THz Spectroscopy of Solvated Ions

Exploring Hydration Dynamics of Aqueous Lanthanides and Transition Metal Halides

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This thesis covers the data and results of my PhD. (doctoral) studies carried out under the supervision of Prof. Dr. Martina Havenith Newen in the group of Terahertz Spectroscopy, Department: Physical Chemistry II, Faculty: Chemistry & Biochemistry, Ruhr University Bochum, Germany between June 15th, 2009 to July 18th, 2013.

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To raise new questions, new possibilities, to regard old problems from a new angle requires creative imagination and marks real advance in science.

.......Albert Einstein
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Overview

Terahertz absorption spectroscopy is a very effective technique for investigation of the hydrogen bond dynamics around ions in aqueous phase. The work in this thesis is mainly devoted to THz spectroscopic study of ion induced effects on the water solvation dynamics by varying the charge state and mass of distinct ions. This study covers investigation of the hydration dynamics of various lanthanide and transition metal ions. The full study is divided into eight chapters and presents the detailed results obtained during the research course.

In Chapter-1, distinct aspects of the ion hydration are presented in order to provide an insight to the ion hydration topic as well as to draw a basic plot which make the thesis structured.

In Chapter-2, the details of the experimental set-up and work functioning of THz narrowband absorption spectroscopy, THz Fourier Transform spectroscopy, low wavenumber Raman spectroscopy as well as the construction of liquid measurement cell are described.

In Chapter-3, the THz hydration modeling methodology is described in detail. This modeling routine allows linking the experimental data with theory, which provides the extended theoretical insight into the hydration dynamics of solvated ions.

In Chapter-4, the results of THz spectroscopic investigations of LaCl₃ and LaBr₃ aqueous solutions are presented. A combined experimental and theoretical analysis was carried out to deconvolute the experimental spectrum into cation, anion and ion pair spectra.

In Chapter-5, the solvation dynamics of aqueous YbCl₃ and YbBr₃ salts is described and discussed. Using the similar physical-chemical analysis like lanthanum, the THz spectral features of Yb³⁺, Cl⁻, Br⁻, YbCl₂⁺ and YbBr₂⁺ were obtained.
In Chapter 6, the results of the THz spectroscopic studies of MnCl$_2$, MnBr$_2$, NiCl$_2$ and NiBr$_2$ salts in aqueous phase are presented. By the proper analysis over the experimental spectra, low frequency resonances of pure Mn$^{2+}$, Ni$^{2+}$, Cl$^-$ and Br$^-$ ions were obtained.

In Chapter 7, the hydration dynamics of ZnCl$_2$ and ZnBr$_2$ salts is discussed. These salts were investigated using THz absorption, THz FT and low frequency Raman spectroscopy. Both zinc halides show strong ion-complexation in aqueous phase. On the theoretical side, Polarization Continuum Modeling was combined with THz hydration modeling to predict the low frequency THz and Raman spectra of pure Zn$^{2+}$ and ion-complex species.

In Chapter 8, general conclusions obtained from the above THz spectroscopic studies of the solvated ions are described. A systematic comparison between the hydration dynamics of aqueous lanthanides and transition metal halides is presented in this chapter.
Chapter 1

Introduction

1.1 Water and solvated ions

Water is the most versatile and pioneer example of hydrogen bonding in liquids [1, 2]. In general perspective, hydrogen bond can be understood as the polar bonding of hydrogen atoms with other electronegative atoms. This specific bonding, which is stronger than Van der Walls bond and weaker than covalent bond is the reason of many special properties of ‘liquid water’, among them high boiling point, large dielectric constant, high viscosity and others [2]. Within the book “The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry”, Linus Pauling has introduced and explained various aspects of hydrogen bonding [3]. This literature demonstrated the large significance and versatility of hydrogen bonding between molecules, and remained successful in originating a new epoch of the studies of hydrogen bond dynamics in liquid phase [3]. Over the years, further scientific advances lead in exploration of the chemical and physical properties of water beyond macroscopic level [4, 5, 6].

With increasing investigations, it has been found that in aqueous state, water molecules behave differently in the vicinity of distinct solute molecules compared to bulk phase. This behavior of water molecules has given rise to the so called “Hydration” phenomenon [6-9]. In further, this has been observed that in order of femto to pico seconds, these hydrogen bonds dynamically break and then reassemble around solute molecules. This continuous mechanism causes the generation of solvation spheres around solute molecules and in general these locally influenced water molecules are defined as the dynamical hydration shell [10, 11, 12].
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This frequent making and breaking of hydrogen bonds between water (H₂O) and solvated chemical species generates some specific vibrations. These vibrations are strongly associated with the microscopic mechanism involved in the interaction between solute and solvent (water) molecules. Resonances generated from these vibrational motions contain significant information about the hydration dynamics of solute molecules. For more specific cases like ionic electrolyte solutions, these vibrational features are also affected by the charge state of the ions, ionic radii, ionic mass, ligand field stabilization effects and exchange kinetics of ligands [13-17].

1.2 Hydration of metal ions and anions

Under the scenario of ion solvation, the most investigated and studied ions in aqueous phase over previous few decades are alkali and earth-alkali metals [8, 13, 14, 18-20]. The origin of these studies can be assigned to the development of ‘Hofmeister Series’ in the nineteenth century [21]. This development demonstrated the significance of solvated ions in the biological systems. Afterwards, these metal ions have been examined by various experimental and theoretical methods over the years due to their high applicability in physical, chemical and biological systems [13, 14, 18, 20-22]. In modern life, their significance is dispersed among all the progressing scientific and technological fields. For example, ion channeling in living organism [23], ionic association for nucleotides [24], electrolyte batteries [25], etc. are some of their prominent applications.

Another class in these ions is the one, which have half or fully filled d-orbitals, popularly manifested as ‘transition metals’. It has been prominently reported that in aqueous phase these ions show strong diversity in their solvation properties [26-28]. Some of these ions show strong ion-complexation with counter anions [29-31], while in some cases very weak or negligible ion-association has been reported [32]. Using distinct experimental and theoretical methods, a number of authors have concluded that the presence of ligand field stabilization effects allows transition metal ions to show a combination of electrostatic and chemical interaction with counter anions [26, 27, 35-36]. However, in spite of these
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scientific efforts, the exact molecular mechanism involved within their hydration dynamics is still not completely understood.

Lanthanides and actinides are the example of ions, which have not been very comprehensively investigated so far in aqueous phase and the knowledge about their solvation dynamics is gradually growing with scientific advancements [17, 38-40, 45]. The trivalent charge state, larger ionic radii, flexible coordination structure and fast ligand exchange kinetics makes their aqueous phase study a challenging task [17, 40]. However, their scientific and technical importance has attracted the attention of researchers over previous few years. Some of the key applications of lanthanides in liquid phase are biomedical luminescence probes [41-42], Magnetic Resonance Imaging (MRI) contrast agents [43], management of radioactive streams [44], etc.

Compared to the metal cations, the hydration behavior of anions (i.e. SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Br$^-$, HPO$_4^{2-}$) shows stronger diversity [8, 11, 13, 19-22]. Some of the anions show negligible or very weak hydration effects on the counter cations [8, 19, 100], while in some cases anions influences the solvation dynamics of cations significantly [18, 20]. Exact structure and dynamics of solvation shell around halide ions is a matter of discussion among various researchers [11, 124, 125]. For example, Kropman et al. [125] have reported that the first solvation shell around Cl$^-$ ion is rigid, while Laage et al. [11] from their MD simulations have concluded that this solvation shell is very labile and shows fast exchanges with second solvation shell.

Probing of ion hydration effects has been facilitated by various experimental techniques over the years. Neutron scattering [27, 33, 46], X-ray solution scattering [45], NMR spectroscopy [17, 43], electrochemical measurements [50, 51], Raman scattering [29, 31, 32], dielectric spectroscopy [47,48] and other methods have been used to investigate significant number of electrolytes in liquid phase. Rather recently, ultrafast and low frequency vibrational spectroscopic methods (i.e. femto-second IR pump probe spectroscopy [20], Optical Kerr Effect spectroscopy [13], 2D IR spectroscopy [49], etc.) have been applied for the investigation of ion induced effects on the solvation dynamics of water molecules. Some of the above mentioned techniques probe rather the static
distribution of water molecules around ions, while the ultrafast vibrational spectroscopic methods probes the dynamics of ions and their solvation shells at different time scales.

In spite of these scientific efforts, many aspects of ion-solvation are still wide open. For example, the exact molecular mechanism involved in the formation of hydration shells around ions is not completely understood [8, 13, 19-20]. In addition to this, it is not entirely clear that why combination of some ions show localized hydration dynamics [13, 14], while in some cases evidence of long range cooperativity has been observed [20]. This is also a fragment of ongoing discussion that, whether the structure and dynamics of the ionic hydration shells only remain intact under ambient conditions or there exists some other aspects at different temperature and pressure conditions [65, 66]. Especially, aqueous transition metal and lanthanide ions offer an open area for precise experimental investigations [17, 40-41]. Under all these aspects, one point which gets highlighted is that, in order to develop better understanding of the solvation properties of these ions in aqueous phase, a detailed experimental and theoretical examination is essential.

On theoretical side, increased computational investigations have remained successful in providing a better understanding of the ion hydration phenomenology up to molecular level. The ab-initio simulations [12], force field based classical and quantum mechanical Molecular Dynamics simulations [10-11, 52-53], micro-solvation model calculations [54] and Polarization Continuum Modeling [55-56] are some of the prominent theoretical methods, which have been utilized in context of ion-solvation so far.

The general conclusions of these investigations indicate that, a combination of techniques is required, in order to understand the different aspects of ion hydration, comprehensively. Reason behind this necessity is that, each experimental technique probes the structuring, distribution and dynamics of hydrogen bonds in a specific spatial, temporal and frequency range. For example, Neutron scattering probes the spatial distribution of water molecules around ions [27, 33], while Optical Kerr Effect spectroscopy provides the information about the collective orientational-diffusion process of a liquid at picoseconds time scales [13]. A key feature of the ionic hydration shells is that, in aqueous phase they are dynamical; i.e. these ions with water molecules undergo various motions, a) vibration, b) libration, c) rotation, d) translation and e) continuous exchange of surrounding water
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molecules. Thus, in order to understand the exact nature of interaction between solvated ions and surrounding water molecules, it is essential to deconvolute the hydration dynamics of ions into distinct components.

1.3 THz spectroscopy and ion hydration

Even in presence of other developing spectroscopic methods, THz spectroscopy has proved itself as a paramount technique to probe the solute induced hydration effects in liquid state [10, 14, 57-59]. The combination of THz p-Ge laser absorption and THz Fourier Transform spectroscopy has strong potential to study the solvation dynamics of complex systems in aqueous phase [14, 58-60, 67]. THz absorption spectroscopy probes the changes in absorption of water due to presence of solute molecules. These changes in the absorption are attributed to the hydration affects induced by the solutes on the water solvation dynamics.

The water absorption spectrum over 1 – 700 cm$^{-1}$ is shown in Figure (1.1). This spectrum was determined by plotting the literature data according to Bertie et al. [61]. Zelsmann et al. [62] have determined the low frequency spectra of pure water and assigned the resonance at 200 cm$^{-1}$ as the hindered translational mode of water molecules. The high frequency large amplitude mode ~ 700 cm$^{-1}$ is attributed to the libration motion of water molecules. Heyden et al. [12] have investigated the solvation dynamics of water molecule using ab-intio simulations, and found an additional mode around 80 cm$^{-1}$. They have assigned this mode as the collective hydrogen bond network motion of water molecules.

THz p-Ge laser absorption spectroscopy probes this collective network motion of water molecules around solutes within 75 – 90 cm$^{-1}$ frequency range (shown as thick orange line in Figure (1.1)). This method allows determining the changes in the absorption within micromolar to molar concentration range. THz Fourier Transform spectroscopy covers a broader frequency range between 50 – 350 cm$^{-1}$ (shown as dark yellow rectangle in Figure 1.1). This technique allows to observe the low frequency resonances generated by the
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solute in aqueous medium and any changes on the hindered translational mode of water at 200 cm\(^{-1}\) [62].

Figure 1.1 Shown above is a schematic overview of the THz (~ \(10^{12}\) Hz) frequency regime (lower panel). The spectra plotted in the upper panel represent the absorption coefficient of pure water over 1 - 700 cm\(^{-1}\) as reported by Bertie et al. [61]. Within the upper plot, the measurement spectral range of THz p-Ge laser spectroscopy between 75- 90 cm\(^{-1}\) (dark orange) and THz FT spectroscopy between 50 – 350 cm\(^{-1}\) (dark yellow) are highlighted. Combination of both these techniques allows to observe the changes in absorption and low frequency resonances of solvated ions in aqueous phase.
Any influences on both these modes of pure water in presence of solutes (ions in the present case) can be well identified and investigated by THz absorption spectroscopy. For an example, in Figure (1.2), low frequency spectra of pure water and 3.3 molar concentration of lanthanum chloride is shown. In presence of LaCl₃, the THz absorption is increased compared to pure water. Additionally, this lanthanide halide salt shows two low frequency resonances at 125 and 210 cm⁻¹.

Figure 1.2: Presented here are the experimental low frequency spectra of pure water (blue) and 3.3 molar concentration of LaCl₃ (red) over 50 – 350 cm⁻¹ frequency range obtained using THz Fourier Transform spectroscopy. THz FT spectroscopy covers this spectral window to observe ion induced changes on the water spectra. From the above spectra it is clear that in presence of lanthanum chloride ions, the 200 cm⁻¹ resonance is increased and blue shifted, as well as an additional mode around 125 cm⁻¹ is visible. The black arrow highlights the frequency range probed by THz p-Ge laser absorption spectroscopy. The change in absorption due to lanthanum chloride is clearly visible around 80 cm⁻¹.

Heugen et al. [58] have investigated the aqueous sugar solutions using THz narrowband absorption spectroscopy. By the application of a complementary three component modeling on the absorption data, they were able to observe the ‘retardation on water solvation dynamics induced by sugar molecules’. Ebbinghaus et al. [59, 63] have investigated the hydration properties of proteins in aqueous phase using THz spectroscopy and observed an
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‘extended solvation shell around proteins’. Using the combination of THz narrowband and broadband spectroscopy, Schmidt et al. [22] were successfully able to explain the hydration dynamics of alkali metal halides. In a continuation to these studies, Funkner et al. [14] had investigated the aqueous earth-alkali halides. Using complementary Molecular Dynamics calculations, they explored and discussed the solvation properties of Mg$^{2+}$ and Ca$^{2+}$ ions, comprehensively. Rather recently, Meister et al. [64] have shown that THz p-Ge absorption spectroscopy is very effective for probing the hydration mechanism of anti-freeze proteins.

In the present study, aqueous lanthanide and transition metal halide salts are investigated using THz p-Ge laser absorption and THz Fourier Transform spectroscopy. All these ionic salts were measured in the combination of La$^{3+}$, Yb$^{3+}$, Mn$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ cations with corresponding Cl$^-$ and Br$^-$ anions in aqueous state. In order to understand the underlying hydration mechanism, the experimental measurements were complemented by proper THz hydration modeling. This conjunction of experimental and theoretical methods allows to explore the solvation dynamics of lanthanide and transition metal ions on a comprehensive level. Resulting from these investigations, the various aspects of the hydration dynamics of these aqueous electrolytes are described and discussed in this study.
2.1 THz narrowband absorption spectroscopy

The p-Ge laser was used as a THz source for performing all absorption measurements over the frequency range 2.3 to 2.8 THz (75 to 90 cm\(^{-1}\)) [67-68]. This technique provides the THz absorption coefficients over a narrow frequency range with very high precision. The pure water has shown very high absorption in this frequency regime. Since all the probe samples (e.g. ionic electrolyte solutions) are dissolved in the pure water, thus very high power of the laser radiation is necessary to penetrate through them. The maximum power of this laser source \(\approx 1\) watt allows such absorption measurements with high accuracy. For performing the concentration dependent absorption measurements, very thin sample layers were used in the measurement cell. Standard commercial Bruker liquid cells with fixed 50 \(\mu\)m Kapton spacers and z-cut quartz windows (4.0 mm \(\pm\) 0.1mm) were used at both the sample and reference cells (see detailed description in section (2.3)).

As this method uses the difference spectroscopy scheme, the absorption coefficients due to solute molecules can be obtained by subtracting the reference contribution from them. As shown in the Figure (2.1), the laser pulse gets reflected and transmitted from first metal chopper alternatively and respective pulses reach at reference and sample measurement channels. After traveling through both (sample and reference) channels the output pulses again get transmitted and reflected by the second metal chopper accordingly and finally get detected at liquid helium cooled Ge photoconductor detector, which is biased at 320 mV with a noise equivalent power of \(10^{-14}\) W Hz\(^{1/2}\) [67-69]. All received signals were averaged over 30,000 laser pulses per channel for each concentration. Since the absorption coefficient value is very sensitive to the external conditions (like humidity, air flow, etc.), the full setup was kept in a closed acrylic glass box. This eliminates any systematic errors due to external atmospheric conditions. For maintaining the selected conditions within the close box chamber, it was purged continuously by dry air and less than 6% humidity was
maintained. The temperature at sample stage was kept at 20.0 ± 0.2 °C using HAAKe, Phoenix II temperature stabilizer during all the measurements. For minimizing thermal fluctuations, both measurement cells were covered with thermal insulating polymer films (Para film). However, manual functioning (filling and mounting sample cells) causes some small temperature variations, which result in a slight change of the value of absorption coefficient. These fluctuations were minimized by waiting six to eight minutes after mounting the sample cell in the holder each time.

Figure 2.1: Schematic diagram of THz p-Ge laser difference spectrometer in transmission mode. The laser pulse from source travels in two paths after reflection from first chopper wheel, a) from sample channel, and b) from reference channel. Both transmitted intensities were detected at a germanium photoconductor detector and get analyzed by connected computer using a LabVIEW program (National Instruments). Using this technique, precise absorption coefficients between 2.3 – 2.8 THz (75 – 90 cm⁻¹) frequency can be obtained, over the concentration range from micromolar to molar [67-70].
For an example, the plot of THz resulting intensities from reference and sample channels over 4000 laser pulses is shown in Figure (2.2). In this case, both channels were filled with water and thus the resulting channel intensities are same.

![Graph showing channel intensities](image)

**Figure 2.2:** Shown here are the resulting channel intensities of THz pulses from sample channel (magenta) and reference channel (green) measured using THz narrow band p-Ge difference spectroscopy. In this case, both channels contain pure water, and within standard deviations, the resulting amplitudes show same value at 20.0 ±0.2 °C.

### 2.1.1 THz p-Ge laser

p-Ge laser is a unique and powerful radiation source in THz frequency range, which uses a semi-conductor active medium for lasing [67]. The doping of semiconductor germanium crystal by p-type donor atoms (beryllium) allows generation of the lasing mechanism by population inversion between light hole and heavy hole bands (Landau levels). The p-Ge crystal is mounted between two NdFeB permanent magnets (which provide a remanent field of 1.4 Tesla) and is simultaneously excited by a pulse generator to deliver THz laser radiation (For a detailed description, refer to Born et al. [69]). This means that, p-Ge crystal
uses a crossed electric and magnetic field configuration for generation of laser pulses in THz frequency range. By proper tuning of electric field, the peak power of the laser is achieved up to 1 W, with maximum duty cycle of 5%. The full laser set up operates at 6 K temperature, which was maintained using liquid helium cooled closed-cycle cryostat (Sumitomo Japan). This laser was originally developed by Bründermann et al. [67] and has been utilized first time in liquid phase studies of various solutes like, sugars [58], ionic salts [14,22], proteins [59,64] in THz frequency range by Havenith and coworkers.

### 2.1.2 Analysis and data evaluation

Since during the measurements, THz intensities are channeled through a difference double beam configuration, it was possible to remove the etalon and reflection effects arriving from the window surface at both channels, simultaneously (see Figure (2.1)). After receiving the resulting intensities from sample and reference channels, the THz absorption coefficient of a particular sample was calculated using Lambert Beer’s law:

\[ I(\omega) = I_0 e^{-\alpha(\omega)d} + S \]  

(2.1)

Where, \(I(\omega)\) and \(I_0\) are final and initial THz intensities, respectively. \(\alpha(\omega)\) is the absorption coefficient, \(d\) is the thickness of the sample layer and \(S\) is the detector offset. The detector offset was removed from both channels by subtracting the background signal from all the measurements, which was obtained by performing the measurements with constant blocking of laser source intensity. For each sample, three independent measurements were performed and error bars were calculated by standard deviation, accordingly. Since, the difference spectroscopic scheme is used here, thus by subtracting the absorption of reference from sample, it was possible to determine the relative THz absorption coefficient of the sample according to the following equations:

\[ \Delta\alpha_{sample} = \alpha_{sample} - \alpha_{reference} \]  

(2.2)

\[ \Delta\alpha_{sample} = -\frac{1}{d} \ln \left( \frac{I_{sample}}{I_0_{sample}} * \frac{I_0_{reference}}{I_{reference}} \right) \]  

(2.3)
In equation (2.2) $\alpha_{\text{sample}}$ and $\alpha_{\text{reference}}$ are the resulting absorptions of sample and reference solutions, respectively. In Equation (2.3), $I_{\text{sample}}$ and $I_{\text{reference}}$ are the respective integrated THz intensities (in the range between 2.3 – 2.8 THz) transmitted alternating through the solutions in the sample cell and the reference cell under identical conditions (humidity, temperature). $I_0_{\text{sample}}$ and $I_0_{\text{reference}}$ signify resulting THz intensities after each subsequent measurement of neat water in the sample and reference channels, respectively, and $d$ is the cell spacer thickness.

For emphasizing the influences due to solvated ions (solutes), the effective ionic absorption ($\alpha_{\text{ion eff}}$) at each concentration was calculated according to:

$$
\alpha_{\text{ion eff}} = (\Delta \alpha_{\text{sample}} + \alpha_{\text{water}}) - c_w \epsilon_{\text{bulk}}
$$

(2.4)

The product $c_w \epsilon_{\text{bulk}}$ describes the absorption due to free water present in a sample solution. The water concentration in a sample solution ($c_w$) was obtained from density measurements (using Anton Paar, DMA 58 density meter), and the extinction coefficient ($\epsilon_{\text{bulk}} = \alpha_{\text{bulk}} / c_{\text{bulk}}$) was determined by independent THz FTS measurements of neat water. The absolute THz absorption of bulk water was used ($\alpha_{\text{water}} = 412 \pm 8$ cm$^{-1}$), as reported by Funkner et al. [14, 70]. The uncertainty ($e$) at a particular intensity ($I$) was calculated by the following formula:

$$
e = - \frac{\Omega}{\sqrt{N}} \sigma
$$

(2.5)

Here, $\Omega$ denotes the Student’s t-factor, for which a value of 1.96 was used for a two sided confidence level of 95%. $N$ denotes the number of pulses in an envelope package and $\sigma$ is the mean standard deviation. The error in the absorption coefficients was calculated according to the following equation:

$$
e_{\alpha} = - \frac{1}{d} \sqrt{\left(\frac{e_{\text{sample}}}{I_{\text{sample}}} \right)^2 + \left(\frac{e_{\text{osample}}}{I_{\text{osample}}} \right)^2 + \left(\frac{e_{\text{reference}}}{I_{\text{reference}}} \right)^2 + \left(\frac{e_{\text{oreference}}}{I_{\text{oreference}}} \right)^2}
$$

(2.6)
2.2 THz Fourier Transform spectroscopy

The p-Ge laser spectroscopy yields precise absorption coefficients in a narrow frequency range. However, for a better understanding of the low wavenumber motions of solute molecules, the information over a broad frequency range is essential. In this respect, for complementing the narrow band absorption method, broad band THz Fourier Transform spectroscopy over 1.5 to 10.5 THz frequency range was performed. This technique allows probing of the low wavenumber resonances due to solvated ions and other solute molecules at different concentrations [14, 22, 68, 70, 72].

A commercial Fourier Transform spectrometer (VERTEX 80V) from Bruker Optics company, attached with a silicon (Si) bolometer was used for detecting the intensities in THz (low wavenumber) frequency range, i.e. 50 to 350 cm$^{-1}$. This instrument works on the basic principle of Michelson’s interferometer (see Figure (2.3)). The source beam gets split into two paths from a Mylar multilayer beam-splitter, in which one get transmitted and travels to a movable mirror, where it again gets reflected. Another beam is reflected from the same half-reflective beam splitter and gets reflected back from a fixed mirror. Thus, this optical arrangement creates a time delay between two travelling beams, which causes interference. By the continuous motion of the movable mirror, successive interference patterns are observed at distinct time intervals (For a detailed description see Krüger et al. [71] and Born et al. [69]). The resulting interferogram is well separated in time domain. With the known speed of the moving mirror, the time and space domain can be correlated to each other. By applying the Fourier Transform, time domain data get converted in frequency domain according to the following equations:

\[ S(t) = \int_{-\infty}^{+\infty} I(v) e^{-iv2\pi t} \, dv \]  
\[ (2.7) \]

\[ I(v) = \int_{-\infty}^{+\infty} S(t) e^{iv2\pi t} \, dt \]  
\[ (2.8) \]
Here $S(t)$ and $I(v)$ are the intensities in time domain and frequency domain, respectively. For probing the aqueous sample solutions in THz frequency range, a silicon carbide or mercury lamp (SiC / Hg) is used as a radiation source. (Note: This source doesn’t have higher power than p-Ge laser around 75 - 90 cm$^{-1}$, but this source allows the probing over a broader frequency range from 50 to 350 cm$^{-1}$). Before guiding the source beam to Michelson interferometer, it is focused on an aperture which can be varied in diameter.

Figure 2.3: Schematic diagram of THz Fourier Transform spectrometer in transmission configuration. A SiC or Hg lamp emits the radiation, which follows the optical path according to Michelson’s interferometer. After interferometer compartment, the radiation light enters sample compartment probing the sample cell in a continuous flowing nitrogen gas atmosphere. Afterwards, the resulting intensity gets detected by a liquid helium cooled Si bolometer and gets analyzed on the connected computer [69-72].

For performing the measurements over 50 to 350 cm$^{-1}$, the commercial Mylar multilayer beam splitter is used. The resulting beam from interferometer section travels through the sample cell and gets detected by a Si-bolometer (detection device). During all
the measurements, the interferometer compartment was kept under vacuum while the sample compartment was maintained under a constant nitrogen gas flow. For this the sample compartment was separated by two polyethylene flaps, which are transparent to the THz radiation. In Si-bolometer, the Si crystal changes the temperature as it receives the resulting signal. Using a biasing voltage, a change in resistance is observed which is proportional to the received intensity of the absorbed THz radiation. For recording the well reproducible THz FT spectrum, each sample was measured three times with 2 cm\(^{-1}\) resolution, and averaged over a total of 384 scans. A running average of 27 cm\(^{-1}\) wavenumber width was taken to smooth out etalon effects resulting from the measurement windows. All measurements over frequency 350 cm\(^{-1}\) were not included in the analysis due to reduced signal to noise ratio in this frequency range because of high water absorption.

### 2.2.1 Analysis and data evaluation

Analysis was initiated by first calculating the THz absolute absorption coefficient of pure water. According to the Lambert-Beer law, the absorption of any liquid sample can be calculated using following equation:

\[
I = I_0 e^{-\alpha(\omega)d}
\]

\[
\Rightarrow \alpha(\omega) = -\frac{1}{d} \ln \left( \frac{I}{I_0} \right)
\]

Here, \(I\) and \(I_0\) are final and initial THz intensities, respectively. \(\alpha(\omega)\) is the absorption coefficient and \(d\) is the thickness of the sample layer. In the resulting spectrum, reflection effects (rising due to change in interface of air/vacuum and due to window material) are present. For ruling out these effects, first the absorption of pure water at 1°C was calculated, because at this temperature signal to noise ratio is significantly improved compared to room temperature [14, 70, 72]. For all low wavenumber THz FT spectroscopic measurements standard Bruker liquid cell was used with CVD - (deposited) diamond windows (0.50 ±0.10 mm thickness; Diamond materials GmbH). The absorption of 1°C water at two different sample layer thicknesses, i) \(d_1 = 39 \pm 2 \, \mu m\) and ii) further smaller thickness of \(d_2 = 25 \pm 2 \, \mu m\) was obtained. Now the absolute absorption coefficient of pure water at 1°C can be expressed:
2. Experimental Methods

\[ \alpha_{\text{water},1^\circ C}(\omega) = -\frac{1}{d_2 - d_1} \ln \left( \frac{I_{d_1}}{I_{d_2}} \right) \]  

(2.11)

Here, the term \( I_o \) gets excluded due to division, and this gives the absolute value of absorption coefficient without interference effects. On assuming that at room temperature, the optical reflection properties of the sample cell remain nearly unchanged, the absolute absorption coefficient of water at 20 °C was determined. The 39 ± 2 μm thick spacer was used to determine the difference \( (\Delta \alpha_{\text{water},20^\circ C,-1^\circ C}(\omega)) \) between the absorption coefficient of water at 20 °C and, that at 1 °C. The absolute absorption of water at 20 °C is represented as:

\[ \alpha_{\text{water},20^\circ C}(\omega) = \alpha_{\text{water},1^\circ C}(\omega) + \Delta \alpha_{\text{water},20^\circ C,-1^\circ C}(\omega) \]  

(2.12)

Or

\[ \alpha_{\text{water},20^\circ C}(\omega) = \alpha_{\text{water},1^\circ C}(\omega) + \frac{1}{d_2} \ln \left( \frac{I_{1^\circ C}}{I_{20^\circ C}} \right) \]  

(2.13)

Here, \( I_{1^\circ C} \) and \( I_{20^\circ C} \) are the resulting THz intensities at 1 °C and 20 °C temperatures, respectively.

Now, for determining the absolute absorption coefficient of sample solutions at 20 °C, a concentration series starting from the pure water measurement to maximum molar concentration of the solute was measured. (Simultaneously, the reference water absorption was measured at each time prior to the sample measurements). In further, this reference water was subtracted from the sample absorption and was added to the absolute water absorption (calculated using Equation (2.13)) according to following equations:

\[ \Delta \alpha_{\text{solute},\text{water}}(\omega) = \alpha_{\text{solute\ sample}}(\omega) - \alpha_{\text{reference\ water}}(\omega) \]  

(2.14)

\[ \alpha_{\text{solute,absolute}}(\omega) = \Delta \alpha_{\text{solute,water}}(\omega) + \alpha_{\text{water},20^\circ C}(\omega) \]  

(2.15)

In this way, the absolute absorption coefficient of the sample solution was determined. In order to calculate the absorption due to solvated ions, scaled water subtraction (similar to p-Ge narrowband data analysis) was carried out. This emphasizes the ionic effects in THz absorption spectrum.
\[ \Delta \alpha(\omega) = \alpha_{\text{solute, absolute}}(\omega) - C' \alpha_{\text{water,20^\circ C}}(\omega) \] (2.16)

The term \( C' \) is the ratio of the concentrations of water molecules in sample solutions \( C_{\text{water, sample}} \) to that in bulk phase \( C_{\text{water, bulk}} \).

\[ C' = \left( \frac{C_{\text{water, sample}}}{C_{\text{water, bulk}}} \right) \] (2.17)

Bulk water concentration was calculated according to the following equation:

\[ C_{\text{water, bulk}} = \left( \frac{\rho_{\text{water, bulk}}}{M_{\text{water, bulk}}} \right) \] (2.18)

Here \( \rho_{\text{water, bulk}} \) denotes the density of the neat water at 20 \( ^\circ \text{C} \), which have a value = 0.99820 g/ml, and \( M_{\text{water, bulk}} = 18.0153 \) g/mol is the molar mass of neat water. The concentration of the water molecules in ionic salt solution can be expressed as:

\[ C_{\text{water, sample}} = \left( \frac{\rho_{\text{salt, sample}} - C_{\text{salt, sample}} \cdot M_{\text{salt, sample}}}{M_{\text{water, bulk}}} \right) \] (2.19)

Here, \( \rho_{\text{salt, sample}} \), \( C_{\text{salt, sample}} \) and \( M_{\text{salt, sample}} \) are density, concentration and molar mass of the salt sample.

**Figure 2.4:** THz effective ionic absorption spectra (left) and THz effective ionic extinction spectra (right) of \( \text{LaCl}_3 \) at 20 ± 0.2°C are shown. The extinction spectra emphasize the non-linear changes in absorption with increasing electrolyte concentration.
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For testing the linear and non-linear contributions in THz absorption spectrum, the THz ionic absorption spectra were normalized by respective molar concentrations. For an ideal ionic salt, THz effective extinction \( (\varepsilon_{\text{ion}}^{\text{eff}} = \alpha_{\text{ion}} / c_{\text{molar}}) \) (concentration normalized THz absorption) spectrum is independent of concentrations. However, if non-linear contributions are observed, then this indicates a significant change in the hydration dynamics around solvated ions. Since, this is the key point of the investigations, wherever required, the effective extinction spectrum \( (\varepsilon_{\text{ion}}^{\text{eff}}) \) of salts were calculated. For an example the THz effective ionic absorption and THz effective ionic extinction spectra of LaCl\(_3\) are shown in Figure (2.4).

### 2.3 Measurement sample cell

A leak proof and easy operational sample cell is required for determination of the absorption coefficients of aqueous solutions with high precision and accuracy. For this purpose, a commercial Bruker fluid cell (A 145) was used for both THz narrowband and broad band measurements, as shown in Figure (2.5). The left and right most holders are made of chromium coated aluminum. Between each quartz window and aluminum holder, Teflon (front) and metal foil covered Neoprene (back) gaskets were used, which provide better temperature isolation and improved fixation of the sample solution between measurement windows. The thickness of the sample layer was maintained by Teflon or Kapton spacer about 39 ± 1µm, and liquid solutions were filled in this using micro syringes [69, 72]. Proper care has been taken while filling the liquid sample because; the presence of any bubble can change the resulting intensity and therefore gives inaccurate value of the absorption coefficient. Another advantage of such small thickness is that, small amount of sample (150 to 350 µl) is required for performing one measurement.

The prepared liquid cell was then mounted on the sample stage, which has magnetic sample holder to fix the cell strongly. This full sample stage was connected to a temperature stabilizer (thermostat) to maintain the constant temperature during all the measurements. For achieving the proper thermal conductivity, the back neoprene gasket was covered by a
thin copper sheet. For THz absorption measurements within 75 - 93 cm\(^{-1}\) frequency range, the 4 mm thick quartz windows were used. For THz FT measurements they were replaced by 0.5 mm thick diamond windows due to increased absorption of quartz after 200 cm\(^{-1}\) frequency.

Figure 2.5: This is a schematic representation of the standard Bruker cell A145 as illustrated in the product operational manual. For THz Fourier Transform measurements, the diamond windows were used, while for THz narrowband absorption measurements the quartz windows were used. Same basic cell construction was used for all the spectroscopic measurements of aqueous sample solutions.

Prior to each measurement, the sample spacer thickness was calculated by obtaining the etalon fringes. For this, the empty cell was scanned over full frequency range of THz FTS under vacuum, which gives the interference pattern as a sinusoidal wave. The spacer thickness \(d\) was determined by the following equation:
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\[ d = \frac{k}{2\eta (\nu_i - \nu_f)} \]  

(2.20)

Here \( \nu_i \) and \( \nu_f \) are the frequencies of two intensity maxima, \( k \) is the number of oscillations between them and \( \eta \) is the refractive index of the medium between the windows, which have a value = 1 for vacuum.

2.4 Raman Spectroscopy

In order to obtain the complementary information to THz Fourier Transform spectra, low frequency Raman spectroscopy of aqueous electrolyte solutions was performed. These measurements were carried out using our commercial confocal Raman microscope (WITec) [73]. For Raman scattering measurements, a frequency-doubled Nd:YAG laser source with a wavelength of 532 nm was used for excitation (P = 45 mW). The laser beam was coupled into the microscope through a single mode optical fiber and then focused on the sample surface. To obtain the proper aperture size and focus of source beam, 20X objective (NA = 0.4) was used. The resulting Raman scattered light was collected with the same objective and registered by a back-illuminated Charged-Coupled Device (CCD) detector (200*1600 pixels, cooled to -60 °C) after passing a multimode fiber (50 µm diameter) and a diffraction grating (600 grooves per mm). The schematic diagram of Raman microscope is shown in Figure (2.6). All measurements were carried out in the spectral range from 200 cm\(^{-1}\) to 1100 cm\(^{-1}\) with an achieved resolution of ± 3 cm\(^{-1}\). The probe concentration series was measured; starting from lowest concentration to that up to solubility limit or to a maximum concentration of 4 M, at room temperature. Each investigated salt solution (50 µL) was placed on a clean piece of silicon wafer. Raman spectra were taken 50 µm below the optical focal plane of the drop with a total integration time of 25 seconds for each spectrum (0.25 seconds, 100 acquisitions). Raman data sets were analyzed using WITec Project 2.08 (2011) software. Prior to any analysis, spectra were treated with user controlled removal of cosmic rays. For background subtraction, areas with no Raman bands were defined in which the Raman intensity values were
averaged. Other areas were interpolated resulting in a background which was subtracted. Prior to each measurement the Raman intensity was pre-calibrated for neat water reference. As required, Raman intensities were normalized by their corresponding molar concentrations for determining the non-linear contributions.

**Figure 2.6:** Shown here is the schematic diagram of a commercial confocal Raman microscope (WITec), coupled with a Nd:YAG laser (532 nm) [73]. This figure is depicted from the operational manual of WI Tec Raman instrument. Each sample concentration was measured over placing a silicon wafer in a back-scattering geometry and prior to each measurement, the Raman intensity was pre-calibrated for the reference (neat water). All Raman data were analyzed using WITec Project 2.08 (2011).

*All Raman measurements were performed with Mr. Eugen Edengeiser (M.Sc.). Author strongly acknowledges his scientific support during the measurements.*
Chapter 3

THz Hydration Modeling

In the following chapters (Chapter 4, 5 and 6), the hydration dynamics of La\(^{3+}\), Yb\(^{3+}\), Mn\(^{2+}\) and Ni\(^{2+}\) cations with counter Cl\(^-\) and Br\(^-\) anions is discussed in terms of THz spectroscopy. On the experimental side, these salts were measured using THz p-Ge laser absorption and THz broad band Fourier Transform spectroscopy. In order to understand the mechanism involved in the origin of their absorption patterns, complementary THz hydration modeling was carried out\(^*\). Most of the THz spectra of these salts show a prominent non-linearity in absorption with increasing salt concentration from 80 to 300 cm\(^{-1}\). These deviations from linearity are mainly attributed to the formation of ion-pairs. (Note: within each chapter, other possible reasons of these non-linear changes are presented and discussed). Under this perspective a detailed description of the THz hydration modeling is presented separately in this chapter.

3.1 Ion-association

The ion-association between metal cation (M) and counter halide ion (X) can be expressed in two ways, first by contact ion-pairing (Equation (3.1)) and second by solvent separated ion-pairing (Equation (3.2)). Both these processes can be represented by the following chemical reactions, respectively.

---

This kind of formalism of the hydration modeling is originally developed by Dr. Gerhard Schwaab and further changed and improved jointly by the author (me) and my colleague Mr. Fabian Böhm. I acknowledge both of them for their strong scientific contributions in the development and implementation of this modeling routine in context of the ion hydration.
3. THz Hydration Modeling

\[
(M(H_2O)_n)^q^+ + X^- \xrightleftharpoons[K]{\approx} (M(H_2O)_{n-1}X)^{(q-1)}^+ + (H_2O) \tag{3.1}
\]

\[
(M(H_2O)_n)^q^+ + X^- \xrightleftharpoons[K]{\approx} (M(H_2O)_nX)^{(q-1)}^+ \tag{3.2}
\]

Here, \( q = 2 \) for a divalent ion (\( \text{Mn}^{2+}, \text{Ni}^{2+} \)) and \( q = 3 \) for a trivalent ion (\( \text{La}^{3+}, \text{Yb}^{3+} \)). The major difference in these two mechanisms is that, in case of contact ion pairing, the halide ion binds directly to the metal center, which results in the release of one water from the first solvation shell of the cation. In case of solvent shared ion-pairing, the cations and anions are separated by solvent water and the resulting complex species incorporates all the coordinating water molecules. To avoid any additional assumptions, any formation of higher ion-pairs is neglected. In both cases, for dilute solutions the equilibrium constant is given by:

\[
K = \frac{\gamma_{\text{pair}}}{\gamma_{\text{cation}}} \frac{c_{\text{pair}}}{c_{\text{cation}} c_{\text{anion}}} \tag{3.3}
\]

Here, \( \gamma \) is described as the mean activity coefficient of the chemical moiety and \( c \) denotes the concentration of the respective chemical species. Considering that solvated cation and ion-pair both have nearly similar chemical structure, Equation (3.3) can be further simplified by assuming: \( \gamma_{\text{pair}} = \gamma_{\text{cation}} \cdot \)

\[
K = \frac{c_{\text{pair}}}{c_{\text{cation}} c_{\text{anion}}} \frac{1}{\gamma_{\text{anion}}} \tag{3.4}
\]

or,

\[
c_{\text{pair}} = K * c_{\text{cation}} * c_{\text{anion}} * \gamma_{\text{anion}} \tag{3.5}
\]
3.1.1 Trivalent electrolyte

Taking into account the conservation of ion number boundary condition, for a trivalent electrolyte, the cation and anion concentrations can be expressed in terms of salt concentration as:

\[ c_{\text{salt}} = c_{\text{cation}} + c_{\text{pair}} = c_{\text{cation}} (1 + K \times c_{\text{anion}} \times \gamma_{\text{anion}}) \]  \hspace{1cm} (3.6)

\[ 3c_{\text{salt}} = c_{\text{anion}} + c_{\text{pair}} = c_{\text{anion}} + K \times c_{\text{cation}} \times c_{\text{anion}} \times \gamma_{\text{anion}} \]  \hspace{1cm} (3.7)

\[ 3c_{\text{salt}} - c_{\text{anion}} = K \times c_{\text{cation}} \times c_{\text{anion}} \times \gamma_{\text{anion}} \]  \hspace{1cm} (3.8)

On equalizing the cation concentration terms from Equation (3.6) and Equation (3.8), the concentration of the anions can be expressed as:

\[ \frac{c_{\text{salt}}}{(1 + K \times c_{\text{anion}} \times \gamma_{\text{anion}})} = \frac{3c_{\text{salt}} - c_{\text{anion}}}{(K \times c_{\text{anion}} \times \gamma_{\text{anion}})} \]  \hspace{1cm} (3.9)

By rearranging Equation (3.9):

\[ K \times c_{\text{anion}}^2 \times \gamma_{\text{anion}} + c_{\text{anion}} (1 - 2 \times c_{\text{salt}} \times K \times \gamma_{\text{anion}}) - 3 \times c_{\text{salt}} = 0 \]  \hspace{1cm} (3.10)

By analytically solving the Equation (3.10), the concentration of the anions in terms of salt concentration and equilibrium constant can be obtained from:

\[ c_{\text{anion}} = \frac{-1 + 2 \times \gamma_{\text{anion}} \times c_{\text{salt}} \times K + \sqrt{1 + 8 \times \gamma_{\text{anion}} \times c_{\text{salt}} \times K + 4 \times \gamma_{\text{anion}}^2 \times c_{\text{salt}}^2 \times K^2}}{2 \times \gamma_{\text{anion}} \times K} \]  \hspace{1cm} (3.11)

The cation concentration can be calculated using Equation (3.6) and Equation (3.11) as:
The concentration of the ion-pairs can be determined using Equation (3.5). The mean activity coefficients of the trivalent lanthanide chlorides were calculated according to Kim et al. [74] using Pitzer’s equation, and lanthanide bromides according to Fukushi et al. [75].

### 3.1.2 Divalent electrolyte

For a divalent electrolyte, the stoichiometry of the salt system is 1 : 2. Hence the relative ratio between the amounts of cation and anion are different than the trivalent salts. For a divalent salt, the cation concentration can be expressed similarly as equation (3.6) by

\[
c_{\text{salt}} = c_{\text{cation}} + c_{\text{pair}} = c_{\text{cation}} (1 + K \cdot c_{\text{anion}} \cdot \gamma_{\text{anion}}) \tag{3.13}
\]

\[
2c_{\text{salt}} = c_{\text{anion}} + c_{\text{pair}} = c_{\text{anion}} + K \cdot c_{\text{cation}} \cdot c_{\text{anion}} \cdot \gamma_{\text{anion}} \tag{3.14}
\]

\[
2c_{\text{salt}} - c_{\text{anion}} = K \cdot c_{\text{cation}} \cdot c_{\text{anion}} \cdot \gamma_{\text{anion}} \tag{3.15}
\]

The anion concentration can be determined by:

\[
\frac{c_{\text{salt}}}{(1 + K \cdot c_{\text{anion}} \cdot \gamma_{\text{anion}})} = \frac{2c_{\text{salt}} - c_{\text{anion}}}{(K \cdot c_{\text{anion}} \cdot \gamma_{\text{anion}})} \tag{3.16}
\]

\[
K \cdot c_{\text{anion}}^2 \cdot \gamma_{\text{anion}} + c_{\text{anion}} (1 - c_{\text{salt}} \cdot K \cdot \gamma_{\text{anion}}) - 2 \cdot c_{\text{salt}} = 0 \tag{3.17}
\]

\[
c_{\text{anion}} = \frac{-1 + \gamma_{\text{anion}} \cdot c_{\text{salt}} \cdot K + \sqrt{1 + 6 \cdot \gamma_{\text{anion}} \cdot c_{\text{salt}} \cdot K + \gamma_{\text{anion}}^2 \cdot c_{\text{salt}}^2 \cdot K^2}}{2 \cdot \gamma_{\text{anion}} \cdot K} \tag{3.18}
\]
Using Equations (3.13 to 3.15) and Equation (3.18), the cation and ion-pair concentrations can be determined. The values of mean activity coefficients of MnCl₂, MnBr₂, NiCl₂ and NiBr₂ were used from the data reported by Goldberg at al. [76-77].

### 3.2 Total absorption

In the previous segment, formulas for the concentrations of the anions, cations and ion-pairs were derived. Both, THz p-Ge absorption and THz FT spectroscopy determine the total absorption of each salt concentration, which are composed of different individual absorption contributions. The total absorption of aqueous electrolyte system contains absorption contributions of: (i) bulk water, (ii) cation, (iii) anion and (iv) ion-pair. In this way, the total absorption of a solvated electrolyte system can be described as:

\[ \alpha_{\text{total}}(\nu) = \alpha_{\text{water}}(\nu) + \alpha_{\text{cation}}(\nu) + \alpha_{\text{anion}}(\nu) + \alpha_{\text{pair}}(\nu) \]  

(3.19)

The concentration of the water molecules \( c_{\text{water}} \) in the salt solution was determined by density measurements (see Section 2.2.1). The distinct absorption terms can be further expressed as the concentration weighted superposition of all the effective extinction \( \epsilon_{\text{eff}} \) components according to:

\[ \alpha_{\text{total}}(\nu) = c_{\text{water}} \epsilon_{\text{bulk}}(\nu) + c_{\text{cation}} \epsilon_{\text{cation}}^{\text{eff}}(\nu) + c_{\text{anion}} \epsilon_{\text{anion}}^{\text{eff}}(\nu) + c_{\text{pair}} K \epsilon_{\text{pair}}^{\text{eff}}(\nu) \]  

(3.20)

### 3.3 THz hydration water

The term \( \epsilon_{\text{eff}} \) used in Equation (3.20) represents the effective extinction due to a chemical species. This term is composed of two parts as described in the following equation:

\[ \epsilon_{\text{eff}} = \epsilon - n \epsilon_{\text{bulk}} \]  

(3.21)
In Equation (3.21), the first part of the right hand side is \( \varepsilon \), which is the extinction component due to solvated ion modes. The second term is a negative component \((- n \varepsilon_{\text{bulk}})\) which itself is composed of two sub-components. The effective number \( n \) describes the amount of THz hydration water molecules influenced in the vicinity of solvated ions defined as ‘hydration water’.

For the determination of THz effective ionic absorption, all the bulk water contributions were subtracted from the total sample absorption (Please refer to Chapter 2, section 2.2.1). However, resulting effective ionic absorption spectra not only contains the contributions from ionic modes but also from the solvation shell water around ions. This hydration water shows lower absorption than bulk water and thus, the total term \((- n \varepsilon_{\text{bulk}})\) represents the extinction contribution of the hydration water molecules, which show less THz absorption than the bulk water. The negative sign is due to the decrease in absorption by the hydration water molecules.

The mathematical interpretation of the quantity hydration water \( n \) is rather straightforward. However, this term lacks the meaning in physical representation. As described here, this is the number of water molecules that show less or no absorption compared to bulk water. This means that, there might exist a stepwise transition from completely transparent to bulk water absorption. This is rather unphysical and more physically meaningful interpretation can be a gradual change in absorption from less absorbing to bulk water absorption. Nevertheless, the quantity \((- n)\) mentioned here represents the lower limit for the number of water molecules in the dynamical hydration shell of ion.

### 3.4 Hydration modeling

In Equation (3.20), the total absorption is deconvoluted in terms of distinct components. Since the total amount of anions and cations is given by the salt concentration \( c_{\text{salt}} \), the ion-pair formation decreases the concentration of the single ions according to the scheme;

\[
c_{\text{cation}} = c_{\text{salt}} - c_{\text{pair}} \quad \text{and} \quad c_{\text{anion}} = 3c_{\text{salt}} - c_{\text{pair}} \quad \text{for trivalent electrolyte}
\]

\[
c_{\text{cation}} = c_{\text{salt}} - c_{\text{pair}} \quad \text{and} \quad c_{\text{anion}} = 2c_{\text{salt}} - c_{\text{pair}} \quad \text{for divalent electrolyte}
\]

Now on
implementing this in equation (3.20), the total THz absorption can be expressed as following:

For trivalent electrolytes:

$$\alpha_{\text{total}}(v) = c_{\text{water}} \varepsilon_{\text{bulk}}(v) + c_{\text{salt}}(\varepsilon_{\text{cation}}^{\text{eff}} + 3\varepsilon_{\text{anion}}^{\text{eff}}) + c_{\text{pair}}(K)(\varepsilon_{\text{pair}}^{\text{eff}} - \varepsilon_{\text{cation}}^{\text{eff}} - \varepsilon_{\text{anion}}^{\text{eff}})$$  (3.22)

For divalent electrolytes:

$$\alpha_{\text{total}}(v) = c_{\text{water}} \varepsilon_{\text{bulk}}(v) + c_{\text{salt}}(\varepsilon_{\text{cation}}^{\text{eff}} + 2\varepsilon_{\text{anion}}^{\text{eff}}) + c_{\text{pair}}(K)(\varepsilon_{\text{pair}}^{\text{eff}} - \varepsilon_{\text{cation}}^{\text{eff}} - \varepsilon_{\text{anion}}^{\text{eff}})$$  (3.23)

In Equations (3.22 and 3.23) the total absorption is expressed in terms of distinct components. In order to perform a nonlinear model fit, this equation can be rewritten as:

$$\alpha(v) = c_{\text{water}} \varepsilon_{\text{bulk}}(v) + c_{\text{salt}} \varepsilon_{\text{single}}^{\text{eff}}(v) + c_{\text{pair}}(K) \varepsilon_{\text{diff}}^{\text{eff}}(v)$$  (3.24)

Here, $$\varepsilon_{\text{single}}^{\text{eff}} = \varepsilon_{\text{cation}}^{\text{eff}} + (q)\varepsilon_{\text{anion}}^{\text{eff}}$$; (q = 2 or 3) emphasizes the pure ionic part of the absorption and $$\varepsilon_{\text{diff}}^{\text{eff}} = \varepsilon_{\text{pair}}^{\text{eff}} - \varepsilon_{\text{cation}}^{\text{eff}} - \varepsilon_{\text{anion}}^{\text{eff}}$$ denotes the difference in the extinction of the ion-pair and single ions (cation and anion). In the following Chapters (4, 5 and 6), the nonlinear model fit was performed according to Equation (3.24). Within this equation, the association constant K, the total extinction due to pure ion modes $$\varepsilon_{\text{single}}^{\text{eff}}$$, and the difference of ion pair and single ion extinctions $$\varepsilon_{\text{diff}}^{\text{eff}}$$ were used as the fitting parameters. The extinction of water ($$\varepsilon_{\text{bulk}}$$) was determined by independent THz FTS measurements of neat water.

### 3.5 Linear part and ionic component

Right hand side of Equation (3.24) contains three components; a) bulk water absorption, b) pure or single ionic absorption and c) ion-pair absorption. As mentioned above, the absorption due to bulk water over 50 – 350 cm⁻¹ frequency range was determined separately.
using THz FT spectroscopy. In all following chapters, the second contribution is defined as linear part/ ionic contribution/ single ion contribution. This term is composed of cation and anion absorptions according to the following equation:

\[ c_{\text{salt}} \varepsilon_{\text{single}} (\nu) = c_{\text{salt}} (\varepsilon_{\text{cation}}^{\text{eff}} + q \varepsilon_{\text{anion}}^{\text{eff}}) \] (3.25)

Here, \( q = 2 \) for divalent ions (\( \text{Mn}^{2+}, \text{Ni}^{2+} \)) and \( q = 3 \) for trivalent ions (\( \text{La}^{3+}, \text{Yb}^{3+} \)).

### 3.6 Non-linear part and ion-pair spectra

The non-linear part of absorption is composed of the following sub components:

\[ c_{\text{pair}} (K) \varepsilon_{\text{diff}}^{\text{eff}} (\nu) = c_{\text{pair}} (K) (\varepsilon_{\text{pair}}^{\text{eff}} - \varepsilon_{\text{cation}}^{\text{eff}} - \varepsilon_{\text{anion}}^{\text{eff}}) \] (3.26)

It is clear from Equation (3.26) that the ion-pairing causes a reduction in the effective extinction of one cation and one anion. As mentioned before that, the term \( (\varepsilon_{\text{eff}}) \) is composed of two components according to: \( \varepsilon_{\text{eff}} = \varepsilon - n \varepsilon_{\text{bulk}} \). The substitution of this in Equation (3.26) yields the following equation:

\[ \varepsilon_{\text{diff}}^{\text{eff}} = (\varepsilon_{\text{pair}} - n_{\text{pair}} \varepsilon_{\text{bulk}}) - (\varepsilon_{\text{cation}} - n_{\text{cation}} \varepsilon_{\text{bulk}}) - (\varepsilon_{\text{anion}} - n_{\text{anion}} \varepsilon_{\text{bulk}}) \] (3.27)

From this, total ion-pair extinction \( (\varepsilon_{\text{pair}}') \) spectra can be calculated according to the following equation:

\[ \varepsilon_{\text{pair}}' = \varepsilon_{\text{diff}}^{\text{eff}} + \varepsilon_{\text{cation}} + \varepsilon_{\text{anion}} = \varepsilon_{\text{pair}} - (n_{\text{pair}} - n_{\text{cation}} - n_{\text{anion}}) \varepsilon_{\text{bulk}} \] (3.28)

The Equation (3.28) gives the total ion-pair spectra.
3.7 Line shape for fitting

All the determined spectra were fitted using minimum number of required modified Lorentzian line shapes and one hydration water contribution. This modification of the Lorentzian line shape by the multiplication of additional ($h_w$) term allows better parameter estimation during the fitting. The equation of the modified Lorentzian is given by:

$$L(\varepsilon_m, h_w, \nu, \nu_m) = \varepsilon_m * h_w * \frac{h_w}{(\nu - \nu_m)^2 + h_w^2} \quad (3.29)$$

Here, $\varepsilon_m$ denotes the amplitude of the resonance, $h_w$ denotes the half width, $\nu$ denotes the frequency and $\nu_m$ denotes the center frequency of the resonance.
4. Hydration of Aqueous Lanthanum Halides

Chapter 4

Hydration of Aqueous Lanthanum Halides

Precise understanding of the hydration dynamics of lanthanide ions in aqueous solution is essential for making progress in various technological applications, e.g. Magnetic Resonance Imaging (MRI), management of radioactive streams, etc. Under this perspective, results of high precision Terahertz (THz) absorption measurements of solvated LaCl$_3$ and LaBr$_3$, using narrow-band (75 - 90 cm$^{-1}$) p-Ge laser and wideband (30 - 350 cm$^{-1}$) Fourier Transform spectroscopy are presented in this chapter. A combined theoretical and experimental analysis in terms of THz hydration model makes it possible to separate the pure ion (cation and anion) and ion pair contributions from bulk water. Resulting from this detailed analysis, distinct aspects of the hydration of lanthanum halides are discussed here.

4.1 Lanthanides in aqueous phase

Significant amount of scientific efforts have been made for understanding the solvation dynamics of alkali, earth-alkali and d-transition metal ions over the years [13, 14, 18-21]. On the other hand, so far rare earth metal ions have not been studied so comprehensively and elementary proceedings of an understanding on the molecular level have started to emerge rather recently [17, 39-40]. The solvation of lanthanides is of prominent importance due to their large applicability in aqueous phase such as: a) aqueous solutions of lanthanides are very useful for chemical and medical applications, (i.e., modern Magnetic Resonance Imaging Contrast Agents (MRI CA) are mainly based on the aqueous Gadolinium (Gd$^{3+}$) complexes [17,43]), b) Due to their luminescent properties, lanthanides are vastly used as luminescent probes [41], c) Increasingly, the high concentration solutions of lanthanides are used in the management of the radioactive streams [44], and others. For making progress in these scientific and technical areas, it is essential to understand the
structure and the hydration dynamics of the solvation spheres around these trivalent cations. In order to achieve this, a systematic probing of lanthanide ions in liquid state is required. It has been found that all these ions preferably have “3+” oxidation states except Eu$^{2+}$ and Ce$^{4+}$ [17]. Under this perspective, measurements were carried out over the first element of this series; which is lanthanum(III) with counter chloride and bromide ions in the present chapter.

### 4.2 Coordination state

The starting element of the lanthanide series (i.e. lanthanum) prefers “3+” oxidation state. It’s coordination structure in aqueous solutions have been reported by distinct experimental techniques in which X-ray solution [46], Neutron scattering [46, 78], Raman Spectroscopy [79], high energy X-ray scattering (HEXS) [80], Nuclear magnetic resonance (NMR) [17, 43] are some. In addition to this, Molecular Dynamics (MD) and Polarizable Continuum Model (PCM) simulations based studies have investigated distinct combinations of lanthanide cations and anions in aqueous phase, in order to get comprehensive theoretical insight [53, 81-83]. Most of the above mentioned techniques found a common conclusion that the preferred coordination state of La$^{3+}$ in water is nine. However, some investigations have shown that, in very dilute solutions, a distribution between eight, nine and ten water coordinated cation species exists [82]. (Note: the coordination state or the first coordination sphere of the ion means the spatial distribution of water (oxygen and hydrogen) molecules around them and this is different than dynamical hydration shell obtained using THz spectroscopic techniques in this chapter.) On extending this aspect over the full lanthanide series; various techniques have reported a change from nine to eight coordination numbers of water molecules from lighter to heavier lanthanides, respectively [38, 39]. However, the exact nature and mechanism involved in this change is still a matter of discussion among them [17, 40].

![Figure 4.1: Lanthanides in periodic table with atomic number. From going left to right the atomic weight increases and the size of the atom decreases.](image-url)
4. Hydration of Aqueous Lanthanum Halides

4.3 Key aspects of hydration dynamics

In spite of this systematic feature of the lanthanide ions, experimentally the investigation and explanation of their complete hydration phenomena is not simple. The reason behind this is that the coordination geometries of lanthanides are not influenced much by the strong ligand field effects. The absence of the strong ligand field stabilization effects, (which is different than the case of transition metal ions, i.e. Ni$^{2+}$, Fe$^{2+}$, Cu$^{2+}$, etc.) makes the coordination structure of lanthanides rather flexible and labile compared to other divalent ions [17]. This allows the generation of distinct geometrical arrangements and coordination numbers, which are very often described as the presence of coexisting equilibria. These flexible structures contain eight, nine and ten water molecules in their first hydration shell over the full lanthanide series. It is often demonstrated using experimental and theoretical methods that, lighter lanthanides are preferably nine coordinated while this number decreases to eight for heavier lanthanides [17, 81, 39]. Strong diversity in results has been reported on whether this change from nine to eight is stepwise or it is rather smooth [17, 39, 40]. Recent review by Helm et al. [17] concluded that this trend shows a smooth decrease in the cation and ligand (water) distance. Schematic representations of exchange pathways reported by them, from eight to nine water coordination of lanthanides are shown in Figure (4.2).

![Figure 4.2: Possible mechanistic paths for water exchange between eight and nine coordinated lanthanides reported by Helm and Merbach [17]. "Adapted with permission from Helm, L., & Merbach, A. E. (2005). Inorganic and bioinorganic solvent exchange mechanisms. Chemical reviews, 105(6), 1923-1960. Copyright (2005) American Chemical Society."](image-url)
This indicates that trivalent lanthanide ions get equilibrated in coupled coordination structures in water at ambient temperatures. The second aspect is that, all these lanthanides ions show very fast ligand exchanges in liquid phase. The residence time of water molecules in the first coordination shell for La$^{3+}$ ion has been reported between 100 to 300 picoseconds [17].

However, this diversity also contains some systematic properties. One of the fascinating features of aqueous lanthanide ions is the reduction of their ionic radii with increasing atomic mass; defined as “lanthanide contraction” [38,39,84]. This behavior allows the sequential investigation of some physical and chemical properties, like ionic radii, Lewis acidity, binding affinities, etc. of the lanthanides [17]. However, some authors have concluded that the complete explanation of the hydration structure of these trivalent ions also requires the inclusion of second and higher coordination shells [55, 85]. This strongly suggests that, the electrostatic interaction between trivalent cations and surrounding chemical species (water, anions, ligands, etc.) significantly affects their solvation dynamics.

### 4.4 Open points and objectives of the study

Although, some of the key aspects of the lanthanides hydration dynamics are well understood, there are some points which still remain ill-known. One of the elementary reasons behind this is that in real systems, these trivalent ions are always present with counter anions and solvent molecules (e.g. water in present case). Thus the separation of the effective hydration mechanism due to individual cations and anions is not a straightforward task. For example, the structure, nature and dynamics of the solvation shell of the lanthanide ions in aqueous phase are still a matter of discussion [40, 81]. The influences of the second and higher solvation shells on the hydration dynamics of water molecules are still not significantly probed by experimental techniques. In addition, the tendency and the nature of ion-complexation between lanthanide and chloride ions are still not entirely clear.

In the following, some literature facts are presented.

The X-ray diffraction investigations by Habenschuss et al. [45] indicate that a large amount of pure hydrated lanthanide ions are present in the concentrated lanthanide chloride aqueous solutions. Allen et al. [86] examined the lanthanide chloride in aqueous phase in
4. Hydration of Aqueous Lanthanum Halides

presence of co-solutes (HCl and LiCl) by EXAFS and XANES techniques. From their measurements, they concluded that in dilute solutions, the ion-association between chloride and lanthanide ion is dominated by the outer sphere complexation. However, the experimental results obtained by Soderholm et al. [80] shows a divergence with conclusions of Allen et al. [86] and Habenschuss et al. [45]. They investigated the acidic aqueous solutions of erbium(III) chloride using high-energy X-ray scattering (HEXS), and concluded that chloride ions form inner sphere complexation with erbium(III). Recently, Diàz-Moreno et al. [78] concluded the presence of contact ion-pairing in 1 molal concentration of LaCl$_3$ using Neutron scattering, X-ray scattering and EXAFS measurements.

Similar to the experimental results, strong contrast is visible in the theoretical calculations. Petit et al. [87] found that two chloride ions bind to La(III) in lithium chloride added aqueous solutions, while Beuchat et al. [53] concluded that no chloride anions are bound to lanthanum at low to moderate concentrations, whereas chloride ions are found in the first coordination shell of erbium even at low concentrations. However, Molina et al. [83] found the ion-complexation, only in case of lanthanum chloride at a concentration of 1.0 molal, while in all other cases of heavier lanthanides, no chloride ions were found to be bound to the metal center.

With this background of knowledge, the hydration of aqueous LaCl$_3$ and LaBr$_3$ solutions was examined using THz absorption and THz Fourier Transform spectroscopy in the present segment. The hydrated lanthanum halide salts (LaCl$_3$*7H$_2$O and LaBr$_3$*7H$_2$O) were purchased from Sigma Aldrich and ABCR Chemicals, respectively. For the liquid measurements, the molar concentration series of the aqueous solutions of LaCl$_3$ and LaBr$_3$ (ranging from 0.15 to 3.3 M) were prepared. The weighed out amount of salt was dissolved in HPLC grade ultra pure water for each concentration. For calculating the partial molar volumes to these electrolytes, density measurements on an Anton Paar DMA 58 density meter at 20 ± 0.2°C were carried out.
4.5 THz (p-Ge laser) absorption measurements

Using THz narrowband spectroscopy [22, 67], the absorption coefficients at different concentrations (between 0.15 M to 3.3 M) of LaCl$_3$ were determined. This method provides averaged THz absorption at a particular concentration of the salt in 75 – 93 cm$^{-1}$ frequency range and thus, the resulting absorption corresponds to the sum of the absorption contributions arriving from the cation, anion and hydration effects. The measured THz absorption pattern of LaCl$_3$ shows a strong non-linearity with increasing molar concentration (see Figure 4.3). For the lower concentrations, the absorption shows a rather linear increase with concentration, while for higher concentrations (> 2M) the slope increases non-linearly. This behavior is prominently

\[
\alpha_{total} \text{ in cm}^{-1}
\]

\[
\text{Concentration in mol / dm}^3
\]

![graph](image)

**Figure 4.3:** Shown above is the experimental total average THz absorption (75 - 93 cm$^{-1}$) of aqueous LaCl$_3$ as a function of salt concentration at a temperature of 20 ± 0.2°C. A growing non-linearity in the absorption coefficients is visible with increasing salt concentration (C > 2M).

...different than the behavior of alkali earth chlorides reported by Funkner et al. [14]. Due to lower charge state of the alkali earth ions (2+) than lanthanide ions (3+), a one to one comparison is not straightforward. However, the trend here provides a clear indication that
4. Hydration of Aqueous Lanthanum Halides

difference in the nature of electrostatic interaction between these different classes of ions with water molecules is affecting the average hydration dynamics significantly.

4.6 THz Fourier Transform measurements

In order to understand the origin of this non-linear behavior of the absorption pattern of LaCl$_3$, complementary THz broadband measurements were performed. For determination of the relative differences due to anions, in addition to LaCl$_3$, the LaBr$_3$ solutions of the same molar concentrations were also measured. In further, the effective THz ionic absorptions at different concentrations of LaCl$_3$ and LaBr$_3$ solutions in the frequency range 50 - 350 cm$^{-1}$ have been determined, which are shown in Figure (4.4) (for details refer to the methods section 2.2.1). One clear difference in both these spectra is that around 200 cm$^{-1}$, LaCl$_3$ shows a vibrational resonance, while LaBr$_3$ shows a nearly zero or slightly partial negative value of absorption. Due to observed non-linearity in the p-Ge spectra, a straight forward assignment of the cation and anion resonances might contain some uncertainty in both cases.

**Figure 4.4:** Presented here are the THz broad band effective ionic absorption spectra of LaCl$_3$ (left) and LaBr$_3$ (right) at different salt concentrations obtained using THz broad band FT spectroscopy at 20 ± 0.2°C.
4.7 THz effective extinctions

In order to assign the resonances properly, the ionic absorptions of LaCl\textsubscript{3} and LaBr\textsubscript{3} were normalized by respective molar concentrations in further (see Figure (4.5)). This yields THz effective molar extinctions of both electrolyte species. Both LaCl\textsubscript{3} and LaBr\textsubscript{3} show strong non-linear changes with increasing salt concentration. In case of LaCl\textsubscript{3}, the non-linearity is prominent between 120 to 200 cm\textsuperscript{-1}, and for LaBr\textsubscript{3} these are mainly centered at 80 cm\textsuperscript{-1} and 200 cm\textsuperscript{-1}. Such strong non-linearity suggests that, these electrolytes are not behaving like an ideal bi-component (cation + anion) system and some additional changes in the average solvation structure are responsible for this. In addition to this, the effective extinction spectra of LaBr\textsubscript{3} show a significant partial negative extinction around 200 cm\textsuperscript{-1}, which changes non-linearly with increasing salt concentration. For assignment of any spectral features of the cation and anion, the separation between the linear and non-linear parts is essential.

![Figure 4.5: Shown here are the THz effective extinction spectra of LaCl\textsubscript{3} (left) and LaBr\textsubscript{3} (right) at different salt concentrations at 20 ± 0.2°C. The non-linear contributions are clearly visible in both spectra.](image)

4.8 Possible reasons for non-linear changes

Prior applying any modeling routine, first it is necessary to estimate the possible reasons behind these non-linear changes. In order to initiate this, it is required to underline the
various cationic, anionic and hydration contributions. Some of the following facts are straightforward to incorporate: a) the positive trivalent charge state of the cation, b) the mass of the lanthanide ion, c) the negative charge state of the halide ion, d) the mass of the anion, e) the increase in the number of solvated ions with increasing salt concentration and f) the decrease in the bulk water concentration with increasing salt concentration.

On the basis of these facts, some of the possible hydration mechanisms are discussed in the following:

1. One of the possible reasons for these non-linear changes can be a change in the coordination number of the water molecules around cation. However, this effect should influence more the cationic resonance than the anionic; while in the spectra (see Figure (4.5)) the non-linear changes are present over the full frequency range.

2. Another important mechanism which can cause these non-linear changes is the hydrolysis reaction in the aqueous solutions of the lanthanum halides. The effects arriving from the hydrolysis can be estimated by the pH measurements because hydrolysis changes the concentration of the hydronium ions in the solution. For solvated lanthanum ion, this can be represented as:

\[
(La(H_2O)_n)^{3+} K (La(OH)(H_2O)_{n-1})^{2+} + (H_3O)^+ \tag{4.1}
\]

From the pH measurements, a value of pH 2 was obtained for 3.3 M concentration of LaCl\textsubscript{3}. However, the 3.3 M concentration of LaBr\textsubscript{3} shows a value of 0.75 pH units. For LaCl\textsubscript{3} this corresponds to hydronium ion concentrations of less than 0.01 M and for LaBr\textsubscript{3} this corresponds to hydronium ion concentrations of lower than 0.2 M. In both cases, compared to the concentration of electrolytes and of bulk water molecules, this concentration is insignificantly small.

3. The third possible mechanism which can produce such non-linear contributions might be a shift in the ionic mode frequencies due to a change in hydrogen bond network strength.

4. The aggregation of the ionic species (of similar charge) can be estimated as the fourth possible mechanism [126]. However, the difference in charge state of both ions (cation (3+) and anion (-)) should prefer a heterogeneous aggregation (cation-anion) compared to the homogeneous (cation-cation- or anion-anion).
Formation of contact or solvent shared ion-pairs can be considered as the fifth possible mechanism, which can cause such deviations in linearity of the extinctions. In the effective ionic absorption spectra, all the contributions of the bulk water molecules have been subtracted and only the ionic and hydration contributions are left. In addition to this, with increasing salt concentration, the amount of bulk water gradually reduces and due to a trivalent charge state, La$^{3+}$ ions have strong electrostatic interaction with neighboring water molecules and counter anions. All these aspects strongly indicate that within the possible mechanisms mentioned in the above section, the ion-pair formation is the process which is mainly contributing in the non-linear changes of the absorption spectra.

### 4.9 Ion-association

The ion-association between lanthanum and halide ions can be represented in two ways, first by a contact ion-pairing (Equation 4.2) and second by solvent separated ion-pairing (Equation 4.3). Both these processes can be represented by following chemical reactions:

\[
(\text{La(H}_2\text{O})_n)^{3+} + X^- \underset{K}{\overset{}\rightleftharpoons} (\text{La(H}_2\text{O})_{n-1}X)^{2+} + (\text{H}_2\text{O}) 
\]

\[
(\text{La(H}_2\text{O})_n)^{3+} + X^- \underset{K}{\overset{}\rightleftharpoons} (\text{La(H}_2\text{O})_nX)^{2+} 
\]

The major difference in these two mechanisms is that, in case of contact ion pairing, the halide ion binds directly to the metal center, which results in the release of one water from the first solvation shell of the cation. While, in case of solvent shared ion-pairing, the cation and anions are separated by solvent water and the complex species incorporates all the coordinating water molecules. Some of the previous studies [79, 88] favor the mechanism of solvent separated ion-pair formation over the contact ion-pairing. In further, all these experimental data were modeled using THz hydration modeling. For a detailed description, please refer to Chapter 3.
4.10 Fitting of narrowband absorption data

First the narrowband absorption spectrum of LaCl₃ was fitted using this hydration model. It’s clear from the Figure (4.6), that, this model is able to fit concentration dependent nonlinear absorption curve of LaCl₃. The fit yields the value of ion-pairing constant $K_{\text{pair}} = 0.13 \pm 0.07 \text{ dm}^3/\text{mol}$. The value of extinction due to pure ionic modes is $\epsilon_{\text{single}}^{\text{eff}} = 61 \pm 3 \text{ cm}^{-1}\text{dm}^3/\text{mol}$, while the difference between the ion-pair and ionic extinction have a value of $\epsilon_{\text{diff}}^{\text{eff}} = 30 \pm 2 \text{ cm}^{-1}\text{dm}^3/\text{mol}$. The numbers mentioned after symbol (±) gives 2σ standard deviation values.

![Graph showing concentration vs. total absorption](image)

**Figure 4.6**: The red line shown here describes a fit to the experimental data of LaCl₃ assuming ion pairing with an association constant of $K_{\text{pair}} = 0.13 \pm 0.07 \text{ dm}^3/\text{mol}$, $\epsilon_{\text{single}}^{\text{eff}} = 61 \pm 3 \text{ cm}^{-1}\text{dm}^3/\text{mol}$, and $\epsilon_{\text{diff}}^{\text{eff}} = 30 \pm 2 \text{ cm}^{-1}\text{dm}^3/\text{mol}$.

4.11 Fitting of THz Fourier Transform data

In order to fit the THz broadband absorption spectra of lanthanide halides, the same fitting procedure like narrowband absorption data was used. Compared to the p-Ge absorption method, the values of the absorption coefficients determined by THz FT spectroscopy
contain larger uncertainty. That’s why the fitting was applied over the each frequency of THz FT spectra of LaCl$_3$ and LaBr$_3$ for all the concentrations within 50 to 350 cm$^{-1}$ frequency range.

A stepwise approach was used here to calculate a value for $K_{\text{pair}}$ and to separate the pure ionic and the ion pair spectra. At first, each frequency within 50 to 350 cm$^{-1}$ range was fitted with a fixed value of $K_{\text{pair}}$ and the obtained values of $\chi^2$ for each $K_{\text{pair}}$ were compared. In the second step, the smallest $\chi^2$ was obtained. Afterwards, these values of $\chi^2$ were used as parameter guesses of a combined fit for all frequencies and concentrations. Due to a calculation over large number of data points, the accuracy level of the determined $K_{\text{pair}}$ is comparable with the values of the p-Ge absorption spectroscopy.

This fit routine yields a value of association constant $K_{\text{pair}} = 0.138 \pm 0.007$ dm$^3$/mol for LaCl$_3$. Within standard deviations, this number is in very good agreement with the value obtained using the THz narrowband p-Ge laser spectroscopy. For LaBr$_3$, the fits yields a smaller ion-pairing constant $K_{\text{pair}} = 0.0141 \pm 0.0009$ dm$^3$/mol, which emphasizes that the ion-complexation tendency with La$^{3+}$ is weaker for Br$^-$ compared to Cl$^-$.

### 4.12 Ionic spectra

![Graph showing the effective single ion extinction spectra of LaCl$_3$ and LaBr$_3$](image)

**Figure 4.7**: Shown here are the effective single ion extinction spectra of LaCl$_3$ (black) and LaBr$_3$ (red) obtained using the THz hydration modeling.
Using this hydration modeling, the ion-pairing constants for aqueous LaCl$_3$ and LaBr$_3$ salts were calculated and the pure ionic and ion-pairing parts were separated. The effective single ion spectra ($\varepsilon_{\text{single}}^{\text{eff}} = \varepsilon_{\text{cation}}^{\text{eff}} + 3\varepsilon_{\text{anion}}^{\text{eff}}$) for LaCl$_3$ and LaBr$_3$ obtained by this model fit are presented in Figure (4.7). Both these spectra contain no contributions due to ion-pairs and thus, they are only composed of La$^{3+}$ and respective 3X$^-$ (X: Cl, Br) ionic modes. The spectrum of LaCl$_3$ shows resonances at 120 and 190 cm$^{-1}$, while for LaBr$_3$ two spectral features are visible at 80 and 120 cm$^{-1}$. In both cases, the resonance at 120 cm$^{-1}$ is attributed to the motion of La$^{3+}$ ions within their hydration cage. In addition to this, a partial negative extinction is visible at 200 cm$^{-1}$ in case of LaBr$_3$.

### 4.13 Effective anion spectra

The main advantage of having the pure ionic spectra is that, the individual cationic and anionic resonances can be extracted from them. For determining this, the $\varepsilon_{\text{single}}^{\text{eff}}$ (LaBr$_3$) spectrum was subtracted from the $\varepsilon_{\text{single}}^{\text{eff}}$ (LaCl$_3$). The resulting spectrum is presented as black thick line in Figure (4.8).

**Figure 4.8:** The difference $\varepsilon_{\text{single}}^{\text{eff}}$ (LaCl$_3$) - $\varepsilon_{\text{single}}^{\text{eff}}$ (LaBr$_3$) shown here is composed of distinct ionic components (see Table 4.1). Positive contribution (green) is attributed to the Cl$^-$ resonance. The negative mode (orange) is due to Br$^-$ resonance. The hydration water component is shown in blue color. The small feature around 120 cm$^{-1}$, is attributed to the effects of anions on the cation.
In order to obtain pure anionic (Cl\(^-\) and Br\(^-\)) resonances, this spectrum was fitted by three modified Lorentz line shapes and one hydration water contribution. The fit yields a strong positive contribution at 190 cm\(^{-1}\) attributed to the rattling mode of chloride ions. The bromide is visible as a weak negative resonance at 80 cm\(^{-1}\) (see Table (4.1)). Due to the trivalent stoichiometry of the electrolyte (LaX\(_3\)), the value of the effective anion extinction is three times the bare anion extinction.

**Table 4.1:** Described here are the center frequency, effective extinction and line width of low frequency vibrational resonances of the anions in lanthanum chloride and bromide obtained using the THz hydration model.

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>contributions</th>
<th>(\nu_m) in cm(^{-1})</th>
<th>(\varepsilon_m) in dm(^3)/mol</th>
<th>(h_w) in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl(_3)</td>
<td>Cl(^-)</td>
<td>188.2 ± 0.1</td>
<td>63.2 ± 0.3</td>
<td>46.9 ± 0.2</td>
</tr>
<tr>
<td>LaBr(_3)</td>
<td>Br(^-)</td>
<td>72.4 ± 0.4</td>
<td>7.2 ± 0.1</td>
<td>28.9 ± 0.9</td>
</tr>
</tbody>
</table>

The small positive shoulder at 120 cm\(^{-1}\) indicates that anions affect the cation resonance. The hydration water \((n_h)\) component (the decrease in the water absorption) shown in blue color is attributed to the relative difference in the number of water molecules influenced in the vicinity of different anions (see Figure (4.8)). The fit yields that per mole salt of LaCl\(_3\) influences about \(n_h\sim3.5\) mole additional water molecules compared to per mole salt of LaBr\(_3\). It is interesting to state here that, on neglecting any effect of the cation on this number, this difference indicates that one Cl\(^-\) ion influences the THz absorption of one additional water compared to a Br\(^-\) ion.

### 4.14 Effective cation spectra

In the upper section, the anionic contributions from the pure ionic spectra were extracted. Now the rest part is attributed to the effective cationic contribution. In order to determine this, the respective anionic contributions were subtracted from the ionic part of the electrolyte spectrum according to the: \(\varepsilon_{\text{single}}^{\text{eff}}\) (LaX\(_3\) - X\(_3\)), where X: Cl\(^-\) and Br\(^-\). The pure La\(^{3+}\) extinction spectra are presented in Figure (4.9). In this figure, the calculated spectrum
of La$^{3+}$ is shown in black for LaCl$_3$ and in red for LaBr$_3$. Both these spectra were fitted by two modified Lorentzian line shapes and one negative hydration water component. In case of LaCl$_3$, the fit yields two resonances of hydrated La$^{3+}$ at 126 and 362 cm$^{-1}$, while for LaBr$_3$, two vibrational resonances at 127 and 355 cm$^{-1}$ were determined (see Table 4.2).

**Figure 4.9:** Plotted here are the pure La$^{3+}$ spectra as obtained from LaCl$_3$ (black) and LaBr$_3$ (red) by subtracting the anion contribution. The respective thick lines show the individual components for LaCl$_3$ and dashed line for LaBr$_3$ obtained by the fit. Two resonances around 126 and 358 cm$^{-1}$ are observed for solvated La$^{3+}$.

Both frequency components of La$^{3+}$ shows higher amplitude and nearly the same line width in case of LaCl$_3$ compared to LaBr$_3$. In addition to this, the high frequency components of La$^{3+}$ show a slight red shift for Br$^-$ compared to Cl$. However, the low frequency components show nearly same resonance frequency position in both cases. This low frequency component can be assigned to a motion of cation, within its water hydration cage.
Table 4.2: Listed here are the center frequency, effective extinction and line width of the low frequency vibrational resonances of La$^{3+}$ for lanthanum chloride and bromide determined by the THz hydration modeling. $n_{\text{salt}}$ refers to the effective number of water molecules influenced per salt entity (LaX$_3$; X: Cl$^-$, Br$^-$).

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>contributions</th>
<th>$v_m$ in cm$^{-1}$</th>
<th>$\epsilon_m$ in dm$^3$/mol</th>
<th>$h_w$ in cm$^{-1}$</th>
<th>$n_{\text{salt}} = n_{\text{cation}} + 3n_{\text{anion}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl$_3$</td>
<td>La$^{3+}$</td>
<td>126.3 ± 0.2</td>
<td>188.8 ± 0.8</td>
<td>36.9 ± 0.3</td>
<td>13.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>361.9 ± 0.9</td>
<td>472.9 ± 3.6</td>
<td>103 ± 1</td>
<td></td>
</tr>
<tr>
<td>LaBr$_3$</td>
<td>La$^{3+}$</td>
<td>127.0 ± 0.2</td>
<td>174.1 ± 0.8</td>
<td>40.3 ± 0.3</td>
<td>9.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>355.0 ± 0.7</td>
<td>446.7 ± 3.2</td>
<td>101 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

On the one hand, the relative differences in both vibrational resonances are rather small, while on the other hand, a prominent difference is visible in the hydration water component of both salts. This number $n_{\text{salt}} = n_{\text{cation}} + 3n_{\text{anion}}$ emphasizes the number of water molecule influenced by one cation and three anions, which show decreased THz absorption compared to bulk water. The fit yields $n_{\text{salt}} = 13.5$ for LaCl$_3$ and $n_{\text{salt}} = 9.8$ for LaBr$_3$.

4.15 Ion-pair spectra

Using the hydration model, the linear and non-linear parts of experimental THz extinction spectra of LaCl$_3$ and LaBr$_3$ were separated. The non-linear part of the spectra contains the contributions of the ion-pairs as well as of the single ions (For analytical details, please see section 3.6 of Chapter 3). The total ion-pair extinction ($\epsilon'_{\text{pair}}$) spectrum was determined according to the following equation:

$$\epsilon'_{\text{pair}} = \epsilon_{\text{diff}} + \epsilon_{\text{cation}} + \epsilon_{\text{anion}} = \epsilon_{\text{pair}} - (n_{\text{pair}} - n_{\text{cation}} - n_{\text{anion}}) \epsilon_{\text{bulk}}$$ (4.5)
The resulting total ion-pair spectra (LaCl$^{2+}$ and LaBr$^{2+}$) are shown as orange thick lines in Figure (4.10 (A and B)). In order to determine the individual resonances present within the curves, both spectra were fitted by the same fitting procedure as described in the above section. Two positive modified Lorentzians at 118.1 and 212.2 cm$^{-1}$ with a negative hydration water component were used to fit LaCl$^{2+}$ spectra. For the fitting of LaBr$^{2+}$, three resonances at 83.7, 118.7, and 186.5 cm$^{-1}$ with hydration water component were necessary (see Table 4.3). The fit yields that the ion-pair LaCl$^{2+}$ binds 1.5 more water molecules than $n_{\text{cation}} + n_{\text{anion}}$, while for LaBr$^{2+}$ a smaller number 0.5 was obtained. Resulting values from the fit are described in Table (4.3).

**Figure 4.10:** Shown here are the ion pair spectra of aqueous LaCl$^{2+}$ in panel (A) and LaBr$^{2+}$ in panel (B) as the thick orange line in both cases. These spectra were fitted using the respective positive modified Lorentzian line shapes and one negative THz hydration water component. The thin black lines for both salts represent the best fit to the ion-pair spectra.
Table 4.3: Described here are the center frequency, effective extinction and line width of low frequency vibrational resonances attributed to ion pairs ((LaCl\textsuperscript{2+})\textsubscript{(aq)} and (LaBr\textsuperscript{2+})\textsubscript{(aq)}) determined using hydration model. The (*) denotes the empirical assignment of the individual resonances present within the ion-pair spectra.

<table>
<thead>
<tr>
<th>ion-pair contributions</th>
<th>(v_m) in (\text{cm}^{-1})</th>
<th>(\varepsilon_m) in (\text{dm}^3/\text{mol})</th>
<th>(h_w) in (\text{cm}^{-1})</th>
<th>(n_\text{diff} = n_\text{pair} - (n_\text{cation} + n_\text{anion}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LaCl\textsuperscript{2+})\textsubscript{(aq)}</td>
<td>(v_1) (La\textsuperscript{3+})*</td>
<td>118.1 ± 0.1</td>
<td>216.7 ± 0.8</td>
<td>32.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>(v_2) (Cl\textsuperscript{-} + H\textsubscript{2}O)*</td>
<td>212.2 ± 0.3</td>
<td>175.4 ± 0.9</td>
<td>56.4 ± 0.6</td>
</tr>
<tr>
<td>(LaBr\textsuperscript{2+})\textsubscript{(aq)}</td>
<td>(v_1) (Br\textsuperscript{-})*</td>
<td>83.7 ± 0.4</td>
<td>80.6 ± 4.5</td>
<td>22.9 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>(v_2) (La\textsuperscript{3+})*</td>
<td>118.7 ± 0.9</td>
<td>90.9 ± 4.2</td>
<td>37.0 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>(v_3) (H\textsubscript{2}O)*</td>
<td>186.5 ± 0.8</td>
<td>94.0 ± 2.0</td>
<td>59.0 ± 0.8</td>
</tr>
</tbody>
</table>

4.16 General discussion and conclusions

Using a combined experimental and theoretical analysis, the linear and non-linear contribution within the THz spectra of LaCl\textsubscript{3} and LaBr\textsubscript{3} were separated. The linear part of the spectrum is composed of the cationic and anionic components. The non-linear part of the spectrum contains the mixture of ion-pair and single ionic contributions. In the following, each of these components is discussed one by one:

(1) Anion contributions: Both anionic spectra are presented in Figure (4.8) and the resulting values are described in Table (4.1). The Br\textsuperscript{-} ions show a weak resonance at 84 cm\textsuperscript{-1}. The Cl\textsuperscript{-} resonance is visible at 188 cm\textsuperscript{-1}. These values are in general agreement with the low frequency resonances of chloride and bromide ions reported by THz FT spectroscopy [14,22]. Schmidt et al. [22] have measured the alkali halide salts using THz absorption spectroscopy and found that chloride and bromide rattling resonances are present around 190 and 90 cm\textsuperscript{-1}, respectively. Funkner et al. [14] have investigated the aqueous solutions of earth-alkali halides and found the similar value of rattling frequencies of both anions. In case of La\textsuperscript{3+}, the rattling resonances of Cl\textsuperscript{-} and Br\textsuperscript{-} are still present well
within the same frequency range, which strongly suggests that these resonances are not much affected by the charge state of the counter cation.

The analysis yields a number of $n_h \approx 3.5$ for the difference between the hydration water of LaCl$_3$ compared to LaBr$_3$. This suggests that one Cl$^-$ influences approximately one more water compared to one Br$^-$. This can be proposed as the lower limit of the number of water molecules affected by Cl$^-$. Tielrooij et al. [89] have investigated the LiCl aqueous solutions using fs-IR pump-probe spectroscopy and found that approximately 2 water molecules are slowed down by one Cl$^-$ ion. This value gives the higher limit of $n_h \approx 6.0$ of the number of water molecules that are influenced in the vicinity of three chloride ions.

(2) Cation contributions: The low frequency spectra of pure lanthanide ions are shown in Figure (4.9) and the respective values of the resonances are described in Table (4.2). The pure La$^{3+}$ ion shows two vibrational modes around 126 and 360 cm$^{-1}$ in both cases (LaCl$_3$ and LaBr$_3$). The low frequency resonance can be assigned to vibration of the cation within its hydration cage. The higher frequency resonance is attributed to the hydrated breathing motion of La$^{3+}$ with surrounding water molecules. This is consistent with previous Raman spectroscopic investigations of glassy and room temperature aqueous solutions of lanthanum halides. [79, 88]

The number of THz hydration water molecules ($n_{salt}$) for LaCl$_3$ and LaBr$_3$ aqueous solutions are given in Table (4.2). The fit yields a value of $n_{salt} = 13.5$ for LaCl$_3$. In case of LaBr$_3$ a comparatively smaller number of $n_{salt} = 9.8$ have been obtained. This means that, in an average lanthanum bromide is weakly hydrated compared to lanthanum chloride. The relative difference of hydration water between 3Cl$^-$ and 3Br$^-$ gives a value of 3.5. With the assumption that, approximately three to six water molecules are affected by the three chloride ions, a value of $n_{cation} = 8.5 \pm 1.0$ THz hydration water molecules can be obtained for one La$^{3+}$. This value is well within the range 8 - 10 as determined by other experimental [17, 45] and theoretical methods [81-83]. An empirical comparison between LaCl$_3$ and LaBr$_3$ clearly indicates that Br$^-$ ions are ill-hydrated compared to Cl$^-$ ions.

Since the lanthanum is a trivalent ion, it is possible that it may exert a strong force on the surrounding water molecules. This can be estimated by a simple calculation by assuming that lanthanum is a particle, which is moving in a harmonic oscillator potential. With $\nu$ as the frequency in hertz and $\mu$ the reduced mass of the system, the force constant can be
4. Hydration of Aqueous Lanthanum Halides

written as: \( k = (2\pi\nu)^2\mu \). The low frequency resonance of \( \text{La}^{3+} \) is present at \( \nu = 126 \text{ cm}^{-1} \) and the reduced mass of the lanthanum surrounded by 9 water molecular system is \( 75 \times 10^{-3} \text{ kg/mol} \). This gives an estimate of the value of \( k \approx 70 \text{ N/m} \). (Note: In this calculation, only the water molecules in the first solvation shell of the lanthanum are considered). Using quantum mechanical based theoretical calculations, Hofer et al. [90] have reported a value of \( k = 53 \text{ N/m} \). Recently, by quantum mechanical charge field (QMCF) MD simulations Lutz et al. [82] have estimated the value of \( k = 110 \text{ N/m} \). A comparison of these numbers suggests that, the value of \( k \) obtained in the present study is well within the range of the theoretical calculations.

(2) Ion Association: Using the hydration modeling, a value of \( K_{\text{LaCl}_3} = 0.14 \text{ dm}^3/\text{mol} \) has been obtained for the \( \text{LaCl}_3 \). The analysis yields a smaller equilibrium constant for \( \text{LaBr}_3 \) (\( K_{\text{LaBr}_3} = 0.013 \text{ dm}^3/\text{mol} \)). This can be correlated from the patterns of THz effective extinctions shown in Figure (4.5). \( \text{LaCl}_3 \) shows non-linear contributions at lower concentrations compared to \( \text{LaBr}_3 \).

One of the non-trivial aspects of the ion-association phenomenon between \( \text{La}^{3+}-\text{halide ions} \) is that whether they form solvent shared ion-pairs or they prefer contact ion-association. Present experimental and theoretical analysis suggests that in lanthanum halide aqueous solutions, solvent shared ion-pairing dominates. This is obtained from the spectra and the fit of the ion-pairs (see Figure 4.10). In case of \( \text{LaBr}_3 \), three components are visible at 84, 119 and 187 cm\(^{-1} \). These modes can be assigned to anionic, cationic and ion-shared water molecule resonances, respectively. Interestingly, the third mode at 187 cm\(^{-1} \), is very close to the hindered translational resonance of water, reported by Zelsmann et al. [62]. In case of \( \text{LaCl}_3 \) the fit yields two resonances at 118 cm\(^{-1} \) and 212 cm\(^{-1} \). The mode at 118 cm\(^{-1} \) is attributed to the cation contribution. The resonance at 212 cm\(^{-1} \) is assumed to be composed of two contributions; a) \( \text{Cl}^- \) and b) ion shared water. The difference between contact ion-pairing and solvent shared ion-pairing between solvated \( \text{La}^{3+} \) and \( \text{Cl}^- \) is illustrated schematically in Figure (4.11).
Figure 4.11: This is a schematic representation of solvent separated (left) versus contact (right) ion pair, between lanthanum and chloride ions. In case of solvent shared ion-association, both cation and anion are separated by solvent (water) molecules, while for contact ion-pairing, the anion replaces one water molecule and binds directly to the metal ion center.

Results presented here are not directly comparable with the results obtained by other measurements [78, 81, 86]. The reason is that, all those measurements were performed on the lanthanide halide aqueous solutions which contain additional co-solutes and significant amount of acids. According to Yaita et al. [91], acidity affects the ion-pairing in aqueous lanthanum halides significantly. Their measurements indicate that the inner-sphere complexes are only present in the hydro chloride acid added LaCl$_3$ solutions, while in presence of lithium chloride; LaCl$_3$ does not show inner sphere complexation. This probably can be linked to the contrasting conclusions of Allen et al. [86] and Diàz-Moreno et al. [78]. Allen et al. [86] have performed EXAFS measurements on lanthanide chloride with 12 M LiCl solutions and found that ion-pairing is dominated by the outer sphere complexation. However, Diàz-Moreno et al. [78] have examined the acidic aqueous LaCl$_3$ solutions by neutron scattering and EXAFS and found that Cl$^-$ ion binds directly to the metal (La$^{3+}$) center, which supports the formation of contact ion-pairing.

Kanno et al. [79] have performed Raman spectroscopic investigations on aqueous and glassy LaCl$_3$ solutions. They do not find any additional resonances, which are expected to originate from the cation-anion direct complexation in these solutions. These conclusions are also consistent with the results of Raman and EXAFS measurements of concentrated aqueous LaCl$_3$ and LaBr$_3$ solutions reported by Alves Marques et al. [88]. On a theoretical perspective, the results presented here are in good agreement with the conclusions of
quantum chemical and classical molecular dynamics studies reported Beuchat et al. [53]. They found inner shell ion pairing in LaCl₃ only for the 5 M concentration (and not at lower concentrations), which is over saturated concentration of the electrolyte because at room temperature the solubility limit of the salt is below 4.5 M. The value of ion-association constants for solvated (LaCl)²⁺ in different strength ionic media is reported between 0.67 to 1.9 dm³/mol by other methods [78, 92-94]. The differences between the other previous studies and the present study are assigned to the direct inclusion of the mean salt activity and to the neglect of the formation of di-chloro or higher order ion complexes in the present case.

In brief, in this chapter LaCl₃ and LaBr₃ aqueous salt solutions were examined by THz absorption spectroscopy and THz Fourier Transform spectroscopy [127]. Using a proper hydration modeling, low frequency cation, anion and ion-pair spectra were extracted from the experimental spectra. The non-linear contributions in the THz spectra were attributed to the ion-association between La³⁺ and halide ions. The combination of all these results suggests that, although lanthanum is a trivalent ion, but it shows rather local influences on the average solvation dynamics of water molecules.
Chapter 5

Hydration of Aqueous Ytterbium Halides

The lanthanides are popularly known for their systematic chemical and physical properties in aqueous phase, e.g. Lewis acidity, binding affinity and others. In Chapter 4 distinct aspects of the hydration dynamics of the lanthanum halides were discussed. In this chapter, this discussion is now extended to another heavier lanthanide ion (ytterbium(III)) with counter bromide and chloride anions. In this segment, combined THz spectroscopy and hydration modeling investigations were carried out on aqueous YbCl$_3$ and YbBr$_3$ solutions. The pure ionic and ion-pair parts of ytterbium halides were separated using the same formalism as lanthanum halides, in order to make both analyses mutually consistent. Distinct spectral contributions resulting from the analysis of ytterbium halides, as well the differences between solvation dynamics of ytterbium and lanthanum ions are described and discussed in this chapter.

5.1 Motivation of the study

Due to the effect of ‘lanthanide contraction’, it has been prominently reported that larger lanthanides prefer ‘9’ water coordination, while smaller lanthanides prefer the ‘8’ coordination state [17, 38-39, 81]. However, the question rises here, that if the charge state is same, and the size of the ion is reduced, actually this should result in a stronger polarization of water molecules. This means that the cation should influence the surrounding water molecules more strongly and more number of water molecules might be influenced. One aspect which could counteract on this process is the increase in the ionic mass. Compared to La$^{3+}$, Eu$^{3+}$, Gd$^{3+}$ and Er$^{3+}$ ions, the experimental investigations of Yb$^{3+}$ ion have not been carried out so comprehensively and only a few techniques have discussed its hydration dynamics [46,86,95]. In comparison to ytterbium(III), the hydration of some neighboring lanthanide ions (erbium, thulium, lutetium) have been investigated rather prominently by different experimental and theoretical methods [45, 53, 80, 83].
experimental side, Allen et al. [86] have examined the aqueous lanthanide chlorides in presence of lithium chloride co-solutes and found that chloride complexation tendency decreases across the lanthanide series. In addition to this, for ytterbium chloride they neither observed Yb$^{3+}$--Cl$^-$ complexation nor any significant loss of coordination water molecules from the solvation shell of the cation. Mayanovic et al. [95] have investigated the aqueous ytterbium chloride solutions using X-ray absorption fine structure (XAFS) technique within 25 – 500 °C temperature range. They observed that below 150 °C, the Yb$^{3+}$ was present as an aqua ion in the solutions while, the ion-complexation had been found only at the higher temperatures (300 – 500 °C). In theoretical perspective, Kowall et al. [85] have investigated the lanthanide ions using classical MD simulations. Their results indicate differences in the hydration behavior of larger and smaller lanthanides. For Yb$^{3+}$ ions they obtained 8 water molecules in the first hydration shell and 15 - 19 water molecules in the second coordination shell. Floris et al. [55] have investigated the hydration of Yb$^{3+}$ ions using ab-initio effective pair potentials based MD calculations. They have found that the first coordination shell of Yb$^{3+}$ contains in between 8 to 9 water molecules, while the second shell of ytterbium contains 11 - 15 water molecules. D’Angelo et al. [96] have investigated the lanthanide ions using a combination of EXAFS technique and MD simulations. They found that, with decreasing size of the lanthanide ionic radii, the ion-coordination water distance gradually decreases. Villa et al. [97] have performed MD simulations using ab-initio based polarization model potentials on Nd$^{3+}$, Gd$^{3+}$ and Yb$^{3+}$ ions. They found that the first coordination shell of ytterbium ions contains 8 water molecules.

This suggests that compared to the experimental investigations, ytterbium ions are more broadly studied by the theoretical methods. In the periodic table, ytterbium is present just before the lutetium, which is the final element of the lanthanide series. In this way, aqueous Yb$^{3+}$ offers a point of interest, which is still open for enhanced experimental investigations. However, in experimental terms, investigation and explanation of the hydration effects due to Yb$^{3+}$ ions is a rather challenging task because the exchange of the water molecules from the ionic first hydration sphere with the bulk water is rather fast [17,85]. In addition to this, the effects rising from the second and higher solvation shells on the experimental spectrum might not be strong enough to observe.
5.2 THz narrow and broad band spectroscopy

In order to understand the hydration dynamics of ytterbium ions, THz spectroscopic investigations were carried out on aqueous YbCl$_3$ and YbBr$_3$. The basic analytical yield of the work in Chapter 4 was that: using a hydration modeling, dissection of the pure ionic contributions from the ion-pairs was carried out. As an extension to this work, in the present segment, a heavier lanthanide (Yb$^{3+}$) with higher charge density is investigated. For lanthanum, the analysis yielded that the interaction between cation and water molecules is dominated by the electrostatic effects. An experimental examination of Yb$^{3+}$ halides with similar analogy allows to test the span of the modeling as well as to see the differences in the solvation mechanism of both cations. In addition to this, it also allows to test the sensitivity of the THz absorption spectroscopy to the ionic influences on the second and higher solvation spheres in aqueous state. A comparison of the two ytterbium halide salts is also essential, because in this way the relative effects induced by the anions on the cations can be explored. The ytterbium halide salts YbCl$_3$ * 6 H$_2$O and YbBr$_3$ * 9 H$_2$O were purchased from commercial suppliers ABCR Chemicals and Alfa Aesar. For a particular concentration, the salts were dissolved in HPLC grade ultra pure water. Density measurements were performed on an Anton Paar DMA 58 density meter at 20 ± 0.2 °C.

5.3 THz (p-Ge laser) absorption measurements

The averaged total THz absorption coefficients of aqueous YbCl$_3$ solutions were determined using narrowband THz absorption spectroscopy. In Figure (5.1) the total absorption coefficients within 0.15 to 3.3 M concentration range are shown. Similar to the LaCl$_3$ (see Figure 4.3), a non-linear increase in the absorption has been observed after 2.5 M concentration. At low concentrations the increase in absorption is rather linear, while after 2.5 M concentration a non-linear rise is observed. This deviation of the absorption
pattern from linearity indicates towards the strong influences of the solutes on the water solvation dynamics.

Figure 5.1: Shown here are the narrowband averaged total THz absorption (75-93 cm$^{-1}$) coefficients of aqueous YbCl$_3$ with increasing electrolyte concentration, determined at a temperature of 20 ± 0.2°C. The solid triangles represent the experimental absorption coefficients obtained using THz (p-Ge laser) absorption spectroscopy, which clearly show growing non-linearity with increasing salt concentration (C > 2.5M).

5.4 THz Fourier Transform measurements

THz broad band absorption measurements were carried out on YbCl$_3$ and its bromide analogue: YbBr$_3$. The broad band (50 - 350 cm$^{-1}$) THz ionic absorption spectra of both ytterbium halides at different concentrations were determined according to the analysis protocol as reported in Methods section (2.2.1). In YbCl$_3$, a broad resonance at 130 cm$^{-1}$ is present (see Figure 5.2). Surprisingly the, Cl$^-$ rattling resonance at 200 cm$^{-1}$ is not visible in this case. However, in YbBr$_3$, two resonances at 85 and 130 cm$^{-1}$ are visible; in addition to this, a strong partial negative absorption has been observed at 200 cm$^{-1}$. Such strong change at this frequency is very different compared to lanthanum bromide (see Figure (4.4)).
Figure 5.2: Presented here are the THz broad band effective ionic absorption spectra of YbCl$_3$ (left) and YbBr$_3$ (right) at different salt concentrations at 20 ± 0.2°C, obtained using THz Broad Band FTS.

5.5 THz effective extinctions

Figure 5.3: Plotted here are the THz effective molar extinction spectra of (A) YbCl$_3$ and (B) YbBr$_3$ at different salt concentrations, obtained using THz FTS at 20 ± 0.2°C. Both spectra emphasize the non-linear changes present in the extinction.
In order to check the presence of non-linear contributions in the absorption spectra, the effective extinctions (molar concentration normalized ionic absorption) for both ytterbium halides were calculated (see Figure 5.3). With increasing concentration, ytterbium chloride shows non-linear changes at 130 and 200 cm\(^{-1}\). Additionally, a general red shift of the mode at 130 cm\(^{-1}\) is visible with increasing electrolyte concentration. In case of YbBr\(_3\), the non-linear changes are centered at 80, 120-130 and 180 cm\(^{-1}\). With increasing concentration of YbBr\(_3\), a general narrowing of the ionic resonances, with a prominent change in the spectra around 200 cm\(^{-1}\) (see Figure 5.3) is observed. In both cases, significant non-linear changes with increasing salt concentration are present.

5.6 pH measurements and reasons of non-linearity

Both the lanthanide ions (La\(^{3+}\) and Yb\(^{3+}\)) have the same surface charge, but they show differences in their experimental THz spectra. In concentrated aqueous lanthanide halide solutions, the positively charge cations and negatively charged anions are present in substantial amount. With increasing electrolyte concentration, the amount of the bulk water in the ionic salt solutions gradually decreases. In addition to this, the trivalent cation induces a strong electrostatic force on the neighboring water molecules and counter anions. Nevertheless, to rule out any affects arising from the acidity, pH measurements of YbCl\(_3\) and YbBr\(_3\) were carried out. The measurement yields the pH 1.4 for 3.3 M concentration of YbCl\(_3\), which corresponds to the concentrations of hydronium ions less than 0.04 M. In case of YbBr\(_3\), 3.3 M concentration of salt shows a value of 1.2 pH, which equals to the hydronium ion concentrations of 0.07 M. In both cases, the salt (cation and anion) and the water concentrations are significantly large compared to these values. This strongly indicates that the ion-pair formation between Yb\(^{3+}\) and counter halide ions is the favorable mechanism, which produces non-linear changes in the THz narrowband absorption and THz FT spectra. In order to identify the underlying reasons of the spectral differences of both lanthanides, ion-association based hydration modeling (similar to lanthanum) was carried out on ytterbium halides. The exact methodology; as described in Chapter 3 was used to model the THz p-Ge and Fourier Transform spectra of YbCl\(_3\) and YbBr\(_3\).
5.7 Fitting of narrowband absorption data

The fitting according to the hydration modeling was performed first on the THz narrowband absorption spectra of YbCl₃. In Figure (5.4), the experimental data, the resulting fit for YbCl₃ and for comparison the LaCl₃ fit results are shown. It is clear from Figure (5.4) that, both data sets can be well represented by these non-linear hydration model fit routines. The fit gives an association constant ($K_{\text{pair}}$) = 0.013 ± 0.006 dm³/mol for YbCl₃. The fit yields as values of the effective extinction for the linear part $\varepsilon_{\text{single}}^{\text{eff}} = 42 \pm 1$ cm⁻¹ dm³/mol, and for the non-linear part $\varepsilon_{\text{diff}}^{\text{eff}} = 26 \pm 5$ cm⁻¹ dm³/mol.

![Graph showing absorption data and fits for YbCl₃ and LaCl₃](image)

**Figure 5.4:** The blue line shown here is a fit to the experimental data of YbCl₃ assuming ion pairing with an association constant of $K_{\text{pair}} = 0.013 \pm 0.006$ dm³/mol, $\varepsilon_{\text{single}}^{\text{eff}} = 42 \pm 1$ cm⁻¹ dm³/mol, and $\varepsilon_{\text{diff}}^{\text{eff}} = 26 \pm 5$ cm⁻¹ dm³/mol. For comparison, the black line plotted here is the resulting fit for LaCl₃ with an association constant $K_{\text{pair}} = 0.13 \pm 0.07$ dm³/mol, $\varepsilon_{\text{single}}^{\text{eff}} = 61 \pm 3$ cm⁻¹ dm³/mol, and $\varepsilon_{\text{diff}}^{\text{eff}} = 30 \pm 2$ cm⁻¹ dm³/mol.
5. Hydration of Aqueous Ytterbium Halides

5.8 Fitting of THz Fourier Transform data

The fit to THz narrow band absorption data gives a value of \( K_{\text{pair}} = 0.013 \pm 0.006 \text{ dm}^3/\text{mol} \) for YbCl\(_3\). This is less than value of \( K_{\text{pair}} = 0.13 \pm 0.07 \text{ dm}^3/\text{mol} \), which have been obtained for LaCl\(_3\) in the previous chapter. For cross confirmation of the value for YbCl\(_3\) and for obtaining the value of equilibrium constant for YbBr\(_3\), in further the corresponding THz broadband FT spectra were fitted according to this hydration modeling. Similar to the lanthanum, both these spectra were fitted using a two step approach. This fitting procedure yields a value of equilibrium constant \( K_{\text{pair}} = 0.015 \pm 0.002 \text{ dm}^3/\text{mol} \) for YbCl\(_3\). This matches well with the value of \( K_{\text{pair}} \) for YbCl\(_3\) obtained using the THz narrowband p-Ge laser spectroscopy. For YbBr\(_3\), the fit gives a value of \( K_{\text{pair}} = 0.015 \pm 0.001\text{dm}^3/\text{mol} \).

5.9 Ionic contributions

Since the different partial contributions of the THz effective extinction spectra are separated, the pure ionic part from the experimental spectrum can be determined. The resulting pure ionic spectrum (\( \varepsilon_{\text{single}}^{\text{eff}} \)) of YbCl\(_3\) and YbBr\(_3\) are shown as black lines in Figure 5.5 (A and B)). For comparison, the effective pure ionic spectra of both respective lanthanum halides (LaCl\(_3\) and LaBr\(_3\)) are also plotted in red color (see Figure 5.5 (A and B)). The pure ionic spectrum of YbCl\(_3\) shows a broad resonance between 100 to 200 cm\(^{-1}\). The positive resonances are attributed to the motions of cations and anions within their hydration water cage. In case of YbBr\(_3\), two positive peaks are visible at 80 and 130 cm\(^{-1}\). In addition to this, a strong partial negative extinction is visible around 190 cm\(^{-1}\) for YbBr\(_3\), which is significantly larger than LaBr\(_3\) (see Figure 5.5 panel B). This indicates that the effect of YbBr\(_3\) on water is larger than LaBr\(_3\).
5.10 Effective anion spectra

For determining the pure anionic resonances, the pure ionic extinction spectrum of YbBr₃ was subtracted from YbCl₃ according to: ε_{\text{single}}^{\text{eff}}(\text{YbCl}_3) - ε_{\text{single}}^{\text{eff}}(\text{YbBr}_3). The resulting spectrum is shown as grey thick line in Figure (5.6). In further, this spectrum was fitted by three modified Lorentzian line shapes and one hydration water component. The fit yields the center frequency of chloride rattling resonance at 197 cm⁻¹, while small bromide rattling mode is visible around 80 cm⁻¹. The small positive shoulder around 130 cm⁻¹ is attributed to the anion induced effect on the cation resonance. The fit yields a value of nₜ ~ 2.8, which expresses the difference in the number of hydration water molecules for YbCl₃ compared to YbBr₃. A detailed list of all the fit results is presented in Table (5.1).
5. Hydration of Aqueous Ytterbium Halides

**Figure 5.6:** The difference in effective pure ionic extinction of $\varepsilon_{\text{eff}}^{\text{single}}(\text{YbCl}_3) - \varepsilon_{\text{eff}}^{\text{single}}(\text{YbBr}_3)$ is shown here, which contains a strong positive contribution of the hydrated Cl$^-$ (green) centered at 197 cm$^{-1}$. The small feature present between 120 – 130 cm$^{-1}$ in the spectrum (brown) is an indication that the anion affects the cation (Yb$^{3+}$) peak. The negative part is composed of a) Br$^-$ rattling mode contribution (orange) at 74 cm$^{-1}$, and of b) the hydration water component (blue).

**Table 5.1:** Described here are the center frequencies ($\nu_m$), effective extinctions ($\varepsilon_m$) and line widths ($h_w$) of low frequency vibrational resonances of the anions in ytterbium chloride and bromide salts, obtained using the hydration model.

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>contributions</th>
<th>$\nu_m$ in cm$^{-1}$</th>
<th>$\varepsilon_m$ in dm$^3$/mol</th>
<th>$h_w$ in cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YbCl$_3$</td>
<td>Cl</td>
<td>196.9 ± 0.2</td>
<td>81.3 ± 0.8</td>
<td>52.0 ± 0.3</td>
</tr>
<tr>
<td>YbBr$_3$</td>
<td>Br</td>
<td>74.0 ± 1.6</td>
<td>7.8 ± 0.9</td>
<td>28.6 ± 3.1</td>
</tr>
</tbody>
</table>

5.11 Effective cation spectra

After determination of the anionic contributions, in further the pure cation (Yb$^{3+}$) spectra were obtained. These spectra were determined by subtracting the anionic contributions from the ionic part of the respective salt spectra in accordance with the scheme:
The calculated effective cation (Yb$^{3+}$) extinction spectra are shown in Figure (5.7). The effective cation (Yb$^{3+}$) spectra in case of YbCl$_3$ and YbBr$_3$ are shown as black and red lines, respectively. In order to fit these spectra, two modified Lorentzians and one negative hydration water component were used. For YbCl$_3$, the fit yields two resonances of solvated Yb$^{3+}$ at 140 and 389 cm$^{-1}$. In case of YbBr$_3$, two resonances at 141 and 386 cm$^{-1}$ are determined. A detailed list of the fit results is presented in Table (5.2). Within standard deviations, both low and high frequency components of cation modes have nearly the same line width, respectively, which is independent of the counter halide anions. The main deference in both spectra is attributed to the change in hydration number ($n_{\text{salt}}$). This is composed of the number of hydration water molecules that are influenced by one Yb$^{3+}$ ion and three counter halide ions. The fit yields a significant difference in $n_{\text{salt}}$ for both ytterbium halides. One mole of YbCl$_3$ salt influences about 21.9 mole of water molecules, while one mole of YbBr$_3$ affects approximately 19.6 mole water molecules. A comparison of $n_{\text{salt}}$ between ytterbium and lanthanum halide salts (YbX$_3$ and LaX$_3$; X = Cl$^-$, Br$^-$) suggests that in an average Yb$^{3+}$ effects more water molecules than La$^{3+}$.

**Figure 5.7**: Displayed here are the pure cation spectra of Yb$^{3+}$ (black for YbCl$_3$ and red for YbBr$_3$) obtained by subtracting the respective anion contributions from the single ion spectra. Within the individual components (comp.), the thick lines show the respective components for YbCl$_3$ and dashed line for YbBr$_3$ obtained according to the fit. In both cases, two resonances of the hydrated Yb$^{3+}$ ions are visible around 141 and 388 cm$^{-1}$. 
Table 5.2: Listed here are the center frequency, effective extinction and line width of the low frequency vibrational resonances of Yb\(^{3+}\) for ytterbium chloride and bromide salts determined by the THz hydration modeling. \(n_{\text{salt}}\) refers to the effective number of water molecules influenced per salt entity (YbX\(_3\); X: Cl, Br).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Contributions</th>
<th>(v_m) in cm(^{-1})</th>
<th>(\varepsilon_m) in dm(^3)/mol</th>
<th>(h_\omega) in cm(^{-1})</th>
<th>(n_{\text{salt}} = n_{\text{cation}} + 3n_{\text{anion}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>YbCl(_3)</td>
<td>Yb(^{3+})</td>
<td>140.2 ± 0.4</td>
<td>243.8 ± 2.7</td>
<td>45.2 ± 0.7</td>
<td>21.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>389.2 ± 3.1</td>
<td>664 ± 13</td>
<td>122.9 ± 2.4</td>
<td></td>
</tr>
<tr>
<td>YbBr(_3)</td>
<td>Yb(^{3+})</td>
<td>141.9 ± 0.3</td>
<td>247.8 ± 2.1</td>
<td>45.7 ± 0.5</td>
<td>19.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>386.1 ± 2.1</td>
<td>668 ± 9</td>
<td>122.4 ± 1.7</td>
<td></td>
</tr>
</tbody>
</table>

5.12 Ion-pair spectra

The total ion-pair spectra of YbCl\(^{2+}\) and YbBr\(^{2+}\) were obtained from the non-linear part of the hydration modeling, (for analysis details please refer to the Chapter 3). The resulting total ion-pair spectra for both ytterbium halides, according to these calculations are shown as orange thick lines in Figure (5.8 (A and B)). The solvated YbCl\(^{2+}\) spectrum was fitted by two positive modified Lorentzians at 127.9 and 217.2 cm\(^{-1}\) and with a negative hydration water component. However, in order to fit the hydrated YbBr\(^{2+}\) spectra three modified Lorentzian line shapes were used at 86.6, 139.5 and 199.1 cm\(^{-1}\) with an additional hydration water component. The numerical results of the fit are described in Table (5.3). The fit routine finds that each YbCl\(^{2+}\) affects \(n_{\text{diff}} = 2.7\) additional water molecules than the linear sum of ions \((n_{\text{cation}} + n_{\text{anion}})\). The ion-pair (YbBr\(^{2+}\)) shows even higher number about \(n_{\text{diff}} = 3.5\), which clearly indicates that in an average both ion-pairs influence more water molecules than pure ions.
5. Hydration of Aqueous Ytterbium Halides

Figure 5.8: Shown here are the ion pair spectra of aqueous YbCl\textsuperscript{2+} in panel (A) and YbBr\textsuperscript{2+} in panel (B) as the thick orange line in both cases. These spectra were fitted using the respective positive modified Lorentzians line shapes and negative THz hydration water component. The thin black lines for both salts represent the best fit to the ion-pair spectra.

Table 5.3: Described here are the center frequency, effective extinction and line width of the low frequency vibrational resonances attributed to ion pairs (YbCl\textsuperscript{2+})\textsubscript{(aq)} and (YbBr\textsuperscript{2+})\textsubscript{(aq)} determined using hydration model. These fits are graphically illustrated in Figure (5.8). The (*) denotes the empirical assignment of the individual resonances present within the ion-pair spectra.
5.13 General discussion and conclusions

In summary, the YbCl$_3$ and YbBr$_3$ aqueous salts were investigated using THz p-Ge laser absorption spectroscopy and THz FT spectroscopy. Implementation of THz hydration modeling, made it possible to deconvolute the experimental spectra into distinct ionic and ion-association contributions. A detailed analysis and discussion of the determined results is presented in the following section. For comparison, a combined list of the key results obtained for lanthanum halides and ytterbium halides are described in Table (5.4).

(1) Anion Spectra: The obtained results of the anion contributions are illustrated in Figure (5.6) and described in Table (5.1). In case of YbCl$_3$, the Cl$^-$ rattling resonance is present at 197 cm$^{-1}$. The Br$^-$ rattling mode is visible on 74 cm$^{-1}$ in case of YbBr$_3$. The calculated difference in number of THz hydration water molecules ($n_{YbCl_3} - n_{YbBr_3} = 2.8$) suggests that each chloride ion influences at least ~ 1 more water molecule than the bromide ion. This is in line with the proposed lower limit of the number of water molecules affected by one Cl$^-$ ion with counter La$^{3+}$ cation, in case of LaCl$_3$ salt in Chapter 4. The determined rattling resonance frequencies are in good agreement with the values reported by Funkner et al. [14] and Schmidt et al. [22]. In addition to this, the general blue shift of both anion resonances with Yb$^{3+}$ compared to La$^{3+}$ indicates that, the average confinement of the anion hydration structures is higher in the vicinity of the lanthanide cation, which has higher charge density.

(2) Yb$^{3+}$ Spectra: The details of the cation spectra are presented in Table (5.2) and shown in Figure (5.7). The extinction spectrum of pure Yb$^{3+}$ shows low and high frequency bands, which are nearly independent of the counter anions. The low frequency modes of Yb$^{3+}$ are observed at 141 cm$^{-1}$ with both counter anions. Both low frequency resonances can be assigned to the vibrational motion of cation within the dynamical hydration shell. The high frequency resonance of Yb$^{3+}$ is observed around 388 cm$^{-1}$, which is in good agreement with Raman measurements of lanthanide halides in glassy and aqueous state [79]. The Kanno et al. [79] have reported the solvated pulsation mode of Yb$^{3+}$ ions at 390 cm$^{-1}$.
Table 5.4: Listed here are the respective contributions, center frequencies ($\nu_m$) in cm$^{-1}$ and hydration water ($n_{\text{hydration}}$) due to distinct hydration species of both lanthanide halides determined from THz hydration modeling. $n_{\text{hydration}}$ refers to the equivalent number of THz hydration water molecules effected by the salt / ion-pair species. The (*) denotes the empirical assignment of the individual resonances present within the ion-pair spectra.

<table>
<thead>
<tr>
<th>species</th>
<th>contributions</th>
<th>$\nu_m$ in cm$^{-1}$</th>
<th>$n_{\text{hydration}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl$_3$</td>
<td>La$^{3+}$</td>
<td>126.3 ± 0.2</td>
<td>13.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$</td>
<td>361.9 ± 0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>188.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>LaBr$_3$</td>
<td>La$^{3+}$</td>
<td>127.0 ± 0.2</td>
<td>9.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>355.0 ± 0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>72.4 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>YbCl$_3$</td>
<td>Yb$^{3+}$</td>
<td>140.2 ± 0.4</td>
<td>21.9 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$</td>
<td>389.2 ± 3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>196.9 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>YbBr$_3$</td>
<td>Yb$^{3+}$</td>
<td>141.9 ± 0.3</td>
<td>19.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>386.1 ± 2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>74.0 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>species</td>
<td>contributions</td>
<td>$\nu_m$ in cm$^{-1}$</td>
<td>$n_{\text{hydration}}$</td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
<td>----------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>(LaCl$^{2+}$)$_{aq}$</td>
<td>$v_1$ (La$^{3+}$)*</td>
<td>118.1 ± 0.1</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$v_2$ (Cl$^- + $H$_2$O)*</td>
<td>212.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>(LaBr$^{2+}$)$_{aq}$</td>
<td>$v_1$ (Br$^-$)*</td>
<td>83.7 ± 0.4</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$v_2$ (La$^{3+}$)*</td>
<td>118.7 ± 0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_3$ (H$_2$O)*</td>
<td>186.5 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>(YbCl$^{2+}$)$_{aq}$</td>
<td>$v_1$ (Yb$^{3+}$)*</td>
<td>127.9 ± 0.1</td>
<td>2.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$v_2$ (Cl$^- + $H$_2$O)*</td>
<td>217.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>(YbBr$^{2+}$)$_{aq}$</td>
<td>$v_1$ (Br$^-$)*</td>
<td>86.6 ± 0.2</td>
<td>3.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>$v_2$ (Yb$^{3+}$)*</td>
<td>139.5 ± 0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v_3$ (H$_2$O)*</td>
<td>199.1 ± 0.8</td>
<td></td>
</tr>
</tbody>
</table>
Both low and high frequency THz modes are blue shifted for Yb$^{3+}$ compared to La$^{3+}$, irrespective of counter halide ions. The fit yields that on average YbCl$_3$ affects $n_{salt} \sim 22$ water molecules, while YbBr$_3$ shows a comparatively weaker hydration by affecting $n_{salt} \sim 19.5$. Both of these numbers are significantly larger compared to their lanthanum analogues because in Chapter 4, LaCl$_3$ was found to be affecting $n_{salt} \sim 13.5$ water molecules and LaBr$_3$, was influencing $n_{salt} \sim 9.8$ water molecules. The comparison in the relative anionic contributions suggests that in both cases the difference in the number of hydration water molecules is similar (about $\sim 3$), which means that the main contribution is induced by the cation hydration.

Similar to the lanthanum, on assuming that three Cl$^-$ affects approximately 3 to 6 water molecules, a value of $n_{cation} = 16$ to 19 is determined for Yb$^{3+}$ ion. Compared to La$^{3+}$ ion $n_{cation} = 7.5$ to 10, this number is large. Neutron scattering [46], EXAFS [86] and theoretical simulations [55, 85, 97] have reported that an average first coordination number of ytterbium ion contains about 8 to 9 water molecules. The number ($n_{cation}$) obtained by THz spectroscopy indicates that Yb$^{3+}$ probably affects water molecules beyond the first solvation shell.

One of the key features to consider in comparison of both the cations is their respective ionic charge density. Both Yb$^{3+}$ and La$^{3+}$ have the same trivalent change state, but the size of the ytterbium is smaller compared to lanthanum due to “lanthanide contraction” [38, 39, 96]. This should result in a strong difference in the binding strength between cation and surrounding water molecules. This can be estimated by the calculation of the effective force constants for both lanthanides within first solvation shell. On assuming that the charged cation moves in a three dimensional harmonic potential, where $\nu$ denotes the harmonic frequency and $\mu$ denotes the reduced mass, the force constant of the system can be expressed as: $k = (2\pi\nu)^2 \mu$. Here $\nu$ and $\mu$ denote the center frequency in Hz, and reduced mass of the hydrated structure, respectively. With the value of $\nu = 141$ cm$^{-1}$ and reduced mass $\mu = 79 \times 10^{-3}$ kg/mol for Yb$^{3+}$ with eight water coordination system, the calculated force constant is $k \approx 92$ N/m. In the previous chapter, similar calculation yielded the value of force constants $k \approx 70$ N/m for nona-water coordinated La$^{3+}$ system. This indicates that ytterbium exerts more force on the hydration water molecules than lanthanum.
This difference can be assigned to the possible reason for the blue shift of the cation resonances, because the low frequency mode for La$^{3+}$ has been observed at 126 cm$^{-1}$, while for Yb$^{3+}$ this mode is present at 141 cm$^{-1}$. This also indicates that the increased effective reduced mass of hydrated Yb$^{3+}$ system than La$^{3+}$ (because ytterbium is heavier than lanthanum) does not significantly drive the shift in the cation frequency. This estimation suggests that the average packing of the first solvation shell of Yb$^{3+}$ is higher compared to La$^{3+}$ in aqueous phase.

Due to higher charge state and larger size compared to the alkali and earth-alkali ions, generally lanthanide ions show stronger hydration effects in aqueous solutions. However, still not much scientific literature is available about the experimental probing of their second or higher solvation shell dynamics. In a theoretical perspective, Kowall et al. [85] and Floris et al. [55] have performed MD simulations to calculate the first and second solvation shell coordination number of Yb$^{3+}$ ion. Kowall et al. [85] have found about 15 – 19 water molecules in the second solvation shell of ytterbium. Floris et al. [55] have reported this number within the range of 11 – 15 by their theoretical calculations. One thing, which is rather simple to understand, is that the higher charge density of ytterbium ion compared to lanthanum affects a larger number of water molecules. However, from the current analysis, it is not so simple to distinguish between the hydration water molecules of cation and anion separately. Nevertheless, the comparison of two lanthanide ions suggests that both these ions show significant differences in their hydration dynamics and the influence on water by Yb$^{3+}$ is probably extended well beyond the first solvation shell.

(3) Ion-pairing: The hydration modeling allows to separate the pure ionic and ion-pair spectra. In the above section, the cation and anion spectra were discussed which clearly indicates that the hydration dynamics of the Yb$^{3+}$ is different compared to La$^{3+}$. In this section, the main focus is on the ion-pair spectra of ytterbium halides. The analysis gives the equilibrium constants $K_{\text{YbCl}_3} = 0.015$ dm$^3$/mol and $K_{\text{YbBr}_3} = 0.015$ dm$^3$/mol, while in the previous chapter, $K_{\text{LaCl}_3} = 0.138$ dm$^3$/mol for LaCl$_3$ and $K_{\text{LaBr}_3} = 0.014$ dm$^3$/mol for LaBr$_3$ were determined. With counter bromide anions, both cations (Yb$^{3+}$ and La$^{3+}$) show very similar ion-pairing tendency. However, with Cl$^-$ ions, lanthanum shows stronger ion-association than ytterbium.
The ion-pair spectra for both ytterbium halides are shown in Figure (5.8) and the fit results are described in Table (5.3). The pure ion-pair spectra of aqueous YbCl$^{2+}$ show two resonances at 127 and 217 cm$^{-1}$, while for YbBr$^{2+}$ three resonances are visible, which are empirically assigned to an anion peak at 87 cm$^{-1}$, Yb$^{3+}$ peak at 140 cm$^{-1}$ and ion-shared solvent water peak at 199 cm$^{-1}$. For YbCl$^{2+}$ the resonance at 127 cm$^{-1}$ is attributed to the cation contribution to the ion-pair, while the peak at 217 cm$^{-1}$ contains both chloride and ion-shared water contributions. In addition to that, the fit yields that an ion-pair of ytterbium halides, affects more water molecules than the linear sum of the water molecules affected by one cation and one anion ($n_{\text{diff}} = n_{\text{cation}} + n_{\text{anion}}$). The obtained value of $n_{\text{diff}} \sim 2.7$ is for YbCl$^{2+}$ and for YbBr$^{2+}$ the value of $n_{\text{diff}} \sim 3.5$ has been determined.

**Figure 5.9:** Schematic illustration of solvent shared ion-pairing of YbCl$^{2+}$ (left) and contact ion-pairing YbCl$^{2+}$ (right) in aqueous phase. Results presented in this chapter are in favor of solvent shared ion-pairing.

Both cases clearly indicate that instead of contact ion-pairing, Yb$^{3+}$ prefers solvent shared ion-pairing with counter halide ions in aqueous phase. A possible schematic illustration of both kinds of ion-pairing between Yb$^{3+}$ and Cl$^-$ ions is presented in Figure (5.9). The comparison in the value of $n_{\text{diff}}$ of ion-pairs, suggests that an ion-pair of ytterbium halide incorporates more water molecules than corresponding lanthanum halide (see Table (5.4)).
Millero et al. [92] have reported the logarithm of the stability constant 0.16 dm$^3$/mol for the ion-association between ytterbium and counter chloride ions. However, this value was obtained in co-solute added solvent media, which is different than the solvent media of the present case (neat water). Since, Yaita et al. [91] have concluded that the ion-pairing in lanthanide halides gets affected significantly by acidic co-solutes, the values of equilibrium constants determined in the present study are not directly comparable with other results. The differences between the value determined in the present study and the value reported by Millero et al. [92] are assigned to the; a) inclusion of the chloride activity and b) to the neglect of the formation of di-chloro or higher order chloride complexation with Yb$^{3+}$ ion. Although, it cannot be completely stated here that any amount of contact-ion pairing does not exist in concentrated ytterbium halide solutions, but the results obtained in this study strongly favors the formation of solvent shared ion-pairing in aqueous ytterbium halides.

In brief, in Chapter 4 and 5, two lanthanide cations (Yb$^{3+}$, La$^{3+}$) and halide anions (Cl$^-$, Br$^-$) in aqueous phase were investigated in terms of THz narrow band absorption and THz FT spectroscopy. A combination of the results for both cases suggests that the effect on the solvation dynamics of water molecules scales with increasing charge density of the cation (going from La$^{3+}$ to Yb$^{3+}$). This clearly indicates that, hydration effects induced by both these lanthanides, ranges from local to locally extended confinement of water molecules around ions. The THz hydration modeling applied on both cases indicates that, this combination of experimental and theoretical analysis has significant potential to provide important information about solvation dynamics of aqueous lanthanide ions. In order to completely explain the interplay between ions and water molecules, a cluster of techniques is required. However, from the present study this can be concluded that; systematic THz spectroscopic examination of a combination of two different lanthanide cations and anions in aqueous phase provides significant insight into their respective hydration dynamics.
Chapter 6

Hydration of Transition Metal Halides

This chapter presents the investigation of the hydration dynamics of two transition metal ions (Mn$^{2+}$ and Ni$^{2+}$) with counter halide ions (Cl$^-$ and Br$^-$) using THz spectroscopy. The combination of p-Ge laser absorption (75 - 90 cm$^{-1}$) and wideband THz Fourier Transform (50 - 350 cm$^{-1}$) spectroscopy was applied to study these salts in aqueous phase. Complementary theoretical analysis based on THz hydration modeling was used to model the experimental data. This analysis allows to determine the low frequency resonances of pure ions and to compare their hydration dynamics in detail. This kind of application of THz spectroscopy on transition metal halides (present Chapter) and on lanthanide halides (in Chapter 4 and 5) shows the effectiveness of the technique in probing the solvation dynamics of ions in aqueous phase.

6.1 Hydration of transition metal ions

Precise probing of ionic influences on solvation dynamics of water molecules has been facilitated by various experimental and theoretical methods over the years [8,13-15,18,19]. The significance of these ionic electrolytes in daily life ranges from activation of neural response in living organism by ion channeling [98] to use of aqueous electrolyte batteries [99]. It is well recognized that distinct cations (e.g. Li$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$, etc.), with counter anions (e.g. Cl$^-$, Br$^-$, SO$_4^{2-}$, NO$_3^-$, etc.) effect the average hydration dynamics of water molecules differently [13, 17-19, ]. It is also prominently reported that in aqueous phase a combination of some of these ions shows "negligible effects" [100] while in some cases ion-complexation [101] has been observed.

One of the basic factors which plays a significant role in determining the chemical and solvation properties of these ions is the dynamics of their hydration shells. Substantial amount of studies have been carried out to understand the different aspects of hydration for
alkali and alkali-earth halides [13-15, 18-20]. Most of these cases manifest that the electrostatic interactions of ions with water molecules govern the hydration mechanism. However, compare to these main group metals, the hydration of transition metal ions is not well understood so far [15, 17, 102, 103]. The complicacy holds due to some additional factors which influences their solvation properties, e.g. ligand field stabilization effects [35-36], higher mass and difference in ligand exchange kinetics compared to alkali and alkali-earth metal ions [15,17]. A schematic illustration of d-orbital structures of Ni$^{2+}$ and Mn$^{2+}$ is presented in Figure (6.1). Manganese ion with its $d^5$ orbital electronic structure offers two possible electron filling schemes; a) Low spin and b) High spin, while nickel ion with its $d^8$ shows only one possible configuration. Under ambient conditions, in dilute solution regime Mn$^{2+}$ ion prefers high spin electronic configuration. It has been previously reported that at same coordination state (i.e., octahedral), this phenomenon gives more stabilization to the hydration structure of transition metal ion, which is prominently defined as the ligand field stabilization affect [15, 35-36]. In addition to this, it has been also reported that, some d-transition metal ions show strong ion complexation with counter anions [29, 31] while for some cases this tendency have been observed to be very week [15, 32].

![Figure 6.1](image)

**Figure 6.1:** This is a schematic illustration of the splitting of d-orbitals based on the crystal field theory. Mn$^{2+}$ with ($d^5$) orbital electronic structure shows two possible (low spin and high spin) configurations. In comparison, for Ni$^{2+}$ with ($d^8$) orbital structure only one configuration is preferred.
6. Hydration of Transition Metal Halides

6.2 Motivation of the study

So far, the aqueous phase studies of transition metal ions have been reported using X-ray scattering [104], Neutron scattering [33], Raman spectroscopy [29, 31], dielectric spectroscopy [48], extended X-ray absorption fine structure (EXAFS) [105], and other methods. The theoretical modeling of these electrolyte systems using molecular dynamics (MD) simulations and ab initio quantum chemical calculations have facilitated the interpretation of hydration effects up to molecular level [34, 54].

Even in presence of these scientific examinations, still some key questions are unanswered. For example, in aqueous phase with increasing salt concentration, the complexation tendency between manganese ions with counter anions is still not well understood. In addition to this, the amount of water molecules influenced in vicinity of these ions and their effective role in governing the ion solvation dynamics is not entirely clear. On experimental side, when any aqueous electrolyte system shows ion-complexation, this clearly means that pure ionic contributions (cation and anion) are coupled with ion-complex spectral features. Very often these interactions result in various different geometrical hydration arrangements and coordination numbers, which are generally described as the presence of large equilibrium of solvated ions. All these components show variety of vibrational resonances which are originated from the motions of the ions, ion-complexes and surrounding water molecules. Thus prior to discussing distinct aspects of the ion hydration dynamics, it is essential to first distinguish the interaction of pure ions from the ion-complexes. However, this extraction is not so straight forward because often these spectral responses are composed of multi components, for example; a) cations, b) counter anions, c) hydration shell water and as well as d) ion complexes in specific cases. All these constraints clearly indicate that the isolation of pure ionic features from ion-complexes requires precise experimental probing and comprehensive theoretical modeling.

In the previous two chapters, lanthanide halides were examined using THz absorption spectroscopy. In this chapter, two transition metal ions (Mn\(^{2+}\) and Ni\(^{2+}\)) with counter chloride and bromide ions is aqueous solutions are investigated using THz p-Ge laser absorption and THz Fourier Transform spectroscopy. The experimental measurements are
complemented by a theoretical hydration modeling. This combination of experimental and theoretical methods allows to identify and separate the low energy vibrational resonances of pure ions from ion-complexes. Resulting from the analysis, the distinct key points of the hydration dynamics of these ions are discussed in detail within this chapter.

Both transition metal halide salts were purchased from commercial suppliers (Sigma Aldrich, and Alfa Aesar) with a purity of > 99 % for MnCl₂, NiCl₂, NiBr₂ and > 98 % for MnBr₂. The weighed amount of salt was dissolved in HPLC grade ultra pure water for each concentration within 0.5 to 4 M concentration range. In order to confirm the salt concentration, density measurements were carried out on an Anton Paar DMA 58 density meter at 20 ± 0.2°C. The amount of free water present in each salt concentration was determined by the density measurements.

6.3 THz (p-Ge laser) absorption measurements

Both transition metal halides (MnX₂ and NiX₂, X: Cl⁻ and Br⁻) were first investigated using THz p-Ge absorption spectroscopy. In order to emphasize the ionic contributions, the respective bulk water absorption was subtracted from each salt concentration. The resulting THz effective ionic absorption coefficients for both manganese and nickel halides within 75 – 90 cm⁻¹ frequency range are shown in Figure (6.2).

Figure 6.2: Plotted here are the experimental averaged ionic THz absorption spectra (75 - 93 cm⁻¹) of aqueous MnCl₂, MnBr₂, NiCl₂ and NiBr₂ with increasing salt concentration at a temperature of 20 ± 0.2°C.
All these ionic salts show higher absorption than the bulk water. In addition to this, within standard errors of the measurements MnCl$_2$, MnBr$_2$, NiCl$_2$ and NiBr$_2$ show a linear rise of absorption with increasing salt concentration. Up to 2 M salt concentration, the absorption of manganese halides is higher than the respective nickel halides: $\alpha$ (MnX$_2$) > $\alpha$ (NiX$_2$) at each concentration. After 2M concentration, NiBr$_2$ is not well soluble in water at 20 °C and MnBr$_2$ aqueous solutions were not measured after 2 M concentration due to presence of strong hydrolysis. The amount of hydrolysis was estimated by pH measurements. 0.5 M MnBr$_2$ shows the pH 2.7, while at 2 M a value of pH 1.3 was obtained. This means that at 2 M salt concentration, the concentration of hydronium ions is below 0.05 M. (However, 4 M concentration of MnB$_2$ shows a value of pH -0.34, which corresponds to $\sim$ 2 M concentration of hydronium ions.) In order to avoid any additional changes in the data due to acidic affects, only concentrations of MnBr$_2$ up to 2 M were measured and analyzed. Because of hydrolysis, the pH changed from pH 6.1 to pH 4.2 for the lowest and highest concentration of MnCl$_2$, respectively, which corresponds to hydronium ion concentrations of lower than 1 millimolar. Similarly, for NiCl$_2$ the pH ranges between pH 4.4 to pH 3.3 and for NiBr$_2$ this ranges from pH 6.5 to pH 5.3 for respective lowest and highest concentrations. In both cases, the concentration of hydronium ions remains lower than 0.6 millimolar and 0.006 millimolar for the highest concentrations, respectively.

### 6.4 THz Fourier Transform measurements

In further, THz broad band absorption measurements were carried out on aqueous MnCl$_2$, MnBr$_2$, NiCl$_2$ and NiBr$_2$ at different salt concentrations. The calculated effective ionic absorption spectra for all the salts are shown in Figure (6.3). MnCl$_2$ shows two well distinguishable low frequency resonances at 130 and 220 cm$^{-1}$. In case of MnBr$_2$, till 2 M concentration, two resonances at 80 and 140 cm$^{-1}$ are visible. For both salts, the absorption increases with increasing salt concentration. Main difference between both these spectra is that manganese chloride shows strong resonance around 200 cm$^{-1}$, while manganese bromide shows partial negative or zero absorption around this frequency. NiCl$_2$ shows two resonances at 170 and 200 cm$^{-1}$ and the total absorption of this salt is lower compared to its manganese analogue; MnCl$_2$, irrespective of the salt concentration.
6. Hydration of Transition Metal Halides

**Figure 6.3:** Shown here are the THz broad band effective ionic absorption spectra of MnCl$_2$ and MnBr$_2$ (upper panel) and of NiCl$_2$ and NiBr$_2$ (lower panel) at different salt concentrations determined using THz FT spectroscopy at 20 ± 0.2°C.

In NiBr$_2$ spectra, up to 2M concentration, two distinguishable resonances are visible on 90 and 170 cm$^{-1}$. In addition to this, for NiBr$_2$ around 200 cm$^{-1}$, absorption is partially negative or zero, which is similar to what has been observed for MnBr$_2$. The absorption of manganese bromide is higher than nickel bromide, irrespective of the electrolyte concentration. These results indicate that low frequency resonances of manganese halides and nickel halides show some differences and some similarities. In order to identify this, all these spectra were normalized by their respective molar concentrations and the resulting THz effective extinctions are presented in the next section.
6.5 THz effective extinctions

The normalization of THz ionic absorption with respective molar concentration gives the THz effective extinction spectrum, which gives the information about the linear and non-linear contributions present in the absorption spectrum.

![Graphs showing THz effective extinctions for MnCl₂, MnBr₂, NiCl₂, and NiBr₂](image)

Figure 6.4: Presented here are the THz effective extinction spectra of MnCl₂ and MnBr₂ (Panel A and B) and of NiCl₂ and NiBr₂ (Panel C and D) at different salt concentrations at 20 ± 0.2°C. Concentration dependent non-linear changes in THz extinction are clearly visible in the spectra of MnCl₂ and NiCl₂.

The calculated THz effective extinctions of MnCl₂, MnBr₂, NiCl₂ and NiBr₂ are shown in Figure (6.4). MnCl₂ shows a prominent non-linear increase of extinction with increasing
electrolyte concentration between 200 – 300 cm\(^{-1}\) frequency range. However, within standard errors of the measurements, MnBr\(_2\) does not show non-linearity up to 2 M concentration. In addition to this, manganese bromide shows a small partial negative or zero extinction around 200 cm\(^{-1}\). Similar trend is visible in case of nickel halides. NiCl\(_2\) shows non-linear rise in extinction at 220 cm\(^{-1}\) with increasing salt concentration, while NiBr\(_2\) does not show any such non-linearity up to 2M concentration. Additionally, NiBr\(_2\) also shows a partial (in comparison of bulk water) negative value of extinction, which is larger than the case of MnBr\(_2\).

This data evaluation indicates that MnCl\(_2\) and NiCl\(_2\) salts show non-linearity in the THz extinction with increasing electrolyte concentration, while for MnBr\(_2\) and NiBr\(_2\), the changes in extinction are rather linear. Prior applying any modeling to these data sets, it is essential to estimate the reasons behind these non-linear changes.

### 6.6 Non-linearity in MnCl\(_2\) and NiCl\(_2\)

MnBr\(_2\) and NiBr\(_2\) do not show any non-linearity in both THz p-Ge absorption and THz FT spectra. However, MnCl\(_2\) and NiCl\(_2\) show divergences from linearity in THz FT spectra. Some of the known facts about these salt systems are following: a) ‘2+’ charge state of the cation, b) ‘-1’ charge state of the anion, c) ligand field stabilizations effects, d) gradual increase in the number of solvated ions with increasing salt concentration and e) decrease in the bulk water concentration with increasing salt concentration. Two additional factors which can influence the ion induced hydration dynamics are discussed in the following:

1. Formation of the ion-complexes with increasing salt concentration. This point is very important in case of transition metal halides, because some of these cations show strong ion-association in aqueous phase, while in some cases ion-complexation tendency have been found to be rather moderate [15].

2. Hydrolysis can produce non-linear changes in the absorption. This affect can be estimated by the pH measurements. The measured pH values of the concentrations for salts (MnX\(_2\) and NiX\(_2\), X: Cl, Br) show that in present study, the acidic affects are very small and do not significantly disturbs the experimental data.
6.7 Ion-complexation

With increasing salt concentration, the amount of bulk water and the inter-ionic distance between cations and anions gradually decreases. This phenomenon increases the possibility that, after a certain limit, both ions (cation and anion) are associated or connected with each other. In comparison to this mechanism, the other affects are moderate because both species present in the aqueous phase (cations and anions) contain opposite charges. The possibility of homogeneous ionic aggregation can be ruled out because the surface charge of electrolytes is significantly higher to make heterogeneous aggregation. Due to all these reasons, in the next section the formation of ion-pairs or ion-complexes will be considered as the main reason producing the non-linear changes in the THz absorption spectra.

6.8 Fitting of the THz Fourier Transform data

The non-linearity is only visible in the THz FT extinction spectra of MnCl$_2$ and NiCl$_2$ around 200 cm$^{-1}$. For only fitting to these spectra, a non-linear model fit was performed. For full details of the modeling, please refer to the Chapter 3. The basic formalism is similar, to what have been used in case of the modeling of lanthanide salts. This fitting procedure gives an association constant of $K_{\text{pair}} = 0.28 \pm 0.09$ dm$^3$/mol for MnCl$_2$ and $K_{\text{pair}} = 0.1 \pm 0.8$ dm$^3$/mol for NiCl$_2$. This indicates that ion-complexation tendency of chloride ions is weaker with nickel compared to manganese ions.

6.9 Ionic spectra

The pure linear (ionic) part of the MnCl$_2$ and NiCl$_2$ spectra is shown in Figure (6.5, Panel A). It’s important to mention here that this model is not applicable for the case of MnBr$_2$ and NiBr$_2$, because within experimental standard errors, both these salts do not show any strong deviation from linearity in THz absorption data (THz p-Ge and THz FT...
spectroscopy) up to 2M concentration. This strongly indicates that within this concentration regime, negligible or very weak ion-pairing is present in these systems. Thus, for both metal bromides, the averaged extinction spectrum of the three concentrations was determined and assigned as pure ionic component.

Figure 6.5: Plotted here are the THz effective ionic extinction spectra Panel (A) of MnCl$_2$ (black) and NiCl$_2$ (red), and Panel (B) of MnBr$_2$ (black) and NiBr$_2$ (red).

The ionic spectra of MnBr$_2$ and NiBr$_2$ are plotted in the Panel B of Figure (6.5). Each spectrum is composed of the cation and anion extinctions according to the:

$$\varepsilon_{\text{ionic}}^{\text{eff}} = \varepsilon_{\text{cation}}^{\text{eff}} + 2\varepsilon_{\text{anion}}^{\text{eff}}$$  \hspace{1cm} (6.1)

MnCl$_2$ shows two resonances centered around 120 and 200 cm$^{-1}$. In case of NiCl$_2$, a broad resonance is visible between 140 - 220 cm$^{-1}$. The averaged ionic extinction spectra of MnBr$_2$ show coupled resonances ranging between 70 - 180 cm$^{-1}$, with a slightly partial negative value of extinction around 200 cm$^{-1}$. The averaged ionic extinction spectra of NiBr$_2$ show two distinct modes centered at 90 and 150 cm$^{-1}$, with a substantial partial negative extinction at 200 cm$^{-1}$.

Since within this study, the experimental THz p-Ge and FT absorption spectra of both metal chlorides and bromides are not accessible up to the same highest concentration (4M), and in low concentration range MnBr$_2$ and NiBr$_2$ do not show non-linear effects.
Thus, in order to avoid any inconsistency in the data analysis, the focus of this modeling is centered on the extraction of the low frequency resonances of the pure ions. Thus the non-linear part of the spectra will not be considered any further.

### 6.10 Low frequency spectra of Cl$^-$ and Br$^-$

In order to determine the pure anionic part from the ionic extinction spectra, the ionic components of both transition metal halides were subtracted according to: $(\varepsilon_{\text{eff single}}^{\text{single}} (\text{MCl}_2) - \varepsilon_{\text{eff single}}^{\text{single}} (\text{MBr}_2)); M = \text{Mn}^{2+}, \text{Ni}^{2+})$. The resulting spectra are shown as the thick gray line in Figure (6.6, Panel (A and B)). This subtraction gives a positive resonance due to Cl$^-$ and negative due to Br$^-$. For fitting these difference spectra by least number of components, two resonances with modified Lorentzian line shapes and one hydration water component were used. Hydration water corresponds to the number of affected water molecules in the vicinity of these ions. Experimental and fitted anionic spectra of both manganese and nickel halide salts are shown in Figure (6.6 (Panel A and B)). In both cases, the most prominent spectral component is the chloride rattling mode at 190 cm$^{-1}$.

**Figure 6.6:** The difference $(\varepsilon_{\text{eff single}}^{\text{single}} (\text{MCl}_2) - \varepsilon_{\text{eff single}}^{\text{single}} (\text{MBr}_2)); M = \text{Mn}^{2+}, \text{Ni}^{2+})$ shown here is composed of distinct ionic components (see Table (6.1)). In both cases, positive contribution (green) is attributed to the Cl$^-$ resonance. The negative mode (orange) is due to Br$^-$ resonance. The hydration water component is shown in blue color.
6. Hydration of Transition Metal Halides

Table 6.1: Described here are the center frequency, effective extinction and line width of the low frequency vibrational resonances of the anions in MnCl$_2$, MnBr$_2$, NiCl$_2$ and NiBr$_2$, obtained using THz hydration model.

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>contributions</th>
<th>$\nu_m$ in cm$^{-1}$</th>
<th>$\varepsilon_m$ in dm$^3$/mol</th>
<th>$h_w$ in cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$</td>
<td>Cl$^-$</td>
<td>188.2 ± 0.2</td>
<td>68.2 ± 0.3</td>
<td>44.5 ± 0.4</td>
</tr>
<tr>
<td>MnBr$_2$</td>
<td>Br$^-$</td>
<td>83.3 ± 1.2</td>
<td>7.3 ± 0.3</td>
<td>30.5 ± 2.6</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>Cl$^-$</td>
<td>184.7 ± 0.1</td>
<td>61.5 ± 0.2</td>
<td>42.1 ± 0.2</td>
</tr>
<tr>
<td>NiBr$_2$</td>
<td>Br$^-$</td>
<td>90.9 ± 0.6</td>
<td>9.8 ± 0.2</td>
<td>37.2 ± 0.1</td>
</tr>
</tbody>
</table>

The bromide is visible as a weak negative resonance at 80 cm$^{-1}$. The third component is assigned to the difference in hydration water of both salts. The fit yields about 3.2 mole additional water molecules per mole salt affected by MnCl$_2$ compared to MnBr$_2$. However, the NiCl$_2$ shows a decreased value of these water molecules about 2.2 compared to NiBr$_2$. In both cases this clearly suggests that in an average a Cl$^-$ ion influences more water molecules compared to a Br$^-$ ion.

6.11 Low frequency spectra of Mn$^{2+}$ and Ni$^{2+}$

Now for obtaining the pure cation spectrum, these anionic contributions were subtracted from their respective effective ionic spectra according to: $\varepsilon_{\text{single}}^\text{eff} (\text{MX}_2 - \text{X}_2)$, which yields the pure Mn$^{2+}$ and Ni$^{2+}$ extinction spectra. The resulting cation spectra for both manganese and nickel ions are plotted in Figure (6.7). For solvated Mn$^{2+}$ ions, two resonances are visible around 134 and 417 cm$^{-1}$, in case of manganese chloride and at 134 and 397 cm$^{-1}$ for manganese bromide. (see Table 6.2). For solvated Ni$^{2+}$ ions, two resonances are obtained, which are centered on 157 and 415 cm$^{-1}$ with counter Cl$^-$ ions and at 157 and 397 cm$^{-1}$ with Br$^-$ ions. Note: the high frequency components in both cases also contain the contributions from the slope of strong libration resonances. The frequency range probed by the present technique does not cover the full spectral range of the libration modes. Thus the center position of high frequency components shows larger uncertainty compared to the values obtained in 50 to 350 cm$^{-1}$ frequency range.
Figure 6.7: Plotted here are the (Panel A) pure Mn$^{2+}$ spectra as obtained from MnCl$_2$ (black) and MnBr$_2$ (red) by subtracting the respective anion contributions, and (Panel B) pure Ni$^{2+}$ spectra as obtained from NiCl$_2$ (black) and NiBr$_2$ (red) by subtracting the respective anion contributions. Within each spectra, the thick solid lines show the individual components for respective metal chlorides (MCl$_2$) and dashed lines for respective metal bromides (MBr$_2$). All the fit results are described in Table (6.2).

Table 6.2: Listed here are the center frequency, effective extinction and line width of the low frequency vibrational resonances of Mn$^{2+}$ for manganese halides and of Ni$^{2+}$ for nickel halides determined by the THz hydration modeling. \(n_{\text{salt}}\) refers to the effective number of water molecules influenced per salt entity (MX$_2$; M: Mn$^{2+}$, Ni$^{2+}$, X: Cl$^-$, Br$^-$).

<table>
<thead>
<tr>
<th>electrolyte</th>
<th>contributions</th>
<th>(\nu_m) in cm$^{-1}$</th>
<th>(\varepsilon_m) in cm$^{-1}$/mol</th>
<th>(h_w) in cm$^{-1}$</th>
<th>(n_{\text{salt}} = n_{\text{cation}} + 2n_{\text{anion}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$</td>
<td>Mn$^{2+}$</td>
<td>134.2 ± 0.3</td>
<td>121.1 ± 0.9</td>
<td>32.9 ± 0.5</td>
<td>8.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>418.8 ± 3.8</td>
<td>438 ± 12</td>
<td>115 ± 1</td>
<td></td>
</tr>
<tr>
<td>MnBr$_2$</td>
<td>Mn$^{2+}$</td>
<td>134.2 ± 0.2</td>
<td>123.4 ± 0.7</td>
<td>35.0 ± 0.4</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>396.1 ± 2.1</td>
<td>371.8 ± 5.6</td>
<td>114 ± 1</td>
<td></td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>Ni$^{2+}$</td>
<td>156.3 ± 0.6</td>
<td>83.6 ± 2.2</td>
<td>38.9 ± 1.3</td>
<td>10.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>415.2 ± 3.8</td>
<td>406.4 ± 8.5</td>
<td>137 ± 2</td>
<td></td>
</tr>
<tr>
<td>NiBr$_2$</td>
<td>Ni$^{2+}$</td>
<td>157.1 ± 0.5</td>
<td>88.3 ± 2.2</td>
<td>40.3 ± 1.2</td>
<td>8.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>406.9 ± 3.1</td>
<td>396.6 ± 6.7</td>
<td>138 ± 2</td>
<td></td>
</tr>
</tbody>
</table>
The substantial difference in both spectra is the change in offset, which is attributed to the difference in the number of water molecules influenced by the distinct ionic salts. The fit yields an estimate of $n_{\text{salt}} = 8.8$ and $5.8$ for MnCl$_2$ and MnBr$_2$, respectively. For NiCl$_2$ and NiBr$_2$ the obtained values are $n_{\text{salt}} = 10.0$ and $8.3$, respectively. Note, that these numbers express the decrease in THz absorption in terms of the equivalent of THz hydration water molecules induced by the one cation and two anions ($n_{\text{salt}} = n_{\text{cation}} + 2n_{\text{anion}}$).

### 6.12 General discussion and conclusions

By the application of THz narrowband absorption and THz Fourier Transform spectroscopy, the low frequency spectra of pure Mn$^{2+}$ and Ni$^{2+}$ cations and respective Cl$^-$ and Br$^-$ anions from experimental extinction spectra were determined. The hydration modeling made it possible to estimate the number of water molecules influenced in the vicinity of these ions. In the following, obtained results are discussed in detail:

**1) Cl$^-$ and Br$^-$ contributions:** The anionic spectra with both counter cations (Mn$^{2+}$ and Ni$^{2+}$) are shown in Figure (6.6). The free Cl$^-$ resonance is present at 188 cm$^{-1}$ with Mn$^{2+}$ and at a peak position of 186 cm$^{-1}$ with Ni$^{2+}$ counter cations (see Table 6.1). The rattling resonance of pure Br$^-$ ions is visible at 83 cm$^{-1}$ in case of MnBr$_2$ and at 91 cm$^{-1}$ in case of NiBr$_2$. This assignment is well within the frequency range reported previously in case of other mono and divalent halides [14, 22]. This suggests that with Mn$^{2+}$ and Ni$^{2+}$ as cations, the average force imposed on the anions by the surrounding water molecules is not significantly changed compared to the other cations. The red shift in the resonance of Br$^-$ compared to Cl$^-$ is attributed to the increase in the anion mass. Analysis yields that one Cl$^-$ ion influences about 1 to 2 additional water molecules compared to one Br$^-$ ion, which is consistent with the value determined in Chapter 4 and 5 with La$^{3+}$ and Yb$^{3+}$ counter cations, respectively. This gives a lower limit of the number of water molecules affected by a Cl$^-$ ion. This also indicates that Cl$^-$ ions are more strongly hydrated compared to Br$^-$ ions.

**2) Low frequency resonances of Mn$^{2+}$ and Ni$^{2+}$:** Mn$^{2+}$ ions show low frequency components at 134 cm$^{-1}$ with both counter Cl$^-$ and Br$^-$ ions. Similarly, the Ni$^{2+}$ display components centered around 157 cm$^{-1}$ for both halides. The details are presented in Figure
Within experimental errors, both low frequency components of Mn\(^{2+}\) and Ni\(^{2+}\) ions with respective Cl\(^-\) and Br\(^-\) ions show nearly the same line shapes and it suggests that these modes are more or less independent from the affects of the counter anions in the aqueous phase. For both ions, these resonances are assigned to a motion of the cation within water hydration cage, similar to that observed in MgCl\(_2\) [14]. However, this could be proposed that due to their higher mass, the mode center frequencies of both Mn\(^{2+}\) and Ni\(^{2+}\) show red shifts compared to Mg\(^{2+}\).

**High frequency resonances of Mn\(^{2+}\) and Ni\(^{2+}\):** For manganese, the high frequency component is present at 419 and 396 cm\(^{-1}\) for MnCl\(_2\) and MnBr\(_2\) salts, respectively. Similarly for Ni\(^{2+}\), the high frequency component is visible on 415 and 407 cm\(^{-1}\) for respective Cl\(^-\) and Br\(^-\) counter anions (see Figure (6.7)). The high frequency resonances of both metal ions show red shift of the center frequency for Br\(^-\) compared to Cl\(^-\). As mentioned earlier that, in this frequency range the contributions from the libration motions of water and hydrated ions are also present, thus exact assignment of these resonances contains larger uncertainty compared to the low frequency modes. Even though it is interesting to mention here that Kano et al. [106] have reported the M-OH\(_2\) (M = Mn\(^{2+}\) and Ni\(^{2+}\)) stretching Raman vibrational frequencies in liquid and glassy state of MnCl\(_2\) and NiCl\(_2\). In liquid state, for MnCl\(_2\) they observed resonance at 358 ± 5 cm\(^{-1}\) and for NiCl\(_2\) at 390 ± 3 cm\(^{-1}\) frequency.

A summary of \(n_{\text{salt}}\) of aqueous MnCl\(_2\), MnBr\(_2\), NiCl\(_2\), and NiBr\(_2\) is given in Table (6.2). MnCl\(_2\) affects ~ 9 water molecules, while MnBr\(_2\) shows a comparatively weaker hydration by affecting about 6 water molecules. Similarly NiCl\(_2\) and NiBr\(_2\) influence \(n_{\text{salt}}\) ~ 10 and 8 water molecules, respectively. General trend indicates that the metal chloride influences more number of water molecules than respective metal bromide. The analysis of the anion spectra yields that one Cl\(^-\) affects at least 1-2 more water molecules than one Br\(^-\). With an assumption that 2 to 4 water molecules affected by 2Cl\(^-\) ions, a number of \(n_{\text{cation}} = 5.5 - 7.5\) hydration water molecules for Mn\(^{2+}\) and \(n_{\text{cation}} = 6.0 - 8.0\) for Ni\(^{2+}\) can be estimated. These values are in general agreement with the results of various other experimental and theoretical methods, which gave the number of water molecules in the first solvation shell of Mn\(^{2+}\) ~ 4 - 6 and of Ni\(^{2+}\) ~ 5 - 7 with counter Cl\(^-\) anions in aqueous phase.[19, 48, 107]. On considering the similar analogy for MnBr\(_2\) and NiBr\(_2\) it can be proposed that, in average one Br\(^-\) ion influences about 0-1 water molecules.
It is a fragment of the ongoing discussion that up to which extent the ligand field stabilizations affects the hydration dynamics of transition metal ions in aqueous phase. In dilute solution regime, it has been previously reported that at divalent charge state the Mn\(^{2+}\) (\(d^5\)) hydrated ions have no additional ligand field stabilizations effects due to their half occupied d-orbital [35]. In contrast, Ni\(^{2+}\) with its (\(d^8\)) configuration shows strong ligand field stabilization effects [15, 36]. Aakesson et al. [35] have determined the hydration enthalpy (\(\Delta H_{\text{hydration}}\)), binding energy (\(\Delta E_{\text{binding}}\)) and solvation energy (\(\Delta E_{\text{solvation}}\)) of the divalent 3d-transition metal ions in gas and solution phases, as shown in Figure (6.8). Their results indicate that, in dilute solution regime, Mn\(^{2+}\) does not have any additional ligand field stabilization effects, while these effects are clearly present in case of Ni\(^{2+}\).

The present experimental and theoretical analysis determines the low frequency resonances of pure Mn\(^{2+}\) and Ni\(^{2+}\) ions at 134 and 157 cm\(^{-1}\), respectively, which are nearly independent from the anionic contributions. These modes can be assigned as the low frequency fingerprint modes of these ions. A blue shift is visible in the center frequency for Ni\(^{2+}\) resonance compared to Mn\(^{2+}\), which could possibly caused by two main factors; a) the change in the force constant between relative motion of ion and water molecules and b) the change in the average reduced mass of the ion–water system. For making an empirical comparison, it can be assumed that the cation make a motion within harmonic potential. The force constant (\(k\)) for this potential is given by \(k = (2\pi\nu)^2\mu\), with \(\nu\) being the harmonic frequency and \(\mu\) the reduced mass. As an estimate it can be considered that in dilute solutions, both Mn\(^{2+}\) and Ni\(^{2+}\) ions contain the 6 water molecules within their first hydration shell. With \(\nu = 134\) cm\(^{-1}\) and a reduced mass of \(36 \times 10^{-3}\) kg/mol for Mn\(^{2+}\) in a cage of six water molecules, this gives a value of \(k = 38\) N/m. Similarly, with \(\nu = 157\) cm\(^{-1}\) and a reduced mass of \(38 \times 10^{-3}\) kg/mol for Ni\(^{2+}\) in a cage of six water molecules, a value of \(k = 55\) N/m is obtained. This correlates with the blue shift in the low frequency resonance of Ni\(^{2+}\) compared to Mn\(^{2+}\), suggesting that average packing of the hydration cage of Ni\(^{2+}\) is higher than Mn\(^{2+}\). This also indicates that in above mentioned two affects, the change in the force constant is mainly driving the blue shift of the frequency. (Note: This analogy was not applied on the high frequency resonances of pure cations because these resonances contain larger uncertainty due to the presence of additional contributions from the slope of strong libration resonance).
6. Hydration of Transition Metal Halides

Figure 6.8: Shown in the figure are the hydration enthalpies ($\Delta H_{\text{hydration}}$) (upper curve), binding energy ($\Delta E_{\text{binding}}$) (middle curve) and solvation energy ($\Delta E_{\text{solvation}}$) (lower curve) of divalent 3-d metal ions, as reported by Akesson et al. [35]. All three curves show three minima respectively for d$^0$, d$^5$ and d$^{10}$ metal ions. In present case, Mn$^{2+}$ ion has d$^5$ configuration, while Ni$^{2+}$ has d$^8$ electronic configuration. For additional details please refer to the article. "Adapted with permission from Aakesson, R., Pettersson, L. G., Sandstroem, M., & Wahlgren, U. (1994). Ligand field effects in the hydrated divalent and trivalent metal ions of the first and second transition periods, *Journal of the American Chemical Society*, 116(19), 8691-8704. Copyright (1994) American Chemical Society."

(4) **Ion-pairing:** The present data analysis suggests that Mn$^{2+}$ shows stronger ion-complexation tendency compared to Ni$^{2+}$ with counter chloride ions. THz hydration model based fit determines an association constant of $k = 0.28$ dm$^3$/mol for MnCl$_2$ and $k = 0.1$
These results are not comparable directly with other reported literature values, because most of those measurements were carried out in presence of perchloric acid and sodium perchloride, and in some cases higher order ion-complexation was also assumed during the calculations. Libus et al. [108] have reported the value of equilibrium constant between 0.14 - 0.50 dm$^3$/mol for MnCl$_2$. Halloff et al. [109] have reported lower value of equilibrium constant within the range -0.015 to + 0.015 for NiCl$_2$ salts. In comparison, Morris et al. [110] have reported a higher value of equilibrium constant 1.7 for nickel chloride. In general, values reported in the present studies are in agreement with the previous literature data. However, the deviations can be assigned to the differences in the technique and timescales of measurements in which these constants have been determined.

On summarizing the results of this study; four transition metal halide salts (MnCl$_2$, MnBr$_2$, NiCl$_2$ and NiBr$_2$) in aqueous state were investigated using THz absorption spectroscopy and THz Fourier Transform spectroscopy. By the application of a THz hydration modeling, low frequency modes of pure Mn$^{2+}$, Ni$^{2+}$, Cl$^-$ and Br$^-$ ions were determined.

In Section (6.10) the low frequency resonances of Cl$^-$ and Br$^-$ ions are presented. Analysis founds that chloride mode is visible at 186 cm$^{-1}$, while the Br$^-$ resonance is present at 87 cm$^{-1}$. Both these values are in good agreement with the results obtained in Chapter 4 and 5 in case of lanthanide halides. By the comparison of manganese with nickel, it can be estimated that a chloride ion influences about one more water molecule than one bromide ion.

In section (6.11), spectral features of pure Mn$^{2+}$ and Ni$^{2+}$ ions were determined. Mn$^{2+}$ shows two low frequencies modes, one at 134 ± 1 cm$^{-1}$ and other broad high frequency mode around 405 ± 15 cm$^{-1}$. Similarly, for Ni$^{2+}$, respective low and high frequency resonances were obtained at 157 ± 1 and 410 ± 5 cm$^{-1}$. These resonances were assigned to the solvation cage vibrational motion and hydration shell breathing vibration of the cation, respectively. The fitting of the pure cation spectra gives an estimate of the number of water molecules affected by one manganese ion between $n_{cation} = 5.5 - 7.5$ and one nickel ion between $n_{cation} = 6.0 - 8.0$. This indicates that Ni$^{2+}$ is slightly more hydrated than Mn$^{2+}$. This hydration study of aqueous manganese and nickel halide salts suggests that compared to Mn$^{2+}$ ions, the average hydration structure of Ni$^{2+}$ is more stabilized, while the ion-association seems to be weaker in NiCl$_2$ solutions compared to MnCl$_2$. 
7. Hydration of Aqueous Zinc Halides

Chapter 7

Hydration of Aqueous Zinc Halides

In this chapter, THz p-Ge absorption and THz FT spectroscopy were applied on ZnCl$_2$ and ZnBr$_2$ aqueous solutions. In addition to this, complementary Raman measurements were carried out to compare low frequency resonances with broadband THz spectra. On theoretical side, Polarizable Continuum Model based calculations were performed to determine, THz and low frequency Raman modes. This combined analysis allows to investigate the exact nature of ion-complexation between Zn$^{2+}$ and halide (Cl$^-$ and Br$^-$) ions. This methodology clearly indicates that THz spectroscopy have significant potential to investigate hydration dynamics of complex systems like zinc halides. Additionally, this analysis also highlights the open perspectives accompanied in the study of hydration dynamics of zinc halides in aqueous phase.

7.1 Introduction

A comprehensive knowledge about the nature of interaction between ions and water molecules is essential for understanding the various aspects of ion hydration in aqueous phase [8, 15, 17, 19, 111]. The mechanisms involved in maintaining the average solvation structure around ions in aqueous phase, have been reported over the years using various experimental techniques [13-14, 18-20]. The main group metal ions (alkali and earth-alkali) probed by THz absorption spectroscopy have clearly shown that in low concentration regime (C < 2M), the absorption contributions of the cations and anions are well separable and can be expressed in terms of the linear superposition of them [14, 22]. However, in some cases this analogy doesn’t hold because over the full periodic table, distinct ions show very different hydration dynamics [15, 17, 20, 29]. For example alkali and earth-alkali metal ions generally show electrostatic interaction with water molecules [8, 19, 22]. Another class in these ionic metals is the one, which contains half or fully filled d-orbital shells, popularly known as the “d-transition metals”. These d-metal ions show strong versatility in their chemical and physical properties; it has been found that in aqueous phase
each individual ion shows a distinct hydration behavior ranging from self confinement of ions to ion-complexation [13, 29, 37]. The probing of their solvation dynamics is a challenging task because with electrostatic interaction they also contain additional stabilization of their hydration structure due to ligand field effects (i.e., Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Cu$^{2+}$) [35, 36]. The hydration dynamics of Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ ions have been reported even further complicated due to their strong complexation tendency with counter anions in aqueous phase [29, 31, 54, 112, 113].

### 7.2 Motivation of the Study

Some of the transition metal (Tm) ions show ion-complexation with counter halide ions [29, 112]; while in some cases weak or negligible ion-association has been observed [32]. The cations which show prominent complexation with counter Cl$^-$ and Br$^-$ anions are In$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ [30, 31, 50, 54]. In addition to this, with increasing salt concentration, these ions form higher order aqueous ion-complex aggregates such as: TmCl$^+$, TmCl$_2^0$, TmCl$_3^-$, TmCl$_4^{2-}$. Zinc halides are considered as the pioneer examples to observe this formalism. It has been previously reported that with increasing salt concentration, the number of anions within the first coordination shell of Zn$^{2+}$ gradually increases [29-31, 54, 112, 113]. The electrochemical measurement have determined a negative cation transport number for ZnCl$_2$ and ZnBr$_2$ aqueous solutions for the concentrations higher than 3 molal [51, 114]. The negative cation transport number means that cation is present on the anode, which is not very usual. In contrast to this, NiCl$_2$ shows a positive cation transport number within this concentration range [115]. The only way in which a divalent cation can be found on the anode is the formation of ZnX$_3^-$ and ZnX$_4^{2-}$ and even higher order ion-complexes.

Weingärtner et al. [50] have reported “unusual behavior of transport coefficients” of zinc chloride compared to the other 4th period transition metal chlorides, which was assigned to the formation of ion-complexes with increasing salt concentrations. Irish et al. [29] have performed Raman measurements on zinc chloride aqueous solutions and found the presence of Zn$^{2+}$ - Cl$^-$ complexes in aqueous phase. Yellin et al. [31] have investigated aqueous ZnBr$_2$ salts using Raman scattering technique and found the existence of strong ion-complexation. Kaatze et al. [112] have investigated ZnCl$_2$ aqueous solutions using
Dielectric spectroscopy and found the presence of $\text{Zn}^{2+} - \text{Cl}^-$ chemical structure. Neutron scattering [113] and EXAFS measurements [30] have further affirmed these conclusions. On a theoretical perspective, Fatmi et al. [34] have investigated structure and dynamics of pure Zn(II) ions in aqueous solution using extended ab initio QM/MM molecular dynamics (MD) simulations. Their calculations have found 6 and 14 water molecules coordinated in the first and second hydration shell of pure zinc ion, respectively. Another theoretical study based on polarizable continuum model (PCM) calculations by Oswald et al. [54] have predicted the presence of $\text{Zn(H}_2\text{O)}_6^{2+}$, $\text{ZnCl}_2$($\text{H}_2\text{O})_2$, $\text{ZnCl}_3$($\text{H}_2\text{O})$-, and $\text{ZnCl}_4^{2-}$ species in the aqueous solution of zinc chloride.

This literature survey clearly indicates the presence of strong ion-complexation between zinc and counter halide ions in aqueous phase. However, in spite of these efforts, there are some basic points which are still unanswered, particularly for aqueous zinc chlorides. For example, the exact mechanism involved in binding of the chloride ions to $\text{Zn}^{2+}$ in aqueous solutions is still not well understood. The precise assignment of distinct $\text{Zn}^{2+}$--$\text{X}_n^-$ ($\text{X} = \text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$; $n = 1$, 2, 3, 4) complexation species as a function of salt concentration and the nature of their collective hydration dynamics is still an open question.

In this chapter, revision of such open questions in terms of a combined experimental and theoretical approach is presented. THz p-Ge laser absorption spectroscopy, wide band THz Fourier Transform (THz FT) spectroscopy, and low wavenumber Raman spectroscopy were employed to probe the hydration mechanism of aqueous zinc halides. Complementary to this, density functional theory (DFT) calculations were carried out to compute normal modes and THz and Raman intensities for comparison and assignment of the experimental data. $\text{Zn}^{2+}$ ion in the form of aqueous solutions of corresponding halide salts ($\text{ZnCl}_2$ and $\text{ZnBr}_2$) was investigated over a range of molar concentrations (0.5 – 4 M), and the absorption patterns and trends along zinc halides were analyzed in terms of THz spectroscopy. The zinc chloride and bromide salts were purchased from Sigma Aldrich, and Alfa Aesar, respectively. The molar concentration series was prepared by dissolving the weighed out amount of ionic salt in the calculated volume of de-ionized HPLC grade ultra pure water. The densities of all concentrations were measured on Anton Paar, DMA 58 density meter. Each sample density was measured at 20 ± 0.2°C temperature with a simultaneous pre calibration of neat water.
7.3 THz p-Ge laser absorption measurements

First, the average THz absorption coefficients of ZnCl$_2$ and ZnBr$_2$ (between 2.3 to 2.8 THz) were determined by THz p-Ge laser spectroscopy. The effective ionic absorptions with increasing molar concentrations of ionic salt are shown in Figure (7.1). Within 0.5 to 4 M concentration range, ZnBr$_2$ shows a linear increase in absorption with increasing electrolyte concentration. However, ZnCl$_2$ shows a non-linearity in absorption after 1.5 M concentration. This non-linear increase has slight convex curvature towards abscissa and the point of inflexion is present between 1 to 2 M concentrations.

![Figure 7.1](image-url)

**Figure 7.1:** Shown here are the experimental averaged THz narrowband (2.3 – 2.8 THz) effective ionic absorption spectra with increasing molar concentrations of ZnCl$_2$ (black) and ZnBr$_2$ (red), determined at 20 ± 0.2°C. The ZnCl$_2$ (black) clearly shows nonlinear change in absorption after 1.5 M concentration.

The effective ionic absorption coefficient $\alpha$ (ZnBr$_2$) is higher than $\alpha$ (ZnCl$_2$), irrespective of the salt concentration. This difference in THz absorption patterns of ZnCl$_2$ and ZnBr$_2$ indicates that average hydration dynamics of both these electrolytes is substantially different.
7.4 THz Fourier Transform measurements

In order to understand the behavior of absorption coefficients over a wide frequency range, the THz Fourier Transform spectroscopy was carried out on both zinc halides. This technique allows observing the vibrational resonances originating from the cations, anions and any ion induced hydration affects over 50 to 350 cm\(^{-1}\) frequency range. Figure 7.2 (A and B) shows the THz FT effective ionic absorption spectra of ZnCl\(_2\) and ZnBr\(_2\) at different salt concentrations. In case of ZnCl\(_2\), two modes are visible at 130 and 300 cm\(^{-1}\). ZnBr\(_2\) shows three resonances centered at 80, 130 and 230 cm\(^{-1}\). For the lowest concentration of ZnCl\(_2\), the mode around 300 cm\(^{-1}\) seems to be very weak. Similarly, the resonance at 230 cm\(^{-1}\) for ZnBr\(_2\) is nearly invisible at 0.5 M concentration. In addition to this, ZnBr\(_2\) shows a slightly partial negative ionic absorption at 200 cm\(^{-1}\).

**Figure 7.2:** Shown here are the THz FT effective ionic absorption spectra (50 – 350 cm\(^{-1}\)) at different salt concentrations of ZnCl\(_2\) (panel A) and ZnBr\(_2\) (panel B), obtained at 20 ± 0.2°C. In case of ZnCl\(_2\), two modes are visible at 130 and 300 cm\(^{-1}\). ZnBr\(_2\) shows three resonances centered at 80, 130 and 230 cm\(^{-1}\).
7.5 THz effective extinctions

For emphasizing the linear and non-linear contributions, in further the THz effective extinctions were determined for both cases (Please refer methods section of Chapter 2 for calculation details). THz effective extinction spectra of ZnCl$_2$ and ZnBr$_2$ are presented in Figure (7.3, Panel A and B). For a standard (cation + anion) electrolyte system, all of the extinction spectra should coincide over the same line shape. However for a general system, non-linear contributions are present in extinction with changing molar concentrations. From Figure (7.3), it is clear that both ZnCl$_2$ and ZnBr$_2$ show significant non-linear changes. For ZnCl$_2$ these are centered mainly around 300 cm$^{-1}$, while for ZnBr$_2$ these are present at 130 and 230 cm$^{-1}$. Within experimental errors, ZnCl$_2$ shows a linearly increasing resonance around 130 cm$^{-1}$, which slightly red shifts as the salt concentration increases. In ZnBr$_2$ a linearly increasing shoulder at 90 cm$^{-1}$ is visible. In addition to this for the lower concentrations of ZnBr$_2$, a substantial partial negative extinction at 200 cm$^{-1}$ is observed. Prior applying and discussing any theoretical modeling it is important to mention here that at ‘2+’ charge state the outermost d-orbital of Zn$^{2+}$ is fully filled and thus in dilute solution regime they do not have any additional ligand field stabilization effects [35, 36].

Figure 7.3: Presented here are the THz effective extinction spectra of ZnCl$_2$ (left) and ZnBr$_2$ (right) over 50 – 350 cm$^{-1}$ frequency range, obtained at 20 ± 0.2°C. Both spectra clearly show the presence of non-linear contributions with increasing salt concentration.
7.6 Raman spectroscopy

In order to comprehensively investigate and assign the low wavenumber vibrational resonances, Raman spectroscopic experiments using a WITec alpha 300 RAS microscope (Ulm, Germany) were carried out. (Please consult methods section for experimental details). These measurements were carried out together with coworker Mr. Eugen Edengeiser. For comparison, the Raman spectra of NiCl$_2$ and NiBr$_2$ were also measured. Till 2 molar concentration, both nickel bromide and chloride show Raman resonances around 400 cm$^{-1}$ (see Figure 7.4 (A and B), shown by vertical arrow), which have been previously reported as Ni$^{2+}$ pulsation mode in surrounding water cage [32]. The spectra of ZnBr$_2$ show two resonances one around 390 cm$^{-1}$ and another at 180 cm$^{-1}$, while ZnCl$_2$ contains two distinguishable resonances one at 390 cm$^{-1}$ and another at 290 cm$^{-1}$ (see Figure 7.4 (C and D)). An empirical comparison of the Raman resonances in all the cases indicates that the vibrational mode between 390 - 400 cm$^{-1}$ is rather weakly / ill dependent on the counter anions.

**Figure 7.4:** Plotted here are the low wavenumber Raman spectra of (A) NiBr$_2$ and (B) NiCl$_2$. The arrow shows the hydrated nickel resonance around 400 cm$^{-1}$ up to 2M concentration. Raman spectra of (C) ZnBr$_2$ and (D) ZnCl$_2$ both show hydrated zinc resonance at 390 cm$^{-1}$, while additional Zn$^{2+}$ --- anion complexation peaks are well visible even at 2M concentration at 180 cm$^{-1}$ and 290 cm$^{-1}$ for zinc bromide and zinc chloride, respectively.
However, the mode at 290 cm\(^{-1}\) in ZnCl\(_2\) and 180 cm\(^{-1}\) in ZnBr\(_2\) seems to be having influences from Cl\(^-\) and Br\(^-\) ions, respectively. A combination of all three findings suggests that Zn\(^{2+}\) and counter halide ions show strong possibility of complexation in concentration range measured here.

### 7.7 Polarizable Continuum Modeling (PCM)*

In order to understand the theoretical origin of these low frequency resonances, a Polarization Continuum Model based calculations of the resonance frequencies and corresponding intensities were carried out.* All these PCM and free energy calculations were performed by the collaborators Dr. R. Schmid, Dr. T.K. Roy and Dr. S. Bureekaew from the Department of Inorganic Chemistry II, Ruhr University Bochum. In aqueous phase, the strong complexation between Zn\(^{2+}\) and counter Cl\(^-\) and Br\(^-\) ions have been observed previously by different experimental techniques [29, 31, 50, 54]. The possible ion-complexation schemes reported there are:

(7.7 A) \[ \text{Zn(aq)}^{2+} \rightleftharpoons \text{ZnCl(aq)}^+ \rightleftharpoons \text{ZnCl}_2(aq)^0 \rightleftharpoons \text{ZnCl}_3(aq)^- \rightleftharpoons \text{ZnCl}_4^{2-}. \]

(7.7 B) \[ \text{Zn(aq)}^{2+} \rightleftharpoons \text{ZnBr(aq)}^+ \rightleftharpoons \text{ZnBr}_2(aq)^0 \rightleftharpoons \text{ZnBr}_3(aq)^- \rightleftharpoons \text{ZnBr}_4^{2-}. \]

The present modeling routine assumes that at the lowest concentration, the pure Zn\(^{2+}\) is coordinated by six (octahedral coordination) water molecules. This is consistent with the results obtained by other experimental and theoretical methods [34, 54, 113]. One of the key points of this scheme is the gradual replacement of the coordination water molecules around cation by the anions with increasing salt concentration. In order to observe this gradual change in the number of hydration water molecules, calculation of free energy of formation for the chemical equilibrium of above mentioned each chemical species were carried out. The tables of these calculations for Zn\(^{2+}\) with both counters anions (Cl\(^-\) and Br\(^-\)) are presented in the following section (7.7.1).

*All PCM and free energy calculations were carried out by the collaborators Dr. R. Schmid, Dr. T.K. Roy and Dr. S. Bureekaew from the Department of Inorganic Chemistry II, Ruhr University Bochum. I very strongly acknowledge them for their scientific support and contributions. This section is included here due to the requirement of these calculations in the further analysis and discussion parts of this chapter.
7. Hydration of Aqueous Zinc Halides

In principle, large numbers of ion-complex species with difference geometric arrangements are possible for this kind of strong ionic association. These calculations allow estimating that which complexes species and structures are favored over the others. For the same ion-complexation pathway, the mechanism which shows more negative value of (ΔG) Gibbs free energy or free energy of formation determines the preferred ion-complex species.

7.7.1 Free energy estimates

Table 7.1: Described here are the free energy estimates of the Zn²⁺ - halide complex formation chemical species. Section (A) shows the calculated (ΔG in kcal/mol) for the substitution of Zn²⁺ coordinated water molecules by chloride ions and Section (B) shows the calculated (ΔG in Kcal/mol) for the substitution of Zn²⁺ coordinated water molecules by bromide ions. In both cases, the octahedral to tetrahedral coordination change of solvated Zn²⁺ is preferred according to the step (2b).

(A) Substitution of water molecules by chloride ions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG in kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Zn(H₂O)₆⁺² + Cl⁻ = ZnCl(H₂O)₅⁺ + H₂O,</td>
<td>-14.29</td>
</tr>
<tr>
<td>(2a) ZnCl(H₂O)₅⁺ + Cl⁻ = ZnCl₂(H₂O)₄ + H₂O,</td>
<td>-13.32</td>
</tr>
<tr>
<td>(2b) ZnCl(H₂O)₅⁺ + Cl⁻ = ZnCl₂(H₂O)₂ + (H₂O)₃,</td>
<td>-21.80</td>
</tr>
<tr>
<td>(3) ZnCl₂(H₂O)₂ + Cl⁻ = ZnCl₃(H₂O)⁻ + H₂O,</td>
<td>-10.87</td>
</tr>
<tr>
<td>(4) ZnCl₃(H₂O)⁻ + Cl⁻ = ZnCl₄²⁻ + H₂O,</td>
<td>-5.94</td>
</tr>
</tbody>
</table>

(B) Substitution of water molecules by bromide ions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG in kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Zn(H₂O)₆⁺² + Br⁻ = ZnBr(H₂O)₅⁺ + H₂O,</td>
<td>-9.63</td>
</tr>
<tr>
<td>(2a) ZnBr(H₂O)₅⁺ + Br⁻ = ZnBr₂(H₂O)₄ + H₂O,</td>
<td>-4.66</td>
</tr>
<tr>
<td>(2b) ZnBr(H₂O)₅⁺ + Br⁻ = ZnBr₂(H₂O)₂ + (H₂O)₃,</td>
<td>-24.23</td>
</tr>
<tr>
<td>(3) ZnBr₂(H₂O)₂ + Br⁻ = ZnBr₃(H₂O)⁻ + H₂O,</td>
<td>-6.90</td>
</tr>
<tr>
<td>(4) ZnBr₃(H₂O)⁻ + Br⁻ = ZnBr₄²⁻ + H₂O,</td>
<td>-3.61</td>
</tr>
</tbody>
</table>
From the above schemes (A and B), it is clear that within paths (2a) and (2b), the (2b) produces more energetically stabilized structure, which indicates that the population of this structure can be estimated rather high compared to the other structure in aqueous phase. However, any existence of the intermediate ion-complex structures cannot be excluded, but in order to minimize the complicacy of the analysis, only these structures will be considered for calculations in further. This also indicates that the change from octahedral to tetrahedral coordination takes place with the inclusion of three or higher X$^-$ ions in the first solvation shell of Zn$^{2+}$. (Note: The presences of other intermediate ion-complex species are also possible, but these calculations suggest the free energy of formation favors the generation of these particular species).

For determination of the chemical geometries, all these structures were fully relaxed using density functional theory (DFT) using the B3LYP hybrid functional [116, 117] with the cc-pVTZ basis sets for all atoms [118]. The further solvation of these systems was described by the PCM implicit solvent model [119]. For all the structures, a normal mode analysis was carried out by an analytic calculation of second derivatives. All calculations were performed with the Gaussian 09 program package [120]. (Note: most these structures show several local minimum geometries, which are due to the rotation of the water molecules in the first solvation shell). In order to obtain absolute global minimum, in principle a Boltzmann-averaged sum of all possible minima would be required. However, in this study further analysis was carried out on the calculated structures.)

In analogy similar to the experimental technique to remove the bulk water absorption, all normal modes related to the changes in the internal water geometry were excluded. For the further analysis, only the low frequencies modes of the solvation cage (water and/or anion motions relative to the metal ion) were extracted. Using this model routine the normal mode center frequencies and THz/Raman intensities were calculated. Due to the model simplifications, anharmonic effects are present in the calculations of vibrational frequencies. These anharmonic effects cause a certain shift of the resonance peak positions with respect to the experimental data. However, this was calibrated by scaling all the computed THz (Far IR) and Raman frequencies by a fixed factor of 1.19, in order to obtain the proper position of the high frequency Zn$^{2+}$--An$^-$ complexation peak obtained from THz FT measurements (see Figure 7.3).
In the following section, Table 7.1, 7.2, 7.3 and 7.4 show the calculated THz ZnCl$_2$, THz ZnBr$_2$, Raman ZnCl$_2$ and Raman ZnBr$_2$ frequencies and their corresponding intensities, respectively for hydrated zinc and zinc-anion complex species. Column one specifies the structure of the chemical species, column two shows corresponding scaled frequencies by a fix factor of 1.19 to assign the complexation peak position in zinc chloride and zinc bromide THz FT spectra. Column three shows the calculated THz and Raman intensities originated from the specific vibrations of the corresponding chemical species. Column four defines the specific nomenclature of the particular vibrations due to presence of coupled vibrational resonances of zinc and surrounding H$_2$O molecules and halide ions. In MX, M denotes mode, X= 1……N, (N$_{max}$= 34) shows number of the particular mode, ‘R’ means rocking, ‘W’ means wagging, ‘T’ means twisting, ‘Sc’ means scissoring, ‘S’ means stretching, ‘Sym’ means symmetric, ‘Asym’ means asymmetric vibrations of the species. Bending vibrations of the pure and complex species are reported as ‘bending’.
7.7.2 Low frequency THz active modes of ZnCl$_2$

Table 7.2: Presented here are the computed Far IR active vibrational frequencies and intensities, of hydrated Zn$^{2+}$ and Zn$^{2+}$—Cl($^-$) complex species in ZnCl$_2$ aqueous solutions determined using PCM model.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Scaled Frequency in cm$^{-1}$</th>
<th>THz (Far IR) Intensity in cm$^{-1}$</th>
<th>Mode Number and Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(H$_2$O)$_6^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>93.88</td>
<td>15.9086</td>
<td>M1 [(R) H$_2$O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>110.92</td>
<td>5.6382</td>
<td>M2 [(R) H$_2$O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>129.17</td>
<td>14.3818</td>
<td>M3 [(R+W) H$_2$O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>135.33</td>
<td>5.0066</td>
<td>M4 [(R+W+T) H$_2$O + O-Zn-O bending]</td>
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<tr>
<td></td>
<td>138.5</td>
<td>8.0672</td>
<td>M5 [(R+W+T) H$_2$O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>148.83</td>
<td>12.9403</td>
<td>M6 [(R+W+T) H$_2$O + O-Zn-O bending]</td>
</tr>
<tr>
<td>ZnCl(H$_2$O)$_5^{+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>67.65</td>
<td>21.67</td>
<td>M7 [(R) H$_2$O+ (R)Cl-Zn + O-Zn-Cl bending]</td>
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<td></td>
<td>89.7</td>
<td>14.92</td>
<td>M8 [(R) H$_2$O+ (R)Cl-Zn]</td>
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<td></td>
<td>100.99</td>
<td>14.68</td>
<td>M9 [(R) H$_2$O+ (R)Cl-Zn + O-Zn-Cl bending]</td>
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<td></td>
<td>122.09</td>
<td>1.13</td>
<td>M10 [(R+T) H$_2$O+ (R)Cl-Zn + O-Zn-Cl bending]</td>
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<td></td>
<td>129.97</td>
<td>11.31</td>
<td>M11 [(R+W) H$_2$O+ (R)Cl-Zn + O-Zn-Cl bending]</td>
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<tr>
<td></td>
<td>147.1</td>
<td>23.30</td>
<td>M12 [(R+T) H$_2$O+ (R)Cl-Zn]</td>
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<td>ZnCl$_2$(H$_2$O)$_2^{0}$</td>
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<tr>
<td></td>
<td>123.07</td>
<td>27.42</td>
<td>M19 [(T) H$_2$O+(W) Cl-Zn-O bending]</td>
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<tr>
<td></td>
<td>123.63</td>
<td>47.33</td>
<td>M20 [(T) H$_2$O+(Sc) Cl-Zn-Cl]</td>
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<td></td>
<td>176.93</td>
<td>4.21</td>
<td>M21 [(Sc) O-Zn-O]</td>
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<td>308.94</td>
<td>34.00</td>
<td>M22 [(Sym S) Cl-Zn]</td>
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<td>329.68</td>
<td>24.00</td>
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<td>ZnCl$_3$(H$_2$O)$_3^{0}$</td>
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</tr>
<tr>
<td></td>
<td>76.12</td>
<td>15.97</td>
<td>M24 [(S) Cl-Zn-Cl]</td>
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<td></td>
<td>96.36</td>
<td>11.49</td>
<td>M25 [(Sc) O-Zn-Cl]</td>
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<td></td>
<td>105.32</td>
<td>73.05</td>
<td>M26 [(W) Cl$_3$-Zn+(W) H$_2$O]</td>
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<td></td>
<td>124.48</td>
<td>11.41</td>
<td>M27 [(Sc) Cl-Zn-Cl+(R) H$_2$O]</td>
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<td></td>
<td>139.73</td>
<td>8.79</td>
<td>M28 [(R) O-Zn-Cl$_3$]</td>
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<td></td>
<td>291.59</td>
<td>23.08</td>
<td>M29 [(Sym S) Cl$_3$-Zn+(Asym S) Zn-O]</td>
</tr>
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<td>312.91</td>
<td>46.88</td>
<td>M30 [(Sym S) Cl-Zn-O]</td>
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<td></td>
<td>330.8</td>
<td>5.38</td>
<td>M31 [(Asym S) Cl-Zn-Cl+(S) Zn-O]</td>
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<tr>
<td>ZnCl$_4^{2-}$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110.63</td>
<td>31.7</td>
<td>M32 [(Bending) 2(Cl-Zn-Cl)]</td>
</tr>
<tr>
<td></td>
<td>295.63</td>
<td>116.86</td>
<td>M33 [(Asym S) Zn-Cl]</td>
</tr>
</tbody>
</table>

In the following Figure (7.5), calculated Far IR intensities of different solvated chemical species as described in Table (7.2) are plotted over the 50 - 350 cm$^{-1}$ frequency range.
Figure 7.5: Shown here are the theoretically calculated Far IR active vibrational low frequencies and intensities of hydrated \( \text{Zn}^{2+} \) and \( \text{Zn}^{2+}-\text{Cl}^- \) complex species in \( \text{ZnCl}_2 \) aqueous solutions.
7. Hydration of Aqueous Zinc Halides

7.7.3 Low frequency THz active modes of ZnBr₂

**Table 7.3:** Presented here are the computed Far IR active vibrational frequencies and intensities, of hydrated Zn²⁺ and Zn²⁺—Br⁻ complex species in ZnBr₂ aqueous solutions determined using PCM model.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Scaled Frequency in cm⁻¹</th>
<th>THz (Far IR) Intensity</th>
<th>Mode Number and Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(H₂O)_₆²⁺</td>
<td>93.88</td>
<td>15.9086</td>
<td>M₁  [(R) H₂O + O-Zn-O bending]</td>
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<tr>
<td></td>
<td>110.92</td>
<td>5.6382</td>
<td>M₂  [(R) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>129.17</td>
<td>14.3818</td>
<td>M₃  [(R+W) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>135.33</td>
<td>5.0066</td>
<td>M₄  [(R+W+T) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>138.5</td>
<td>8.0672</td>
<td>M₅  [(R+W+T) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>148.83</td>
<td>12.9403</td>
<td>M₆  [(R+W+T) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td>ZnBr(H₂O)₅⁺</td>
<td>65.7</td>
<td>14.01</td>
<td>M₇  [(R) H₂O+ (R) Br-Zn + O-Zn-Br bending]</td>
</tr>
<tr>
<td></td>
<td>98.92</td>
<td>21.12</td>
<td>M₈  [(R) H₂O+ (R) Br-Zn + O-Zn-Br bending]</td>
</tr>
<tr>
<td></td>
<td>107.67</td>
<td>21.84</td>
<td>M₉  [(R) H₂O+ (R) Br-Zn + O-Zn-Br bending]</td>
</tr>
<tr>
<td></td>
<td>121.85</td>
<td>23.65</td>
<td>M₁₀ [(R+W) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>129.82</td>
<td>21.95</td>
<td>M₁₁ [(R+W+T) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>171.15</td>
<td>2.41</td>
<td>M₁₂ [(R+W+T) H₂O + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>194.99</td>
<td>17.73</td>
<td>M₁₃ [(R+T) H₂O⁺ (S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>274.53</td>
<td>21.76</td>
<td>M₁₄ [(R+W) H₂O⁺ (Sym S) O-Zn-O]</td>
</tr>
<tr>
<td></td>
<td>313.57</td>
<td>40.10</td>
<td>M₁₅ [(R+W) H₂O⁺ (Asym S) O-Zn-O]</td>
</tr>
<tr>
<td></td>
<td>335.45</td>
<td>79.84</td>
<td>M₁₆ [(R+W) H₂O⁺ (Asym S) O-Zn-O]</td>
</tr>
<tr>
<td>ZnBr₂(H₂O)₄⁻</td>
<td>95.96</td>
<td>15.05</td>
<td>M₁₇ [(R) O-Zn-O⁺ (Sc) Br-Zn-Br]</td>
</tr>
<tr>
<td></td>
<td>110.44</td>
<td>22.56</td>
<td>M₁₈ [(R) O-Zn-O⁺ (Sc) Br-Zn-Br]</td>
</tr>
<tr>
<td></td>
<td>216.82</td>
<td>11.28</td>
<td>M₁₉ [(Sym S) Br-Zn + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>289.7</td>
<td>48.16</td>
<td>M₂₀ [(S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>311.91</td>
<td>100.58</td>
<td>M₂₁ [(T) H₂O⁺ (Asym S) Br-Zn-Br]</td>
</tr>
<tr>
<td>ZnBr₃(H₂O)⁻</td>
<td>65.45</td>
<td>7.18</td>
<td>M₂₂ [(Sc) Br-Zn-Br]</td>
</tr>
<tr>
<td></td>
<td>102.39</td>
<td>22.16</td>
<td>M₂₃ [(Sc) O-Zn-Br]</td>
</tr>
<tr>
<td></td>
<td>128.02</td>
<td>3.01</td>
<td>M₂₄ [(Sc) O-Zn-Br]</td>
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<td></td>
<td>174.45</td>
<td>18.56</td>
<td>M₂₅ [(Sym S) 3Br-Zn]</td>
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<tr>
<td></td>
<td>238.57</td>
<td>101.65</td>
<td>M₂₆ [(Asym S) 3Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>256.06</td>
<td>88.27</td>
<td>M₂₇ [(Asym S) 3Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>298.74</td>
<td>42.53</td>
<td>M₂₈ [(Asym S) 3Br-Zn]</td>
</tr>
<tr>
<td>ZnBr₄⁻</td>
<td>71.57</td>
<td>8.72</td>
<td>M₂₉ [(Bending) 2(Br-Zn-Br)]</td>
</tr>
<tr>
<td></td>
<td>71.6</td>
<td>8.72</td>
<td>M₃₀ [(Bending) 2(Br-Zn-Br)]</td>
</tr>
<tr>
<td></td>
<td>90.7</td>
<td>3.25</td>
<td>M₃₁ [(Bending) 2(Br-Zn-Br)]</td>
</tr>
<tr>
<td></td>
<td>221.49</td>
<td>99.24</td>
<td>M₃₂ [(Asym S) 2(Br-Zn-Br)]</td>
</tr>
<tr>
<td></td>
<td>221.5</td>
<td>99.25</td>
<td>M₃₃ [(Asym S) 2(Br-Zn-Br)]</td>
</tr>
<tr>
<td></td>
<td>234.21</td>
<td>95.76</td>
<td>M₃₄ [(Asym S) 2(Br-Zn-Br)]</td>
</tr>
</tbody>
</table>

In the following Figure (7.6), calculated low frequency IR intensities of different solvated chemical species as described in Table (7.3) are plotted over the 50 - 350 cm⁻¹ frequency range.
Figure 7.6: Shown here are the theoretically calculated Far IR active vibrational low frequencies and intensities of hydrated Zn$^{2+}$ and Zn$^{2+}–$Br$^-$ complex species in ZnBr$_2$ aqueous solutions.
7.7.4 Low frequency Raman active modes of ZnCl$_2$

Table 7.4: Presented here are the low wavenumber Raman vibrational frequencies and intensities of hydrated Zn$^{2+}$ and Zn$^{2+}$—Cl$^-$ complex species in ZnCl$_2$ aqueous solutions determined using PCM model.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Scaled Frequency in cm$^{-1}$</th>
<th>Raman Intensity</th>
<th>Mode Number and Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(H$_2$O)$_6^{2+}$</td>
<td>275.79</td>
<td>0.09</td>
<td>M1 [(Asym S) O-Zn-O]</td>
</tr>
<tr>
<td></td>
<td>277.52</td>
<td>0.11</td>
<td>M2 [(T) H$_2$O+ (Asym S) O-Zn-O]</td>
</tr>
<tr>
<td></td>
<td>390.04</td>
<td>4.44</td>
<td>M3 [(W) H$_2$O+ (Sym S) O-Zn-O]</td>
</tr>
<tr>
<td>ZnCl(H$_2$O)$_5^{+}$</td>
<td>213.61</td>
<td>0.44</td>
<td>M4 [(R) H$_2$O]</td>
</tr>
<tr>
<td></td>
<td>225.52</td>
<td>0.19</td>
<td>M5 [(R) H$_2$O+ (S) Zn-O+ (S) Cl-Zn]</td>
</tr>
<tr>
<td></td>
<td>249.88</td>
<td>0.23</td>
<td>M6 [(R) H$_2$O+ (S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>348.89</td>
<td>3.95</td>
<td>M7 [(S) Zn-O+ (S) ZnCl]</td>
</tr>
<tr>
<td></td>
<td>368.26</td>
<td>3.40</td>
<td>M8 [(Sym S) Zn-O]</td>
</tr>
<tr>
<td>ZnCl$_3$(H$_2$O)$_2^{0}$</td>
<td>308.94</td>
<td>6.02</td>
<td>M9 [(Sym S) Cl-Zn-Cl + O-Zn-O bending]</td>
</tr>
<tr>
<td></td>
<td>383.61</td>
<td>4.54</td>
<td>M10 [(Sym S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>397.93</td>
<td>1.34</td>
<td>M11 [(W) H$_2$O+ (Asym S) Cl-Zn]</td>
</tr>
<tr>
<td>ZnCl$_4$(H$_2$O)$^-$</td>
<td>291.59</td>
<td>4.53</td>
<td>M12 [(Sym S) 3Cl-Zn+ (S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>312.91</td>
<td>5.15</td>
<td>M13 [(Sym S) Cl-Zn+ (Sym S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>330.8</td>
<td>2.85</td>
<td>M14 [(Asym S) 3Cl-Zn+ (S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>360.39</td>
<td>1.84</td>
<td>M15 [(Asym S) 3Cl-Zn+ (S) Zn-O]</td>
</tr>
<tr>
<td>ZnCl$_4^{2-}$</td>
<td>295.63</td>
<td>1.01</td>
<td>M16 [(Sym S) 4Cl-Zn]</td>
</tr>
<tr>
<td></td>
<td>307.11</td>
<td>12.2</td>
<td>M17 [(Sym S) 4Cl-Zn]</td>
</tr>
</tbody>
</table>

In the following Figure (7.7), calculated low frequency Raman intensities of different solvated chemical species as described in Table (7.4) are plotted over the 150 - 500 cm$^{-1}$ frequency range.
7. Hydration of Aqueous Zinc Halides

Figure 7.7: Shown here are the theoretically calculated Raman active vibrational low frequencies and intensities of hydrated Zn$^{2+}$ and Zn$^{2+}$—Cl$^-$ complex species in ZnCl$_2$ aqueous solutions.
### 7.7.5 Low frequency Raman active modes of ZnBr$_2$

*Table 7.5:* Presented here are the low wavenumber Raman vibrational frequencies and intensities of hydrated Zn$^{2+}$ and Zn$^{2+}$—Br$^-$ complex species in ZnBr$_2$ aqueous solutions determined using PCM model.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Scaled Frequency in cm$^{-1}$</th>
<th>Raman Intensity</th>
<th>Mode Number and Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(H$_2$O)$_6^{2+}$</td>
<td>275.79</td>
<td>0.09</td>
<td>M1 [(Asym S) O-Zn-O]</td>
</tr>
<tr>
<td></td>
<td>277.52</td>
<td>0.11</td>
<td>M2 [(T) H$_2$O+ (Asym S) O-Zn-O]</td>
</tr>
<tr>
<td></td>
<td>390.04</td>
<td>4.44</td>
<td>M3 [(W) H$_2$O+ (Sym S) O-Zn-O]</td>
</tr>
<tr>
<td>ZnBr(H$_2$O)$_5^+$</td>
<td>194.99</td>
<td>0.89</td>
<td>M4 [(R+T) H$_2$O+ (S) Zn-O+ (S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>245.78</td>
<td>0.75</td>
<td>M5 [(R+T) H$_2$O+ (S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>274.53</td>
<td>2.97</td>
<td>M6 [(R+T) H$_2$O+ (S) Zn-O+ (S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>335.45</td>
<td>0.21</td>
<td>M7 [(Asym S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>365.5</td>
<td>2.96</td>
<td>M8 [(Sym S) Zn-O]</td>
</tr>
<tr>
<td>ZnBr$_2$(H$_2$O)$_4^-$</td>
<td>216.82</td>
<td>8.50</td>
<td>M9 [(Sym S) Br-Zn + O-Zn-O bend]</td>
</tr>
<tr>
<td></td>
<td>289.7</td>
<td>0.99</td>
<td>M10 [(W) H$_2$O+ (S) Zn-O]</td>
</tr>
<tr>
<td></td>
<td>311.91</td>
<td>1.05</td>
<td>M11 [(T) H$_2$O+ (Asym S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>352.79</td>
<td>2.13</td>
<td>M12 [(S) Zn-O]</td>
</tr>
<tr>
<td>ZnBr$_3$(H$_2$O)$^-$</td>
<td>174.45</td>
<td>7.72</td>
<td>M13 [(Sym S) 3Br-Zn + (S)Zn-O]</td>
</tr>
<tr>
<td></td>
<td>258.57</td>
<td>1.24</td>
<td>M14 [(T) H$_2$O+ (Asym S) 3Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>256.06</td>
<td>1.59</td>
<td>M15 [(W) H$_2$O+ (Asym S) 2Br-Zn + (S)Zn-O]</td>
</tr>
<tr>
<td></td>
<td>298.74</td>
<td>3.25</td>
<td>M16 [(S) Zn-O]</td>
</tr>
<tr>
<td>ZnBr$_4^{2-}$</td>
<td>179.04</td>
<td>1.91</td>
<td>M17 [(Sym S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>221.49</td>
<td>0.4</td>
<td>M18 [(Asym S) Br-Zn]</td>
</tr>
<tr>
<td></td>
<td>221.5</td>
<td>0.4</td>
<td>M19 [(Asym S) Br-Zn]</td>
</tr>
</tbody>
</table>

In the following Figure (7.8), calculated low frequency Raman intensities of different solvated chemical species as described in Table (7.5) are plotted over the 150 - 500 cm$^{-1}$ frequency range.
Figure 7.8: Shown here are the theoretically calculated Raman active vibrational low frequencies and intensities of hydrated Zn$^{2+}$ and Zn$^{2+}$—Br$^-$ complex species in ZnBr$_2$ aqueous solutions.
7.8 Hydration model

By the application of PCM modeling, the low frequency vibrational frequencies and their corresponding THz and Raman intensities were determined in the previous section. In order to connect these frequencies to the experimental spectra a hydration modeling over Zn$^{2+}$ and Zn$^{2+}$-anion complexes have been carried out. The main aim of this approach is to find out the spectral contributions of distinct ionic and ion-complex species within the experimental spectra. For the ion-complexation between Zn$^{2+}$ and counter halide ions (Cl$^-$ and Br$^-$), the following reactions are considered:

\[
\begin{align*}
Zn^{2+}(H_2O)_6 + X^- & \rightleftharpoons K_1 Zn^{2+}(H_2O)_5X^- + H_2O \quad (7.1) \\
Zn^{2+}(H_2O)_5X^- + X^- & \rightleftharpoons K_2 Zn^{2+}(H_2O)_4(X^-)_2 + 3 H_2O \quad (7.2) \\
Zn^{2+}(H_2O)_4(X^-)_2 + X^- & \rightleftharpoons K_3 Zn^{2+}H_2O(X^-)_3 + H_2O \quad (7.3) \\
Zn^{2+}H_2O(X^-)_3 + X^- & \rightleftharpoons K_4 Zn^{2+}(X^-)_4 + H_2O \quad (7.4)
\end{align*}
\]

Here, $K_i$ denotes the equilibrium constant of the reaction (i) and X denotes the halide ion. This model assumes that the octahedrally coordinated $Zn^{2+}(H_2O)_5X^-$ changes to tetrahedral coordination $Zn^{2+}(H_2O)_2(X^-)_2$ by the addition of second anion. This is based on the free energy calculations of PCM model (see section (7.7.1)) and this is consistent with *ab Initio* Hybrid Microsolvation/Continuum approach of Oswald et al. [54].

The corresponding equilibria for zinc chloride and bromide systems are given by:

\[
\begin{align*}
K_1 & \quad K_2 & \quad K_3 & \quad K_4 \\
Zn(H_2O)_6^{2+} & \rightleftharpoons ZnCl(H_2O)_5^{+} & \rightleftharpoons ZnCl_2(H_2O)_2^{0} & \rightleftharpoons ZnCl_3(H_2O)^{-} & \rightleftharpoons ZnCl_4^{2-} \\
Zn(H_2O)_6^{2+} & \rightleftharpoons ZnBr(H_2O)_5^{+} & \rightleftharpoons ZnBr_2(H_2O)_2^{0} & \rightleftharpoons ZnBr_3(H_2O)^{-} & \rightleftharpoons ZnBr_4^{2-}
\end{align*}
\]
7.9 Equilibrium constants

The next aim is to determine the concentrations of the pure ionic and distinct ion-complex species. Equations (7.1) to (7.4) can be expressed in terms of the respective equilibrium constants according to:

\[ [\text{Zn}^{2+}(\text{H}_2\text{O})_5\text{X}^-] = K_1 \frac{[\text{Zn}^{2+}(\text{H}_2\text{O})_6][\text{X}^-]}{[\text{H}_2\text{O}]} \]  \hspace{1cm} (7.5)  

\[ [\text{Zn}^{2+}(\text{H}_2\text{O})_2(\text{X}^-)_2] = K_2 \frac{[\text{Zn}^{2+}(\text{H}_2\text{O})_5\text{X}^-][\text{X}^-]}{[\text{H}_2\text{O}]^3} \]  \hspace{1cm} (7.6)  

\[ [\text{Zn}^{2+}\text{H}_2\text{O}(\text{X}^-)_3] = K_3 \frac{[\text{Zn}^{2+}(\text{H}_2\text{O})_2(\text{X}^-)_2][\text{X}^-]}{[\text{H}_2\text{O}]} \]  \hspace{1cm} (7.7)  

\[ [\text{Zn}^{2+}(\text{X}^-)_4] = K_4 \frac{[\text{Zn}^{2+}\text{H}_2\text{O}(\text{X}^-)_3][\text{X}^-]}{[\text{H}_2\text{O}]} \]  \hspace{1cm} (7.8)  

Here, \( \gamma \) denotes the mean activity coefficient of the salt. The values of the mean activity coefficients for ZnCl\(_2\) and ZnBr\(_2\) were used from the reported data \[121\]. For a given salt concentration \( c \), the cation and anion concentrations can be obtained using the ion number conservation boundary condition.

The cation concentration:

\[ [\text{Zn}^{2+}(\text{H}_2\text{O})_6] + [\text{Zn}^{2+}(\text{H}_2\text{O})_5\text{X}^-] + [\text{Zn}^{2+}(\text{H}_2\text{O})_2(\text{X}^-)_2] + [\text{Zn}^{2+}\text{H}_2\text{O}(\text{X}^-)_3] + [\text{Zn}^{2+}(\text{X}^-)_4] = c \]  \hspace{1cm} (7.9)  

The anion concentration:

\[ [\text{X}^-] + [\text{Zn}^{2+}(\text{H}_2\text{O})_5\text{X}^-] + 2[\text{Zn}^{2+}(\text{H}_2\text{O})_2(\text{X}^-)_2] + 3[\text{Zn}^{2+}\text{H}_2\text{O}(\text{X}^-)_3] + 4[\text{Zn}^{2+}(\text{X}^-)_4] = 2c \]  \hspace{1cm} (7.10)  

In order to determine the concentrations of the different hydrated components, this set of equations was solved numerically. For zinc chloride, the estimated equilibrium constants are \( K_1 \approx 0.68, K_2 \approx 1.86, K_3 \approx 0.38, K_4 \approx 1.41 \) and for zinc bromide are \( K_1 \approx 0.61, K_2 \approx 1.32, K_3 \approx 0.38, K_4 \approx 1.18 \).
7.10  Prediction of the low frequency spectra

In further, efforts have been made to link these theoretical results (calculated frequencies) to the experimental spectra using the determined value of equilibrium constants. However, spectral prediction is clearly not a simple task because approximately ~ 33 different THz resonances have been predicted by theoretical calculations for both zinc halide species. Similar to this, for aqueous ZnCl\textsubscript{2} and ZnBr\textsubscript{2}, about ~18 low frequency Raman resonances have been determined by PCM modeling. On a technical side, only five Gaussian line shapes are required to fit each of the spectra because the spectral features are rather broad, but in reality our calculations suggests that large number of individual resonances are present under these broad vibrational modes. In order to predict the ionic and ion-complex spectra, following stepwise approach was used:

(1) In the first step, the values of the equilibrium constants for ZnCl\textsubscript{2} given by Maciel et al. [122] were used as the guess parameters. These values were further iteratively modified in order to achieve a better fit to the experimental spectra.

(2) In the second step, the concentrations of the hydrated pure Zn\textsuperscript{2+} and ion-complex species were calculated using these values of equilibrium constants according to the Equations (7.9, 7.10).

(3) In the third step, for every salt concentration, all the calculated THz and Raman intensities of each species were multiplied by their relative amount of the concentrations. This gives the final intensity of each mode.

(4) In further, all the frequencies and respective intensities were plotted using a Gaussian line shape. For all the resonances the half width (FWHM) was kept at 30 cm\textsuperscript{-1}.

For zinc chloride, the estimated equilibrium constants are $K_1 = 0.68$, $K_2 = 1.86$, $K_3 = 0.38$, $K_4 = 1.41$ and for zinc bromide are $K_1 = 0.61$, $K_2 = 1.32$, $K_3 = 0.38$, $K_4 = 1.18$. These equilibrium constants give the concentrations of the zinc and ion-complex species for both zinc halides, which are described in Table (7.6) and (7.7).
Table 7.6: Calculated contributions according to the hydration model for hydrated zinc and zinc-chloride complex species at different concentrations in ZnCl₂ aqueous solutions.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Zn(H₂O)₆²⁺ (M)</th>
<th>ZnCl(H₂O)₅⁺ (M)</th>
<th>ZnCl₂(H₂O)₂⁻ (M)</th>
<th>ZnCl₃(H₂O)⁻ (M)</th>
<th>ZnCl₄²⁻ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.16</td>
<td>0.03</td>
<td>0.025</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
<td>0.08</td>
<td>0.08</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>0.75</td>
<td>0.32</td>
<td>0.12</td>
<td>0.15</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>1</td>
<td>0.38</td>
<td>0.16</td>
<td>0.22</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>1.25</td>
<td>0.44</td>
<td>0.19</td>
<td>0.29</td>
<td>0.12</td>
<td>0.19</td>
</tr>
<tr>
<td>1.5</td>
<td>0.50</td>
<td>0.22</td>
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Table 7.7: Calculated contributions according to the hydration model for hydrated zinc and zinc-bromide complex species at different concentrations in ZnBr₂ aqueous solutions.

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<th>Concentration (M)</th>
<th>Zn(H₂O)₆²⁺ (M)</th>
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</table>
7. Hydration of Aqueous Zinc Halides

All the theoretical THz and Raman intensities were multiplied by the relative amount of the zinc and ion-complex species at a given salt concentration. In order to predict the spectra, these intensities were multiplied by an arbitrary scaling factor. This scaling factor just scales the relative strengths of the resonances equally, and for the prediction of full concentration series (between 0.25 to 4 M) only one individual scaling factor was used. (Note: this is different than the scaling factor for the resonance frequencies which have a fix value of 1.19). The individual scaling factors used for scaling only the intensities (not center frequencies) are 1.9, 1.4, 7 and 20 for THz FT ZnCl$_2$, THz FT ZnBr$_2$, Raman ZnCl$_2$ and Raman ZnBr$_2$, respectively.

7.11 Line shape

All these mode predictions were made using Gaussian line shapes according to the following equation:

$$G (I_G, h_G, \nu_0, \nu) = I_G \exp\left[\frac{-\log[2] \ast (\nu - \nu_0)^2}{h_G^2}\right]$$ (3.12)

Here, $G$ corresponds to the ionic absorption, amplitude ($I_G$) denotes the calculated THz / Raman intensity, $\nu$ denotes the frequency, $\nu_0$ denotes the center frequency of the mode and $h_G$ denotes the full width at half maximum. The spectral estimation was performed using N Gaussian oscillators (N corresponds to the number of predicted vibrational modes) with a fix half width of 30 cm$^{-1}$. The resulting fitted and experimental spectra of all zinc halide species are shows in Figures (7.9) – (7.12).
Figure 7.9: Illustrated here are the experimental THz modes (black), theoretically predicted IR active modes (red) of hydrated Zn$^{2+}$ and Zn$^{2+}$—Cl$^-$ complexes. The blue dashed lines correspond to the individual frequency components described in Table (7.2).
Figure 7.10: Illustrated here are the experimental low frequency Raman modes (black) and theoretically predicted Raman active modes (red) of hydrated Zn$^{2+}$ and Zn$^{2+}$—Cl$^-$ complexes. The blue dashed lines correspond to the individual frequency components described in Table (7.4).
Figure 7.11: Illustrated here are the experimental THz modes (black), theoretically predicted IR active modes (red) of hydrated \( \text{Zn}^{2+} \) and \( \text{Zn}^{2+} - \text{Br}^- \) complexes. The blue dashed lines correspond to the individual frequency components described in Table (7.3).
Figure 7.12: Illustrated here are the experimental low frequency Raman modes (black) and theoretically predicted Raman active modes (red) of hydrated Zn$^{2+}$ and Zn$^{2+}$—Br$^-$ complexes. The blue dashed lines correspond to the individual frequency components described in Table (7.5).
7.12 General discussion and outlook

This combined experimental and theoretical analysis of zinc halides indicates that Zn$^{2+}$ with counter Cl$^-$ and Br$^-$ ions shows strong ion-complexation in aqueous phase. This tendency gradually scales larger with increasing salt concentration. Theoretical analysis allows assigning the resonances attributed to distinct ion-complex species within the experimental spectra. Although this methodology requires more theoretical support to completely dissect the ionic and ion-complex spectra. Nevertheless, the conclusions of the present study are discussed in the following segment:

(1) Zn$^{2+}$ and Cl$^-$ complexation: THz p-Ge laser absorption spectra of ZnCl$_2$ show non-linear change in absorption with increasing electrolyte concentration (see Figure 7.1). The slope of the absorption gradually decreases after 1.5 M concentration. The THz effective extinction spectra of ZnCl$_2$ show two ionic resonances centered at 120 and 300 cm$^{-1}$ (see Figure 7.3). The low frequency mode shows linear change with salt concentration, while the increase in high frequency mode is rather non-linear. Theoretical calculations suggest that high frequency resonance is attributed only to the zinc – chloride complex species (all), since pure Zn$^{2+}$ ion do not show any resonance after 180 cm$^{-1}$ (see Figure 7.5, uppermost panel). This could also be assigned as the reason of very weak strength of 300 cm$^{-1}$ at 0.5 M concentration of ZnCl$_2$, where probably very weak ion-complexation is present (see Figure 7.3, panel A). However, the analysis indicates that pure Zn$^{2+}$ as well as ion-complexes show contributions within the low frequency mode. Both these spectra clearly indicate that ZnCl$_2$ makes strong ion-complexes in liquid phase. The low frequency Raman spectra show a strong resonance at 300 cm$^{-1}$, which indicates that this resonance is THz as well as Raman active. In addition to this, a weak Raman resonance is also visible at 390 cm$^{-1}$ (see Figure 7.4).

The results of Raman measurements are in good agreement with the previous studies [29, 37]. Irish et al. [29] have investigated the aqueous zinc chloride using Raman spectroscopy. They found a resonance at 390 cm$^{-1}$, which was assigned to the water cage motion of Zn$^{2+}$.
ion (see Figure 7.4 Panel (D), shown by vertical arrow). This assignment is consistent with the Raman spectroscopic investigations of Macklin et al. [37]. Both of them have concluded that the mode at 300 cm⁻¹ is attributed to the zinc and chloride complexation.

**2) Zn²⁺ and Br⁻ complexation:** The THz p-Ge spectra of ZnBr₂ show a linear trend with increasing concentration, while the non-linear changes are clearly visible in the THz FT spectra (see Figure 7.1 and 7.3, respectively). The reason behind this is that, the resonance of the pure bromide ion is present between 80 – 90 cm⁻¹ wavenumber, which exactly matches with the frequency of the p-Ge laser source [14, 22]. This technique is very sensitive to the collective water network mode around the solvated ions as reported by Schmidt et al. [22]. Due to simultaneous presence of two effects, both these vibrational modes mask the contributions of each other, and thus any estimation only based on this data analysis can be ambiguous. In order to avoid this, all these salts were examined and analyzed over the broader frequency range using THz FT spectroscopy. THz effective extinction spectra of ZnBr₂ show three resonances centered at 90, 130 and 220 cm⁻¹ (see Figure 7.3, panel B). Additionally, this spectra show a partial negative extinction on 200 cm⁻¹, which is clearly different compared to its chloride analogue; ZnCl₂.

Low frequency Raman spectra of ZnCl₂ and ZnBr₂ are presented in Figure (7.4, Panel C and D). The zinc bromide shows two resonances at 180 and 390 cm⁻¹. In case of ZnCl₂ two resonances are visible at 300 and 390 cm⁻¹. For comparison, the Raman spectra of NiCl₂ and NiBr₂ are also plotted in the left column of Figure (7.4). By combining the Raman spectra of zinc halides and nickel halides, following conclusions can be made:

1) In all the cases, the high frequency component seems to be nearly independent of the choice of the counter halide ion. This is consistent with previous Raman studies [29, 31-32].

2) Up to 2 M concentration, both NiCl₂ and NiBr₂ do not show any additional low frequency Raman resonances, while these modes are clearly visible in case of ZnCl₂ and ZnBr₂.

3) The Raman mode at 300 cm⁻¹ for ZnCl₂ seems to be red shifted for ZnBr₂ at 180 cm⁻¹ with the change of the respective anion (see Figure 7.4). This trend is consistent with the
shift in THz modes from 300 to 225 cm\(^{-1}\), on going from ZnCl\(_2\) to ZnBr\(_2\) (see Figure 7.3). Although, the shift in both cases is not equal, it strongly suggests that all these modes are substantially dependent on the choice of the counter anion. The red shift in the modes correlates with the increase in the ionic mass of the anion (Br\(^-\) is heavier compared to Cl\(^-\)).

4) A gradual change of the extinction at 200 cm\(^{-1}\) in THz FT spectra of ZnBr\(_2\) clearly indicates that ions significantly affect the hindered translation mode \([62]\) of bulk water.

(2) **Comparing experimental and theoretical results:** Experimental data indicates the formation of strong ion-complexes in aqueous solutions of zinc halides. In order to understand this complexation mechanism comprehensively, the PCM and THz hydration modeling were carried out. The experimental and theoretical THz FT spectra of ZnCl\(_2\) and ZnBr\(_2\) are presented in Figure (7.9) and (7.11), respectively. In order to understand the similarities and differences of the spectra, the features of both the spectra are discussed in the following.

Experimental THz spectra of zinc halides is composed of the following vibrational components; a) pure Zn\(^{2+}\), d) pure anions (Cl\(^-\) or Br\(^-\)), c) large number of modes generated from distinct ion-complex species, d) any change in the solvation water spectra. In comparison the theoretical spectra contains, a) pure Zn\(^{2+}\) and b) ion-complex resonances. (Note: The numbers of resonances determined by the theoretical analysis are only attributed to the estimated chemical species. However, in real systems this number can be large due to the presence of intermediate complex species.) Thus at this point, estimation of the anion contribution and determination of the changes in the solvation water is still an open question. However, this analysis is a successful effort to link the THz spectroscopy directly to the theoretical data. This analogy holds for all the predicted and experimental spectra. It is clearly visible from the spectra shown in Figures (7.9), (7.10), (7.11) and (7.12) that predictions are not completely coinciding and center frequencies and intensities are shifted. This can be assigned to the presence of anharmonic effects in the theoretical analysis due to model simplifications. However, the overall predicted modes are in qualitative agreement with the THz spectra. The similar analogy holds for the theoretically and experimentally determined low frequency Raman spectra of ZnCl\(_2\) and ZnBr\(_2\) salts. The theory is able to
represent the experimental spectra qualitatively, while the differences are attributed to the lacking knowledge of unknowns.

The estimated values of equilibrium constants for zinc chloride are in general agreement with the reported literature data [122]. For zinc chloride, the analysis yields equilibrium constants; $K_1 = 0.68$, $K_2 = 1.86$, $K_3 = 0.38$, $K_4 = 1.41$ and for zinc bromide; $K_1 = 0.61$, $K_2 = 1.32$, $K_3 = 0.38$, $K_4 = 1.18$. The comparison between the equilibrium constants of ZnCl$_2$ and ZnBr$_2$ ion complexation schemes indicates that, Zn$^{2+}$ favors stronger association with Cl$^-$ ions compare to Br$^-$. However, these numbers are not exactly comparable with the values reported by other methods [122, 123], because each technique probes this ion-association mechanism at different timescales. Maciel et al. [122] have used NMR technique to obtain the association constant, $(K_1 = 0.48$, $K_2 = 1.86$, $K_3 = 0.56$, $K_4 = 1.40)$ which probes the water exchanges at the order of nanoseconds. In comparison, THz spectroscopy measures the ion hydration dynamics over sub-picoseconds time scales. Sillén et al. [123] have determined the equilibrium constant by assuming only three steps of the ion-complexation mechanism, which is different than the present case. In addition to this, within the present study the strong change in the solvation shell of Zn$^{2+}$ was estimated by the theoretical calculations, going from octahedral coordination to tetrahedral by the inclusion of third halide ion. This inclusion is different than the mechanism reported by the above mentioned both authors [122, 123].

In brief, this study is an effort to understand the theoretical origin of the experimental spectra of complex electrolyte salts in aqueous phase. The main gain of this investigation is that by combining THz spectroscopy with a proper theoretical analysis, hydration dynamics of zinc halides can be explored comprehensively. This combined experimental and theoretical analysis also allows to understand the molecular mechanism involved in the generation of the low frequency vibrations of solvated zinc halides, which gives an opportunity to extract some physically meaningful quantities, like equilibrium constant, free energy of formation, etc. The efforts to improve the agreement between experiment and theory and are under continuous progress. This kind of study allows extending the effectiveness of THz spectroscopy to a more quantitative level in context of the solvation of ions.
Chapter 8

General Conclusions and a Perspective: Ion Hydration

The main focus of this study was to investigate the hydration dynamics of solvated ions in aqueous phase by the application of THz p-Ge laser absorption and THz Fourier Transform spectroscopy. Both these techniques were implemented to investigate and analyze the low frequency vibrational resonances originated from the motion of ions in water solvent media. On the one hand, p-Ge laser narrow band (75 – 90 cm\(^{-1}\)) absorption spectroscopy was used to probe the effects induced by the ions on the collective network mode of water molecules [12, 14, 22]. This technique allows to observe the changes in the absorption with an increase in the electrolyte concentration. On the other hand, THz FT spectroscopy is very sensitive to the low frequency vibrations of the ions as well as to the ion induced influences on the hindered translational mode of water (184 cm\(^{-1}\)) [62]. This technique covers a broader frequency range (50 – 350 cm\(^{-1}\)) compared to the first method and gives continuous absorption bands originated from the motions of the solvated ions.

On a theoretical side, all these experimental results were complemented using the THz hydration modeling. This modeling was an effort to understand the underlying molecular mechanism involved within these spectral features as well as to extract some physically meaningful information, (i.e., single ionic spectra, ion-pair spectra, equilibrium constants, etc.) from the experimental data. In all cases, each metal ion was measured with two counter anions (Cl\(^-\) and Br\(^-\)). This analogous combination of ions allows to separate the effects of pure cation as well as to determine the influences of both anions on the cation and on the solvation dynamics of water molecules. This combined experimental and theoretical study covers ten different ionic salts which were composed of the combination of five different cations (La\(^{3+}\), Yb\(^{3+}\), Mn\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\)) and two different halide anions (Cl\(^-\) and Br\(^-\)).

In the first step, LaCl\(_3\) and LaBr\(_3\) salts were investigated in aqueous phase. Non-linear changes in the absorption with increasing salt concentration were observed by both narrowband and broad band THz spectroscopy. For both lanthanum halides, the non-
linearity in the THz extinction was attributed to the formation of ion-pairs. THz hydration modeling based on this ion-association mechanism was implemented on the experiment data to separate the spectral features of pure ions and ion pairs. This analysis gives the minimum value (1 - 2) of water molecules influenced by one chloride ion. Pure La\textsuperscript{3+} spectrum shows two low frequency resonances at 127 and 360 cm\textsuperscript{-1}. A proper fitting of the cation spectra yields an estimate of 7.5 - 10 water molecules affected around one La\textsuperscript{3+}. In further, low frequency spectra of ion pairs (aqueous LaCl\textsuperscript{2+} and LaBr\textsuperscript{2+}) were determined, which indicate towards the formation of solvent shared ion-pairs. A combination of all these results suggests that, under ambient conditions the effect of La\textsuperscript{3+}, on the average water structure is restricted to the local regime.

In the second step, YbCl\textsubscript{3} and YbBr\textsubscript{3} salts were investigated using both THz spectroscopic techniques. THz p-Ge laser spectra as well as THz FT spectra show strong deviations from the linearity in the concentration dependent absorption patterns of ytterbium halides. Using a similar ion-association based THz hydration modeling as for lanthanum, the THz spectral features of pure ions (Yb\textsuperscript{3+}, Cl\textsuperscript{-} and Br\textsuperscript{-}) and ion-pairs (YbCl\textsuperscript{2+} and YbBr\textsuperscript{2+}) were determined. A comparison of Yb\textsuperscript{3+} with La\textsuperscript{3+} yields that the ion-pairing with counter Cl\textsuperscript{-} ions is weaker for ytterbium. However, the ion-association tendency of both Yb\textsuperscript{3+} and La\textsuperscript{3+} seems to be rather similar with Br\textsuperscript{-} ions. In both cases, solvent separated ion-pairing was observed. The low frequency absorption bands of Yb\textsuperscript{3+} were obtained at 141 and 388 cm\textsuperscript{-1}. The analysis gives the minimum number of 16 – 19 water molecules affected by one Yb\textsuperscript{3+} ion in aqueous phase. By the comparison of bromides with chlorides, a lower limit of 0 – 1 hydration water molecules was proposed for one Br\textsuperscript{-} ion.

A combination of the results in Chapters 4 and 5 suggests that influence of Yb\textsuperscript{3+} ions on the water is by far stronger than La\textsuperscript{3+}. The blue shift of both the low frequency resonances of Yb\textsuperscript{3+} compared to La\textsuperscript{3+} correlates with the increase in the effective force constant of the resonance, which is attributed to the increase of the cation charge density. The general blue shift of both anionic resonances with Yb\textsuperscript{3+} compared to La\textsuperscript{3+} indicates that, the average confinement of the anion hydration structures is higher in the vicinity of the lanthanide cation, which has higher charge density. Values of the determined association constants indicate that binding affinity of La\textsuperscript{3+} with Cl\textsuperscript{-} ions seems to be stronger compared to Yb\textsuperscript{3+} ions. The larger number of THz hydration water for Yb\textsuperscript{3+} compared to La\textsuperscript{3+} indicates that in case of ytterbium ions the locality of the interaction between cation and surrounding water
molecules is extended beyond the first solvation shell, which is driven by the charge density of the ion.

In the third part, these physical-chemical studies were extended on the transition metal ions. These studies were initiated by THz spectroscopic measurements of aqueous MnCl$_2$ and MnBr$_2$. In order to understand the hydration dynamics of these ions, hydration modeling based theoretical analysis was carried out on both manganese halides. The Mn$^{2+}$ ions show a significant ion-pairing with counter Cl$^-$ ions. However, in case of MnBr$_2$ strong increases in the pH value with increasing salt concentration have been observed, which clearly suggests that cations species are significantly hydrolyzed. Due to this complicity only the ion-pair spectra of aqueous MnCl$^+$ was determined. By the proper analysis of the experimental data, the low frequency resonances of pure Mn$^{2+}$, Cl$^-$ and Br$^-$ ions were obtained. Solvated Mn$^{2+}$ ions show one rattling mode at 134 cm$^{-1}$ and another large amplitude resonance at 405 cm$^{-1}$. The analysis yields that each Mn$^{2+}$ ion influences about 4 to 6 water molecules. A comparison with results of other techniques indicates that the hydrations dynamics of the solvation shell of Mn$^{2+}$ ions at sub pico-second time scales can be well explained by THz spectroscopy.

In the fourth part, the hydration dynamics of Ni$^{2+}$ ions with counter Cl$^-$ and Br$^-$ ions was discussed. By a combined THz absorption and Fourier Transform spectroscopy, the concentration dependent absorption spectra of NiCl$_2$ and NiBr$_2$ were determined. Using a similar analysis like Mn$^{2+}$, the two low frequency resonances of pure aqueous Ni$^{2+}$ ion have been obtained at 157 and 410 cm$^{-1}$. In aqueous state, NiCl$_2$ shows the formation of ion-pairs with increasing electrolyte concentration. However, up to 2M concentration, the NiBr$_2$ does not show ion-association. By complementary theoretical analysis, a minimum number of about 5 – 7 THz affected water molecules were obtained in the vicinity of one Ni$^{2+}$ ion. In this case, the low frequency resonances of Cl$^-$ and Br$^-$ ions were determined at 84 and 188 cm$^{-1}$, respectively.

A comparison of association constants of MnCl$_2$ and NiCl$_2$ suggests that the ion-pairing with Cl$^-$ ions is stronger for Mn$^{2+}$ than Ni$^{2+}$ ions in aqueous solutions. The low frequency rattling resonance of pure Mn$^{2+}$ was observed at 134 cm$^{-1}$, while in case of Ni$^{2+}$ this mode was blue shifted at 157 cm$^{-1}$. Since the charge state of both the cations is same; this blue shift in the resonance was proposed to be the effect of additional ligand field stabilization.
on the hydration structure of the ion. The numbers of estimated THz hydration water molecules indicate that each nickel ion influences one additional water molecule compared to one manganese ion. A combination of the results of both transition metal halides suggests that Mn$^{2+}$ and Ni$^{2+}$ ions show differences in their hydration dynamics, which can be probed and differentiated by THz absorption spectroscopy.

In the fifth section, ZnCl$_2$ and ZnBr$_2$ salts were investigated using THz p-Ge absorption and THz FT spectroscopy. The narrowband absorption spectra of zinc chloride show strong deviation from linearity with increasing salt concentration. Broadband THz FT spectra show strong non-linear changes in extinction for both zinc halides, which were attributed to the formation of the ion-complexes. In order to understand the origin of low frequency resonances, complementary low frequency Raman spectra of ZnCl$_2$ and ZnBr$_2$ were determined at different salt concentrations. On the theoretical side, the low frequency THz and Raman modes were determined by Polarizable Continuum Modeling. In addition to this, efforts were made to combine these theoretical modes with an ion-complexation based hydration model, which allows to predict the low frequency THz and Raman spectra of pure Zn$^{2+}$ and ion-complexes. All these results clearly indicate that in aqueous phase zinc forms strong ion-complexes with counter halide ions.

Systematic attempts to improve the link between experimental and theoretical results of zinc halides are under continuous progress. In order to do that, linear superposition of all the theoretical modes of each complex species (for example ZnCl$^+$) will be calculated. This improvement will be helpful to extract and assign the low frequency features of the ionic and each ion-complex species in aqueous phase.

In brief, the investigations and results obtained in this study demonstrate the effectiveness of THz spectroscopy in context of the ion hydration. The combination of THz p-Ge laser absorption spectroscopy and THz FT spectroscopy provides complementary and comprehensive information about ion-solvation dynamics. The supplementary low frequency Raman measurements affirm the conclusions of THz FT spectroscopy and provide a better understanding of the low frequency ionic resonances. The conjunction of THz hydration modeling with experimental data allows to explore the underlying molecular mechanism of the ion hydration with higher precision, which complements other techniques like; Optical Kerr Effect spectroscopy, THz dielectric relaxation spectroscopy, etc. The systematic investigations of aqueous lanthanides and transition metal halides by THz
spectroscopy demonstrate that ionic charge, ionic radii, ionic mass and ligand field stabilization effects significantly influence the dynamics of the hydration shells of ions. These studies confirm that, with a proper and consistent experimental and theoretical analysis, the solvation of ions can be explored on a quantitative level. These investigations of the electrolyte salt solutions provide an improved understanding of their solvation properties and affirm that in aqueous phase, distinct combination of ions affects the solvation of water differently.
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### Acronyms

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<th>Description</th>
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<td>Terahertz Fourier Transform Spectroscopy</td>
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<td>H-bond</td>
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<td>MRI</td>
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<td>Optical Kerr Effect Spectroscopy</td>
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<td>2D IRS</td>
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<td>MD</td>
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<td>PCM</td>
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<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>ND: YAG</td>
<td>Neodymium-doped Yttrium Aluminum Garnet</td>
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<td>EXAFS</td>
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<td>Quantum Mechanics/Molecular Mechanics</td>
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<tr>
<td>DFT</td>
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<td>p-Ge</td>
<td>p-Germanium</td>
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<td>NMR</td>
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- Interdisciplinary: In the organization committee of Sections Days – 2010 Natural activity Sciences, by Ruhr University Research School, at Ruhr University, Bochum, Germany
Publications

The work presented in this dissertation is based on the following publications:


- Sharma V., Schwaab G., Seitz M., Böhm F., Havenith M., Extended locality of ionic influence on water: A THz study of ytterbium (III) hydration, to be submitted soon.


Author has also contributed in the following papers:

- Böhm F., Schwaab G., Sharma V., Havenith M., Investigating ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ions in aqueous solution via THz spectroscopy, in preparation.
