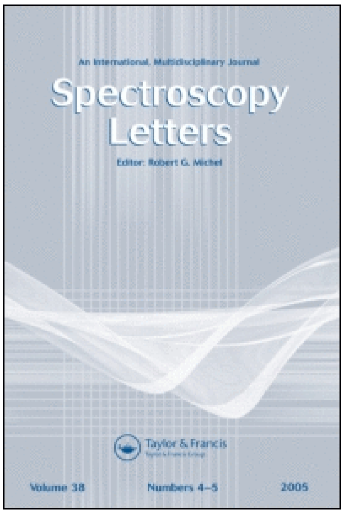

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FLUORESCENCE ENHANCEMENT OF Eu^{3+} IN $POCl_3$:$SnCl_4$ AND OF Sm^{3+} in $POCl_3$:$ZrCl_4$.

by

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The fluorescence efficiency of the rare-earth ions in organic solvents depends strongly upon the solvent molecules in the primary solvation sphere and to a lesser extent upon the molecules located in the secondary solvation sphere of the ion(1-4). The fluorescence efficiency of the rare-earth ions in many organic solvents is relatively low probably due to an efficient electronic excitation energy transfer from the lowest excited state of the rare-earth ion to the organic solvent, via some high overtones of certain vibrational modes associated with the solvent under consideration. Contrary to this behavior, solutions of the rare-earth ions in solvents associated with very low-energy vibrational modes, "aprotic" solvents, like $POCl_3$:$SnCl_4$, $POCl_3$:$ZrCl_4$, $POCl_3$:$SbCl_5$ etc., exhibit a remarkable enhancement in both the fluorescence efficiencies and lifetimes of the rare-earth ions(5). Neither the organic nor the "aprotic" solvents used absorb light in the excitation region i.e., 370 mμ to 410 mμ. Since the absorption spectra of these solvents appear at wavelengths shorter than 300 mμ one may rule out both energy transfer from the solvent to the rare-earth ion and decreased light absorption by the ion due to the presence of the solvent. The "aprotic" solvents do not have groups containing H-atoms, i.e. $\longrightarrow$C-H, -O-H, >N-H etc., which are associated with high energy vibrational modes. The importance of such "aprotic" solvents is not associated only with a mere fluorescence enhancement. Both the fluorescence efficiencies and lifetimes depend upon the composition of these solvents(5).

Europium oxide (99.9 to 99.99% purity) was dissolved in a mixture of $POCl_3$ and $SnCl_4$, under refluxing conditions at 80-90°C, in the absence of water vapor and CO_2. Transparent solutions containing up to 3×10^{-1}M Eu^{3+} were prepared. The solubility of Eu_2O_3 was found to decrease at lower $[SnCl_4]$, whereas at higher $[SnCl_4]$ a precipitate, probably of the type $(POCl_3)_2 \cdot SnCl_4$, was formed, which was soluble in an excess of $POCl_3$.

$$2\ POCl_3 + SnCl_4 \rightleftarrows (POCl_3)_2SnCl_4 \longrightarrow 2\ POCl_2^+ + SnCl_6^=$$

$$Eu_2O_3 + 6\ POCl_2^+ \longrightarrow 2\ Eu^{3+} + 4\ POCl_3 + P_2O_5 \qquad (1)$$

The role and the effect of P_2O_5 upon the fluorescence efficiency of Eu^{3+} is uncertain. One can eliminate this problem provided that anhydrous $EuCl_3$ is employed.

$$EuCl_3 + 3\ POCl_2^+ \text{ — } Eu^{3+} + 3\ POCl_3$$

However, despite our continuous attempts to use either commerically labeled "anhydrous" $EuCl_3$ or anhydrous salts prepared via a stepwise removal of the water present, at low temperatures and low pressures, we have been unable to attain transparent solutions. It appears that in both cases some small amounts of oxychloride, EuOCl, were present in sufficient quantities to give rise to slightly cloudy solutions. Furthermore, Reaction (1) is not completely unambiguous. The solvation species could be either $POCl_2^+$, the complex $(POCl_3)_2 \cdot SnCl_4$ or both. The main argument supporting the existance of Reaction (1) is that Eu_2O_3 is insoluble in both pure $POCl_3$ and pure $SnCl_4$, which are associated with very low conductivities i.e. $1.6\times10^{-6}\ \Omega^{-1}cm^{-1}$ and $1\times10^{-8}\ \Omega^{-1}cm^{-1}$, respectively, whereas $POCl_3$ with 6% (in moles) of $SnCl_4$ has a conductivity of $6\times10^{-6}\Omega^{-1}cm^{-1}$(6).

Eu^{3+} IN $POCl_3$:$SnCl_4$ AND Sm^{3+} IN $POCl_3$:$ZrCl_4$

The emission spectra of 2×10^{-1}M Eu^{3+} in $POCl_3$:$SnCl_4$ at a $\left[POCl_3\right] / \left[SnCl_4\right]$ ratio of 11.0 (optimum ratio) are shown in Figure (1A). Spectrum (a) was taken at about -2°C (freezing point of the sample), spectrum (b) was taken

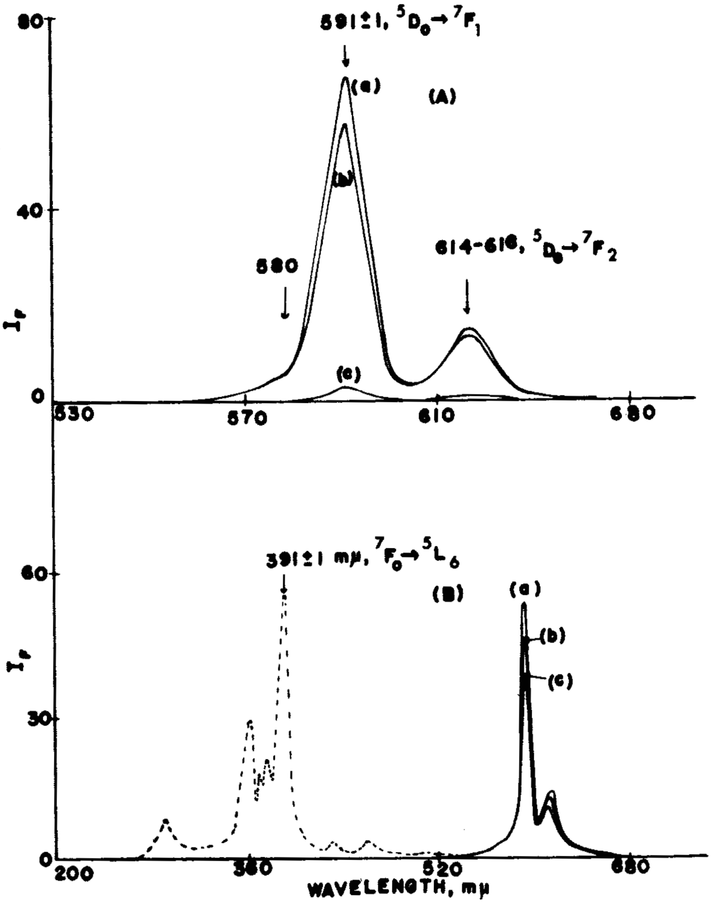


Figure 1. Emission spectra of Eu^{3+} in $POCl_3$:$SnCl_4$; uncorrected. (A) 2×10^{-1}M Eu^{3+} in $POCl_3$:$SnCl_4$ at $\left[POCl_3\right] / \left[SnCl_4\right] = 11.0$; $\lambda_{exc} = 391 \pm 1$ mμ. (a) at about -2°C (b) at 25°C and (c) emission spectra of 2×10^{-1}M $EuCl_3$ in aqueous solutions (magnified by a factor of 10). (B) 5×10^{-2}M Eu^{3+} in $POCl_3$:$SnCl_4$ at various $\left[POCl_3\right] / \left[SnCl_4\right]$ ratios; $\lambda_{exc} = 391 \pm 1$ mμ. (a) $\left[POCl_3\right] / \left[SnCl_4\right] = 11.0$, (b) $\left[POCl_3\right] / \left[SnCl_4\right] = 11.5$ and (c) $\left[POCl_3\right] / \left[SnCl_4\right] = 19.1$ and 23.5.

at 25°C, whereas spectrum (c) represents the emission of $2\times10^{-1}M$ $EuCl_3$ in aqueous solution (25°C) under identical conditions and magnified by a factor of 10. An enhancement of about 220 is apparent as far as the fluoresence efficiency of Eu^{3+} in $POCl_3$:$SnCl_4$ (at a molar ratio of 11.0) is concerned, relative to that in aqueous solutions, under identical conditions. An additional enhancement of about 17% is also observed by lowering the temperature from 25°C to -2°C. Lower temperatures could not be employed because the freezing point of the samples was about -2°C. Both enhancements are much lower that the corresponding fluoresence intensifications for Sm^{3+} in $POCl_3$:$SnCl_4$ (at a $[POCl_3]/[SnCl_4]$ ratio of 10.34$^{(5)}$). Figure (1B) depicts the appropriate emission spectra of Eu^{3+}in $POCl_3$:$SnCl_4$ at various $[POCl_3]/[SnCl_4]$ ratios and at 25°C. The fluoresence efficiency of Eu^{3+} increases as the $[POCl_3]/[SnCl_4]$ ratio decreases. The $[POCl_3]/[SnCl_4]$ ratios vary from 11.0 to 23.5 (in moles), whereas the approrpriate changes in the fluorescence efficiencies of Eu^{3+} are rather small, namely 30 to 40%. Since the transition probabilities were found to be almost the same for different $[POCl_3]/[SnCl_4]$ ratios $^{(5)}$, the changes observed may be attributed to a weak fluoresence quenching by the $\gt P = 0$ group of the $POCl_3$ molecules which predominate at high $[POCl_3]/[SnCl_4]$ ratios. This speculation is based on the fact that the fundamental frequency of the stretching vibrational mode of the $\gt P = 0$ group is about 1300 cm^{-1} $^{(7,8)}$ and therefore, it should not be completely ignored.

Figure (2A) exhibits similar emission spectra of Sm^{3+} in $POCl_3$:$ZrCl_4$, where $ZrCl_4$ is a Lewis acid replacing $SnCl_4$. Samarium oxide (99.9-99.99% purity) is dissolved by $POCl_3$:$ZrCl_4$ using the same conditions as those used for $EuCl_3$ in $POCl_3$:$SnCl_4$, namely

$$2\ POCl_3 + ZrCl_4 \rightleftarrows (POCl_3)_2 \cdot ZrCl_4 \longrightarrow 2\ POCl_2^{+} + ZrCl_6^{=}$$

$$Sm_2O_3 + 6\ POCl_2 \longrightarrow 2\ Sm^{3+} + 4\ POCl_3 + P_2O_5 \qquad (2)$$

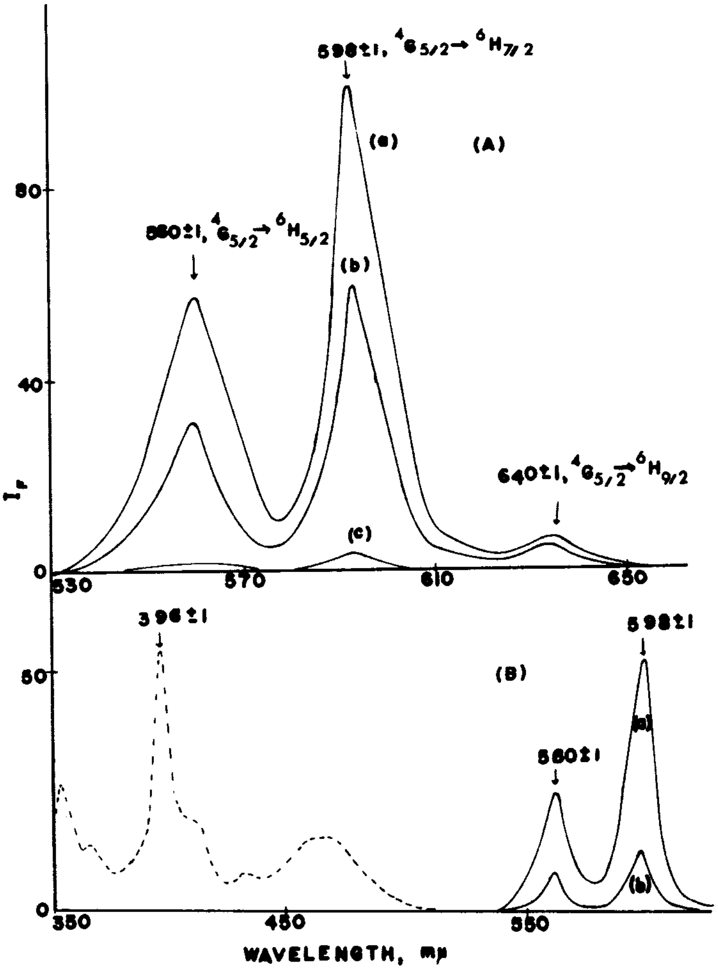


Figure 2. Emission spectra of Sm^{3+} in $POCl_3:ZrCl_4$. (A) $2\times10^{-1}M$ Sm^{3+} in $POCl_3:ZrCl_4$ at $[POCl_3] / [ZrCl_4] = 30$; $\lambda_{exc} = 396\pm1$ mμ. (a) at about 0°C, (b) at 25°C and (c) emission spectra of $2\times10^{-1}M$ $SmCl_3$ in aqueous solution (magnified by a factor of 10). (B) Emission spectra of $4\times10^{-2}M$ Sm^{3+} (a) in $POCl_3:SnCl_4$ at $[POCl_3] / [SnCl_4] = 28$ and (b) in $POCl_3:ZrCl_4$ at $[POCl_3] / [ZrCl_4] = 30$; $\lambda_{exc} = 396\pm1$ mμ; uncorrected. Spectrum in dashed lines represents the fluorescence excitation spectrum (uncorrected).

Spectrum (a) shows the emission of $2x10^{-1}$ M Sm^{3+} at about 0°C (freezing point of the sample), spectrum (b) exhibits the emission of Sm^{3+} at 25°C whereas (c) represents the emission spectrum of $2x10^{-1}$M $SmCl_3$ in aqueous solutions, magnified by a factor of 10, under identical conditions. An enchancement of about 300 is apparent in the fluoresence intensity of Sm^{3+} in $POCl_3:ZrCl_4$ relative to that in aqueous solutions, whereas an enlargement of about 70% was observed by lowering the temperature from 25°C to 0°C. The emission spectra exhibit only three bands associated with the transitions $^4G_{5/2} \longrightarrow {}^6H_{5/2}$, $^4G_{5/2} \longrightarrow {}^6H_{7/2}$ and $^4G_{5/2} \longrightarrow {}^6H_{9/2}$, respectively. The additional bands are not shown because they appear at wavelengths longer than 650 mμ, a region in which our 1P21 phototube has practically zero response. The fluoresence enhancement of Sm^{3+} in $POCl_3:ZrCl_4$ is smaller than the corresponding enhancement observed for Sm^{3+} in $POCl_3:SnCl_4$ under identical conditions (Figure (2B)).

The changes observed in the fluoresence efficiencies of the rare-earth ions in "aprotic" solvents relative to those in aqeuous solutions are not matched with appropriate changes in the absorption spectra. Figure (3) shows a comparison between the ultraviolet and the visible spectra of $SmCl_3$ in H_2O and in $POCl_3:ZrCl_4$ at $\left[POCl_3\right]/\left[ZrCl_4\right] = 30$. These absorption spectra are expressed in terms of their molar exctinction coefficient, ϵ. Intensity-wise there is a very minor (almost negligible) increase in the value of ϵ for Sm^{3+} in $POCl_3:ZrCl_4$. On the other hand, a considerable splitting is observed in the case of Sm^{3+} in $POCl_3:ZrCl_4$ whose origin is not clear at the present time. A similar but better defined splitting was observed in the case of Sm^{3+} in $POCl_3:SnCl_4$(5). Figure (4) shows the complete absorption spectra of

Sm^{3+} in $POCl_3$:$ZrCl_4$ at $\left[POCl_3\right] / \left[ZrCl_4\right] = 30$. Figure (4A) shows the spectrum at 0°C, whereas Figure (4B) depicts the spectrum of Sm^{3+} at 25°C.

If we examine the last four absorption bands of Figure (4), namely the bands which are associated with the transitions $^6H_{5/2} \longrightarrow {}^6F_{7/2}$, $^6H_{5/2} \longrightarrow {}^6F_{5/2}$, $^6H_{5/2} \longrightarrow {}^6F_{3/2}$ and $^6H_{5/2} \longrightarrow {}^6F_{1/2}$, respectively, we can

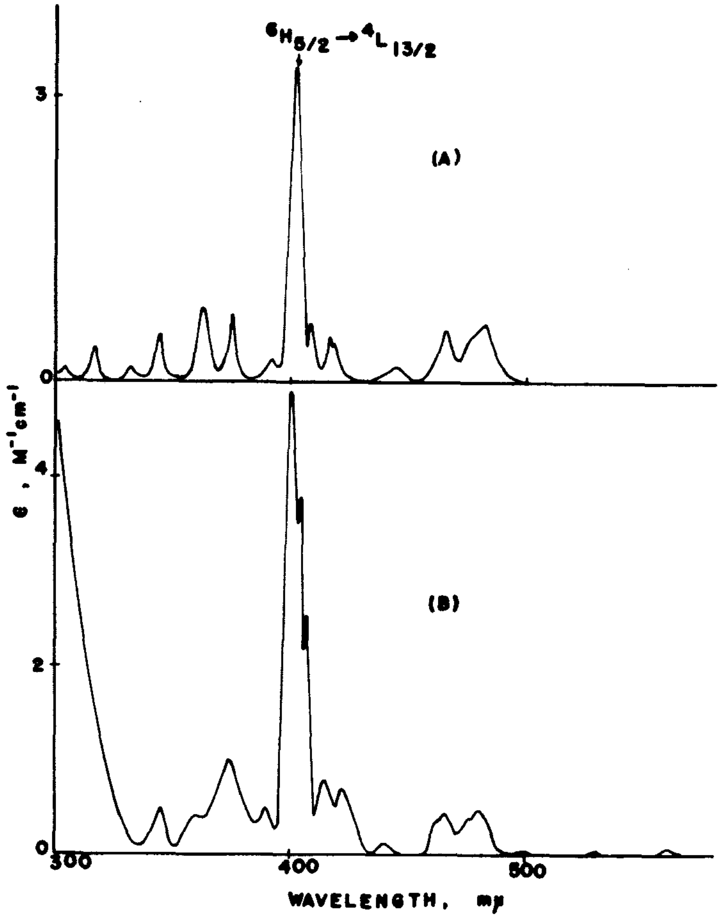
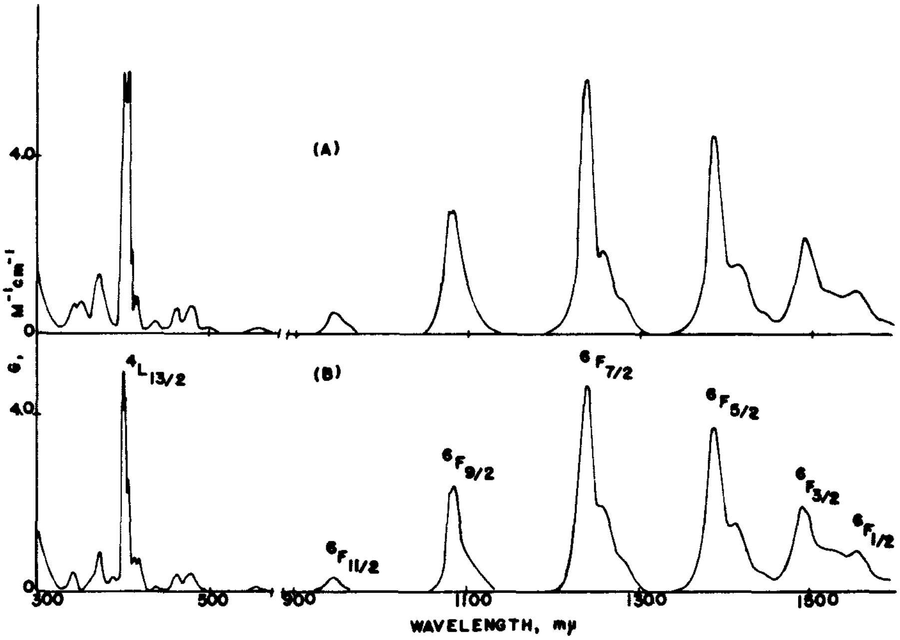


Figure 3. (A) Absorption spectrum (ultraviolet and visible) of Sm^{3+} in aqueous solutions (in terms of ε) (B) Absorption spectrum (ultraviolet and visible) of Sm^{3+} in $POCl_3$:$ZrCl_4$ at $\left[POCl_3\right] / \left[ZrCl_4\right] = 30.0$ in terms of ε . Room temperature.

observe that all these bands (which correspond to single transitions) exhibit the same pattern i.e. the main peak accompanied by a weak side band, red-shifted by about 150 cm^{-1} and a much weaker shoulder, red-shifted by about 290 cm^{-1}. If we plot these four bands on a $\Delta\bar{v}$ scale in such a way that the four main peaks are superimposed ($\Delta\bar{v}=0$), the other two components of the bands under consideration are also almost superimposed at $\Delta\bar{v} = -150$ cm^{-1} and $\Delta\bar{v} = -290$ cm^{-1}, respectively, (Figure (5)). The minus sign indicates a red shift, whereas the positive sign implies a blue shift.



<u>Figure 4</u>. (A) Absorption spectrum of Sm^{3+} in $POCl_3$:$ZrCl_4$ at $[POCl_3]/[ZrCl_4]=30$ and at 0°C. (B) Absorption spectrum of Sm^{3+} in $POCl_3$:$ZrCl_4$ at $[POCl_3]/[ZrCl_4]=30$ and at 25°C. Both spectra are given in terms of ε vs the wavelength.

These results may indicate a possible quasimolecular nature for Sm^{3+} in $POCl_3$:$ZrCl_4$, in which the ion is weakly bonded, or pseudobonded, to the solvent. Such a bond or pseudobond will be very weak and the two side bands may represent the fundamental and the first overtone of this bond, respectively, (vibronic structure). Another alternative could be the participation of the $^6H_{7/2}$ and $^6H_{9/2}$ states of Sm^{3+} as initial states. However, the state $^6H_{7/2}$ lies about 1000 cm^{-1} above the ground state of Sm^{3+}, $^6H_{5/2}$ (9). Therefore, unless one may postulate a strong

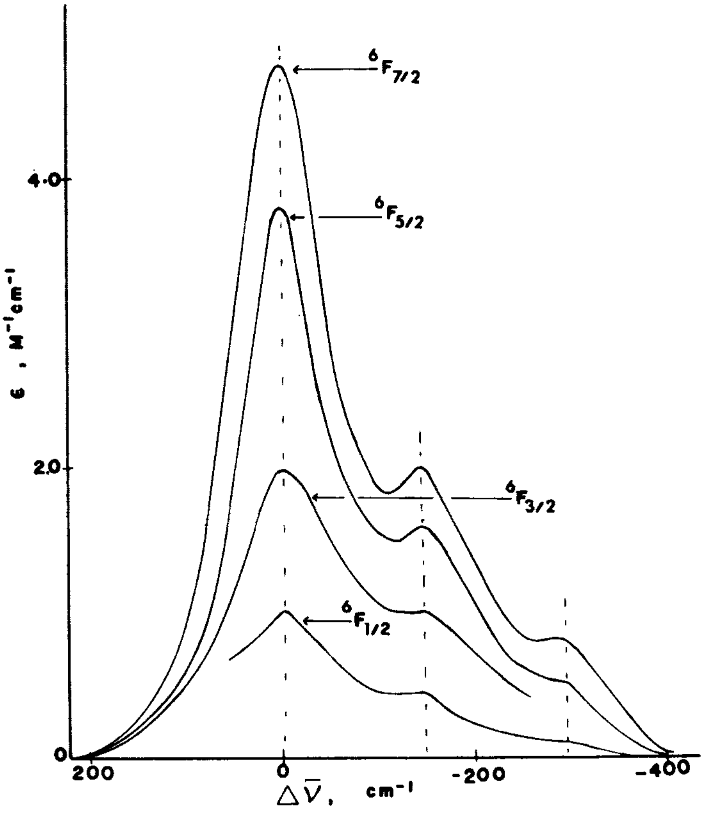


Figure 5. Absorption bands associated with transitions from the $^6H_{5/2}$ state of Sm^{3+} to the $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$ and $^6F_{1/2}$, respectively, in $POCl_3$:$ZrCl_4$ at $[POCl_3]$ / $[ZrCl_4]$ = 30, plotted on a differential wavenumber scale, $\Delta\bar{v}$; room temperature.

Stark splitting of the $^6H_{7/2}$ in which some low energy components appear above the ground state by about 150 and 290 cm^{-1}, the role of the $^6H_{7/2}$ and $^6H_{9/2}$ should be ruled out at room temperature. On the other hand, Stark splitting of the $^6H_{5/2}$ may also give rise to such two side bands. The answer to this problem is not available at the present time. These side bands have not been observed so far by Raman spectroscopy. However, their detection may be very difficult due to their weakness and low energies. Studies using far infrared are also under way. Similar vibronic structure was not observed in the case of Eu^{3+} in $POCl_3$:$SnCl_4$, although it was observed for Sm^{3+} in $POCl_3$:$SnCl_4$ associated with slightly different red shifts. The reason for the absence of such a structure for Eu^{3+} in $POCl_3$:$SnCl_4$ may be that the low energy of such bands make it almost absolutely necessary to search for them in the near or regular infrared. Whereas Sm^{3+} has a number of fairly narrow absorption bands in this region, Eu^{3+} is associated with two very broad absorption bands ranging from 1.7 μ to 2.4 μ. Any weak vibronic bands could be lost under these strong and very broad bands.

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