr(III) ion in barium nitrate and acetate solution have been studied in the UV and visible regions. From the observed spectra, and values of Slater-Condon spin-orbit and Judd-Ofelt parameters have been calculated. The experimentally measured energies and spectral intensities agree with theoretical data. From the magnitude of the bonding parameter the nature of bonding in the complex has been suggested. From the observed intensity parameters, the values of the lifetimes for various fluorescent levels of Pr(III) ion in barium acetate and barium nitrate have been predicted.

INTRODUCTION

THE optical spectra of lanthanides in various solutions of complexes[1-5] and laser liquids[6-10] have been reported earlier. However the spectra of Pr(III) ion in $Ba(C_2H_3O_2)_2$ and $Ba(NO_3)_2$ have not been reported and the present work is an attempt to fill this gap.

EXPERIMENTAL

To a saturated solution of acetate and nitrate of barium, 0.2 m % of praseodymium acetate and nitrate were added. The UV visible absorption spectra were recorded on a Perkin-Elmer 551 spectrophotometer. For the observed four bands, the spectral intensities are calculated from the expression[11]

$$f_{exp} = 4.32 \times 10^{-9} \int \varepsilon(v) \, dv,$$

where (v) is the extinction coefficient value for a band whose energy is $v(cm^{-1})$, and dv is the bandwidth at the half height and these values are presented in table 1. The refractive indices of barium acetate and nitrate are 1.500 and 1.572 respectively.

RESULTS AND DISCUSSION

From the UV visible spectra of Pr(III) complexes about four energy levels have been observed and identified as $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ from the ground state $^3H_4$.

Energy levels: The measured energies of the observed levels have been compared with theoretical energies, by following the procedure of Wong[12]. From this energy level fitting, the Slater-Condon (F_k) and spin-orbit (ξ_{4f}) energy level parameters are calculated and presented in table 3. The measured values of energies, extinction coefficient, band halfwidths and oscillator strengths of bands for Pr(III) in barium acetate and barium nitrate are given in table 1. The theoretically evaluated energies and oscillator strengths are shown in table 2 for Pr(III) in barium acetate and barium nitrate.

Spectral intensities: The intensity parameters (T_2, T_4 and T_6) evaluated[13-15] for the observed spectra of Pr(III) complex are given in table 3.

Bonding: According to procedures reported earlier[16,17], the bonding parameter (δ) of the complexes is said to suggest the covalent or ionic nature of the bond depending on the sign of δ. Since in the present work the δ parameters for the two complexes are negative, the bonding has been inferred to be ionic in nature.

Lifetime: Recently, theoretical prediction of lifetimes (T_R) of the fluorescent levels for each of the rare earth elements has been reported[18] where the Judd-Ofelt parameters have been used for theoretically evaluating the lifetimes. We have followed their method for calculating the lifetimes of the fluorescent levels known as $^3P_{1,0}$ and $^1D_2$ of Pr³⁺ in barium acetate and barium nitrate using our data given in table 3 and the results are presented in table 4.

CONCLUSIONS

Since the observed levels and the spectroscopic parameters (F_2, F_4, F_6 and ξ_{4f}) are equal in number, an accurate energy level fitting has been made possible with zero as the r.m.s. deviation (tables 1 and 2).

Table 1 *Measured values of energies (E), extinction coefficient (ϵ), band halfwidths (dv) and oscillator strengths (f) of bands for Pr (III) in barium acetate and barium nitrate*

Energy levels from $^3H_4$	E		ϵ		dv		$f_{exp} \times 10^6$	
	Barium acetate (cm^{-1})	Barium nitrate (cm^{-1})	Barium acetate	Barium nitrate	Barium acetate	Barium nitrate	Barium acetate	Barium nitrate
$^3P_2$	22567	22567	2.60	4.55	457	305	5.13	5.99
$^3P_1$	21361	21407	1.10	1.95	413	302	1.96	2.71
$^3P_0$	20741	20784	0.75	1.55	172	129	0.55	0.86
$^1D_2$	16973	17002	0.50	0.85	458	345	0.98	1.26

Table 2 *Calculated values of energies (E) and spectral intensities ($f \times 10^6$) for Pr^{3+} in barium acetate and barium nitrate*

Energy level from $^3H_4$	E (cm^{-1})		f_{cal} ($\times 10^6$)	
	Barium acetate	Barium nitrate	Barium acetate	Barium nitrate
$^3P_2$	22567	22567	5.13	6.00
$^3P_1$	21361	21407	1.24	1.77
$^3P_0$	20741	20784	1.22	1.74
$^1D_2$	16972	17001	0.97	1.24

Table 3 *Calculated Slater-Condon (F_2, F_4, F_6), spin-orbit (ξ_{4f}), Judd-Ofelt(T_2,T_4,T_6) refractive index(n), intensity ($\Omega_2,\Omega_4,\Omega_6$), nephelauxetic ($\bar{\beta}$) and bonding ($\delta$) parameters for Pr^{3+} in barium acetate and barium nitrate*

Complexes	F_2	F_4	F_6	ξ_{4f}	T_2	T_4	T_6	n	Ω_2	Ω_4	Ω_6	$\bar{\beta}$	δ
Pr^{3+} in barium acetate	315.31	62.44	5.79	763.5	−11.89	0.34	1.58	1.500	−73.7	2.11	9.85	1.00	−0.309
Pr^{3+} in barium nitrate	316.04	45.62	4.66	741.6	−11.81	0.48	1.83	1.572	−69.3	2.85	10.70	1.00	−0.457

Table 4 *Lifetimes (τ_R) for the electronic excited states $^3P_1$, $^3P_0$ and $^1D_2$ for Pr^{3+} in barium acetate and barium nitrate*

Fluorescent levels	τ_R (μsec)	
	Pr^{3+}: Barium acetate	Pr^{3+}: Barium nitrate
$^3P_1$	57.4	54.0
$^3P_0$	69.9	64.0
$^1D_2$	1046.0	990.0

The influence of the environment on the observed intensities is clear from table 3. Among the three Judd-Ofelt parameters, T_2 has a negative sign in both the hosts. Similar observation was made by Tandon *et*

al[19]. From table 4, it is noted that the lifetimes of the fluorescent levels $^3P_{1,0}$ and $^1D_2$ appear to be approximately the same, whereas the T_R values for $^1D_2$ is about 20 times greater compared to $^3P_{1,0}$. The reasons

for such a behaviour might be due to the higher values of reduced matrix elements $||U||^2$ for $^1D_2$ and its lower lying levels, and also due to the influence of T_4 and T_6 on these reduced matrix elements. In both the hosts, the trend in lifetime is as follows:

$$^1D_2 \gg {}^3P_0 > {}^3P_1.$$

Similar trends have been reported for Pr(III) earlier[1,5,6].

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NEWS

CREATING AN ENVIRONMENTAL ETHIC

. . . "Despite all that has been done to identify and to solve the environmental problems of the nation and the world, the argument can be and is being made that the scales are still precariously tipped in favor of exploitation. The seriousness and gloominess of this conclusion have been reinforced in numerous ways in just the last half-dozen years as ecological research and understanding have focused public attention on such global problems as the buildup of carbon dioxide in the atmosphere, world population, and desertification. . . . In 1981, the Natl. Academy of Sciences concluded in a report on energy, 'We are exhausting fossil fuels, ruining soil fertility, unbalancing ecosystems, and distorting human values and institutions in the greatest energy-spending spree of all time.' The fact that so many governmental and nongovernmental institutions have come to accept the need for a broader perspective and for worldwide action is an encouraging sign. But understanding the global dimensions of the environmental crisis is merely a realistic observation about the scale of the planet's mismanagement. What is also needed, as many others have noted, is a deeper, more spiritual approach to nature from which we can derive an environmental ethic."

[(Peter Borrelli in *Amicus Journal* 7(3): 34–41, Winter 1986 (See also: E. Garfield. The Natural Resources Defense Council, Inc.: scientists and lawyers go to court in defense of the environment. *Essays of an information scientist*. Philadelphia: ISI Press, 1981, Vol. 4, p. 323–32.) Reproduced with permission from Press Digest, *Current Contents*®, No. 19, May 12, 1986, p. 13 (Published by the Institute for Scientific Information®, Philadelphia, PA, USA))]