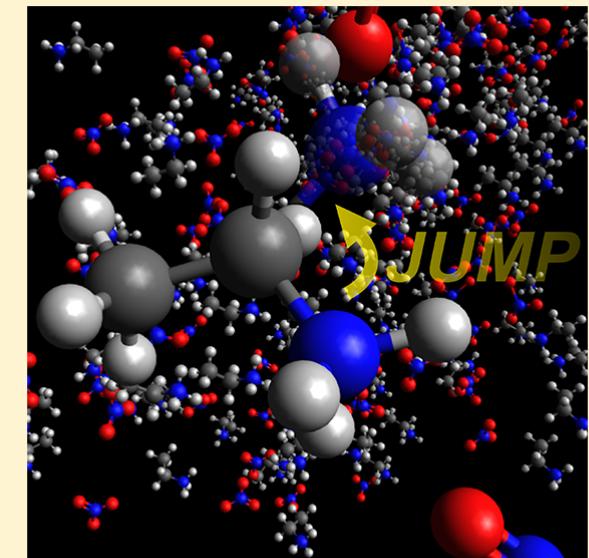


# Hydrogen-Bond Dynamics in a Protic Ionic Liquid: Evidence of Large-Angle Jumps

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**ABSTRACT:** We study the molecular rotation of the protic room-temperature ionic liquid ethylammonium nitrate with dielectric relaxation spectroscopy and femtosecond-infrared spectroscopy (fs-IR) of the ammonium N–H vibrations. The results suggest that the rotation of ethylammonium ion takes place via large angular jumps. Such nondiffusive reorientational dynamics is unique to strongly hydrogen-bonded liquids such as water and indicates that the intermolecular interaction is highly directional in this class of ionic liquids.

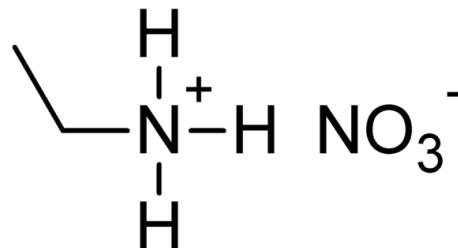


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**SECTION:** Spectroscopy, Photochemistry, and Excited States

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# Motivation : Why do they want to show the jump of protic ILs?



Ethylammonium nitrate (EAN)

$[\text{C}_2\text{H}_5\text{NH}_3][\text{NO}_3]$

: first reported RTIL (Walden, *Bull. Acad. Imp. Sci. St-Petersbourg* (1914))

Brønsted Acid & Base Pair : when an acid and a base react with each other, the acid forms its conjugate base, and the base forms its conjugate acid by **exchange of a proton**.

- Promote the aggregation of amphiphilic molecules ([Chem. Rev. 2008](#))
- Extraordinary high charge mobility ([Acc. Chem. Res. 2007](#))
- Dissolve protein and enzymes ([Curr. Opin. Biotechnol. 2002](#))

Directional interionic interaction was not measured yet

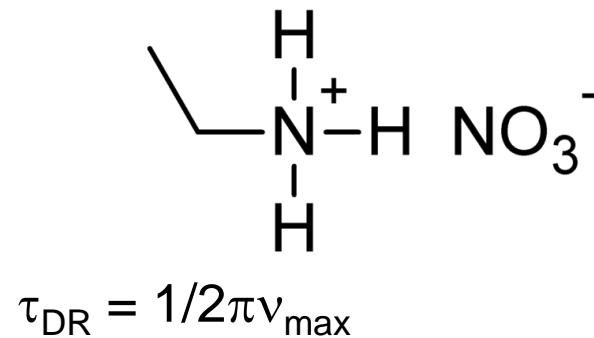
→ Jump-like molecular reorientation need to be observed like water

([Chem. Rev. 1993](#), [Science 2006](#))

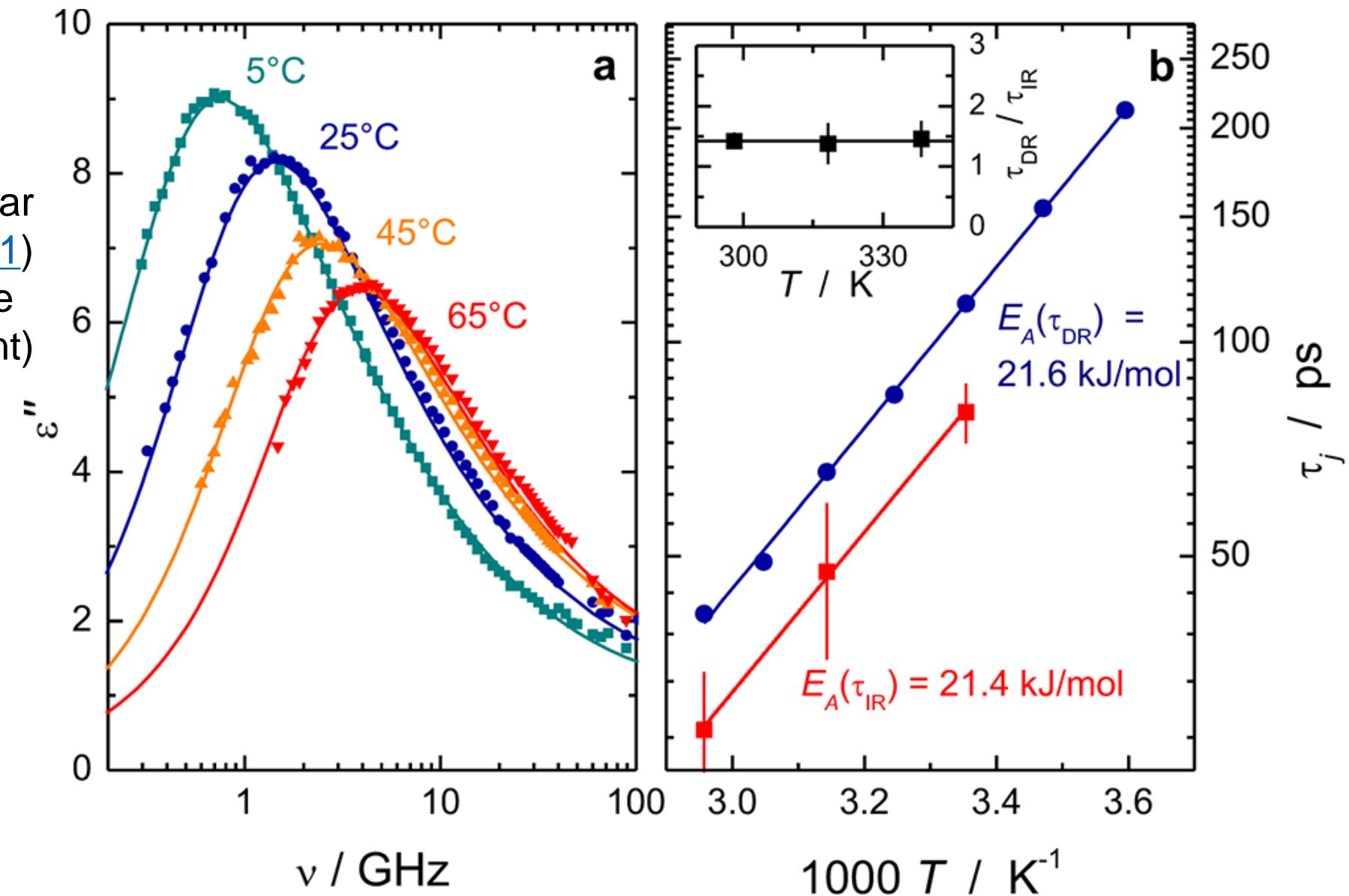
# Dielectric Spectroscopy

$\epsilon''$  : absorptive term  
in dielectric spectrum

- Rotation motion of dipolar ions for PIL ([PCCP 2011](#))
- $\text{NO}_3^-$  does not contribute (zero net dipole moment)

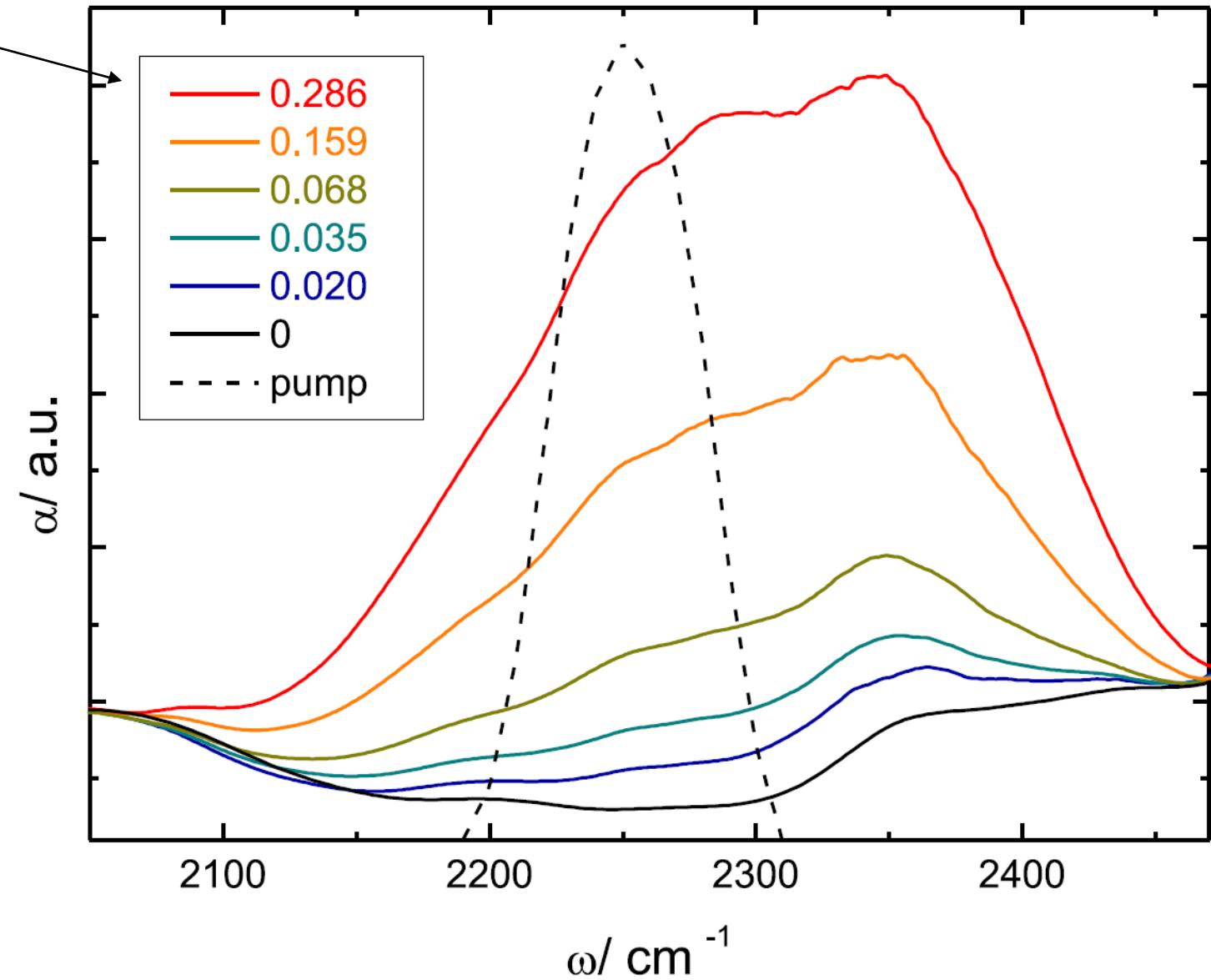
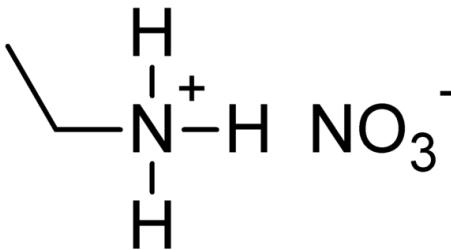


$$\tau_{\text{DR}} = 1/2\pi\nu_{\text{max}}$$

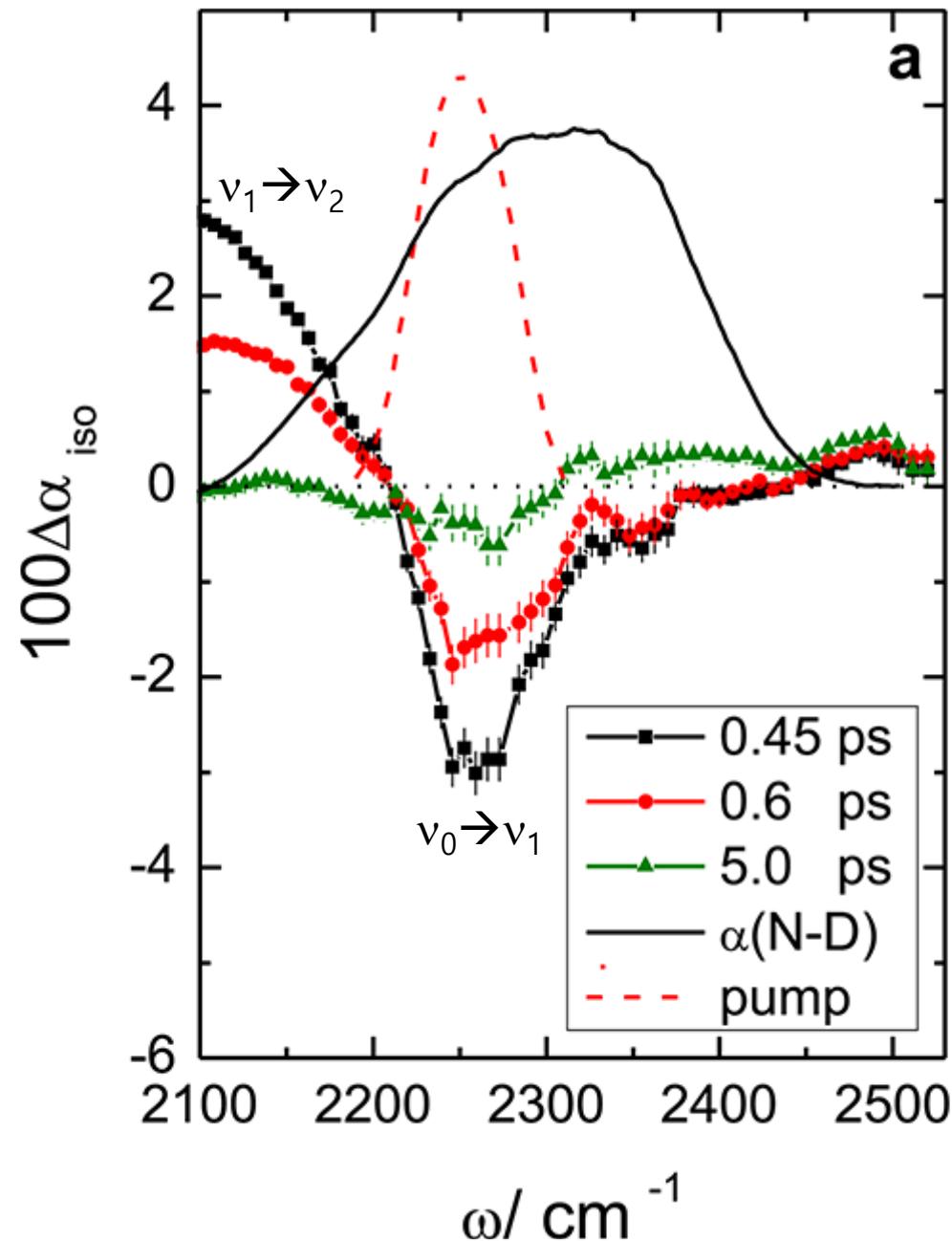


# IR Absorption Spectra

Isotopic Exchange Ratio  
 $[C_2H_5NH_{3-x}D_x][NO_3]$

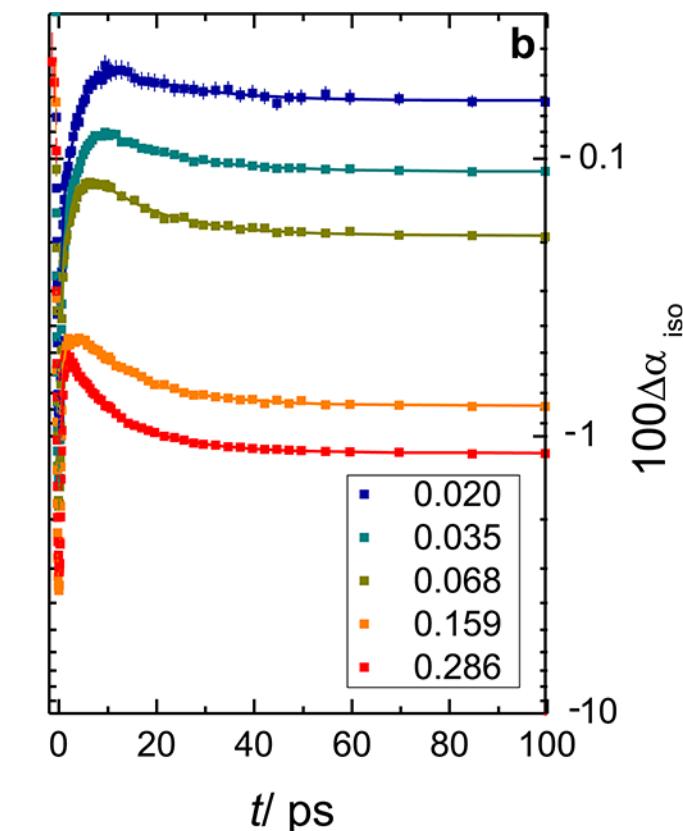


# IR Pump-Probe Experiments

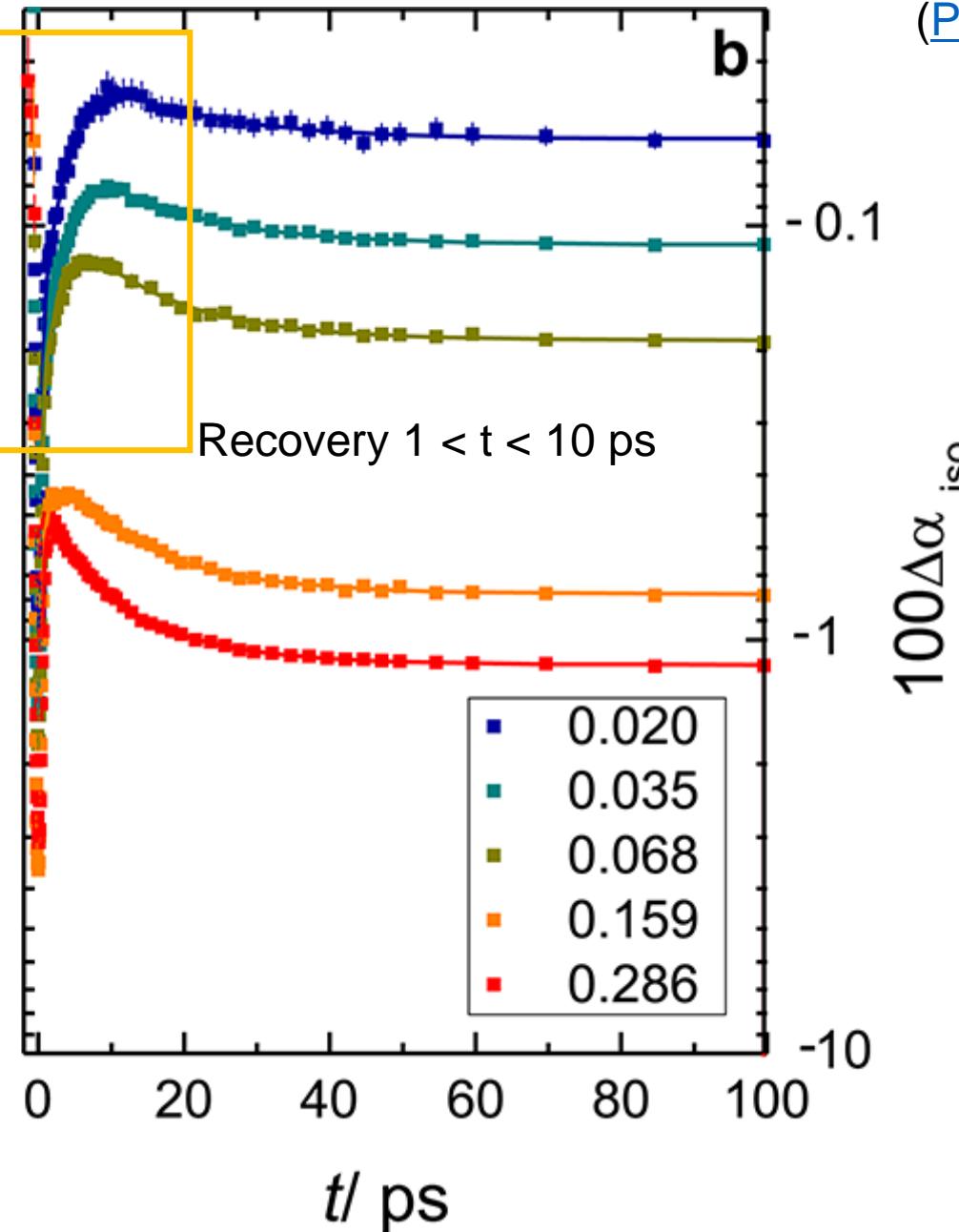


The bandwidth of bleach does not broaden significantly ( $t < 1 \text{ ps}$ )  
→ No spectral diffusion  
→ Heterogeneous & quasi-static local structures of EAN

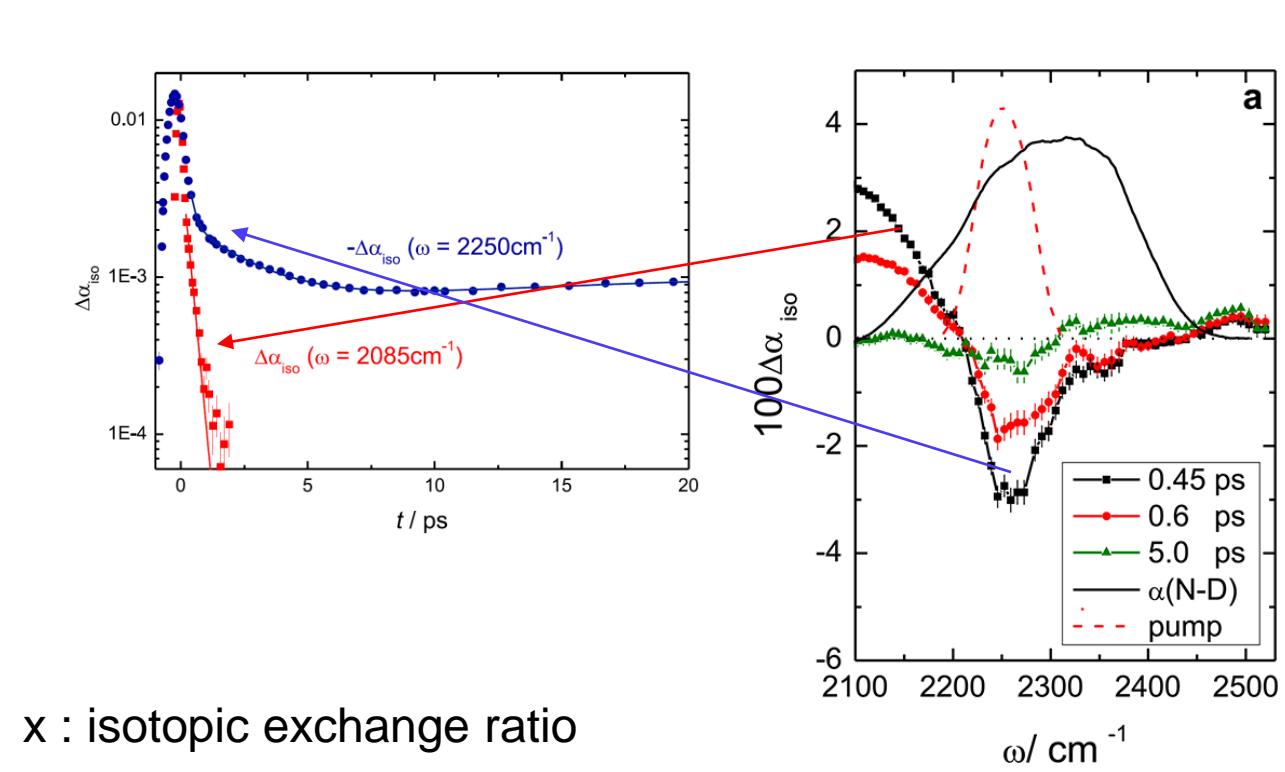
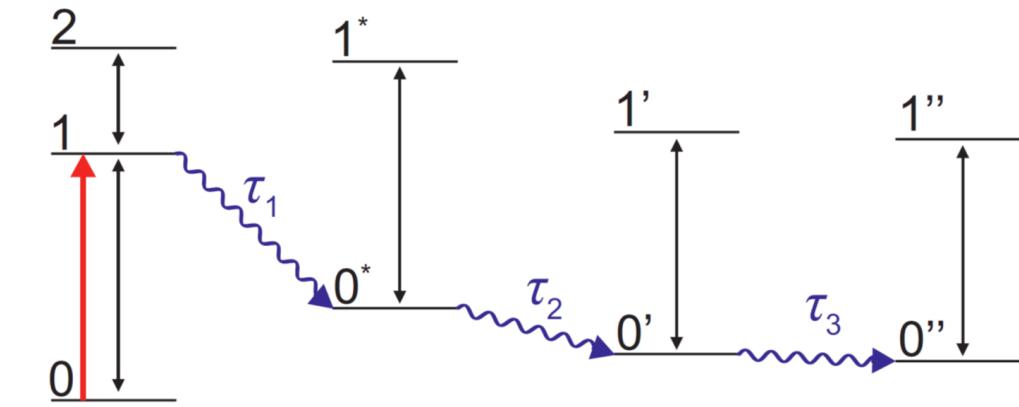
$$\tau_1 = (200 \pm 40) \text{ fs} : \text{independent of temperature/x}$$



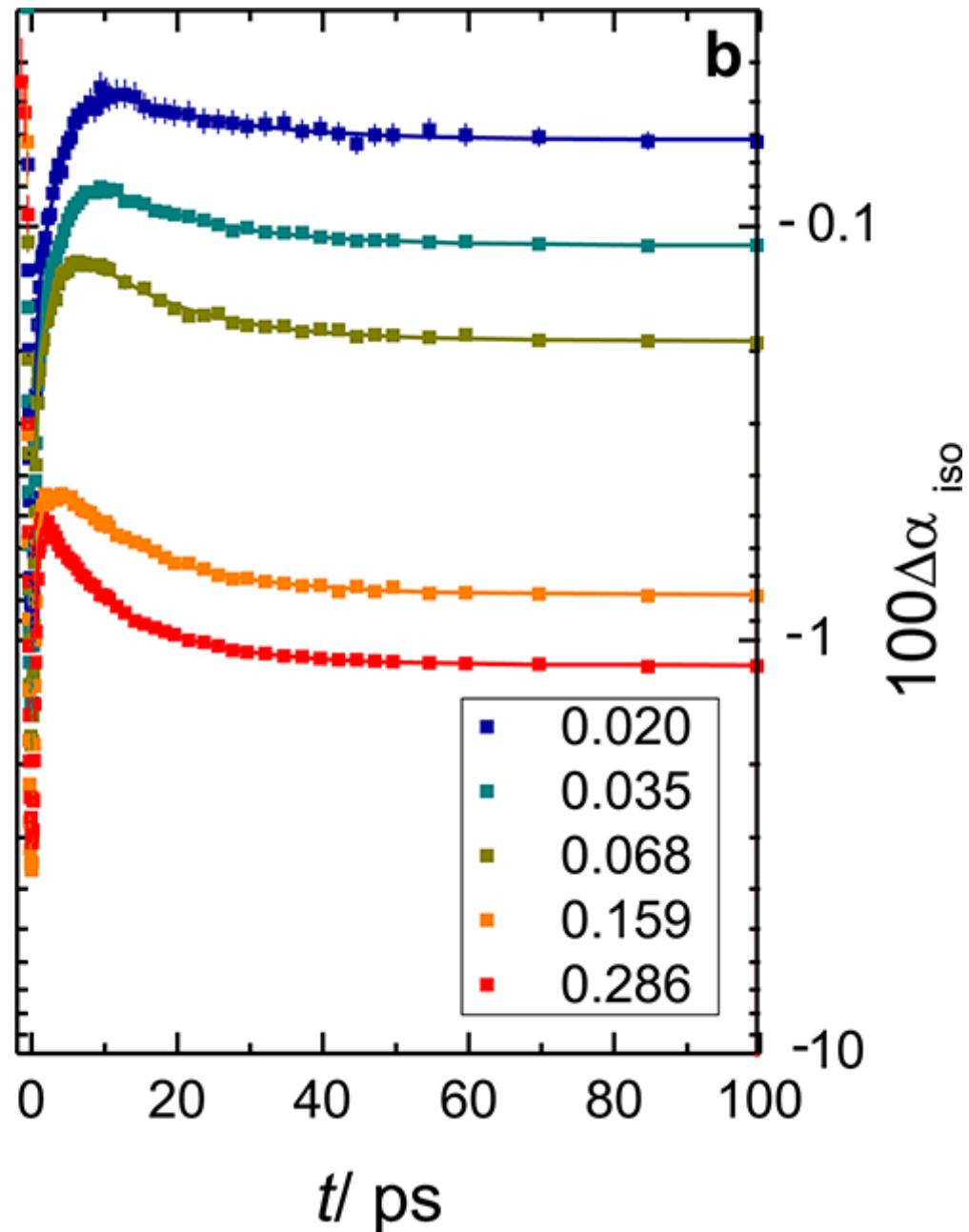
# IR Pump-Probe Experiments



$\tau_2 = (2.5 \pm 0.6) \text{ ps}$  : independent of temperature/x  
[\(PCCP 2012\)](#)



# IR Pump-Probe Experiments



Slow thermalization dynamics  
(final equilibrium reached at > 50 ps)

$$\tau_3 = (15.7 \pm 1.2) \text{ ps for } 25 \text{ deg}$$

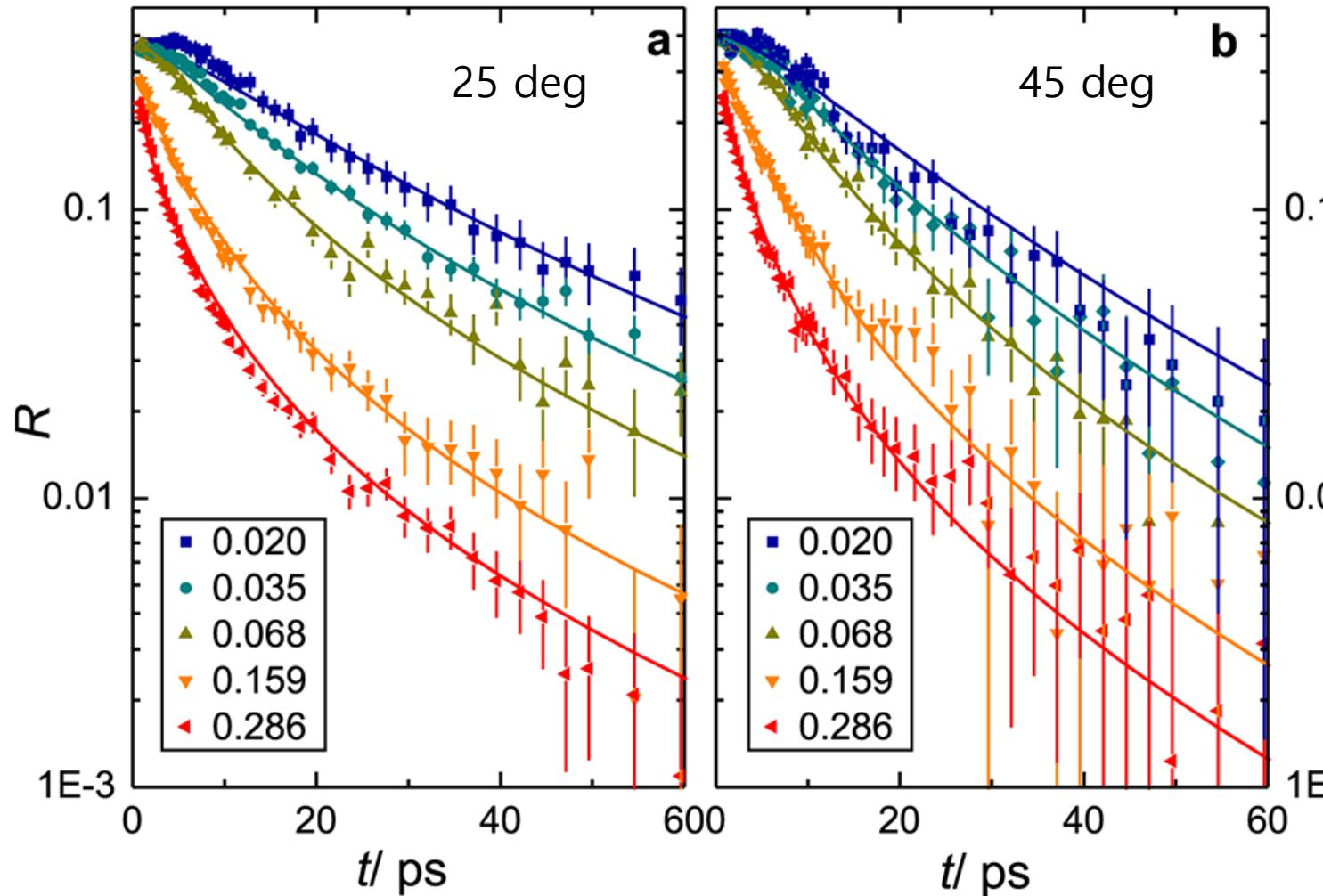
$$\tau_3 = (13.4 \pm 2.4) \text{ ps for } 45 \text{ deg}$$

$$\tau_3 = (11.7 \pm 0.9) \text{ ps for } 65 \text{ deg}$$

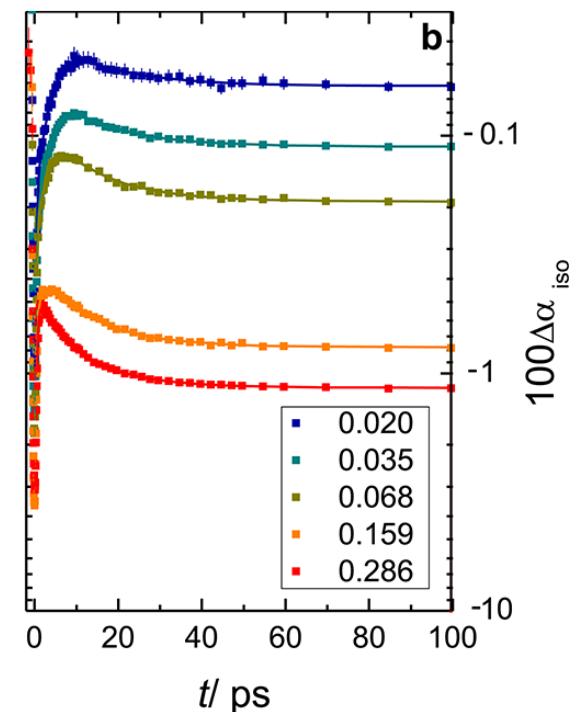
3D RTIL structure becomes more flexible for higher temperature

# IR Pump-Probe Anisotropy Experiments

$$R(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) - \Delta\alpha_{\perp}(\omega, t)}{3\Delta\alpha_{\text{iso}}(\omega, t)}.$$

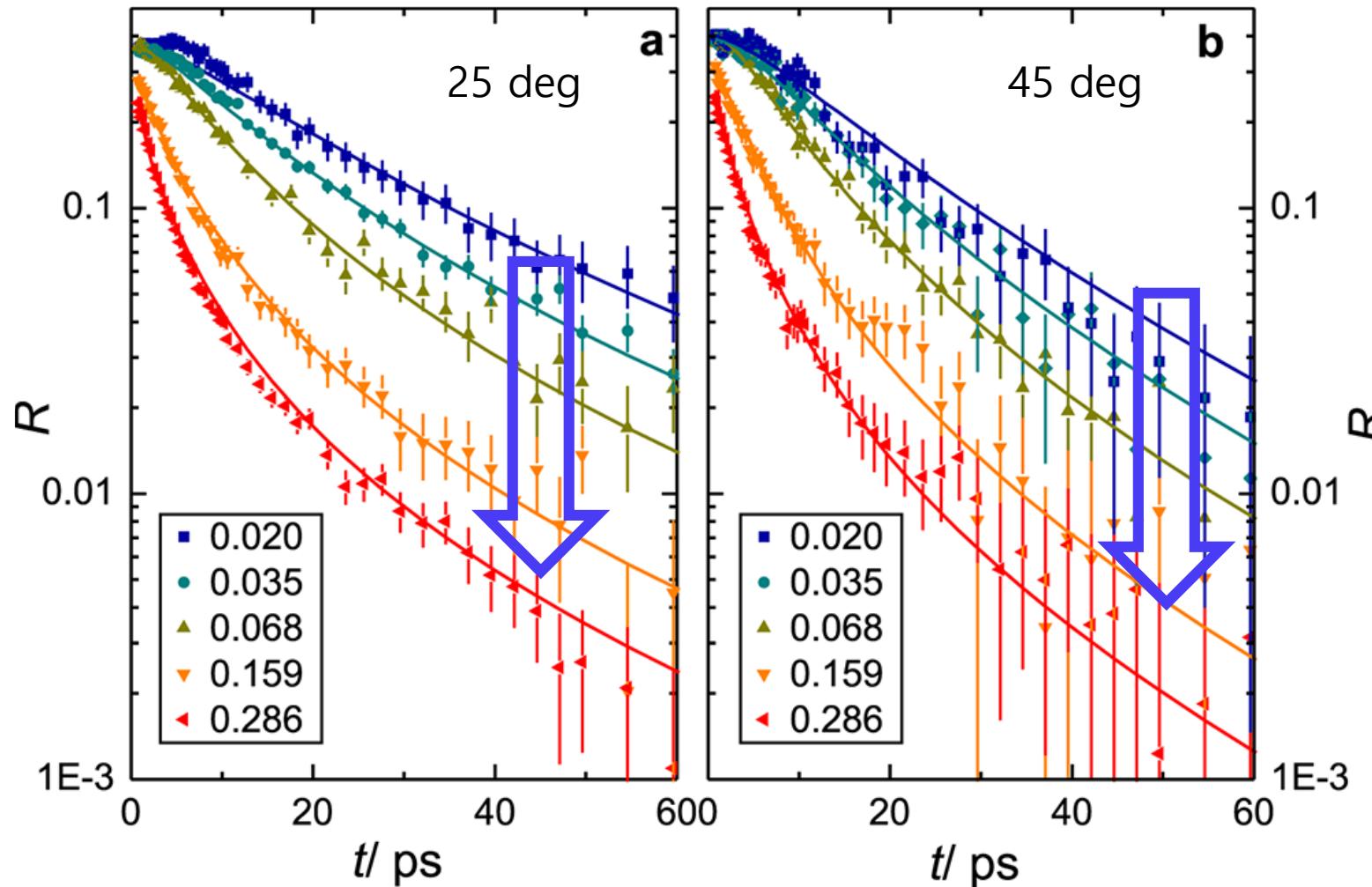


>> Long-live



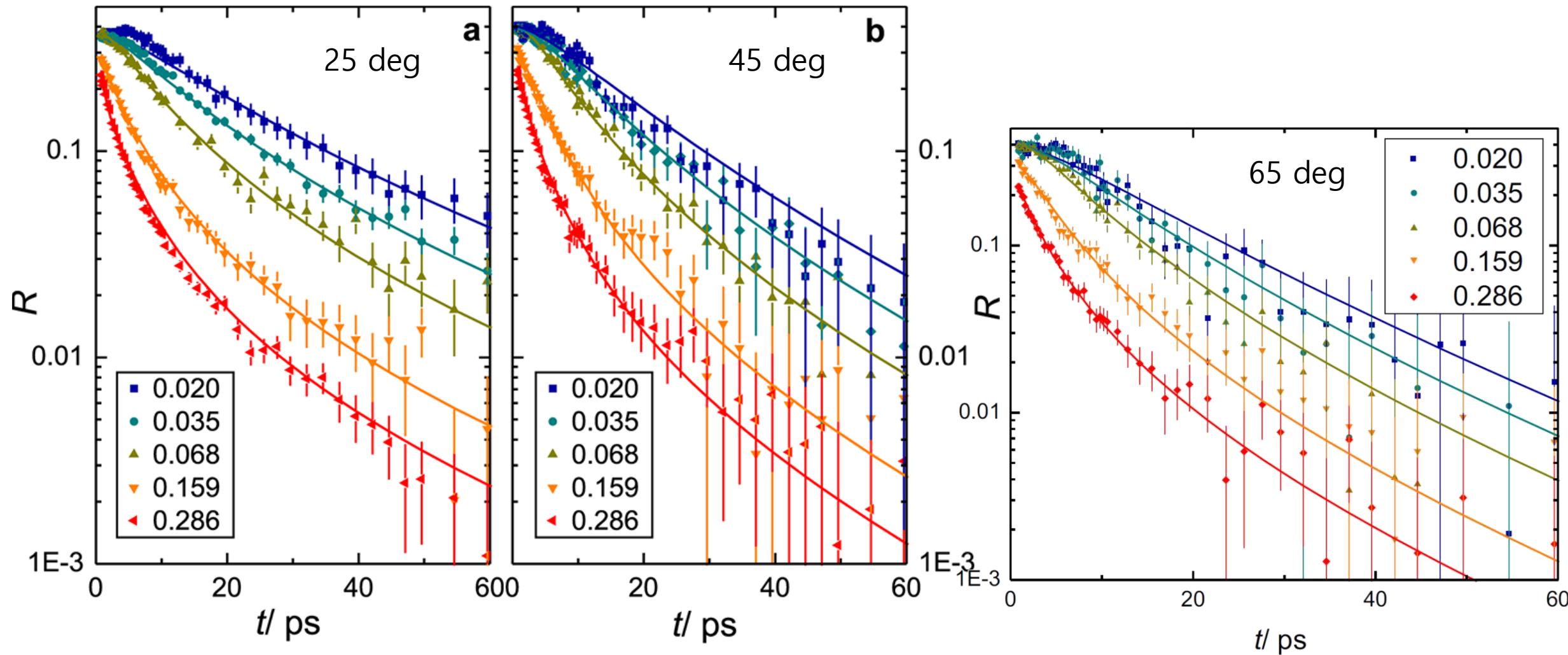
# IR Pump-Probe Anisotropy Experiments

Decay Mechanism 1 : Thermal energy diffusion  
N-D<sub>excited</sub> to N-D<sub>ground</sub> by diffusion : depending on the # of N-D  
Larger x decay faster

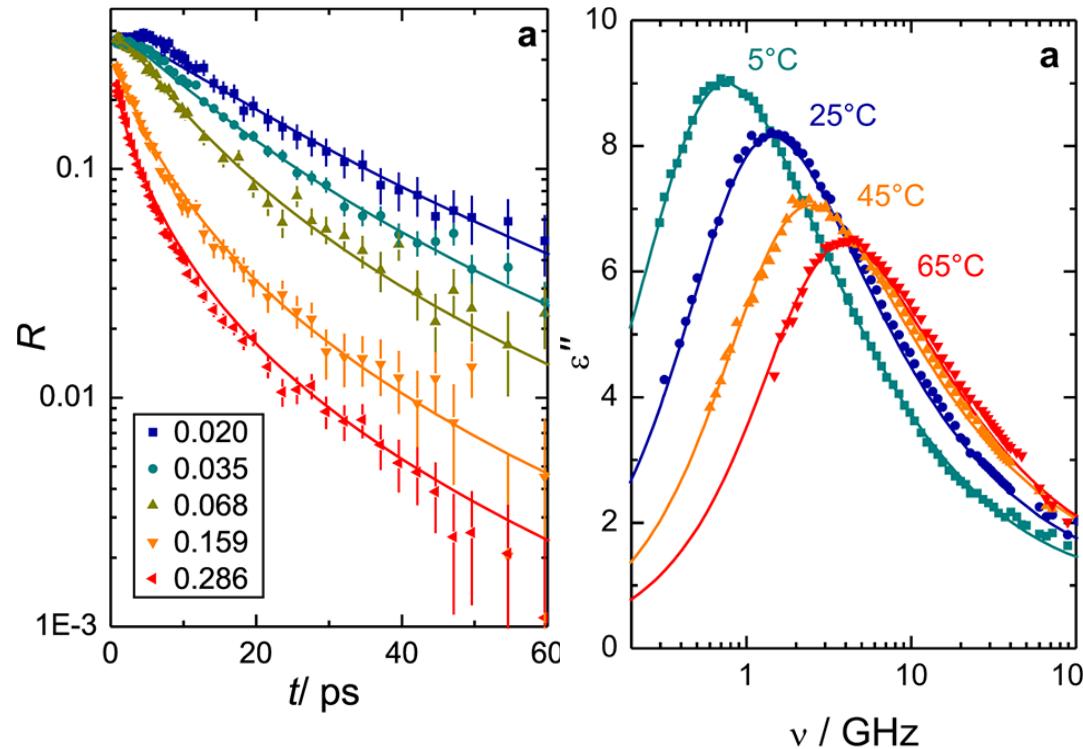


# IR Pump-Probe Anisotropy Experiments

Decay Mechanism 2 : Rotation of the excited ammonium group



# Comparison between DS and fs-IR Spectroscopy



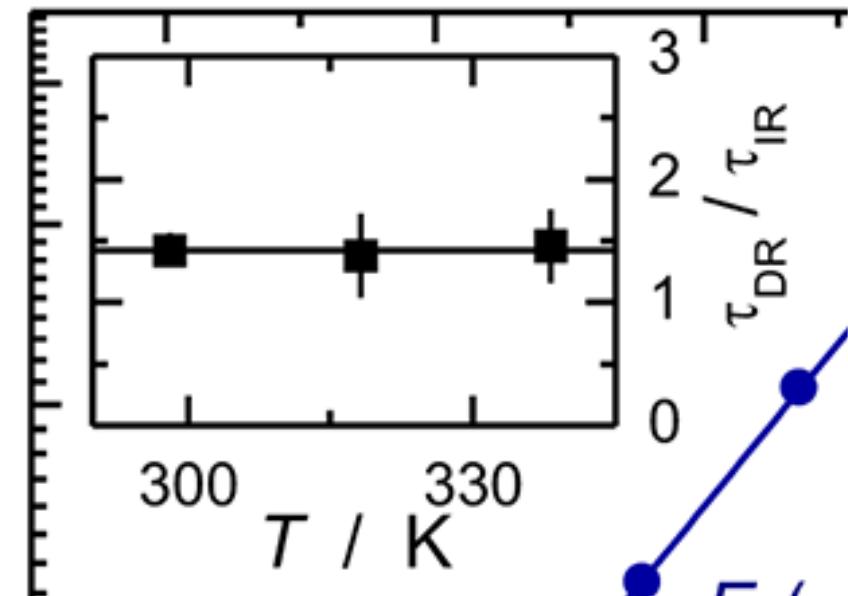
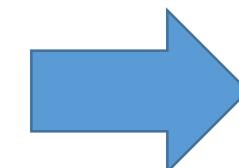
JCP 125 061102 (2006) H. Kim

$$C_l(t) \equiv \langle P_l[\cos \theta(t)] \rangle; \quad \tau_R^{(l)} = \int_0^\infty C_l(t) dt$$



$$C_l(t) = \exp[-l(l+1)D_R t]; \quad \tau_R^{(l)} = \{l(l+1)D_R\}^{-1},$$

Rotational diffusion limit



$\tau_{DR}/\tau_{IR} \sim 1.4$  : observed  
 $\tau_{DR}/\tau_{IR} \sim 3$  : Theory

IR : 1<sup>st</sup> order rotational correlation  
 DR(NMR, OHD-OKE...) : 2<sup>nd</sup> order rotational correlation

# Comparison between DS and fs-IR Spectroscopy

DR: 1<sup>st</sup> order rotational correlation

IR(OKE, NMR...) : 2<sup>nd</sup> order rotational correlation

JCP 125 061102 (2006) H. Kim

$$C_l(t) \equiv \langle P_l[\cos \theta(t)] \rangle; \quad \tau_R^{(l)} = \int_0^\infty C_l(t) dt$$



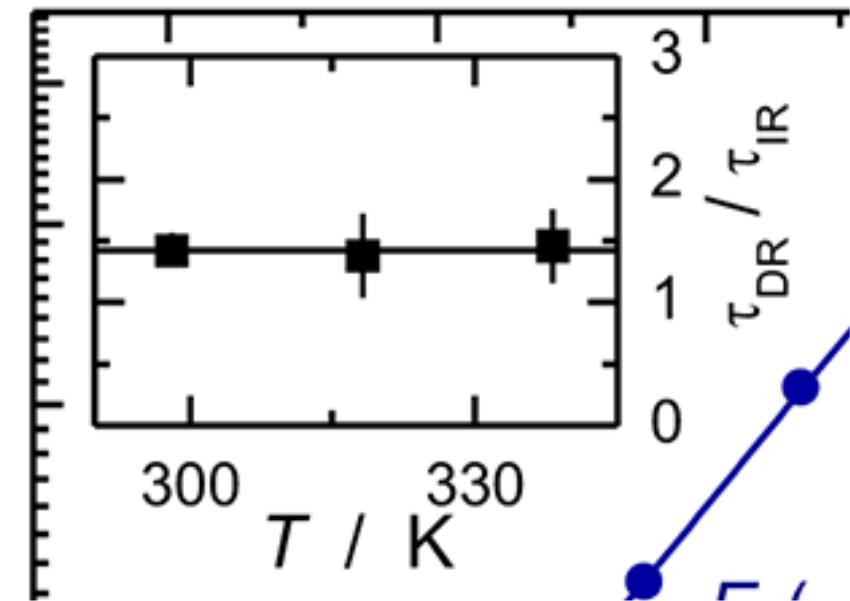
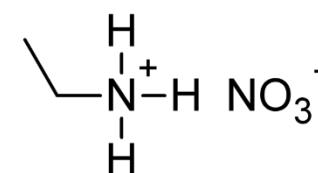
$$C_l(t) = \exp[-l(l+1)D_R t]; \quad \tau_R^{(l)} = \{l(l+1)D_R\}^{-1},$$

Rotational diffusion limit

$\tau_{DR}/\tau_{IR} \sim 1.4$  : observed

→ jump angle : 106 deg

→ Related to tetrahedral structure of ammonium?



$\tau_{DR}/\tau_{IR} \sim 1.4$  : observed

$\tau_{DR}/\tau_{IR} \sim 3$  : Theory for isotropic liquids

$\tau_{DR}/\tau_{OKE} < 3$  : [Ethylene Glycol](#)

$\tau_{(2)}/\tau_{(1)} \sim 2$  : [\[EMIM\]\[PF<sub>6</sub>\] \(MD\)](#)

$\tau_{DR}/\tau_{OKE} \sim 2$  : [\[EMIM\]\[PF<sub>6</sub>\]](#)



# Pump-probe Experiments

## One Color Pump-probe Experiments

Regenerative Amplifier (800 nm, 1 kHz)

→ 2250 cm<sup>-1</sup> (FWHM ~ 100 cm<sup>-1</sup>), 150 fs, ~ 5 μJ

→ probe (~ 4%), reference (~ 4%), pump (~ 92%)

## Two Color Pump-probe Experiments

mid-IR probe & reference (~ 0.2 μJ)

→ ~ 50 fs (FWHM ~ 300 cm<sup>-1</sup>), 2150 cm<sup>-1</sup> to 2400 cm<sup>-1</sup>

mid-IR pump (~ 25 μJ)

→ 2250 cm<sup>-1</sup> (FWHM ~ 100cm<sup>-1</sup>), ~ 50 fs

**Pump to probe : 45 deg**

**LN cooled MCT detector with dispersed spectrometer**