

Dielectric Relaxation of HCl and NaCl Solutions Investigated by Terahertz Time-Domain Spectroscopy

Wenchao Qiao · Kejian Yang · Arne Thoma · Thomas Dekorsy

Abstract We have used Terahertz time-domain spectroscopy (THz-TDS) to investigate the complex dielectric function of water solutions containing different ions. Using HCl and NaCl solutions with different concentrations we study the changes of the dielectric response introduced by the ions. We find a linear increase of the real and imaginary part of the dielectric function compared with pure water with increasing ion concentrations. We use an expanded model for fitting the dielectric function based on a combination of a Debye relation and damped harmonic oscillators for the anions and cations. A good agreement between the model and the experimental results is obtained.

Keywords Terahertz time-domain spectroscopy · Water solution · Dielectric function · Oscillation

1 Introduction

As one of the most important substances on our planet water has been studied extensively in the past. Many different methods have been applied for the studies of water and water based solutions. Among those techniques, Terahertz time-domain spectroscopy (THz-TDS) has become important, since the relaxational response associated with intermolecular fluctuations of polar liquids can be observed with THz spectroscopy. Hence this method provides access to the understanding of the physical and chemical properties of liquids on a molecular level. Rønne *et al.* and Jepsen *et al.* have used THz-TDS in reflection geometry to study the dielectric response of liquid water including the temperature dependence and also some organic solutions [1–5]. Hirori *et al.* and Ngai *et al.* have built an attenuated total reflection THz-TDS system to study water dynamics and biological solutions at THz frequencies [6–9]. Tielrooij *et al.* have built a THz-TDS system in transmission geometry to study the THz dynamics of ions in water [10, 11].

W. Qiao (✉) · K. Yang · A. Thoma · T. Dekorsy
Department of Physics and Center for Applied Photonics, University of Konstanz, 78457 Constance,
Germany
e-mail: wenchao.qiao@uni-konstanz.de

Ions solutions such as acid, alkali and salt solutions are of great relevance in biological systems. Compared to pure water, ions provide electrical conductivity to the solution and cause a rearrangement in the hydrogen bond network which makes intermolecular interactions much more complicated. Charged ions can induce electric fields which will reorient the dipoles of the surrounding water molecules, hence the charge will be screened and long-range interaction between cations and anions is reduced [12]. Protons (H^+) play different roles compared with regular positive ions. It was revealed by de Grotthuss in 1806 that hydronium (H_3O^+) can form covalent and hydrogen-bonds (H-bonds) with adjacent molecules, through which protonic charge can be transferred via a rearrangement of the covalent and hydrogen-bonds [13]. This is the reason why the conductivity of protons in water is much larger than through other ions under similar conditions [11, 12]. In dilute solutions cations and anions are relatively isolated in a “cage” formed by surrounding water molecules [14]. However, at high concentrations, hydronium and chloride ions can also be connected by interaction via hydrogen bonds [15–17]. The same situation applies also to sodium ions (Na^+).

A double Debye model is adopted and commonly used for the analysis of the dielectric response of water and related solution systems [2–5, 7–10, 18–21]. This model works well for pure water in the low frequency range, but it is inadequate to describe the solutions since ions introduce conductivity, polar interactions and will give contributions to the dielectric relaxation. Diedrich *et al.* and Dodo *et al.* described a model to explain the change of the absorption coefficient of solutions with different concentrations [14, 22]. However, there is still no model entirely describing the dielectric relaxation of the solutions.

In this paper, we measured the dielectric function of HCl and NaCl solutions with concentrations in the range from 0.1 mol/l to 3 mol/l by employing a reflection geometry THz-TDS system. A combined model based on the combination of the Debye model and damped harmonic oscillators was developed to explain the dielectric response of solutions for different ion concentrations. The fitting obtained by the model is in good agreement with experimental results obtained in the frequency range from 0.1 THz to 2.7 THz at room temperature.

2 Experimental set up

The experimental set up is depicted in Fig. 1. The solution is enclosed in a reservoir beneath a high resistivity Si wafer. The spectral response of the Si-solution interface is measured in a THz-TDS system. Compared with THz-TDS in transmission geometry, our setup is especially applicable to highly absorbing liquids. In reflection geometry from the Si-liquid interface with HCl and NaCl solutions we do not have to consider the thickness of the sample and the reduction of the signal quality by strong absorption as compared to transmission geometry.

In order to perform experiments with a good long-term stability and a high signal-to-noise ratio, our THz-TDS system employs high-speed asynchronous optical sampling (ASOPS). ASOPS uses two mode-locked femtosecond oscillators working at 1 GHz repetition rate with a fixed repetition frequency difference around 2 kHz as sources of pump and probe pulses, generating and detecting the THz pulses, respectively [23].

A copper sample holder was used which was equipped with a front window made of double polished, high resistivity silicon wafer with a thickness of 260 μm . Two small holes are drilled on the side of the sample holder through which we can inject liquid samples without any further mechanical changes to the set up. THz pulses are generated from a large area photoconductive THz emitter [24]. P-polarized THz pulses are focused on the silicon window of the sample cell with an incident angle around 60° . The THz pulse is partially

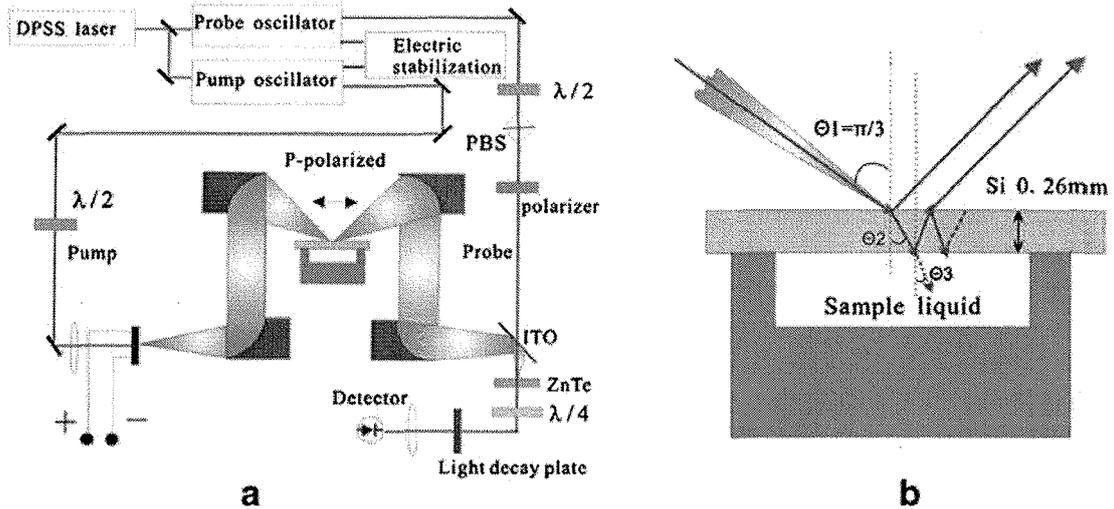


Fig. 1 (a): Set up based on two separate Ti:sapphire fs lasers (pump and probe laser) pumped by a diode pumped solid state laser (DPSS) and the ASOPS technique. (b): detailed view of the sample holder and the THz beam path.

reflected at the air-silicon interface, while a second reflection takes part at the silicon-liquid interface. Both pulses can be clearly separated in time as can be seen in Fig. 2. We use the pulse with no liquid filled in as a reference and the pulse measured with liquid as signal pulse. The second pulse contains the information about the complex dielectric constant of the liquid. Hence we can determine the complex dielectric constant of the liquid from the Fresnel reflection coefficients [2].

3 Experimental results and analysis

Our THz-TDS system provides good stability and high-speed data acquisition. We performed a series of measurements of solutions with concentrations varied from pure water to 3 mol/l at room temperature. Each measurement was repeated four times with

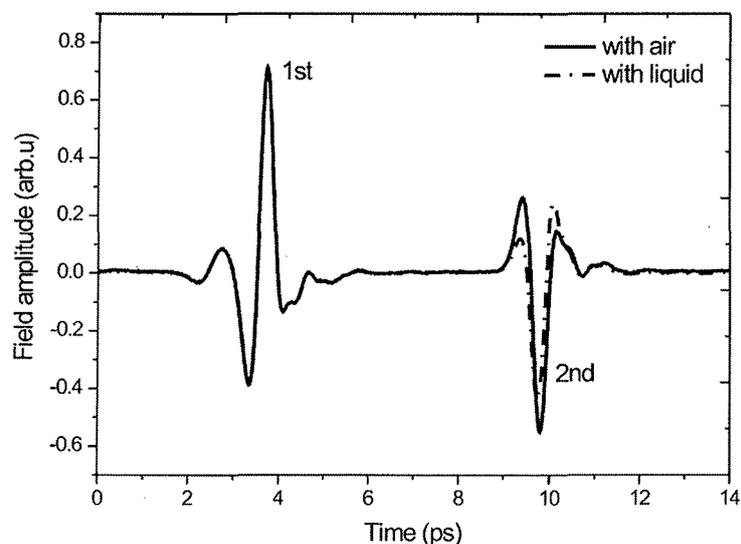


Fig. 2 THz time trace with the 1st and 2nd reflection of the THz pulse from the Si surface and Si-water interface, respectively. The solid line corresponds to the empty cell, the dashed line to the cell filled with water.

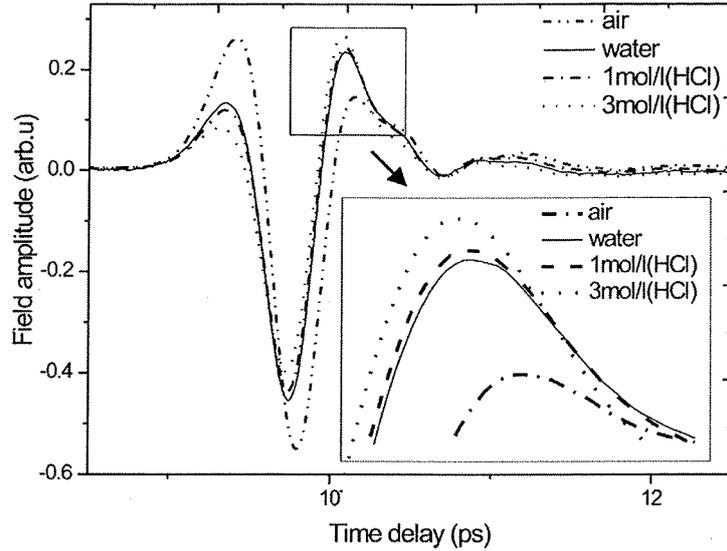


Fig. 3 Terahertz pulses (2nd pulse) reflected by an empty vessel and by vessel filled with pure water as well as 1 mol/l, 3 mol/l HCl water solutions.

each for 512000 averages. The results shown in the following are the average values of the four measurements. As a typical measurement, we show in Fig. 3 the reflected THz pulses from an empty vessel and from vessels filled with pure water as well as 1 mol/l, 3 mol/l HCl solutions. To clarify the stability of our system we show in Fig. 4 the obtained complex dielectric constant of pure water with error bars. These error bars are the standard deviations. The uncertainty of the measurements was caused by the fluctuations of the laser power and the temperature variation.

The refractive index and the absorption coefficient in the range from 0.2 THz to 2.7 THz are obtained quantitatively from these measurements. In Fig. 5(a) and (b) the refractive index and the absorption for different concentrations of the HCl-water solutions are shown. The concentration has been increased by steps of 0.5 mol/l. Clearly both the refractive index and the absorption coefficient of the HCl solutions

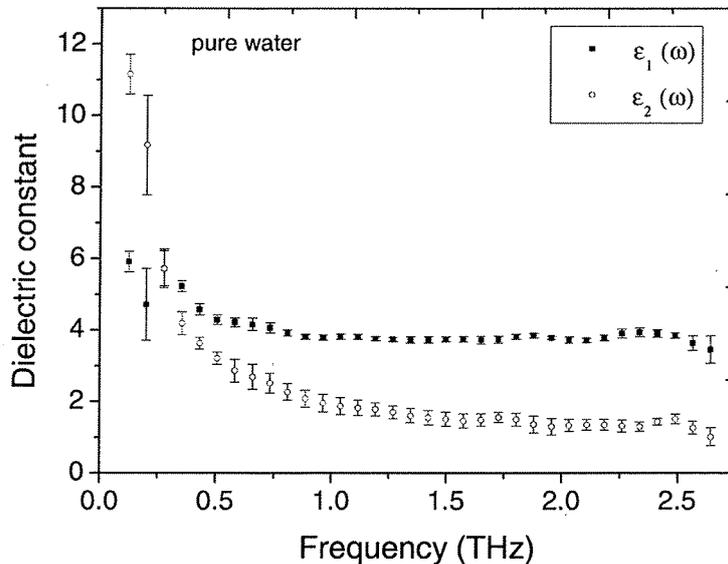


Fig. 4 Complex dielectric constants of pure water with error bars.

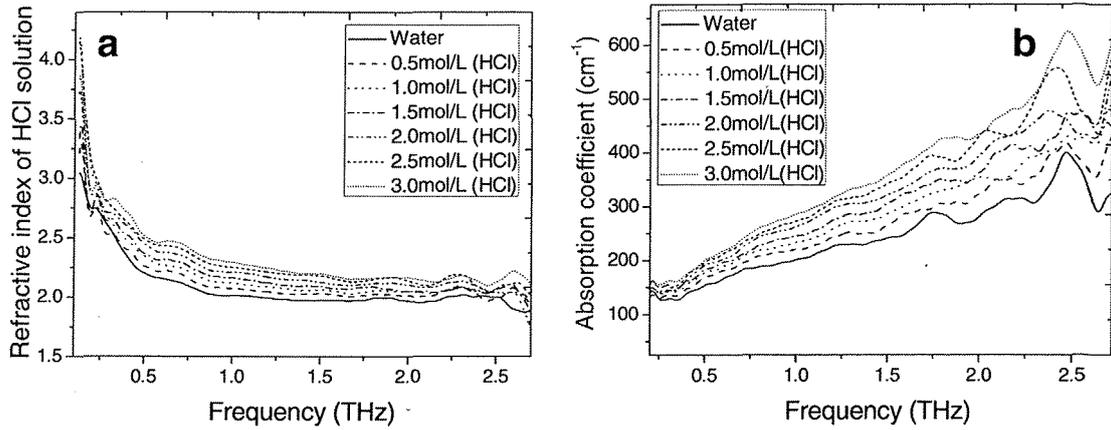


Fig. 5 (a): Refractive index of HCl solutions with different concentrations from 0.5 to 3 mol/l. (b): Absorption coefficient of HCl solutions with different concentrations from 0.5 to 3 mol/l.

have a gradual and monotonic increase with higher concentrations in the whole THz region.

The complex dielectric function $\varepsilon(\omega, c) = \varepsilon_1(\omega, c) + i\varepsilon_2(\omega, c)$ of HCl solutions as a function of concentration and frequency are shown in Fig. 6. Similar to pure water, the real and imaginary parts of the dielectric function decrease with frequency. For increasing ions concentrations they both increase. There are several oscillatory structures and dips on the spectra shown in Fig. 5 and Fig. 6 as deviations from a smooth curve. These stem primarily from the Fourier transforms in the data evaluation and an increased noise level at low (<500 GHz) and higher (>2 THz) frequencies. However these deviations from a smooth curve do not have a physical origin and do not influence the trends of the main spectral features.

The complex dielectric function of NaCl solutions shows a similar gradual increase as the HCl solutions concerning the dependence on concentration. As the tendency of the dielectric constant with concentration is almost consistent in the whole frequency range, we choose the data at 1 THz in order to compare the results. Figure 7 shows the real and imaginary part of the dielectric function at the frequency of 1 THz. Both the HCl and NaCl solutions show a linear increase with increasing concentrations. This behavior is consistent with the results from Tielrooij *et al.* [10].

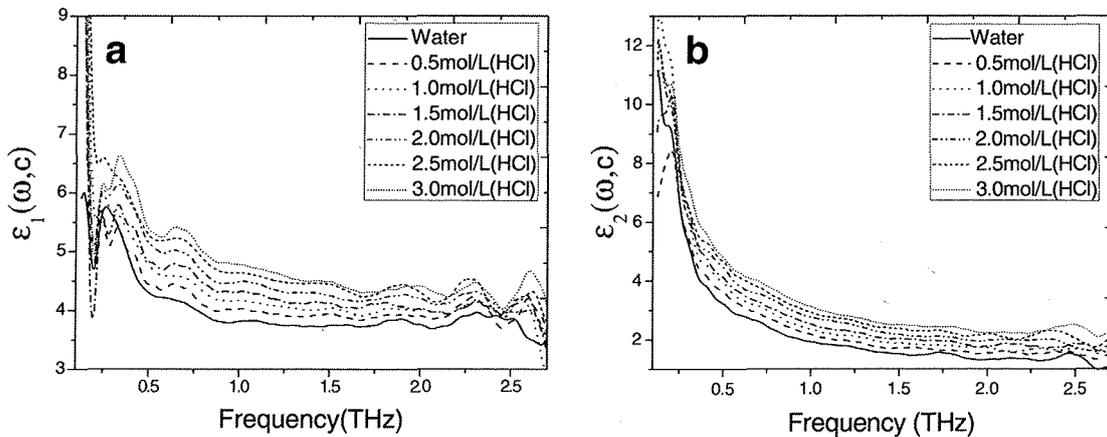


Fig. 6 (a) The real part of the complex dielectric function $\varepsilon_1(\omega, c)$ shown as a function of frequency for different concentrations of HCl. (b) The imaginary part of the complex dielectric function $\varepsilon_2(\omega, c)$ for different concentrations.

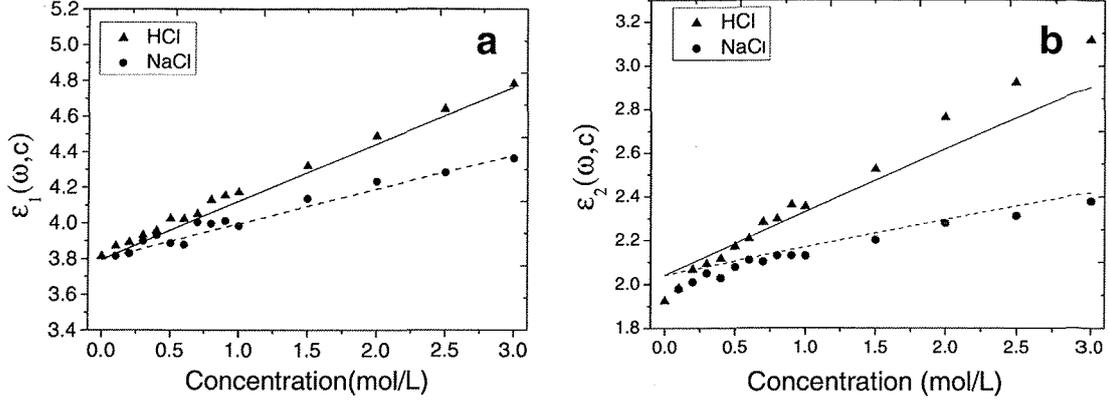


Fig. 7 (a), (b) dependence of real and imaginary part of dielectric constant $\epsilon_1(\omega, c), \epsilon_2(\omega, c)$ of HCl and NaCl solutions, respectively, with concentration, with data measured (points) and theoretical fits (solid line for HCl and dash line for NaCl).

A double Debye model has been shown to describe very well the dielectric function of bulk water with three components [2–5, 7–10, 18–21]:

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_1}{1 + i\omega\tau_D} + \frac{\epsilon_1 - \epsilon_\infty}{1 + i\omega\tau_2}, \quad (1)$$

where ϵ_∞ is the high-frequency limit of complex permittivity, ϵ_s also called the static permittivity is the low-frequency limit of permittivity describing the response of a medium to static electric fields, τ_D and $\epsilon_s - \epsilon_1$ are the relaxation time and the strength of the rotational Debye relaxator, respectively, and τ_2 and $\epsilon_1 - \epsilon_\infty$ are those of the second Debye relaxator. The dielectric constants of bulk water in our measurements (in Fig. 5 and Fig. 6) are 10 % smaller than the results from Rønne *et al.* [2], but are in quite good consistent with results from Masaya *et al.* [7] and even much earlier results from Afsar *et al.* [25]. Using this model to fit the dielectric constant of our results on water we obtain fitting parameters as listed in Table 1. The slow and fast relaxation times τ_D and τ_2 are 8.2 ps and 0.39 ps, respectively, which are slightly different from Masaya's work, in which their parameters are 9.36ps and 0.30ps. The high-frequency limit ϵ_∞ in our simulation is 3.53 which is higher than their value of 2.5 [7] but consistent with Jepsen *et al.* [5].

The experimental data reveal that the dielectric function of solutions shows the same frequency dependence as bulk water and a gradual and monotonic increase for increasing concentrations as seen in Fig. 6 and Fig. 7. We assume that the dielectric response of the water molecules remains unchanged in dilute solution at the investigated ion concentrations. To simulate the experimental data, we used a model based on the following assumptions: the frequency dependent molar dielectric function cross sections σ_{ec} and σ_{ea} of cations and anions, respectively, are described by a reduced-mass resonance which describes the anions and cations as damped harmonic oscillators [14, 22]. So the obtained total dielectric function is a linear superposition of the individual contributions

$$\epsilon(\omega) = \left(1 - \frac{C_s}{W_{mc}} \frac{(\phi_{v,s}^0 + \sqrt{C_s} S_{v,s}^*)}{V_{w0}}\right) \left(\epsilon_\infty + \frac{\epsilon_s - \epsilon_1}{1 + i\omega\tau_D} + \frac{\epsilon_1 - \epsilon_\infty}{1 + i\omega\tau_2}\right) + \frac{\sigma_{ic} C_s}{i\omega\epsilon_0} + \sigma_{ec}(\omega) C_s + \sigma_{ea}(\omega) C_s \quad (2)$$

where C_s is the concentration of ionic compounds, W_{mc} is the water concentration of pure water at room temperature, V_{w0} is the molar volume of pure water, $\phi_{v,s}^0$ is the ions apparent

Table 1 Fit parameters for reduced-mass resonance and the dielectric function of ionic solutions.

Fitting parameters	HCl	NaCl
W_{mc} (mole/liter)	55.51	55.51
m_a (amu)	35.45	35.45
m_c (amu)	19.02	22.99
$\phi_{v,s}^0$ ($cm^3/mole$)	17.8	16.62
$S_{v,s}^*$ ($cm^3 liter^{1/2} mole^{-3/2}$)	1.884	1.884
ϵ_∞	3.53	3.53
ϵ_s	80.3	80.3
ϵ_1	5.2	5.2
τ_D (ps)	8.2	8.2
τ_2 (ps)	0.39	0.39
V_{w0} ($cm^3/mole$)	18.02	18.02
σ_{ic} (literHz/mole)	19.4±0.3	4.3
γ_A (THz)	15.46	15.46 [14]
k_A (kg/s^2)	7.3	7.3
γ_C (THz)	6.5±0.4	10.62 [14]
k_C (kg/s^2)	10.6±0.2	63.08 [14]
s_c (g/mol)	40.12	40.12 [14]

molar volume at infinite dilution, and $S_{v,s}^*$ is the experimental slope of the Masson equation [14, 22]. The first term of Eq. (2) is the dielectric contribution of water molecules to the solutions. σ_{ic} is the ion induced electrical conductivity [10, 18] with different values for different ions (see Table 1), and ϵ_0 is the vacuum permittivity. σ_{ei} is the frequency dependent molar dielectric constant cross sections expressed by:

$$\sigma_{ei} = \frac{10^3 N_A e^2}{\epsilon_0} \frac{\mu_i \omega^2 - k_i + i \mu_i \omega \gamma_i}{(\mu_i \omega^2 - k_i)^2 + \mu_i^2 \omega^2 \gamma_i^2}, \quad (3)$$

where N_A is Avagadro's number, $\mu_i = (m_i * s_i) / (m_i + s_i)$ is the reduced mass of the ion with a reduced-mass fitting parameter s_i . γ_i is the damping constant of the oscillations and k_i is the force constant describing the strength of confinement of the ions due to the interaction with the surrounding water molecules [14, 22, 26]. Besides the double Debye model included in this model, we used five adjustable parameters to fit the frequency dependent molar dielectric constant cross section which are all shown in Table 1. We are aware of the fact that this large number of fitting parameters opens a large parameter space for fitting the experimental data. However, we believe that the model as a combination of two known description reflects well the complex dynamics.

This model agrees well with HCl and NaCl solutions as shown in Fig. 8, which depicts the theoretical calculations together with the measured complex dielectric functions of both solutions.

In order to study the contributions of the different part of Eq. (2) to the complex dielectric constant of the solution, we plot the different contributions in Fig. 9. Comparing each contribution to the complex dielectric function by the chloride, hydronium and sodium ions, the chloride ions have a 10 times higher contribution than the sodium ions to the real part of the dielectric function, and 100 times higher for the imaginary part, respectively. This means

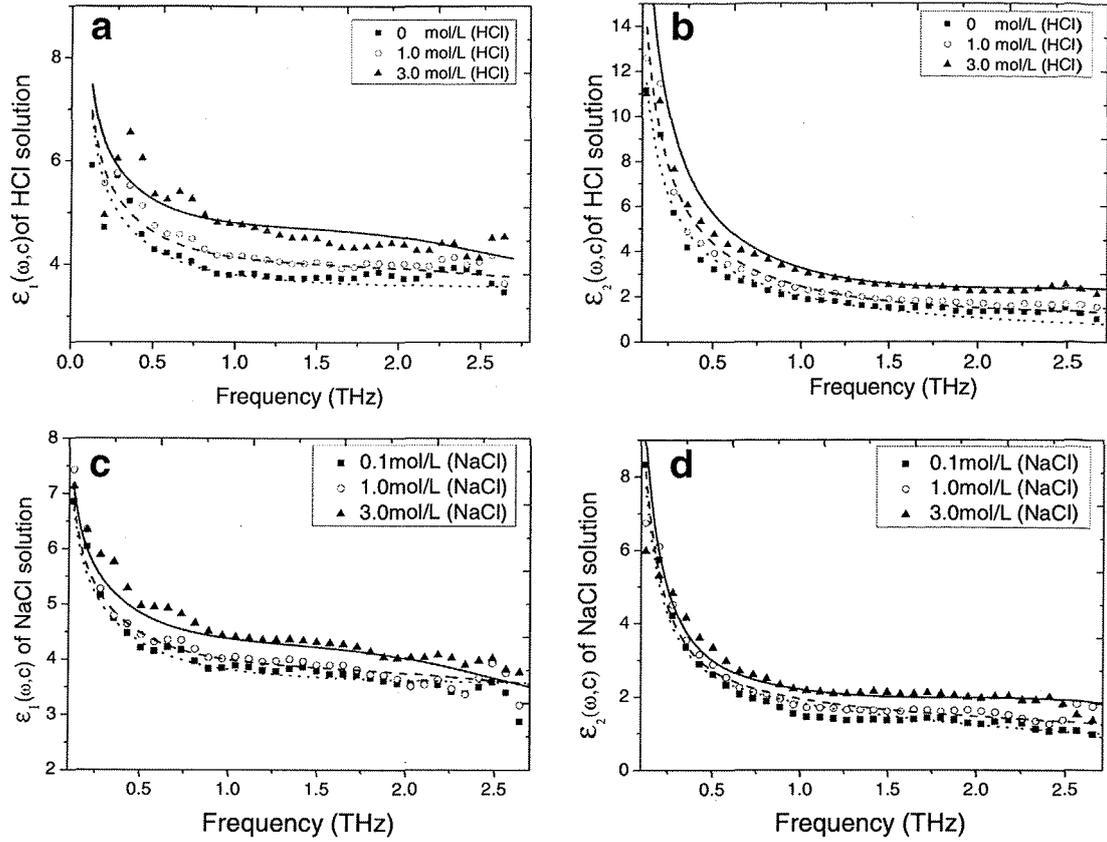


Fig. 8 (a), (b) real and imaginary part of dielectric constant $\epsilon_1(\omega,c), \epsilon_2(\omega,c)$ of HCl solutions for different concentration, with data measured (points) and theoretical fits (solid line for 3.0 mol/L, dashed line for 1.0 mol/L and dotted line for water), (c) and (d) for the NaCl solutions (dotted line for 0.1 mol/L).

that in NaCl solution the increase of dielectric constant is mainly caused by the contributions from chloride ions. The contribution of hydroniums has the same value scale as the contribution from the chloride ions. This is expected because of the much stronger interactions with surrounding water molecules.

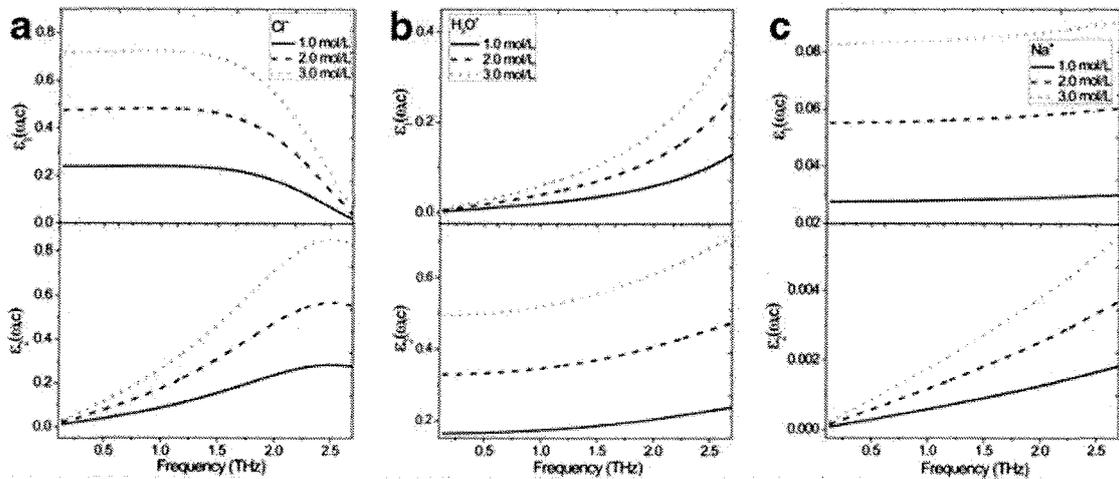


Fig. 9 Ions contributions to the real and imaginary part of dielectric constant $\epsilon_1(\omega,c), \epsilon_2(\omega,c)$ in corresponding solutions. (a), (b) and (c) are chloride ions, hydronium, and sodium ions, respectively. (solid line for 1.0 mol/L, dashed line for 2.0 mol/L and dotted line for 3.0 mol/L).

In the NaCl solution, anions and cations can be certainly described as damped harmonic oscillators in the cage, as they do affect less the dynamics of hydrogen bonds of surrounding water molecules [14]. However, circumstances are different in the HCl solutions. The proton (H^+) can form a covalent bond with a water molecule turning to be hydronium (H_3O^+) which can also form hydrogen bonds with surrounding water molecules and reorient the dipoles of water molecules further due to the induced electric field. This gives a much stronger effect to the relaxation of water molecules and causes the value of the dielectric function of HCl solution to be much larger than NaCl with the same concentration (Fig. 7). It is assumed that the protonic charge is transferred from the hydronium to the surrounding molecules by rearrangement of covalent and hydrogen bonds, thus resulting in σ_{ic} of HCl solution much higher than σ_{ic} of NaCl solution under the same concentration [10, 12].

Although the hydronium changes the hydrogen bond network, it is assumed that the effect to surrounding water molecules gets weaker at increased distance. Hydrogen bonds are formed and broken on picosecond time scales in the water network, hence the configuration of surrounding water molecules around the hydronium is assumed to remain constant. Therefore we can still treat the system as damped harmonic oscillators. The relevant arrangement of protons in water solution is still under debate: It has been proposed that the most relevant configuration is either as hydronium (H_3O^+) as Zundel cation ($H_5O_2^+$) or Eigen cation ($H_9O_4^+$) and more [10, 12]. In our model of damped harmonic oscillators we used the hydronium configuration. The force constant k_C of hydronium due to the interaction with surrounding water molecules is quite different from that of sodium ions due to the difference of the covalent and hydrogen bonds. The main parameters for fitting the model to the experimental data are the mass, the force constant k_C and the electrical conductivity σ_{ic} . Best results are obtained by setting the hydronium mass $m_c=19.02$, and force constant $k_C=10.6$, and the electrical conductivity $\sigma_{ic}=19.4$ for HCl.

Summarizing our experimental results and the theoretic analysis, we conclude that for acid and salts water solutions, the THz complex dielectric constant can be described as a linear supposition of contributions of bulk water and ionic oscillations in a water cage defined by the solvating water as well as induced electrical conductivity. A linear increase of the dielectric function compared with pure water with increasing ion concentrations is verified by both the experiment and theoretic analysis. Within this model hydroniums can also be described as damped harmonic oscillators with compensated fitting parameters although they are associated with more complex dynamics compared to other positive ions.

4 Conclusion

We have performed measurement of HCl and NaCl solutions with different concentrations at room temperature in the range from 0.1 THz to 2.7 THz using an ASOPS based Terahertz time-domain reflection spectroscopy set up. A model based on the Debye model as well as damped harmonic oscillators for the ions was developed and the obtained fits are in good agreement with the complex dielectric constant of the solutions. Our system provides a useful method to study the dynamics of aqueous solutions for different concentrations, temperatures *etc.*

Acknowledgments The authors acknowledge financial support by the Center for Applied Photonics (CAP) and China Scholarship Council (CSC). We also thank M. Bonn, H. J. Bakker, and M. Havenith for fruitful discussions. KY acknowledged the Alexander-von Humboldt foundation for support.

References

1. L. Thrane, R. H. Jacobsen, P. Uhd Jepsen, and S. R. Keiding, "THz reflection spectroscopy of liquid water," *Chemical Physics Letters* **240**, 330 (1995).
2. Cecilie Rønne, Lars Thrane, Per-Olof Åstrand, Anders Wallqvist, Kurt V. Mikkelsen, and Søren R. Keiding, "Investigation of the temperature dependence of dielectric relaxation in liquid water by THz reflection spectroscopy and molecular dynamics simulation", *J. Chem. Phys.* **107**, 5319 (1997).
3. Cecilie Rønne, Per-Olof Åstrand, and Søren R. Keiding, "THz-Spectroscopy of H₂O(l) and D₂O(l)", *Phys. Rev. Letters*. **82**, 2888 (1999).
4. C. Rønne and S. R. Keiding, "Low frequency spectroscopy of liquid water using THz-time domain spectroscopy," *J. Mol. Liq.* **101**, 199 (2002).
5. Peter Uhd Jepsen, Uffe Møller, and Hannes Merbold, "Investigation of aqueous alcohol and sugar solutions with reflection terahertz time-domain spectroscopy," *Opt. Express* **15**, 14717 (2007)
6. Hideki Hirori, Kumiko Yamashita, Masaya Nagai and Koichiro Tanaka, "Attenuated Total Reflection Spectroscopy in Time Domain Using Terahertz Coherent Pulses", *Jpn. J. Appl. Phys.* **43**, 1287 (2004).
7. M. Nagai, H. Yada, T. Arikawa, K. Tanaka, "Terahertz Time-Domain Attenuated Total Reflection Spectroscopy in water and biological solution", *Int. J. IRMMW.* **27**, 505 (2006)
8. H. Yada, M. Nagai, and K. Tanaka, "Origin of the fast relaxation component of water and heavy water revealed by terahertz time-domain attenuated total reflection spectroscopy", *Chemical Physics Letters* **464**, 166 (2008).
9. H. Yada, M. Nagai, and K. Tanaka, "The intermolecular stretching vibration mode in water isotopes investigated with broadband terahertz time-domain spectroscopy", *Chemical Physics Letters* **473**, 279 (2009).
10. K.J. Tielrooij, R.L.A. Timmer, H.J. Bakker and M. Bonn, "Structure dynamics of the proton in liquid water probed with terahertz time-domain spectroscopy", *Phys. Rev. Lett.*, **102**.198303 (2009).
11. K.J. Tielrooij, N. Garcia-Araez, M. Bonn and H.J. Bakker, "Cooperativity in ion hydration", *Science*, **328**. 1006 (2010).
12. J.M.J. Swanson, C.M. Maupin, H.N. Chen, M.K. Petersen, J.C. Xu, Y.J. Wu, and G.A. Voth. "Proton solvation and transport in aqueous and biomolecular systems: Insights from computer simulations", *J. Phys. Chem. B*, **111**. 4300 (2007).
13. de Grothuss, C.J.T.. "Sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique". *Ann. Chim.* **58**, 54 (1806).
14. Diedrich. A. Schmidt, Özgür Birer, Stefan Funkner, and Martina Havenith. "Rattling in the cage: Ions as probes of sub-picosecond water network dynamics", *J.AM.CHEM.SOC.***131**, 18512 (2009).
15. A. Botti, F. Bruni, S. Imberti, and M. A. Ricci, "Ions in water: The microscopic structure of a concentrated HCl solution", *Journal of Chemical Physics.* **121**, 7840 (2004).
16. C. Lee, C. Sosa, M. Planas, and J. J. Novoa, "A theoretical study of the ionic dissociation of HF, HCl, and H₂S in water clusters", *J. Chem. Phys.* **104**, 7081 (1996).
17. R. Triolo and A. H. Narten, "Diffraction pattern and structure of aqueous hydrochloric acid solutions at 20 °C", *J. Chem. Phys.* **63**, 3624 (1975).
18. Peter Uhd Jepsen and Hannes Merbold, "Terahertz reflection spectroscopy of aqueous NaCl and LiCl solutions," *J Infrared Milli Terahz Waves*, **31**, 430 (2010)
19. J. T. Kindt and C. A. Schmittenmaer, "Far-infrared dielectric properties of polar liquids probed by femtosecond terahertz pulse spectroscopy", *J. Phys. Chem.* **100**, 10373 (1996).
20. U. Møller, D. G. Cooke, K. Tanaka, and P. Uhd Jepsen, "Terahertz reflection spectroscopy of Debye relaxation in polar liquids," *Journal of the Optical Society of America B* **19**, A113 (2009).
21. Mattijs Koeberg, Chien-Ching Wu, Doseok Kim and Mischa Bonn, "THz dielectric relaxation of ionic liquid:water mixtures," *Chemical Physics Letters* **439**. 60 (2007).
22. Taro Dodo, Masao Sugawa, Eiji Nonaka, and Hiroshi Honda, "Absorption of far-infrared radiation by alkali halide aqueous solutions," *J.Chem.Phy.*,**102**, 6208 (1995).
23. Bartels, A., Cerna, R., Kistner, C., Thoma, A., Hudert, F., Janke, C., and T. Dekorsy, "Ultrafast time-domain spectroscopy based on high-speed asynchronous optical sampling," *Rev. Sci. Instrum.*, **78**, 035107 (2007).
24. A. Dreyhaupt, S. Winnerl, T. Dekorsy and M. Helm, "High-Intensity Terahertz radiation from a micro-structured large-area photoconductor," *Applied Physics Letters* **86**, 121114 (2005)
25. M. N. Afsar and J. B. Hasted, "Measurements of optical-constants of liquid H₂O and D₂O between 6 and 450 cm⁻¹", *J. Opt. Soc.Am.* **67**, 902 (1977)
26. Mark Fox, "Optical Properties of Solid", pp. 29–32 (Oxford, New York 2001)