The vibrational studies on the water channel in LiTFSI aqueous electrolyte system

Joonhyung Lim[1,2], Kwanghee Park[1], Hochan Lee[1], Jungyu Kim[1,2], Kyungwon Kwak[1,2] and Minhaeng Cho[1,2]

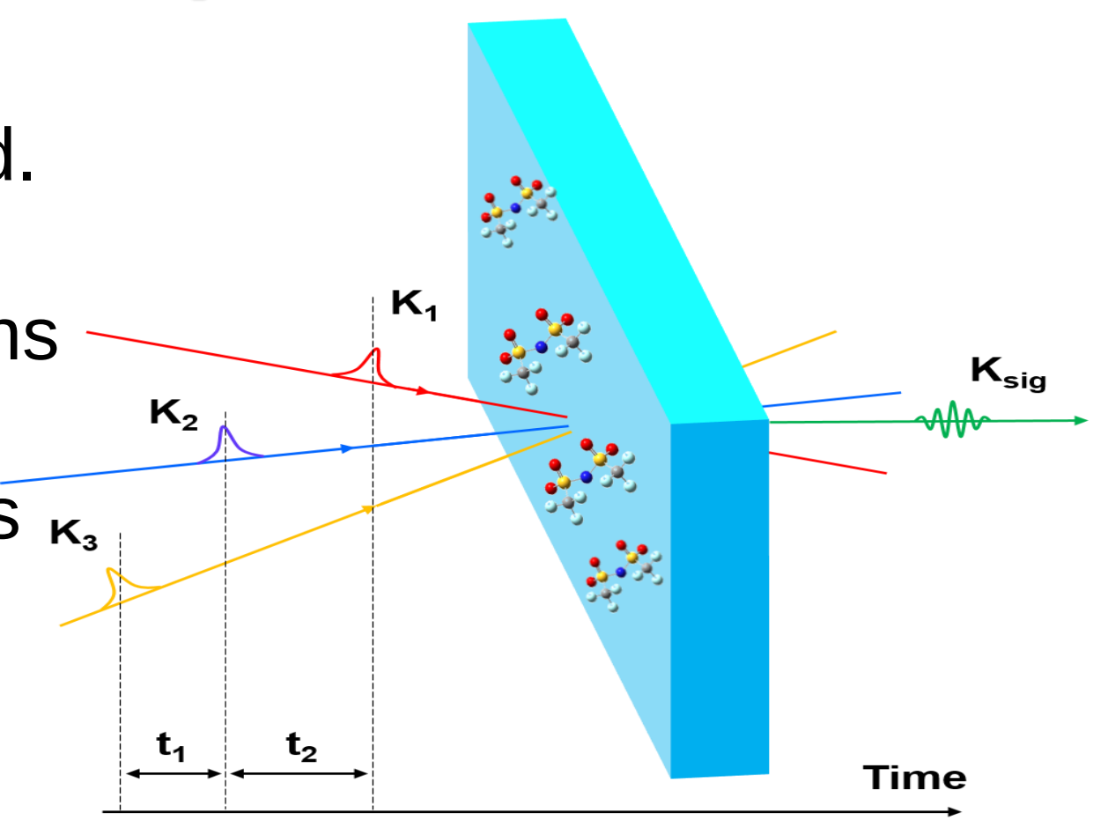
1. Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, Republic of Korea,

2. Department of Chemistry, Korea University, Seoul 02841, Republic of Korea, Email:kmno0831@korea.ac.kr

Abstract

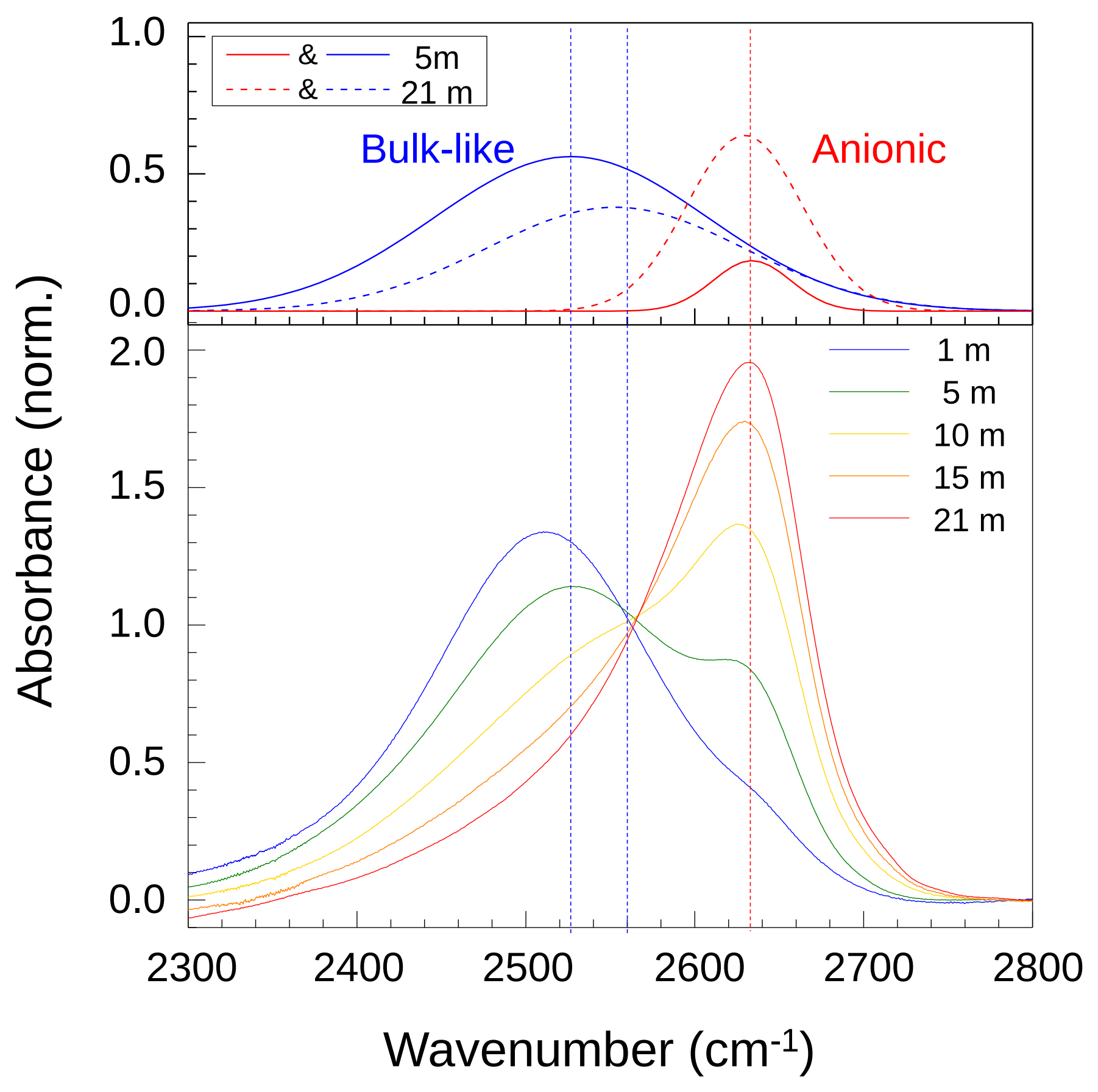
The highly concentrated LiTFSI (Lithium bis(trifluoromethanesulfonyl)imide) aqueous electrolyte overcome the electrochemical stability limit of water (1.23 V) with the formation of LiF-based SEI. This noble electrochemical property presents the possibility of aqueous electrolyte as a replacement for nonaqueous electrolytes currently used. Many studies have focused on the electrochemical properties (i.e. formation of SEI) and there is a lack of research on how Li ions can transport rapidly in highly viscous enviroment. In here, we have investigated the role of water to transport Li$^+$ in highly viscous condition. Linear IR, PSPP, and 2D-IR were performed on various concentrations of electrolyte. The results of time-resolved IR experiment revealed that a considerable amount of water exhibited bulk-like properties, indicating the existence of a water channel in the electrolyte. Furthermore the interfacial water, located between water and TFSI$^-$ domain, were also observed. With PSPP and 2D-IR, the anionic water acts as a lubricant to prevent electrostatic drag resulting in the fast transport of Li ion. Moreover, MD simulations of LiTFSI solutions were performed to gain a deeper insight into morphological aspects of both water H-bonding networks and ion aggregates. The the water channel and TFSI- domain were observed by MD simulation and movement of Li cation in water channel shows fast diffusional properties, emphasizing the importance of water domain to transport the Li cation.

Experimental scheme



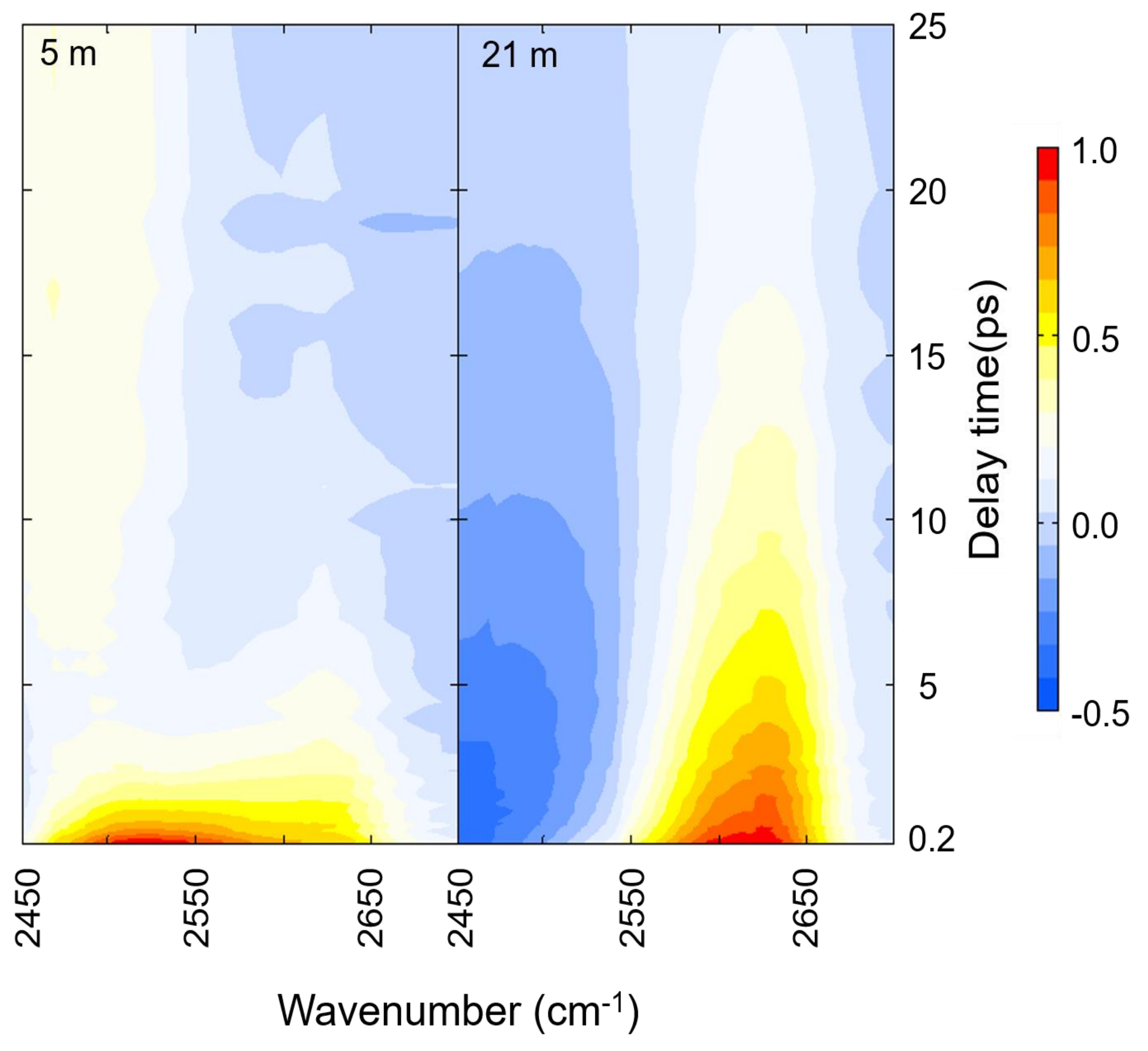
Experimental results

FT-IR spectra

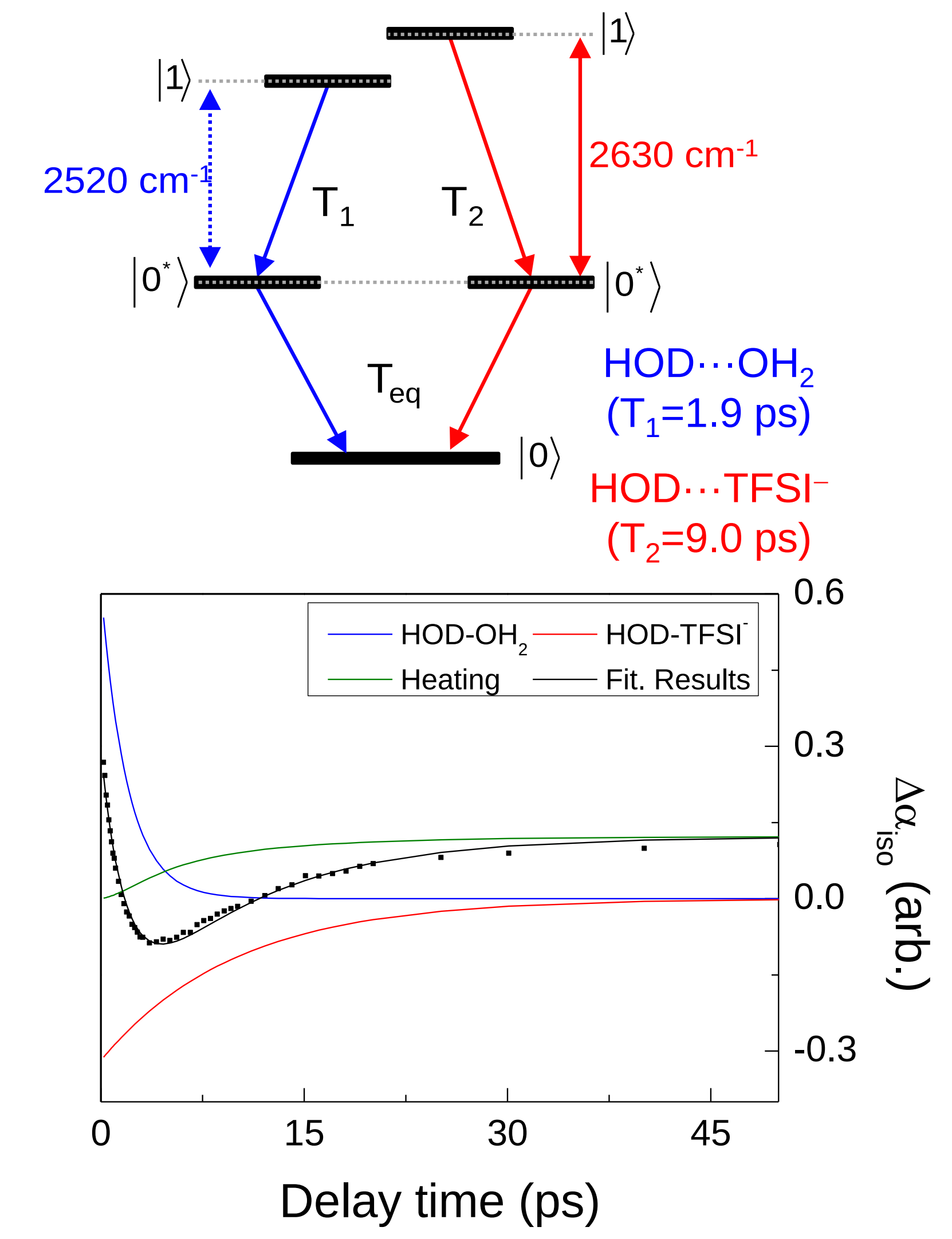


FT-IR spectra of OD stretches in various concentrated LiTFSI aqueous electrolyte (1~21 m, lower pannel) and Gaussian fitting results (5 and 21 m, upper pannel).

IR PP spectra

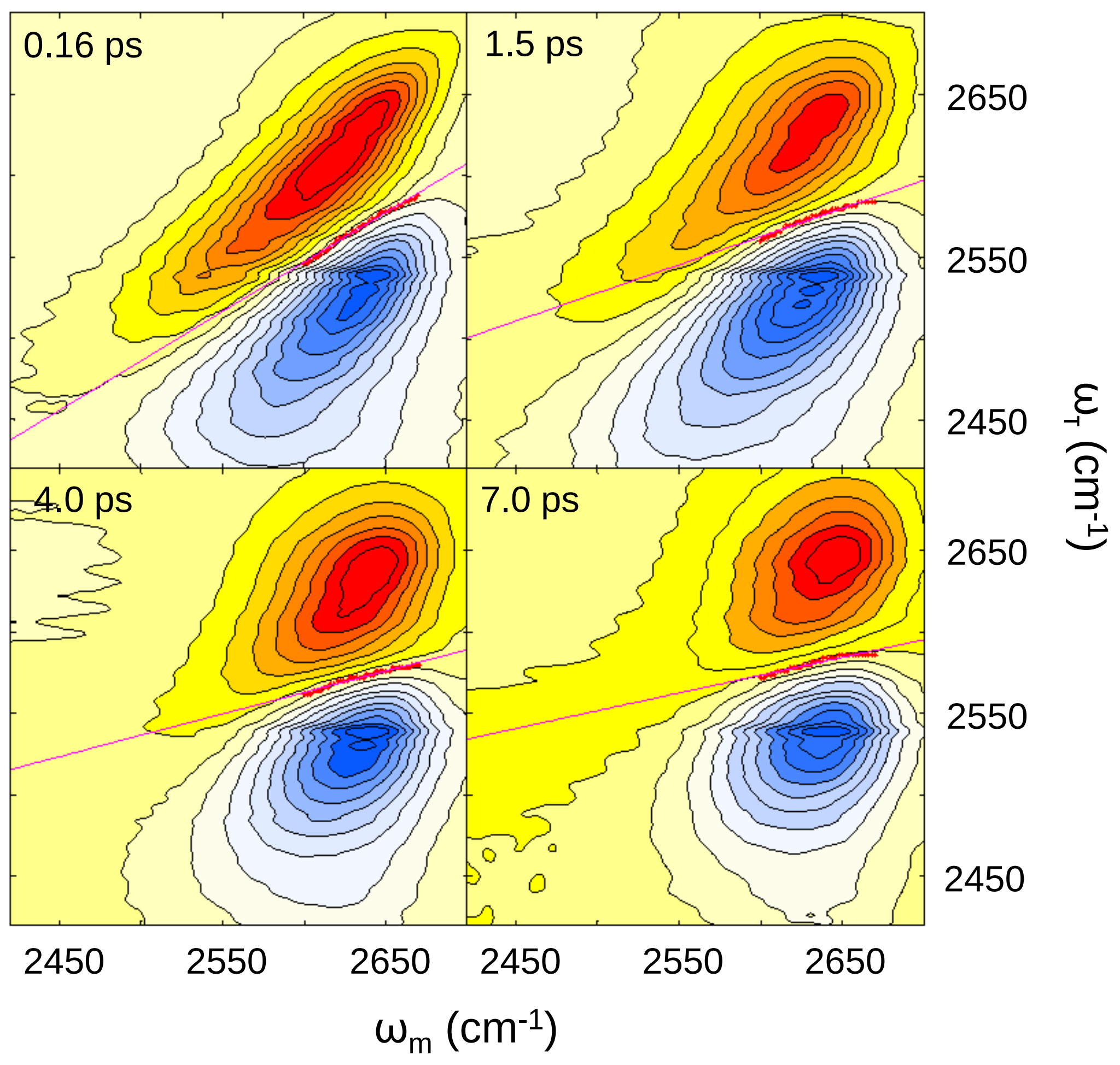


The contour plot of isotropic signal of various concentrated LiTFSI aqueous electrolyte (5 and 21 m) from 0.2 ps to 25 ps.



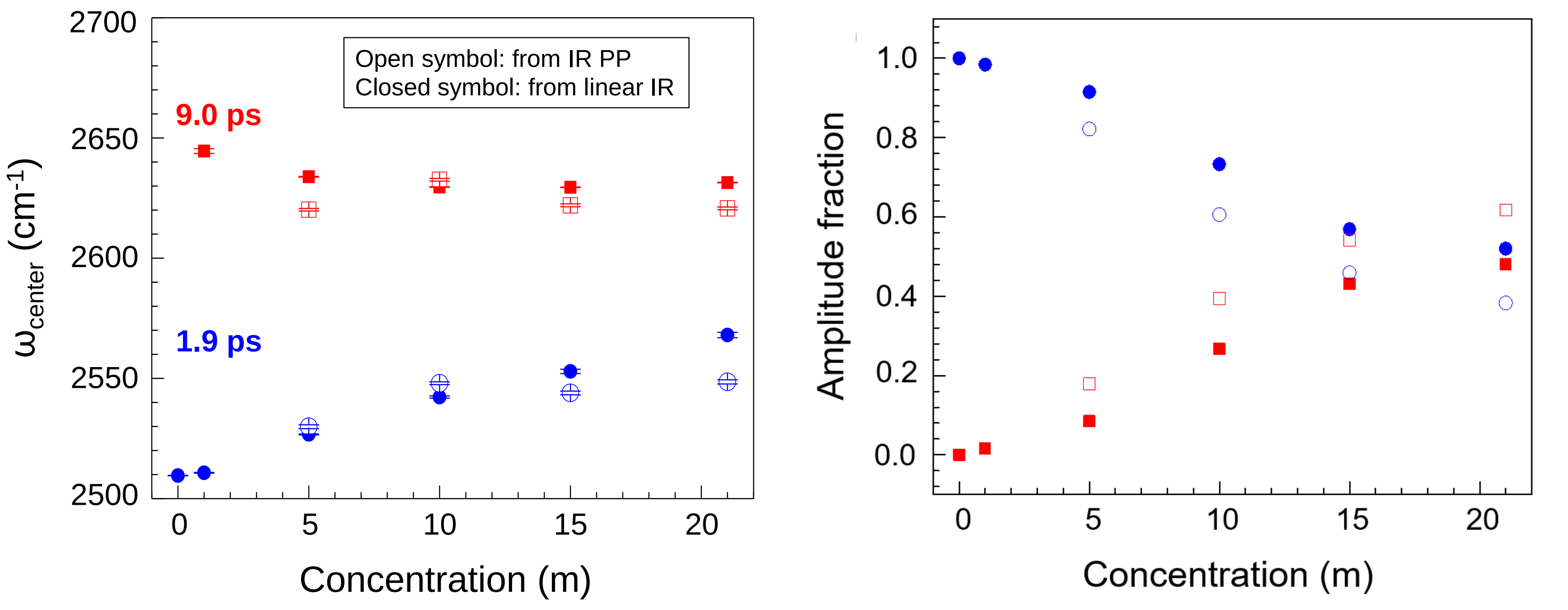
Scheme of global fit to remove the induced heating effect on the isotropic signal and results of fitting w/ Bakker's model (J. Chem. Phys. 125, 144512 (2006))

2D IR spectra

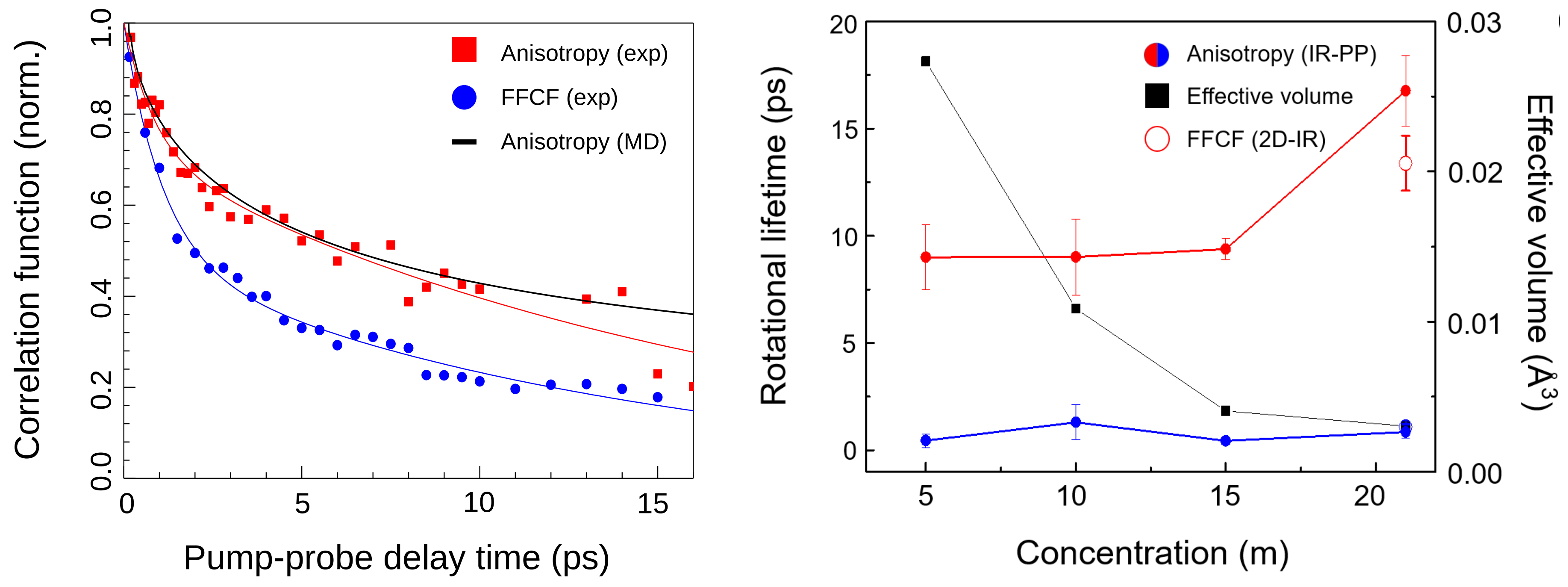


2D-IR spectra of 21 m LiTFSI aqueous electrolyte at four representative T_w and corresponding nodal line (related with the FFCF)

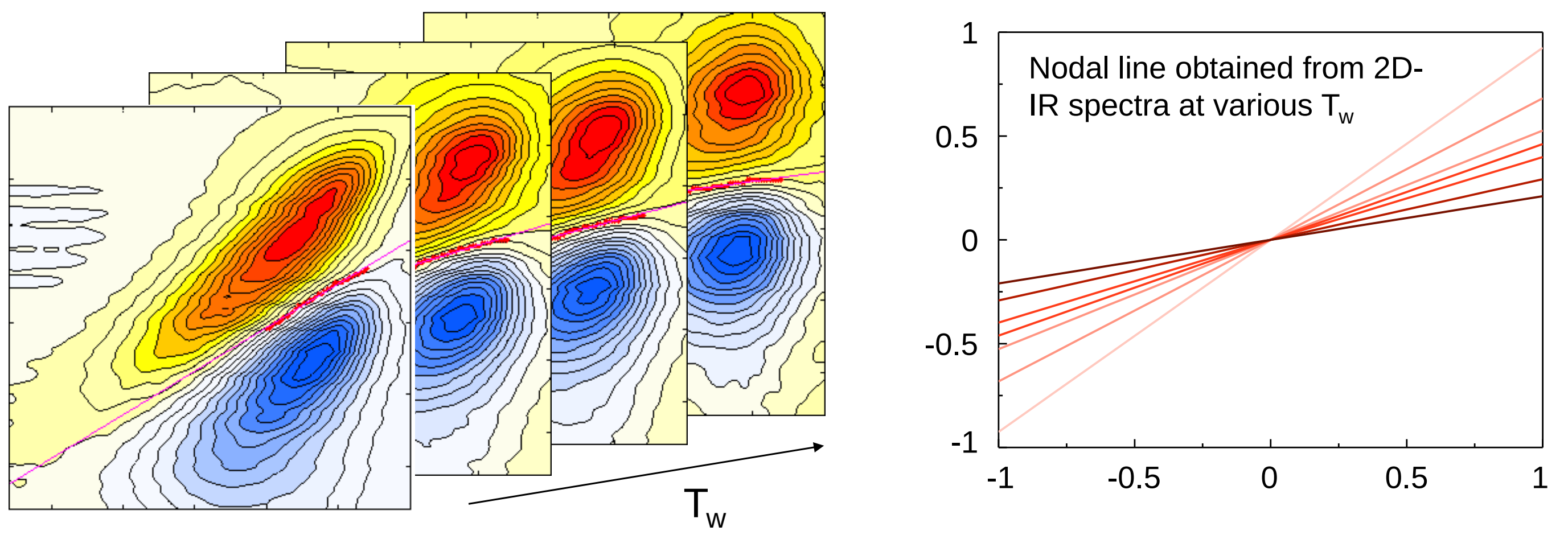
Analysis



(Left) Center peak frequency and (Right) amplitude fraction of water species
Both information was obtained by Gaussian fit on FT-IR and isotropic signal at several concentration (5~21 m).



(Left) Rotational (anisotropy, PSPP) and spectral diffusion (FFCF, 2D-IR) correlation function and (Right) rotational decaying constant and corresponding effective volume of water in ionic system.



Debey-Stokes-Einstein relation

$$\tau_D = \left[\frac{k_B T}{V_{eff}\eta}\right]$$

Anisotropy

$$R(t) = 0.4C_2(t) = \left[\frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{3P(t)}\right]$$

MD simulation

MD simulation method

- ✓ Various LiTFSI moleculse(1, 5, 10, 15, 21 m) was dissolved in 1000 H_2O molecules
- ✓ Energy minimization (steepest & conjugate gradient method)
- ✓ NTP equilibration(10 ns)
- ✓ NVT equilibration(200 ns)
- ✓ Production NVT MD (800 ns) cutoff = 10 Å / at T = 298 K, P = 1 atm

QM calculation

- ✓ Atomic charges of the two ions are the restrained electrostatic potential (RESP) charges obtained by carrying out B3LYP/6-311++G(3df, 2pd) calculations with Gaussian 09 program.

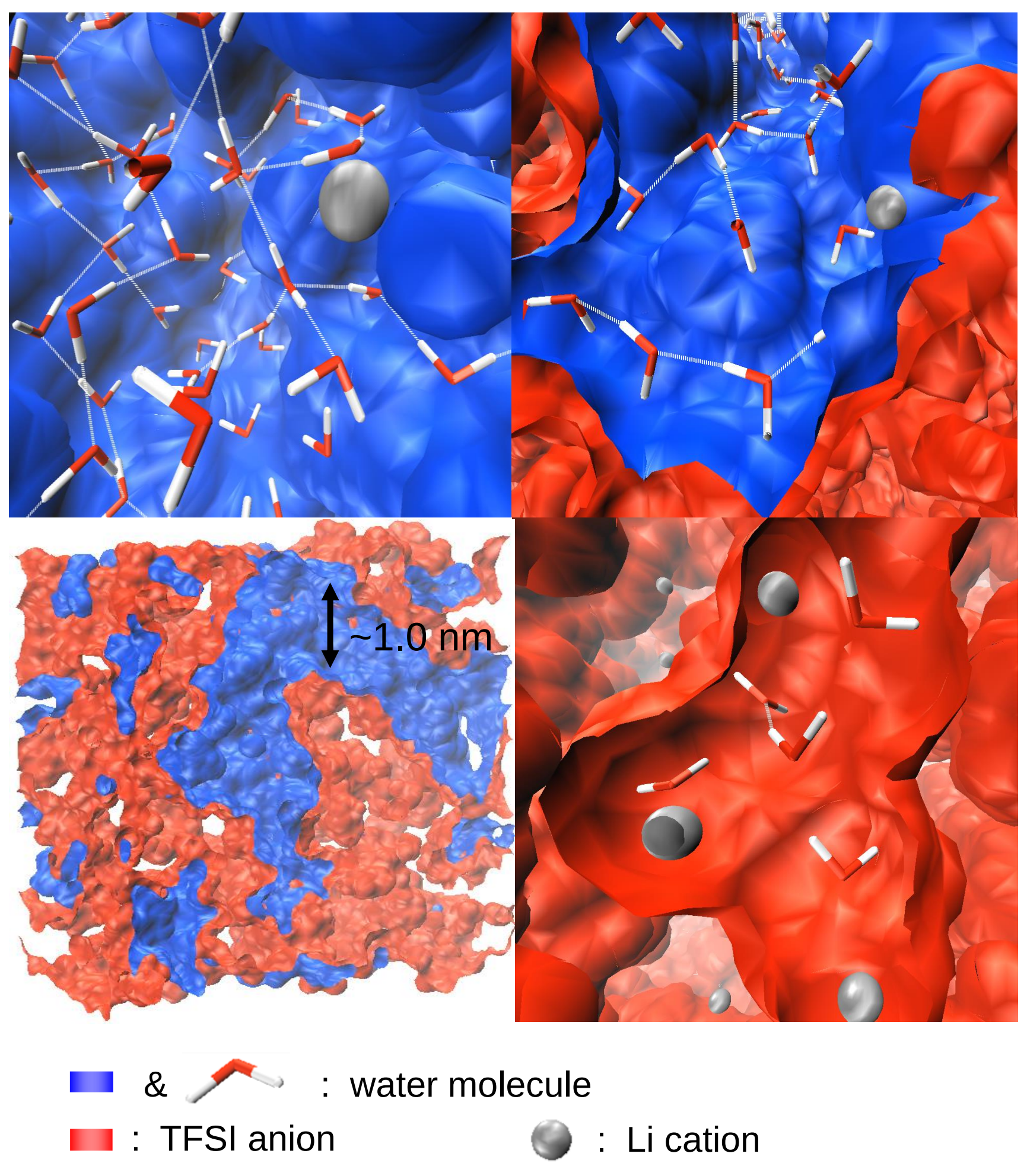
Conc. (m)	D (10^{-10} m²/s) Simulation	D Experiment		k (mS/cm) Simulation	k Experiment
5	5.04	3.21[a]	4.12[b]	69.00	49.2
10	2.21	1.67[a]	2.27[b]	33.80	32.9
15	0.96	1.08[a]	1.15[b]	-	-
21	0.35	0.394[a]	0.52[b]	6.40	8.2

[A] 20 °C; [b] 30 °C

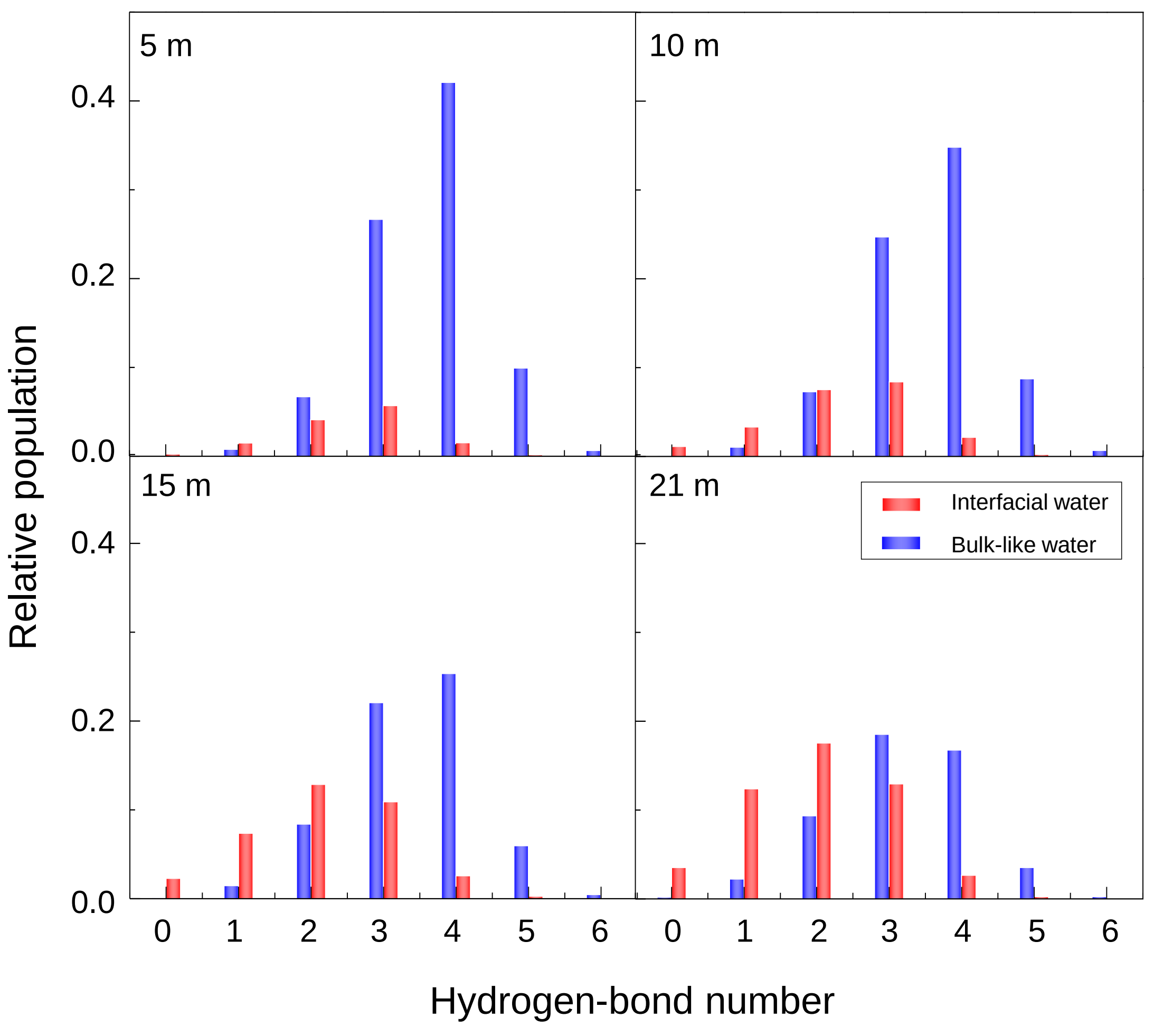
$$D = \lim_{t\to\infty}\frac{1}{6}\sum_{i=1}^{N}\frac{t}{dt} < [R_i(t) - R_i(0)]^2 >$$

D : Diffusion coefficient
κ : Ion conductivity

$$\kappa = \lim_{t\to\infty}\frac{e^2}{6tkBVT}\sum_{i,j=1}^{N} z_i z_j < [R_i(t) - R_i(0)] >< [R_j(t) - R_j(0)] >$$

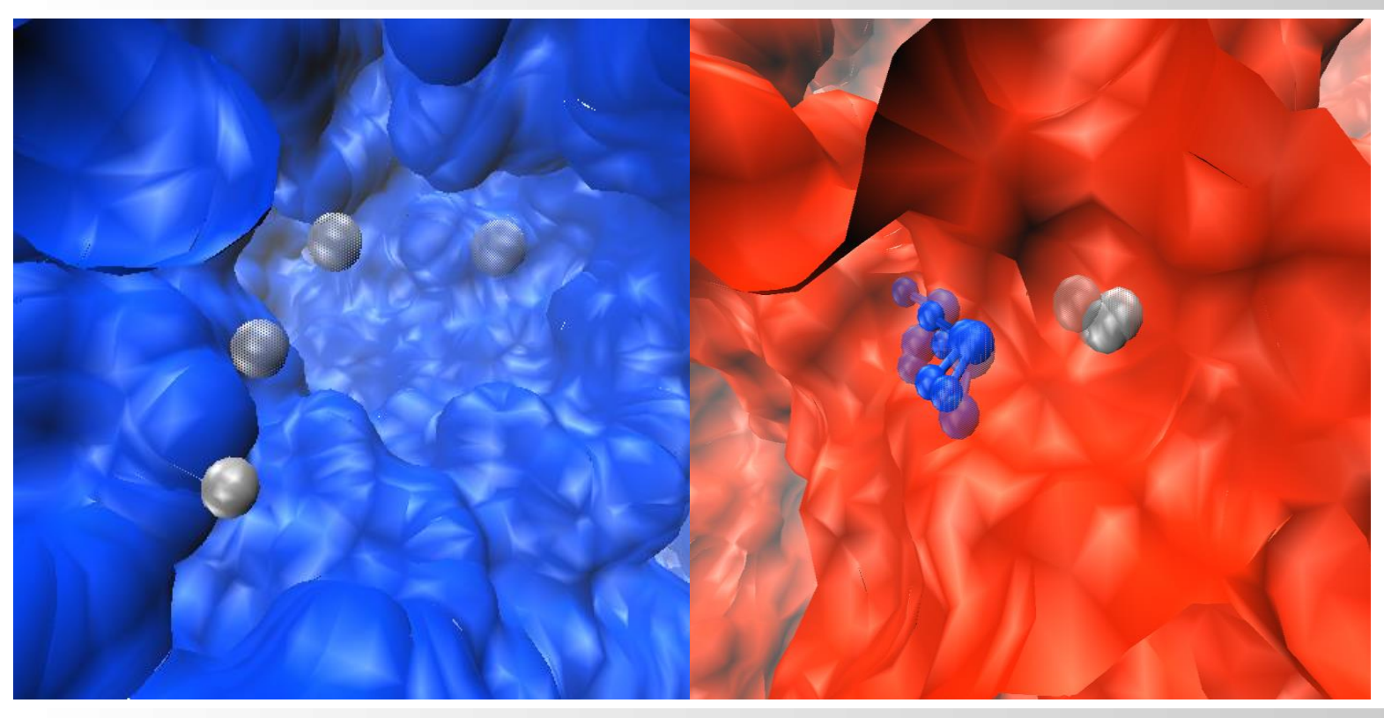


MD snapshot of 21 m LiTFSI aqueous solution. (In clockwise) water channel, interface, anionic domain and whole shot.



Histogram of H-bond number per water molecule and relative population of bulk-like water and interfacial water molecules

Discussion & Conclusion



- ✓ With the local sensitivity of OD stretch, it was revealed that the substantial amount of water still remained as 'bulk-like' water even at 21 m concentrated LiTFSI aqueous electrolyte.
- ✓ The anisotropy(rotational dynamics) and 2D-IR spectra figured out there are two rotational relaxation pathway; one is wobbling-in-a cone (the rotation of OD is restricted in cone) and the jump rotation of OD to another S=O functional group.
- ✓ With MD simulation, the bulk-like water is expected to plays important role to transport the Li$^+$ ion and anionic water will be the lubricant for transporting the Li cation by preventing the direct coulombic interaction between Li cation and TFSI anion.

This work was supported by the Institute for Basic Science (IBS) R023-D1