Raman spectroscopic study of trivalent lanthanides in concentrated aqueous solutions

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Abstract. The Raman spectra in the region of the O-H stretching vibration band are used to investigate the effect of lanthanide (III) ions on liquid water structure in concentrated aqueous solutions of CeCl₃ and GdCl₃ (C~0.5–3 M). The differential spectra, derived from the consequent Raman spectra, have reflected the substantial discrepancy between the spectra of lanthanide (III) salt solutions and pure water as well as the spectra of standard LiCl (C~1.5–9 M) solutions. The new sharp bands (ν[max]~ 3180–3190 cm⁻¹) and (ν[max]~3360 cm⁻¹), observed in the differential spectra, are assumed to two types of aqua-ions: Ln³⁺[H₂O]ₘH₂Oₙ and Ln³⁺[H₂O]ₘCl⁻ₚ having a difference in the 2nd coordination sphere. The discrepancy, observed in the spectra of the equimolar CeCl₃ and GdCl₃ aqueous solutions, is interpreted as a result of the different hydration numbers and ion radiiuses of Ce³⁺ₐq and Gd³⁺ₐq.

1. Introduction

Despite the fact that the influence of inorganic as well as organic solutes on the liquid water structure has been intensively investigated by various methods, including X-ray, NMR and IR/Raman spectroscopy, some aspects of the phenomenon still remain uncertain [1-8]. In this connection studying the Raman spectra of aqueous solutions is considered to be rather informative owing to high sensitivity of the O-H stretching band (ν~2800–3800 cm⁻¹) to the local environment of water molecules. The O-H stretching band shape were established to reflect interactions between water molecules and solutes, polymers, biological molecules, etc., however, the main problem remains to select and/or identify every bonding effect, especially when the band intensity is employed as a standard in spectrofluorometry or lidar measurements [8].

In absolute majority of previous works pure water (or dilute aqueous inorganic salt solution) is generally regarded as a compound of differently sized hydrogen bonded water clusters, which bonds may be broken with the temperature increasing. Some soluted ions were established demonstrating a similar perturbing effect but its distinction from that of temperature has been rarely shown clearly yet [1, 4-8]. The influence of halogen anions upon the water Raman spectra was appeared to be much stronger than that of cations and increased in the sequence of Cl⁻ < Br⁻ < I⁻. At the same time the role of metal ions in water bonding was not adequately investigated and the similar sequences for single- or doubly charged cations were difficult to obtain exactly because of their effects insignificance [1, 4, 8].
In this study the O-H stretching Raman spectra in the range of ν~2500–4000 cm\(^{-1}\) were used to determine the effect of lanthanide (III) chlorides on the water microstructure.

2. Experimental
Raman spectra have been measured using a thermostatted cell at 20±0.05ºC under continuous argon laser excitation (Spectra Physics, \(\lambda=514, 488\) nm, \(P=1\)W) and registered by the optical system: a double monochromator Aston and an optical multi-channel analyzer OMA-1 (PARS, USA).

Cerium (III), Gadolinium (III) and Lithium chlorides of high analytical purity grade and doubly distilled water were used for the solutions preparing. The lanthanide (III) salts solutions were prepared to be equimolar along the concentration sequence of 0.53, 1.06, 2.12 and 3.18 M, where the highest concentration was close to the solubility limit. The comparative LiCl solutions were three times higher in concentration for having equal anion amounts.

3. Results
The Raman spectra of CeCl\(_3\), GdCl\(_3\) and LiCl water solutions in the range of \(\nu=2700-3800\) cm\(^{-1}\) measured under equal excitation conditions are presented at Figures 1-3. At the Figures 1b-3b the differential spectra are shown that were derived from the consequent spectra of lanthanides salt solutions and pure water. Tables 1, 2 contain the main spectral parameters. All intensities of the Raman as well as differential spectra are normalized to the peak height of pure water Raman spectrum. Figure 4 shows the differential spectra obtained subtracting the LiCl and CeCl\(_3\) solutions spectra, consequently, from that of CeCl\(_3\) and GdCl\(_3\) solutions.

![Figure 1](https://i.imgur.com/3J5J5J.png)  
**Figure 1.** O-H stretching Raman spectra of CeCl\(_3\) aqueous solutions (1a) and differential spectra of CeCl\(_3\) - pure water (1b): 1 – pure water, 2- 0.529 M, 3- 1.059 M, 4- 2.177 M, 5 – 3.176 M

Our findings manifest the increasing dissolved lanthanide salt concentration leads to monotonous changing of the O–H stretching Raman spectra. The intensity of the low-frequency band shoulder \(\nu \sim 3200\) cm\(^{-1}\) decreases whereas the maximum intensity occurring near \(3405 \pm 5\) cm\(^{-1}\) increases significantly up to 30-40%. Furthermore, in comparison with the pure water spectrum the weak high-frequency band shoulder at \(\nu \sim 3650\) cm\(^{-1}\) practically disappears so the total band width decreases from \(\Delta\nu \sim 360\) cm\(^{-1}\) to \(\Delta\nu \sim 240-270\) cm\(^{-1}\) but the spectra of the salts solutions change in such a way that the spectral band areas remain constant to a high degree of accuracy (±0.1%).

Observed changes in general are similar to spectra transformation registered for LiCl solutions having the equal anion concentrations (see Table 1) but in the case of the lanthanide (III) chlorides the spectra maximums are shifted to low frequencies (\(\Delta\nu \sim 20\) cm\(^{-1}\) ) while their band widths are distinctly higher.

Much more clear the spectral band modification can be seen from the differential spectra (Figures 1b-3b, Table 2). An important fact is that in all cases under salt concentration increase opposite...
whereas the spectra maximums for higher concentrations shift to low frequencies (solutions the differential concentration are presented at Figure 5 showing at the concentration rise the dependencies tend to a plateau but none satiation limit has been achieved.

In contrast, for the lanthanide (III) chlorides there was observed a substantial behaviour discrepancy between the water solutions spectra of lanthanide (III) chlorides and that of LiCl.

Table 1. O-H stretching Raman spectra parameters of concentrated aqueous solutions of Ce(III), Gd(III) and Li(I) chlorides

| Solution    | C_{sols} M | C_{anions} M | ν_{max} cm^{-1} | Δν, cm^{-1} | I_{max} |
|-------------|------------|--------------|-----------------|-------------|---------|
| Pure H_{2}O | 0          | 0            | 33 97.2         | 395.2       | 1       |
| LiCl in H_{2}O | 1.588      | 1.588        | 3409.3          | 350.8       | 1.136   |
|              | 3.176      | 3.176        | 3417.3          | 314.6       | 1.239   |
|              | 6.352      | 6.352        | 3425.4          | 242.0       | 1.446   |
|              | 9.528      | 9.528        | 3425.4          | 221.8       | 1.530   |
| CeCl_{3} in H_{2}O | 0.529      | 1.587        | 3405.2          | 358.9       | 1.121   |
|              | 1.059      | 3.177        | 3409.3          | 326.7       | 1.206   |
|              | 2.117      | 6.351        | 3409.3          | 270.2       | 1.352   |
|              | 3.176      | 9.528        | 3401.2          | 242.0       | 1.426   |
| GdCl_{3} in H_{2}O | 0.530      | 1.590        | 3405.2          | 362.9       | 1.098   |
|              | 1.059      | 3.177        | 3409.3          | 334.7       | 1.172   |
|              | 2.118      | 6.354        | 3405.2          | 290.4       | 1.268   |
|              | 2.987      | 8.961        | 3401.2          | 274.2       | 1.301   |

Table 2. The parameters of ‘positive’ (ν_{max}, I_{max}) and ‘negative’ (ν_{min}, I_{min}) bands in differential spectra of concentrated aqueous solutions of Ce(III), Gd(III) and Li(I) chlorides and pure water

| Solution    | C_{sols} M | C_{anions} M | ν_{max} cm^{-1} | I_{max} | ν_{min} cm^{-1} | I_{min} | N_{isosb} cm^{-1} |
|-------------|------------|--------------|-----------------|---------|-----------------|---------|------------------|
| LiCl in H_{2}O | 1.588      | 1.588        | 3437.5          | 0.15    | 3191.5          | 0.12    | 3320.5           |
|              | 3.176      | 3.176        | 3441.5          | 0.27    | 3195.5          | 0.21    | 3324.6           |
|              | 6.352      | 6.352        | 3437.5          | 0.48    | 3195.5          | 0.34    | 3324.6           |
|              | 9.528      | 9.528        | 3437.5          | 0.58    | 3195.5          | 0.40    | 3320.5           |
| CeCl_{3} in H_{2}O | 0.529      | 1.587        | 3429.4          | 0.13    | 3191.5          | 0.11    | 3316.5           |
|              | 1.059      | 3.177        | 3425.4          | 0.23    | 3191.5          | 0.18    | 3316.5           |
|              | 2.117      | 6.351        | 3421.4          | 0.37    | 3191.5          | 0.27    | 3308.5           |
|              | 3.176      | 9.528        | 3405.2          | 0.44    | 3191.5          | 0.30    | 3300.4           |
| GdCl_{3} in H_{2}O | 0.530      | 1.590        | 3437.5          | 0.11    | 3195.5          | 0.10    | 3312.5           |
|              | 1.059      | 3.177        | 3437.5          | 0.19    | 3195.5          | 0.17    | 3308.5           |
|              | 2.118      | 6.354        | 3417.3          | 0.27    | 3195.5          | 0.25    | 3300.4           |
|              | 2.987      | 8.961        | 3405.2          | 0.30    | 3195.5          | 0.26    | 3292.3           |

changes occur simultaneously at three comparatively narrow spectral intervals: intensity increase in the range of 3330-3550 cm^{-1} and intensity decrease in the regions of 2950-3330, 3550-3700 cm^{-1} but there was observed a substantial behaviour discrepancy between the water solutions spectra of lanthanide (III) chlorides and that of LiCl.

In the differential spectra of LiCl solutions: the maximum (ν ~ 3437 cm^{-1}), the high- and low-frequency minimums (ν ~ 3600 and 3195 cm^{-1}) as well as the isosbestical point (ν ~ 3324 cm^{-1}) do not change their positions via concentration changing. In contrast, for the lanthanide (III) chlorides solutions the differential spectra minimum position (ν ~ 3192 - 3195 cm^{-1}) remains unchanged whereas the spectra maximums for higher concentrations shift to low frequencies (Δν ~ 25-30 cm^{-1}) and the isosbestical points are not pronounced.

The areas of the differential spectra positive bands (ν ~ 3437 cm^{-1}) as a function of the anion concentration are presented at Figure 5 showing at the concentration rise the dependencies tend to a plateau but none satiation limit has been achieved.
Figure 2. O-H stretching Raman spectra of GdCl$_3$ aqueous solutions (2a) and differential spectra of GdCl$_3$ - pure water (2b) 1 – pure water, 2- 0.530 M, 3- 1.059 M, 4- 2.118 M, 5 – 2.987 M

Figure 3. O-H stretching Raman spectra of LiCl aqueous solutions (3a) and differential spectra of LiCl - pure water (3b) 1 – pure water, 2- 1.588 M, 3- 3.176 M, 4- 6.352 M, 5 – 9.527 M

Thus, the differential spectra evidence that at equal Cl$^-$ concentrations the O-H stretching Raman spectra of lanthanide (III) chloride solutions and their behavior under the concentration growth differ from that of LiCl and that the discrepancy between CeCl$_3$ and GdCl$_3$ solutions spectra are also observed.

4. Discussion
The halogenides of alkali metals, alkaline metals and the first-row transition metals are known to act upon the water O-H stretching Raman spectra in the similar way [1, 4, 6-8].

As proposed, the effect of halogen anions on the water structure consists in breaking water-water hydrogen bonds and on the other hand in forming the hydrogen bonds between anions and water molecules that results in the specific changing of the O-H stretching band contour [1, 8, 9].

The metal ions (cations) effects are not perfectly understood yet, though some differences were observed between the O-H stretching Raman spectra of the aqueous solutions with monovalent (Na$^+$, K$^+$, Li$^+$) and divalent (Mg$^{2+}$, Ca$^{2+}$, Mn$^{3+}$) or trivalent (Al$^{3+}$, Fe$^{3+}$) cations. The strength of metal ion effects was found depending on the ionic charge, the outmost electronic structure and ionic size, the
ionic charge to be most important, nevertheless, no metal ion solvated forms or their specific impacts have been registered [1, 4, 8].

Figure 4. Differential spectra, obtained by the Raman spectra subtraction in solution pairs: (a) – CeCl₃ (C=2.177 M) and LiCl (C=6.352 M); (b) - GdCl₃ (C=1.694 M) and CeCl₃ (C=1.694 M)

Figure 5. The area of the differential spectra ‘positive’ band as a function of the anion concentration.

We have also to assume that in the case of LiCl solutions Cl⁻ anions break the hydrogen-bonded (tetrahedral etc.) water-water (H₂O)ₙ structures and make the hydrogen-bonded anion-water (H₂O)Cl⁻ complexes while the Li⁺ ions do not sufficiently affect the O–H stretching Raman spectra (the sub-symbols ‘r’ and ‘s’ represent numbers of water molecules associated into the cluster). Thus, the increasing with Cl⁻ concentration rise ‘positive’ band at ν~3430 cm⁻¹ in the LiCl-H₂O differential spectra (see Figure 3b) should be assigned to the anion-water complexes (H₂O)Cl⁻, whereas the ‘negative’ bands low-frequency at ν~3195 cm⁻¹ and high-frequency at ν~3650 cm⁻¹ belong probably to the decreasing both anion-free, consequently, hydrogen-bonded water-water structures (H₂O)ₙ and non-bonded free single water molecules, H₂O. As long as the satiation plateau of the differential spectrum changing were not achieved even at the highest concentration of 9.53 M (see Figure 5), we can not assume the total disappearing of the hydrogen-bonded anion-free water-water forms and their conversion into the anion-bonded structures.

Now, if we have recourse to the Gaussian analysis, which is usually applied to analyze the O–H stretching Raman band for more information of water structure and where the band contour is deconvoluted into 5, 4, 3, or 2 Gaussian components [1], we should assume that the number of components change from 5 or 4 to 2 as the anion concentration increase from 0+0.5 to 9+10 M. In that way for the highest LiCl concentration of 9.53 M we have got two Gaussian components: 1) νmax = 3420±10 cm⁻¹, Δν=170±10 cm⁻¹, 80% of the total spectra area; and 2) νmax = 3240±10 cm⁻¹, Δν=140±10 cm⁻¹, 18%, which conform well to the positive and main negative differential spectral bands, consequently. As may be seen, this model neglects the impact of Li⁺ cations, which may probably reduce to a slight maximum shift and broadening of the hydrogen-bonded water-water components spectrum.

Undoubtedly, the breaking of water-water hydrogen bonds as well as making of anion-water hydrogen-bonded complexes (H₂O)ₙCl⁻ take also place in aqueous solutions of lanthanide (III) chlorides but our data obtained for the CeCl₃ and GdCl₃ solutions show a sufficient distinction in comparing with LiCl. The differences between the O-H stretching Raman spectra of CeCl₃ and GdCl₃ solutions are also observable but much slighter. These results denote the formation of some new hydrated forms influencing the Raman spectra of lanthanide (III) chlorides in aqueous solutions.

The difference between the Raman spectra of CeCl₃ and LiCl aqueous solutions, having the equal Cl⁻ concentration of 6.35 M, in the case of CeCl₃ solution demonstrates the intensity deficiency in the spectral area belonging to anion-water (H₂O)ₙCl⁻ complexes (ν ~ 3465 cm⁻¹) and the intensity excess in
the spectral interval of $\Delta \nu = 3250\,\text{--}\,3440\ \text{cm}^{-1}$, where two overlapping ‘positive’ bands appear with maxima at 3192 and 3324 cm$^{-1}$ (see Figure 4a).

From the Figure 4b, where the differential spectrum is shown of the CeCl$_3$ and GdCl$_3$ equimolar aqueous solutions ($C = 1.694\ \text{M}$), one can see in the case of CeCl$_3$ the concentration decrease in the anion-water (H$_2$O)$_m$Cl complexes (the ‘positive’ band $\nu_{\text{max}} \approx 3498\ \text{cm}^{-1}$) and the increase in anion-free water-water (H$_2$O)$_n$ clusters ($\nu_{\text{max}} \approx 3179\ \text{cm}^{-1}$) as well as the appearing of a new sharp separate spectral band at $\nu_{\text{max}} \approx 3360\ \text{cm}^{-1}$.

To interpret these spectral data we should attract the results obtained by various methods on the coordination of trivalent lanthanide ions (Ln$^{3+}$) in solutions [2, 3, 10, 11].

According to the majority of previous results, in dilute aqueous solutions any Ln$^{3+}$ ion forms a surroundings, which is called as ‘the 1$^\text{st}$ coordination sphere’, with the hydration number changing from nine for the light ions (La$^{3+}$ - Nd$^{3+}$) to eight for the heavy ions (Tb$^{3+}$ - La$^{3+}$). In the Eu-Tb regions of the lanthanide (III) series the intermediate (between 9 and 8) hydrated numbers are proposed [10].

Our early investigations of the Ce$^{3+}$ ion coordination in aqueous solutions and neat inorganic acids [12, 13], using the methods of UV-absorption and luminescence spectroscopy, deduced that: 1) in dilute aqueous solutions a temperature dependent equilibrium exists of the hydrated Ce$^{3+}$ forms with different numbers of water molecules in the 1$^\text{st}$ coordination sphere, Ce$^{3+}$[H$_2$O]$_m$→Ce$^{3+}$[H$_2$O]$_n$, by our estimation at room temperature the concentration percentage of the Ce$^{3+}$[H$_2$O]$_m$ form does not exceed 1.2% in CeCl$_3$ solution (C~10$^{-3}$ M); 2) at concentrations C < 6 M inorganic monovalent inorganic anions such as ClO$_4^-$ or Cl$^-$ do not enter the 1$^\text{st}$ coordination sphere; 3) in neat inorganic acids, such as HCl (C~11 M), anion enters the 1$^\text{st}$ coordination sphere that drastically changes the UV spectra and luminescence characteristics of the Ce$^{3+}$aq.

Some authors have registered an outer-sphere Ln$^{3+}$-Cl$^-$ complexes at lower concentrations (~5 M) [2] but the inner-sphere Ln$^{3+}$-Cl$^-$ complexation have been fixed for La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$ and Eu$^{3+}$ in 14 M aqueous solution of LiCl only [3].

We carried out an additional investigation having shown no changes in the Ce$^{3+}$aq spectral or luminescence characteristics (UV absorption and luminescence spectra, quantum yield and decay time of luminescence) up to Cl$^-$ concentrations ~6.6 M. The measurements were made for CeCl$_3$ + CaCl$_2$ aqueous solutions at room temperature.

Our data correspond with the results, obtained in [14] for aqueous solutions of the dysprosium (III) chloride using the UV-vis/near-IR, time-resolved laser-induced fluorescence spectroscopy experiments and molecular-dynamic calculations conducted for dilute to concentrated solutions (ca. 3.1 mol kg$^{-1}$). The authors concluded that the 1$^\text{st}$ coordination sphere of Dy$^{3+}$aq was filled with 8 water molecules, while there were 17±18 molecules in the 2$^\text{nd}$ sphere; when the solution concentration was increased to 3.1 mol kg$^{-1}$ the average number in the second sphere decreased from 17.5 to 10 and the average number of Cl$^-$ ions increased from 0.5 to 6.3; up to concentrations C~3 M the chloride ion did not form the inner-sphere complexes with dysprosium (III) [14].

Taking into account all these results, we can interpret our data in the following way:

1) Apart from the hydrogen-bonded anion-free water-water (H$_2$O)$_s$ and anion-water (H$_2$O)$_c$Cl$_{\text{aq}}$ forms in the solutions of lanthanide (III) chlorides the Ln$^{3+}$[H$_2$O]$_n$H$_2$O$_m$ and Ln$^{3+}$[H$_2$O]$_n$Cl$_p$ forms arise, where [H$_2$O]$_n$ represents the 1$^\text{st}$ coordination sphere of lanthanide (III) ion; these spheres include 9 water molecules in the case of Ce$^{3+}$aq and between 9 and 8 for Gd$^{3+}$aq, n~10±18, p~1±3; the appearing of inner-sphere Ln$^{3+}$-Cl$^-$ complexes at used concentration range seemed to be not likely.

2) The spectral band (c$\nu_{\text{max}} \approx 3180\,\text{--}\,3190\ \text{cm}^{-1}$), appearing at the differential spectra between CeCl$_3$, LiCl and CeCl$_3$-GdCl$_3$ solutions (Figure 4), corresponds most likely to the new anion-free Ln$^{3+}$[H$_2$O]$_n$H$_2$O$_m$ forms. This band is slightly low-shifted regarding to the band (c$\nu_{\text{max}} \approx 3195\ \text{cm}^{-1}$) assumed to the ‘traditional’ anion-free water-water (H$_2$O)$_c$Cl$_p$ clusters.

3) The second type of new bands at the Figure 4 ($c\nu_{\text{max}} \approx 3360\ \text{cm}^{-1}$) can be assigned to outer-sphere complexes Ln$^{3+}$[H$_2$O]$_n$Cl$_p$. The band maximum is also low-shifted, comparing with the band at c$\nu \approx 3430\ \text{cm}^{-1}$ which represents the anion-water (H$_2$O)$_c$Cl$_p$ forms.
4) The differences, observed in the spectra of the equimolar CeCl$_3$ and GdCl$_3$ aqueous solutions (see Figure 4), may be interpreted as a result of the discrepancy in hydration numbers (9 and 8) and ion radiiues of Ce$^{3+}$aq and Gd$^{3+}$aq.

4) All Raman O-H stretching spectra differences, reflected by the differential spectra, and their behavior under the solution concentration growth may be interpreted in terms of the equilibrium of four main hydrated forms: (H$_2$O)$_m$[Ln$^{3+}$]$_n$H$_2$O$_m$, Ln$^{3+}$[H$_2$O]$_m$Cl$_p$ and (H$_2$O)$_m$Cl$^-$, two of which are the kinds of lanthanide (III) aqua-ions having a difference in the 2$^{\text{nd}}$ coordination sphere ion.

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