



Characteristics of the energy bands and the spectroscopic parameters of Pr³⁺ ions in PrCl₃ mixed methanol, iso-propanol and butanol solutions

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ABSTRACT

An investigation on the absorption spectra of the praseodymium chloride (PrCl₃) in methanol, iso-propanol and butanol is carried out between 190 nm and 1100 nm. We have observed and assigned six energy bands of the 4f² electronic configuration of the Pr³⁺ ion in the visible to near-infra-red and one due to 4f5d configuration in the ultraviolet region. The 4f5d band has been detected properly for low concentration of PrCl₃. We have also constructed a free-ion Hamiltonian and calculated the energy levels of the 4f² configuration theoretically. Hence, the best fit free-ion parameters are deduced.

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1. Introduction

Research on lanthanides in complex matrices like gels and glasses is demanding remarkable attention because of their important practical utility. Many of the organically modified glass matrices are being developed by applying the alcohol method of synthesis. In order to explain the optical properties of the rare earth metal ion in these systems, studies on lanthanides in alcoholic solution become suitably important. Although the spectroscopic properties of some praseodymium complexes in alcohols have been studied, namely, on Pr (NO₃)₃ · 6H₂O [1], praseodymium perchlorates [2], anhydrous and hydrated praseodymium chlorides (PrCl₃) [3,4], however, rigorous investigations specifically on the aspects of the energy level characteristics as well as various spectroscopic parameters of the Pr³⁺ ions in alcohols are rather scarce. Besides, the characteristics of the 4fⁿ⁻¹5d electronic configuration of the trivalent rare earths are becoming attractive because of their wide applications in the vacuum ultraviolet region, e.g., development of plasma display panels and mercury-free fluorescent tubes. Among the rare earth ions, Pr³⁺ ion bears a unique feature, which is due to the proximity of the 4f¹5d configuration with the ¹S₀ state of the 4f² electronic configuration [5,6].

Hence, to get an insight regarding the properties of the energy bands of the 4f² and 4f5d configurations of the Pr³⁺ ion, in this paper, we represent the absorption spectra of various concentrations of PrCl₃ in methanol, iso-propanol and butanol solvents. The observed energy bands for both configurations are detected and analyzed. Adopting a free-ion Hamiltonian of the 4f² electronic configuration, we have calculated the energies theoretically and hence estimated the best fit parameters. The free-ion Hamiltonian is constructed by incorporating the electrostatic Slater, spin-orbit, configuration interaction, the spin-spin and spin-other-orbit, i.e., Marvin interactions, and the two-body electrostatically correlated magnetic interactions.

2. Experimental

In our experiment three different alcohols viz., methanol [CH₃OH], 2-propanol i.e., iso-propanol [(CH₃)₂CHOH] and butanol [CH₃(CH₂)₃OH] (Guaranteed Reagent grade, Merck, India) were taken as organic solvents. High purity anhydrous praseodymium chlorides (PrCl₃, Indian Rare Earth Ltd., purity 99.9%) were dissolved with different concentrations from 0.00125 M to 0.02 M in the alcohols, according to the requirements (where M indicates the Molar solution). Because of the hygroscopic nature of the PrCl₃, the samples were prepared in a dry box in the laboratory.

Absorption spectra were measured at room temperature (300 K) by a UV-Visible Spectrometer (Perkin Elmer, Model: Lambda 45) in

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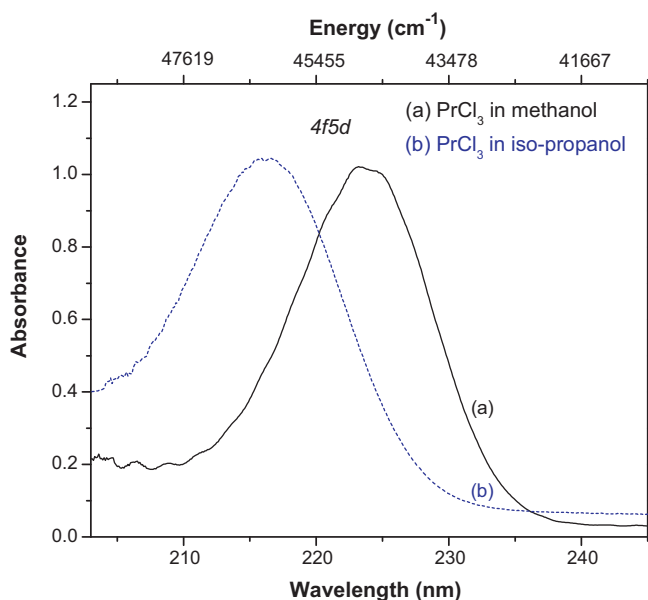


Fig. 1. Absorption spectra observed at room temperature in the ultraviolet region corresponding to the $4f5d$ configuration for 0.00125 M concentration of PrCl_3 in (a) methanol and (b) iso-propanol solutions.

the region 190–1100 nm. The PrCl_3 mixed alcoholic solutions were taken in a quartz cuvette having a path length of 10 mm. Observed spectra were recorded in the double-beam spectrometer, taking respective alcohol as the reference.

3. Results and discussions

3.1. Analysis of the observed spectra

The spectral characteristics of the anhydrous praseodymium chloride in three different alcohols are focused in the ultraviolet (UV), visible and near infra-red (NIR) regions.

Absorption spectra of PrCl_3 in methanol and iso-propanol in the UV region (between 200 and 250 nm) are depicted in Fig. 1. The signature of the peak of the band becomes prominent as the concentration of the PrCl_3 is reduced to 0.00125 M. We find the appearance of peaks in methanol at 223.2 nm (i.e., at energy 44803 cm^{-1}) and in propanol at 215.83 nm (46333 cm^{-1}). These energy bands correspond to the $4f5d$ electronic configuration of the Pr^{3+} ion. It is interesting to note that the intensity of absorption observed for this inter-configurational transition ($4f^2-4f5d$) is stronger than that of visible and NIR regions, since this band is *electric dipole allowed* transition. The occurrence of the $4f5d$ energy band around this wavelength is supported by various works on solutions as well as solid host matrices [2–7]. We have observed a positional shift of the peak towards the higher energy when the solvent is changed from methanol to iso-propanol. The shift of energy for this transition towards the UV region confirms the effect of mixing of the opposite parity configuration [2].

The possibility of $^3\text{H}_4 \rightarrow ^1\text{S}_0$ transition is curtailed here, because it is very weak due to the strongly forbidden character. Our theoretical calculation also indicates that the $^1\text{S}_0$ energy level is situated at a higher region [8]. It is to be mentioned here that we experienced difficulties in recording the $4f5d$ absorption band in butanol, since the cutoff wavelength of this solvent is 215 nm.

The energy bands which arise due to the electronic transitions for the $4f^2-4f^2$ configuration of the Pr^{3+} ion are represented in Figs. 2–4 below.

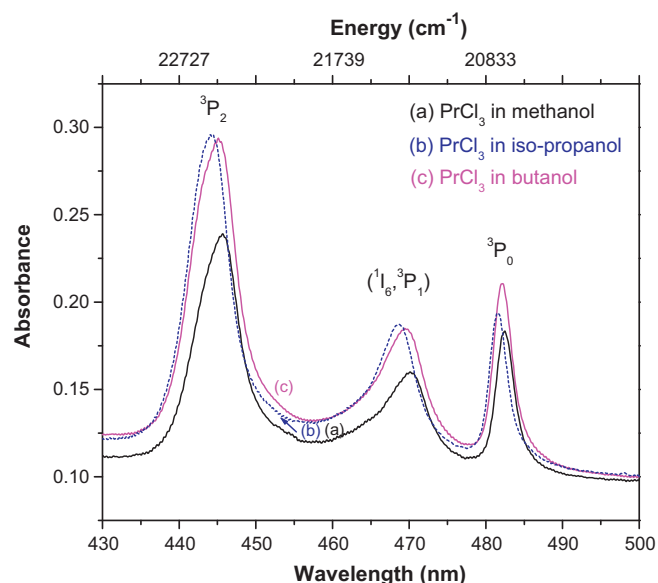


Fig. 2. Observed energy bands for $^3\text{H}_4 \rightarrow (^3\text{P}_2, ^1\text{I}_6, ^3\text{P}_1, ^3\text{P}_0)$ transitions for 0.02 M of PrCl_3 dissolved in (a) methanol (b) iso-propanol and (c) butanol solvents, respectively.

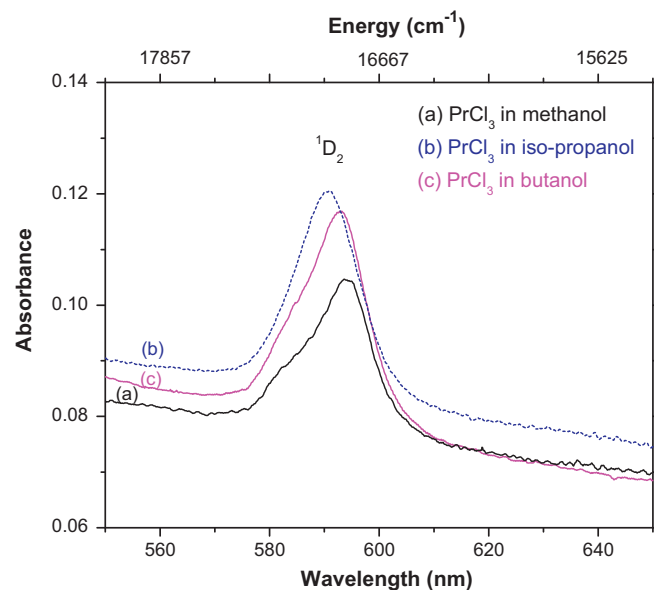


Fig. 3. Experimental absorption for 0.02 M of PrCl_3 in (a) methanol (b) iso-propanol and (c) butanol, respectively, indicating $^3\text{H}_4 \rightarrow ^1\text{D}_2$ transition at room temperature.

Fig. 2 shows the absorption spectra in the visible region between 430 nm and 500 nm, for 0.02 M concentration of PrCl_3 solutions. Here we have observed transitions from the ground state $^3\text{H}_4$ to the excited $^3\text{P}_2$, $^1\text{I}_6$, $^3\text{P}_1$ and $^3\text{P}_0$ multiplets. The $^3\text{P}_2$ band has comparatively wide bandwidth [i.e., *full width at half maximum (FWHM)*] and it occurs at 445.68 nm (22438 cm^{-1}) in methanol, at 444.08 nm (22518 cm^{-1}) in iso-propanol and at 445.10 nm (22467 cm^{-1}) in butanol, respectively. The $^1\text{I}_6$, $^3\text{P}_1$ energy bands become unresolvable and they arise at 470.11 nm (21272 cm^{-1}), 468.70 nm (21336 cm^{-1}) and 469.43 nm (21302 cm^{-1}), respectively in methanol, iso-propanol and butanol. The spectra having small bandwidth are observed at 482.48 nm (20726 cm^{-1}), 481.52 nm (20768 cm^{-1}) and 482.19 nm (20739 cm^{-1}) corresponding to $^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition, respectively, in those alcohols.

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