Electronic Absorption Spectra of Praseodymium in Molten Chlorides

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Z. Naturforsch. **62a,** 733 – 738 (2007); received June 13, 2007

Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

Electronic absorption spectra of trivalent praseodymium in various alkali chloride melts were precisely measured. The oscillator strength of the hypersensitive transition, $^3F_2 \leftarrow ^3H_4$, showed a clear decrease with increasing temperature. This temperature dependence was the inverse of reported cases for other trivalent lanthanoides. The Judd-Ofelt parameter was analysed, and the calculated oscillator strength showed quite good agreement with the experimentally obtained oscillator strength. However, the Ω_2 parameter, which is sensitive to the ligand environment change, showed a clear decrease with increasing temperature and negative values at high temperature. We found that the $^3P_0 \leftarrow ^3H_4$ transition and its shoulder peak are quite sensitive to the coordination circumstance change of the $[PrCl_6]^{3-}$ complex in molten chlorides. These intensities could be correlated with the octahedral symmetry of $[PrCl_6]^{3-}$.

Key words: Molten Salt; Praseodymium; Electronic Absorption Spectrometry; Judd-Ofelt Parameter Analysis.

1. Introduction

Electronic absorption spectrophotometry has been used to study the characteristics of chemical species in molten salts. To reinforce the basic knowledge for pyrochemical reprocessing, we investigated the behaviour of trivalent f-elements in molten salts by using this analytical technique. We have focused on the hypersensitive transition of neodymium, and studied the structural property of the $[NdCl_6]^{3-}$ complex in various molten chlorides [1]. The highly symmetric octahedral coordination has been confirmed in an NaCl-2CsCl eutectic and in CsCl. Adding LiCl to CsCl resulted in the distortion of the symmetry. The octahedral symmetry of $[NdCl_6]^{3-}$ was also found to be distorted with increasing temperature. These findings were demonstrated for other trivalent lanthanoides [2], Sm(III), Dy(III), Ho(III), and Er(III), in chloride melts, which supports the results of studies [3 – 5] on Nd(III) and Ho(III). Investigating these characteristics is useful for understanding the thermochemical stabilities of f-elements in melts, which greatly influence the performance of the reprocessing process.

In this paper we report absorption characteristics of Pr(III) in chloride melts that seem to be quite unusual among other lanthanoides. Radiative transition probabilities of f-f transitions in spectra of lanthanoide compounds have been successfully analysed by the Judd-Ofelt theory [6, 7]. However, Pr(III) is known to be notorious for the inconsistency of the transition probability between the Judd-Ofelt theory and experimental values [8 – 10]. The discrepancy has been reported for various praseodymium compounds [8 – 10]. Since the Judd-Ofelt parameter analysis is effective in discussing the ligand environment of Nd(III) and Ho(III) in chloride melts [3 – 5], it is of interest to check the effectiveness for Pr(III) in chloride melts.

2. Experimental

Anhydrous alkali chlorides, 3LiCl-2KCl eutectic mixture (mole ratio of lithium to potassium = 59/41), NaCl-2CsCl eutectic mixture (mole ratio of sodium to cesium = 1/2), LiCl, CsCl, $CaCl_2$, and anhydrous praseodymium trichloride, $PrCl_3$, were products of Anderson Physics Laboratory Engineered Materi-

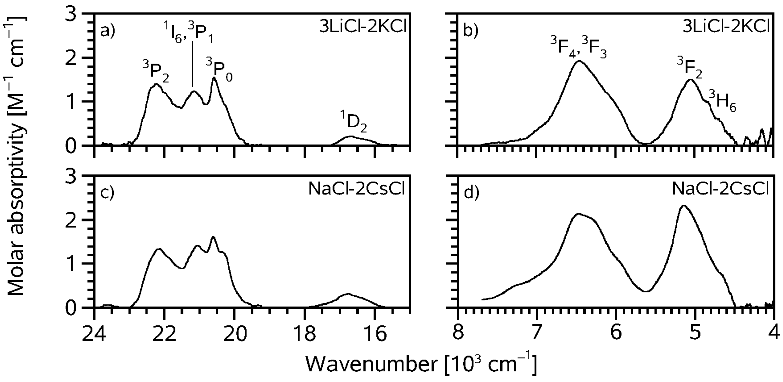

Fig. 1. Electronic absorption spectra of Pr(III) in molten chlorides at 873 K. (a, b) 3LiCl-2KCl eutectic; (c, d) NaCl-2CsCl eutectic. The ground energy state is $^3H_4$.

als. The 3LiCl-2CsCl eutectic mixture (mole ratio of lithium to cesium = 3/2) was prepared by mixing pure LiCl and CsCl.

All experiments were carried out in a glove box system filled with dry Ar continuously purified to remove oxygen and humidity. The content of O_2 and H_2O in the inside atmosphere was continuously maintained at less than 1 ppm. Absorbance measurements (UV/Vis/NIR spectrometer, V-570, JASCO) were performed with various molten chlorides containing ca. 0.1 mol dm^{-3} (M) $PrCl_3$. The details of our experimental apparatus and the procedure for absorbance measurements can be seen elsewhere [1, 11]. The temperature of the sample during the experiment was controlled to the desired value within ±3 K.

3. Results and Discussion

The typical absorption spectra of Pr(III) in molten chlorides are shown in Figure 1. The obtained spectra reproduce well the reported spectrum of molten $PrCl_3$ [12]. The f^2 configuration of a free Pr^{3+} ion involves 13 energy levels. The ground term appears to be $^3H_4$. All the absorption bands for Pr(III) in solutions and crystals in the Vis/NIR region correspond to the transitions from the ground state. The transition to the highest $^1S_0$ level, which lies in the near UV region, cannot be observed, as it is masked by the f-d transition in the same region [13]. As shown in Fig. 1, the absorption spectra of Pr(III) in molten chlorides in the Vis/NIR region involve 7 bands, in which the J-level splitting components for two pairs of levels, $^1I_6$–$^3P_1$ and $^3F_4$–$^3F_3$, are considered to be overlapped [13]. The electric dipole transitions between f-orbitals, that show abnormal variations in intensity, are classified as hypersensitive transitions. These variations are attributed to the action of an inhomogeneous electromagnetic field in the surrounding medium. Since the hypersensitive transition is sensitive to the coordination circumstances, it is commonly used to examine the coordination of trivalent lanthanoides. From the selection rule stated by Jørgensen and Judd [14], i. e., $|\Delta J| = 2$, $|\Delta L| \leq 2$, $\Delta S = 2$, the $^3F_2 \leftarrow {}^3H_4$ transition is the hypersensitive transition of Pr(III). Though transitions $^3P_2 \leftarrow {}^3H_4$ and $^1D_2 \leftarrow {}^3H_4$ do not comply with the selection rule, they are sometimes classified as the pseudo-hypersensitive transitions due to their sensitivities to the coordination circumstance [15]. These pseudo-hypersensitive transitions were, however, not sensitive in the present study.

The predominant species of trivalent lanthanoides in molten chloride is $[LnCl_6]^{3-}$ (Ln = lanthanoide) with the octahedral symmetry (O_h) [1, 3 – 5, 12]. According to a computer simulation [16] on $LnCl_3$ in CsCl at mole fractions up to 25 mol% $LnCl_3$, the certain coordination number of Ln in the Ln complex is six. A higher coordination number has been calculated for mole fractions over 25 mol% $LnCl_3$ [16], but this is inconsistent with the six-fold coordination experimentally obtained for pure $LnCl_3$ [5, 12]. Since the present study is performed with diluted Pr(III) molten chlorides, the predominant Pr(III) species should be $[PrCl_6]^{3-}$.

To discuss the coordination change, we evaluated the oscillator strength for the hypersensitive transition, $^3F_2 \leftarrow {}^3H_4$. The oscillator strength can be defined as [4]

$$f_{\text{exp}} = 4.319 \cdot 10^{-9} \frac{9n}{(n^2+2)^2} \int \varepsilon(\nu)\mathrm{d}\nu, \quad (1)$$

where $\varepsilon(\nu)$ is the molar absorptivity at energy ν (cm^{-1}) and n the refractive index of the solvent medium. The n value of the eutectic was estimated

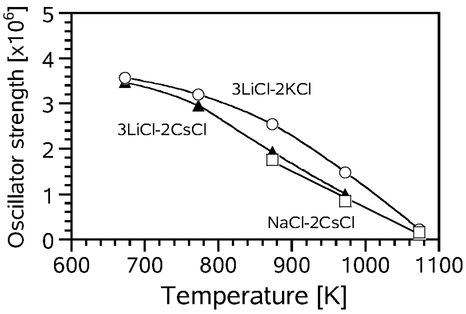

Fig. 2. Oscillator strength for the hypersensitive $^3F_2$,$^3H_6$ ← $^3H_4$ transition.

by a linear interpolation between the n values of pure alkali chlorides [17]. We calculated $f_{\rm exp}$ for the $^3F_2$,$^3H_6$ ←$^3H_4$ transition (Fig. 2). Though the difference was small, the $f_{\rm exp}$ value at a fixed temperature was found to increase in the order of NaCl-2CsCl < 3LiCl-2CsCl < 3LiCl-2KCl. In general [4], distortion of the octahedral symmetry results in an increase of oscillator strength of hypersensitive transitions. The NaCl-2CsCl eutectic can be treated as molten elpasolite ($Cs_2NaLnCl_6$), in which the elpasolite provides highly symmetric octahedral coordination of $[LnCl_6]^{3-}$ in its crystal matrix [3]. Hence, the smallest $f_{\rm exp}$ values found for the NaCl-2CsCl eutectic are reasonable and this supports that the highly octahedral symmetry of $[PrCl_6]^{3-}$ is kept in the NaCl-2CsCl eutectic. The octahedral symmetry is known to be distorted by adding cations with higher polarizing power like Li^+ [1]. The $f_{\rm exp}$ value was found to increase in the order of polarizing power ($1/r^+$) of alkali chloride eutectics. This is consistent with the studies on other lanthanoides [1, 2]. An unexplained phenomenon in the present study is the temperature dependence of $f_{\rm exp}$. The oscillator strength of hypersensitive transitions generally increases with temperature [1, 5], which can be interpreted as the increase of anharmonic vibrations of $[LnCl_6]^{3-}$. As shown in Fig. 2, $f_{\rm exp}$ ($^3F_2$,$^3H_6$ ←$^3H_4$) for each system shows an opposite temperature dependence. This discrepancy suggests that the Pr(III)-molten chloride system may be an exceptional case for applying the Judd-Ofelt theory.

From the Judd-Ofelt theory [6, 7], the oscillator strengths of f-f transitions can be expressed as

$$f_{\rm calc} = \frac{8\pi^2 m_{\rm e} c\nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \cdot \sum_{\lambda=2,4,6} \Omega_\lambda (f^n\psi J \| U^{(\lambda)} \| f^n\psi' J')^2, \quad (2)$$

Table 1. Intensity parameters for Pr^{3+} in molten chlorides.

Temperature [K]	Ω_2 [10^{-20} cm^2]	Ω_4 [10^{-20} cm^2]	Ω_6 [10^{-20} cm^2]
a) 3LiCl-2KCl eutectic			
673	2.79	8.79	2.44
773	2.20	8.02	2.53
873	0.094	8.11	2.29
973	−2.99	8.17	1.52
1073	−6.09	7.68	0.45
b) 3LiCl-2CsCl eutectic			
673	5.50	5.52	2.02
773	3.75	5.57	1.99
873	0.44	5.65	1.90
973	−2.55	5.95	1.33
c) NaCl-2CsCl eutectic			
873	1.33	4.17	1.53
973	−1.89	4.84	0.918
1023	−4.36	5.80	−0.246

where c is the light velocity, J the total quantum number of the ground state, and $(f^n\psi J\|U^{(\lambda)}\|f^n\psi' J')$ the reduced matrix element of the respective unit tensor operator $U^{(\lambda)}$. The $U^{(\lambda)}$ values have been tabulated by Carnall and co-workers [18]. Ω_λ ($\lambda = 2$, 4, and 6) are the phenomenological intensity parameters determined by a least-squares fit. We performed the Judd-Ofelt parameter analysis for $f_{\rm exp}$ values in the four transition regions, ($^3P_2$,$^1I_6$,$^3P_1$,$^3P_0$ ←$^3H_4$), ($^1D_2$ ←$^3H_4$), ($^3F_4$,$^3F_3$ ←$^3H_4$), and ($^3F_2$,$^3H_6$ ←$^3H_4$). The determined intensity parameters are given in Table 1. The experimentally obtained oscillator strengths and those calculated by the Judd-Ofelt parameters are shown in Table 2. As given in Table 2, quite good agreement between $f_{\rm calc}$ and $f_{\rm exp}$ can be seen. Though the breakdown of the Judd-Ofelt parameter analysis for Pr(III) has been reported [8 – 10], it is effective for evaluating the f-f transition intensity of Pr(III) in molten chlorides.

The important point of the Judd-Ofelt theory is that the intensity of hypersensitive transitions is associated with the Ω_2 parameter which appears to be rather sensitive to the ligand environment. In other words, the Ω_2 parameter has a close relation to the nephelauxetic effect of f orbitals. As shown in Table 1, for each eutectic system, Ω_2 shows a clear change while the Ω_4 and Ω_6 parameters are found to be less sensitive. The Ω_2 parameters determined in this study (Table 1) are graphically shown in Figure 3. It has been reported [3, 12] that the Ln–Cl distance of $[LnCl_6]^{3-}$ is shorter in heavier alkali chlorides and the shortening of the Ln–Cl distance increases the Ω_2 values. This indicates that Ω_2 shows a larger value for Ln(III) in a matrix chloride

Temperature [K]	$^3P_2,^1I_6,^3P_1,^3P_0 \leftarrow ^3H_4$ (436 – 523 nm)		$^1D_2 \leftarrow ^3H_4$ (573 – 633 nm)		$^3F_4,^3F_3 \leftarrow ^3H_4$ (1300 – 1782 nm)		$^3F_2,^3H_6 \leftarrow ^3H_4$ (1777 – 2213 nm)	
a) 3LiCl-2KCl eutectic								
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
673	10.55	10.55	0.85	0.81	5.18	5.19	3.57	3.57
773	9.75	9.73	1.02	0.75	4.98	4.99	3.20	3.20
873	9.69	9.69	0.63	0.60	4.66	4.66	2.54	2.54
973	9.42	9.40	0.72	0.33	3.75	3.76	1.48	1.48
1073	8.44	8.40	0.70	0.00	2.41	2.42	0.22	0.23
b) 3LiCl-2CsCl eutectic								
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
673	6.88	6.89	0.61	0.77	3.95	3.95	3.47	3.47
773	6.89	6.89	0.55	0.68	3.83	3.82	2.95	2.94
873	6.87	6.87	0.56	0.48	3.55	3.55	1.93	1.93
973	6.93	6.91	0.55	0.25	2.91	2.92	1.00	1.00
c) NaCl-2CsCl eutectic								
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
873	5.15	5.14	0.61	0.43	2.81	2.81	1.75	1.76
973	5.59	5.57	0.42	0.19	2.23	2.24	0.84	0.85
1023	6.15	6.12	0.46	0.00	1.28	1.29	0.15	0.16

Table 2. Measured and calculated polarized oscillator strength [$\cdot 10^6$] for Pr^{3+} in molten chlorides.

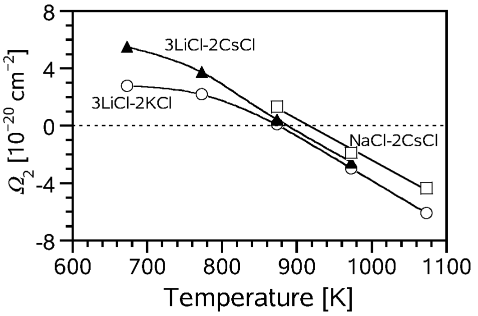

Fig. 3. Judd-Ofelt parameter Ω_2 as a function of the temperature. The values of the Judd-Ofelt parameters are listed in Table 1.

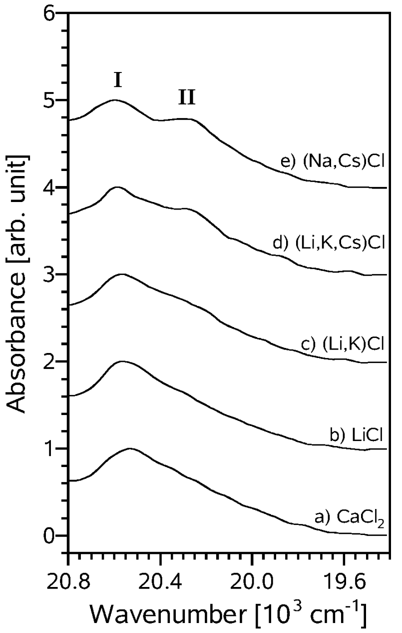

Fig. 4. Electronic absorption spectra of the $^3P_0 \leftarrow ^3H_4$ transition of Pr(III) in molten chlorides. (a) $CaCl_2$ (1075 K); (b) LiCl (973 K); (c) 3LiCl-2KCl eutectic (978 K); (d) mixture of 3LiCl-2KCl eutectic and CsCl (973 K, mole fraction of CsCl is 28%); (e) NaCl-2CsCl eutectic (923 K). Absorbance at the maximum of peak I is normalized to be unity.

with smaller polarizing power ($1/r^+$). Though the difference is small, Ω_2 was found to increase in the order, 3LiCl-2KCl < 3LiCl-2CsCl < NaCl-2CsCl. This property is consistent with the reported Ω_2 characteristics [3]. However, the temperature dependence of Ω_2 is totally inconsistent with the reported Ω_2 characteristics [3]. Furthermore, Ω_2 values at high temperature showed negative values. As shown in Fig. 2, f_{exp} of the $^3F_2 \leftarrow ^3H_4$ transition in the NIR region drastically decreased with increasing temperature, and this should be the origin of the specific change in Ω_2. The transition in the NIR region may have been interfered by vibrational motions, e. g., overtone vibrations or combination tone vibrations. The fundamental vibrational frequency of the $[PrCl_6]^{3-}$ complex is, however, much smaller [19, 20] than the $^3F_2 \leftarrow ^3H_4$ transition energy.

In this paper, we present a new idea: to investigate the ligand environment of $[PrCl_6]^{3-}$ via the $^3P_0 \leftarrow ^3H_4$ transition in the visible region. As shown in Fig. 1, a characteristic difference in the absorption spectra between the 3LiCl-2KCl eutectic and the NaCl-2CsCl eutectic is the right side (lower energy side) shoulder of the $^3P_0 \leftarrow ^3H_4$ transition. This re-

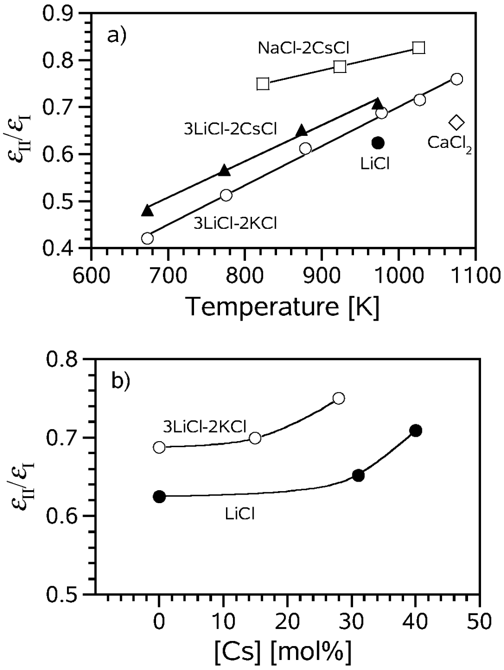

Fig. 5. Ratio of molar absorptivities of the $^3P_0 \leftarrow ^3H_4$ transitions of Pr(III) in molten chlorides. (a) Temperature dependence; (b) concentration dependence of Cs. ε_I, molar absorptivity at peak I; ε_{II}, molar absorptivity at $20.28 \cdot 10^3$ cm^{-1} (493 nm).

gion is enlarged and shown in Figure 4. From spectra (a) to (e), the absorbance of a shoulder peak at $20.28 \cdot 10^3$ cm^{-1} (493 nm) increases. It should be noted that this unknown peak has never been observed in aqueous systems [8] or molten PrCl$_3$ [3]. Since this peak is very clear for Pr(III) in the NaCl-2CsCl eutectic, it is suggested that its appearance is attributable to the highly O_h symmetry of the $[PrCl_6]^{3-}$ complex. We evaluated the ratio of the molar absorptivities for these two transition bands, $\varepsilon_{II}/\varepsilon_I$, where transition I means the possible $^3P_0 \leftarrow ^3H_4$ transition, and transition II the shoulder peak at 493 nm. The obtained ratios are shown in Figure 5a. At a fixed temperature, $\varepsilon_{II}/\varepsilon_I$ clearly increases in the following order: CaCl$_2$ and LiCl < 3LiCl-2KCl < 3LiCl-2CsCl < NaCl-2CsCl. It should be noted that this is the identical order of the electron donating ability [4] of Cl$^-$ to Pr^{3+} (this electron donating ability is in inverse relation to the polarizing power of cations of matrix molten chlorides). In other words, $[PrCl_6]^{3-}$ is considered to keep the highly octahedral symmetry following this order. The $[LnCl_6]^{3-}$ complex keeps highly octahedral symmetry in solvent melts with small polarizing power such as the NaCl-2CsCl eutectic and CsCl, but the symmetry is distorted in melts of strong polarizing cations such as Li$^+$ and Ca^{2+} [1]. This trend can also be seen in Fig. 5b: $\varepsilon_{II}/\varepsilon_I$ increases with Cs$^+$ content, in which the $[LnCl_6]^{3-}$ complex keeps higher octahedral symmetry. We therefore point out that the $^3P_0 \leftarrow ^3H_4$ transition can provide information on the coordination circumstance of $[PrCl_6]^{3-}$ in molten chlorides. Since the Judd-Ofelt parameter analysis possesses an imperfect aspect for Pr(III), our proposal may be useful for discussing its ligand environment.

As a final note, we discuss what the shoulder peak of the $^3P_0 \leftarrow ^3H_4$ transition means. Two possibilities can be expressed as the origin of this unknown peak. One possibility is the splitting of the electronic energy levels. The P$_0$ term is the singlet Γ_1, while the ground energy state $^3H_4$ consists of four levels (Γ_1, Γ_4, Γ_3, and Γ_5, from the lower to the upper level), which are clearly split under the O_h crystal field of the elpasolite crystal, Cs$_2$NaPrCl$_6$ [19,21]. The $^3P_0 \leftarrow ^3H_4$ transition has been assigned as $^3P_0(\Gamma_1) \leftarrow ^3H_4(\Gamma_1)$ [21] or $^3P_0(\Gamma_1) \leftarrow ^3H_4(\Gamma_4)$ [19]. If both transitions are permissible for Pr(III) in molten chlorides, the main peak and shoulder peak may be assigned as the $^3P_0(\Gamma_1) \leftarrow ^3H_4(\Gamma_1)$ and $^3P_0(\Gamma_1) \leftarrow ^3H_4(\Gamma_4)$ transitions, respectively. From Fig. 4, the energy difference between the two peaks is estimated to be 250–300 cm^{-1}. This energy is similar to the reported energy difference between $^3H_4(\Gamma_1)$ and $^3H_4(\Gamma_4)$ for the Cs$_2$NaPrCl$_6$, that is $\sim$275 cm^{-1} [19]. If this is the origin, more precise peak position analysis will be required, because the splitting energy must be affected by the ligand field change. The transition probabilities from $^3H_4(\Gamma_1$ and $\Gamma_4)$ must also be theoretically clarified in order to explain the change in $\varepsilon_{II}/\varepsilon_I$.

The other possibility is the association with vibrational energies. The $^3P_0 \leftarrow ^3H_4$ transition for $[PrCl_6]^{3-}$ complexes in solutions or solids shows vibrational structures [20]. The absorption spectrum of Pr(III) in Cs$_2$NaPrCl$_6$ shows two intensive peaks [17, 18], in which the higher energy band and the lower one are associated with the ν_3 stretching mode and ν_4 bending mode, respectively. If this absorption characteristic remains in our molten chloride systems, especially in the NaCl-2CsCl eutectic, two intensive peaks can be seen in the $^3P_0 \leftarrow ^3H_4$ region. The vibrational frequencies for $[PrCl_6]^{3-}$ in Cs$_2$NaPrCl$_6$ may be evaluated: $\nu_3 = 271$ cm^{-1} and $\nu_4 = 121$ cm^{-1} (4.2 K [21]), or $\nu_3 = 225$ cm^{-1} and $\nu_4 = 100$ cm^{-1} (room temperature [19]). If the peak position difference we estimated at 250 – 300 cm^{-1} (Fig. 4) means the energy difference between ν_3 and ν_4, our estimated value is about twice as large as the reported values [19, 21]. Further theoretical study will be required for the certain assignment of this transition peak.

4. Conclusions

The hypersensitive transition $^3F_2 \leftarrow ^3H_4$ of Pr(III) was nearly independent of the type of the matrix molten chlorides, and its temperature dependence was inconsistent with the cases found for other lanthanoides. The Judd-Ofelt parameter analysis showed a breakdown. The Ω_2 parameter showed a clear decrease with increasing temperature and negative values at high temperature. The intensities of the $^3P_0 \leftarrow ^3H_4$ transition and its shoulder peak were sensitive to the coordination circumstance change of the $[PrCl_6]^{3-}$ complex. We found that the ratio of their molar absorptivities can provide information on the octahedral symmetric property of $[PrCl_6]^{3-}$ in molten chlorides.

Acknowledgement

The authors wish to thank George N. Papatheodorou for his insightful suggestions which were given at the EUCHEM conference. T. F. thanks Takaumi Kimura and Ryuji Nagaishi for their comments on the Judd-Ofelt analysis. The authors wish to thank Roy Jacobus for his help in improving the English of this paper.

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