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^{2}H NMR study of structure, hydrogen bond dynamics and phase transition in a model ionic liquid electrolyte

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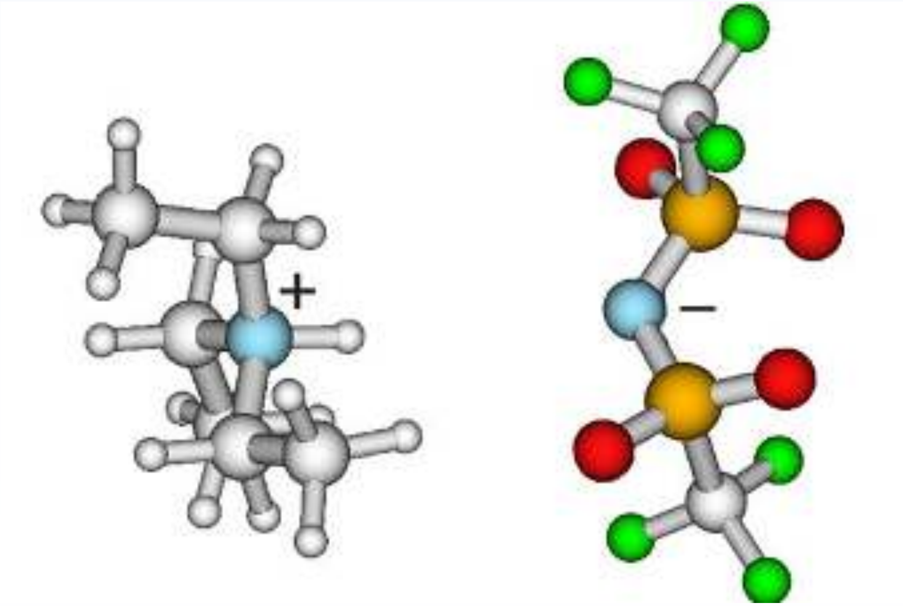
Ionic liquids

- Melting temperature is lower than 373 K
- Vast number of compounds
- Low vapor pressure ("green" chemistry)
- High thermal and charge conductivity (working fluids, electrochemical devices)
- Catalytic activity

Organic cation Anion



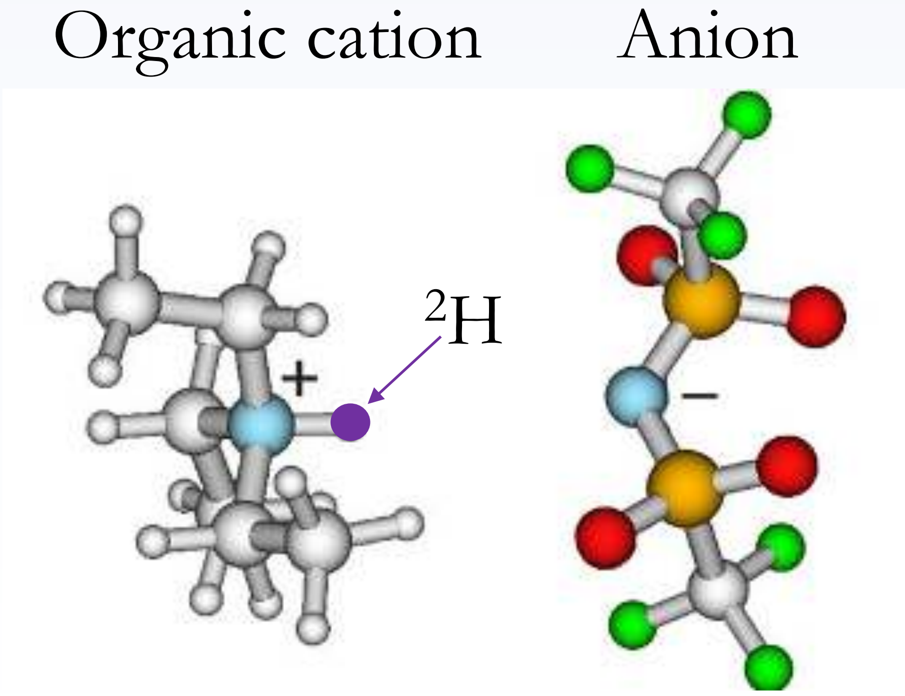
$[TEA]^+$ $[NTf_2]^-$

Ionic liquids

- How are diffusion and ionic mobility organized in ILs?
- Does it form a glass or crystal upon cooling?
- Is IL homogeneous in the solid state?
- Are there domains of different dynamics?

[TEA] = triethylammonium

$[NTf_2]$ = Bis(trifluoromethanesulfonyl)imide



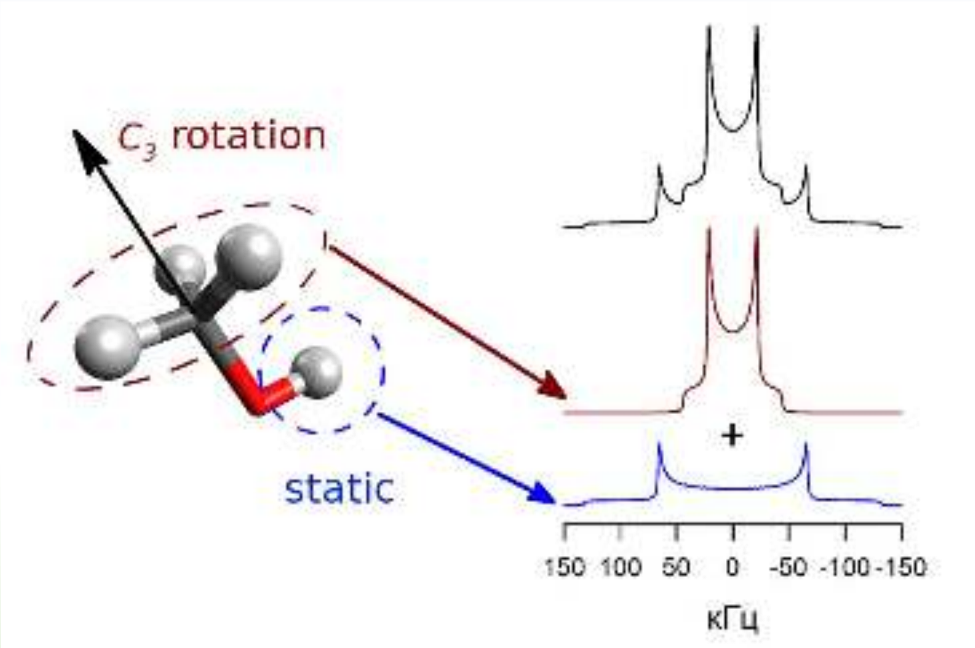
$[TEA]^+$ $[NTf_2]^-$

^{2}H NMR

$$\hat{H}_Q = \frac{e^2 \rho_{ZZ} Q}{8I(2I-1)} (3I_0^2 - I(I+1))(3\cos^2\theta - 1 - \eta \sin^2\theta \cos(2\varphi))$$

Quadrupole constant $\mathbf{C_Q}$ → efg tensor magnitude (O-D, C-D, H-bonds)

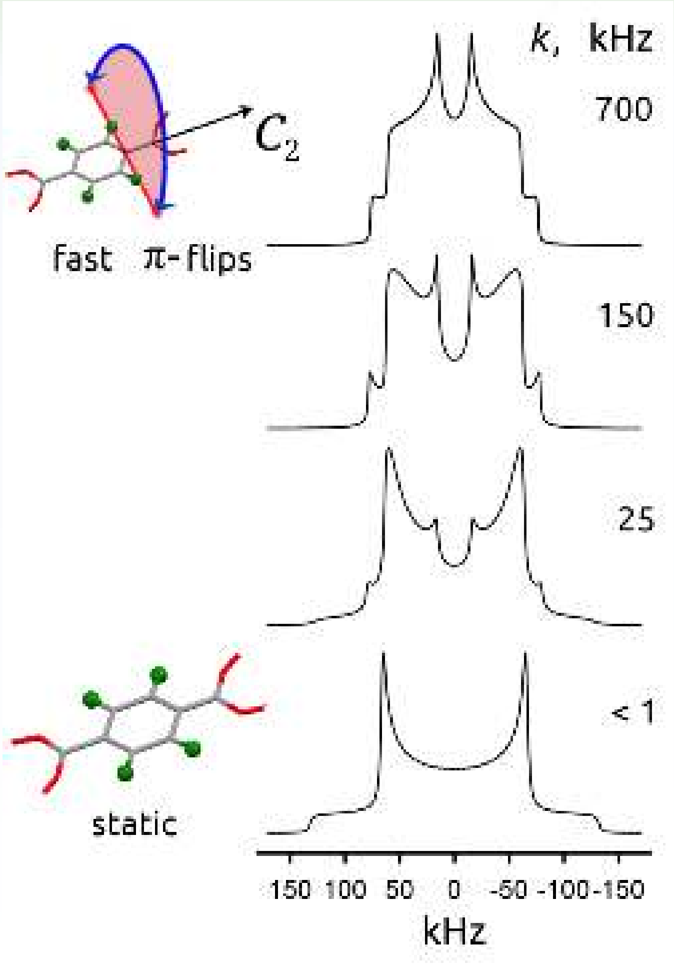
Orientational dependence → information about rotational dynamics



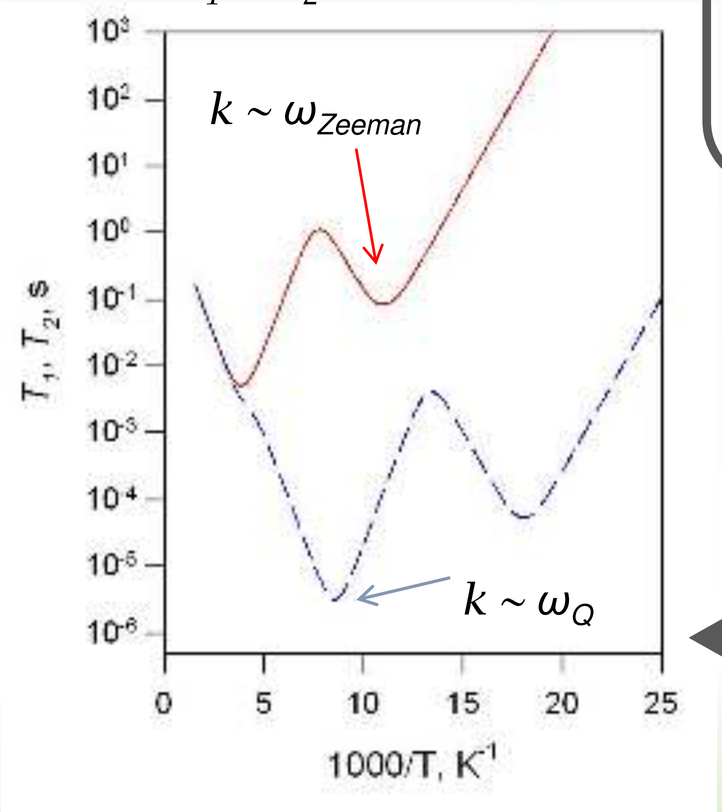
^{2}H NMR

Spectrum line shape:

- Sensitive to the geometry and rate of motions
- Rate constant 10^3 - 10^7 Hz



$T_1 = T_2$ in fast limit



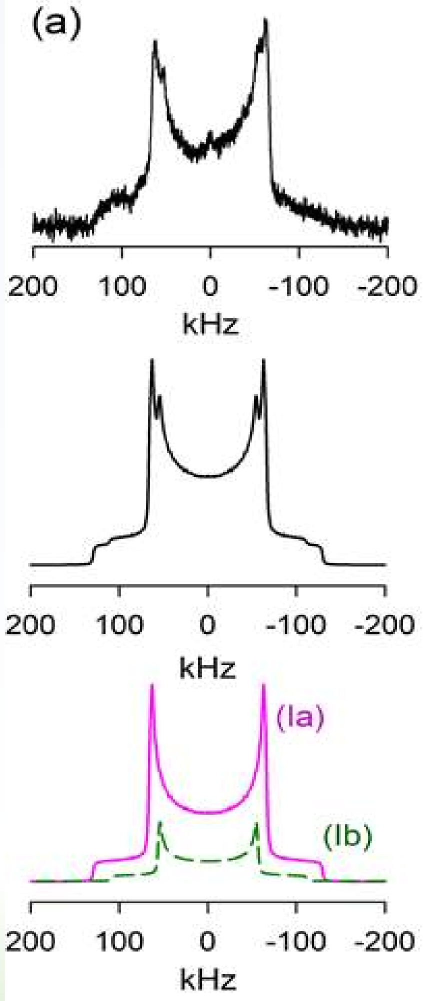
Spin relaxation:

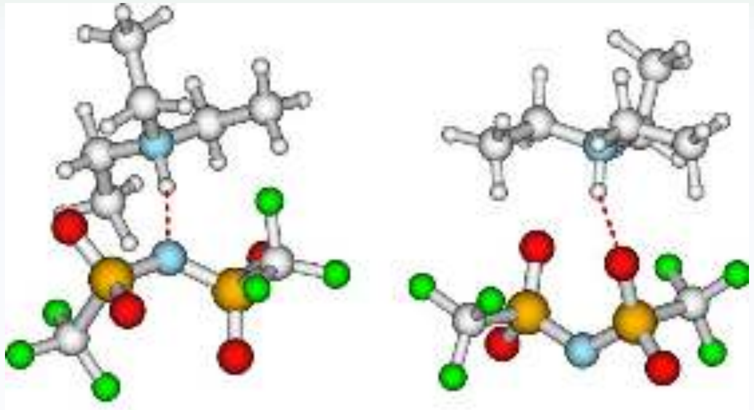
- Applicable for isotropic motion
- Rate constant 10^5 - 10^{10} Hz

Line shape analysis

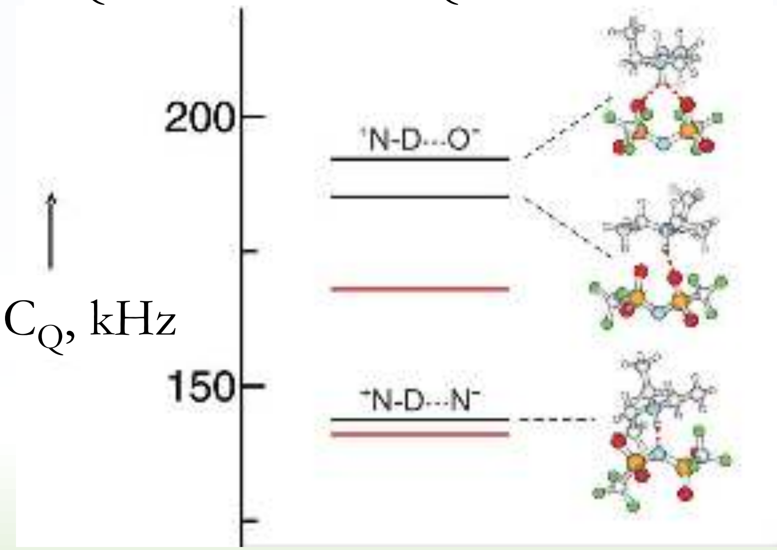
- 2 NMR signals correspond to 2 kinds of hydrogen bond
- Smaller C_Q refers to stronger hydrogen bond
- ^{2}H NMR data are consistent with DFT calculations

223 K





C_Q = 145 kHz C_Q = 175 kHz



Line shape analysis

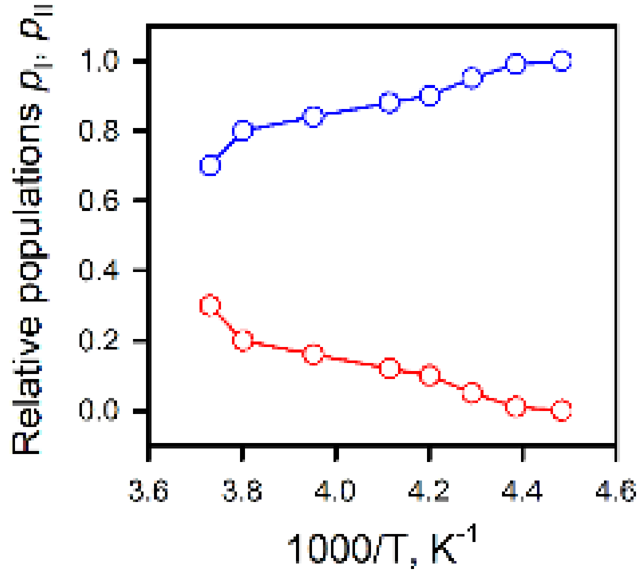
- Ionic liquid melts through dynamically heterogeneous state
- $K = p_{II}/p_{I}$ – equilibrium constant
- Melting occurs in two stages:

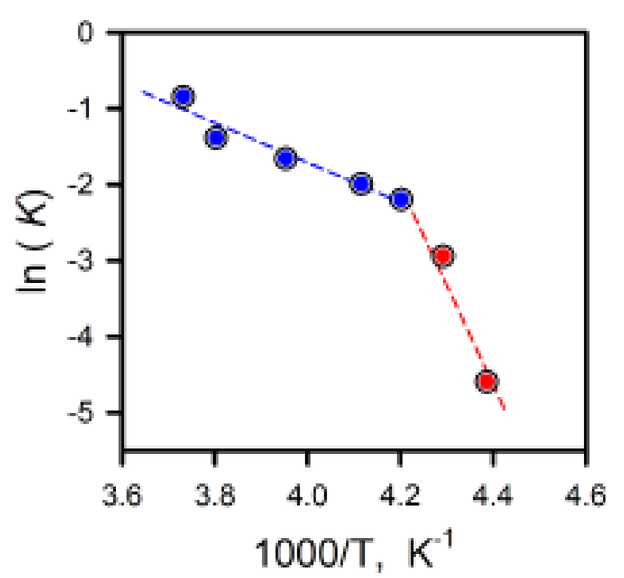
T < 238 K

$\Delta H_1 = 110 \pm 20$ kJ mol^{-1}

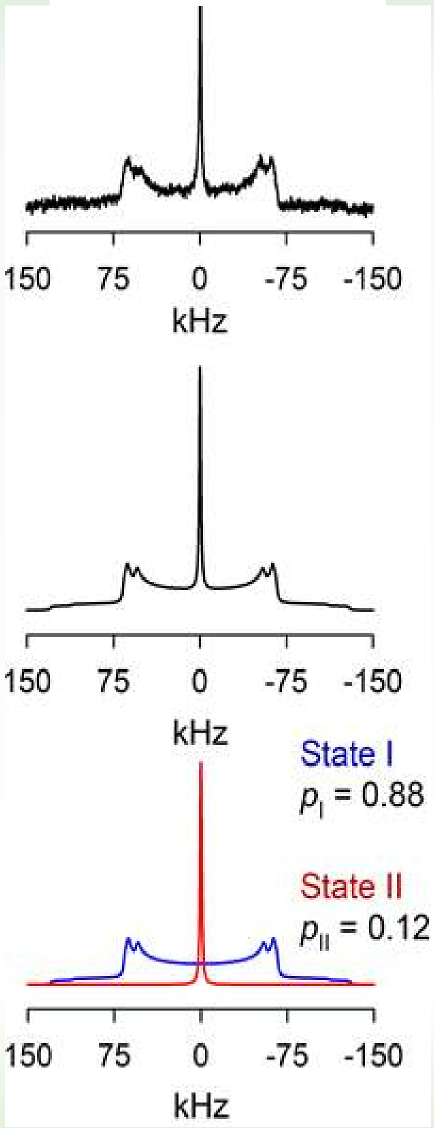
T > 238 K

$\Delta H_2 = 22 \pm 5$ kJ mol^{-1}





233 - 283 K



Spin relaxation analysis

T_1 relaxation: inversion recovery

$180°_x$ - t_d - $90°_x$ - τ - $90°_y$ - τ - acquisition

T_2 relaxation: CPMG pulse sequence

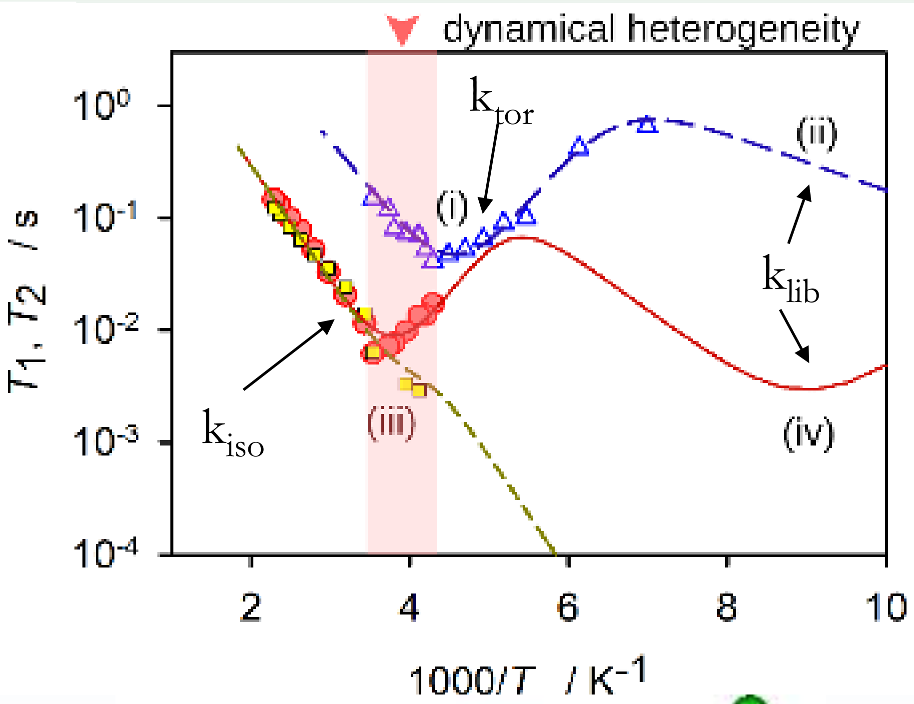
$90°_x$ – (t_d - $180°_y$ - t_d $)_n$ – acquisition

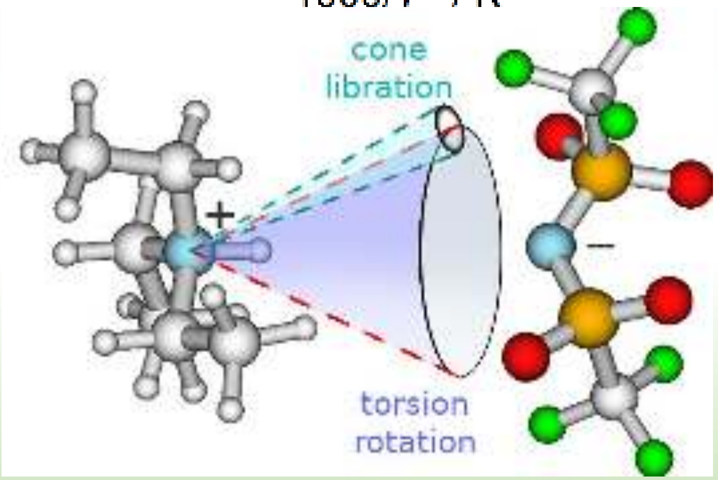
Solid state:

Torsional rotation (k_{tor}) + cone libration (k_{lib})

Liquid state:

Isotropic rotation (k_{iso}) + cone libration (k_{lib})



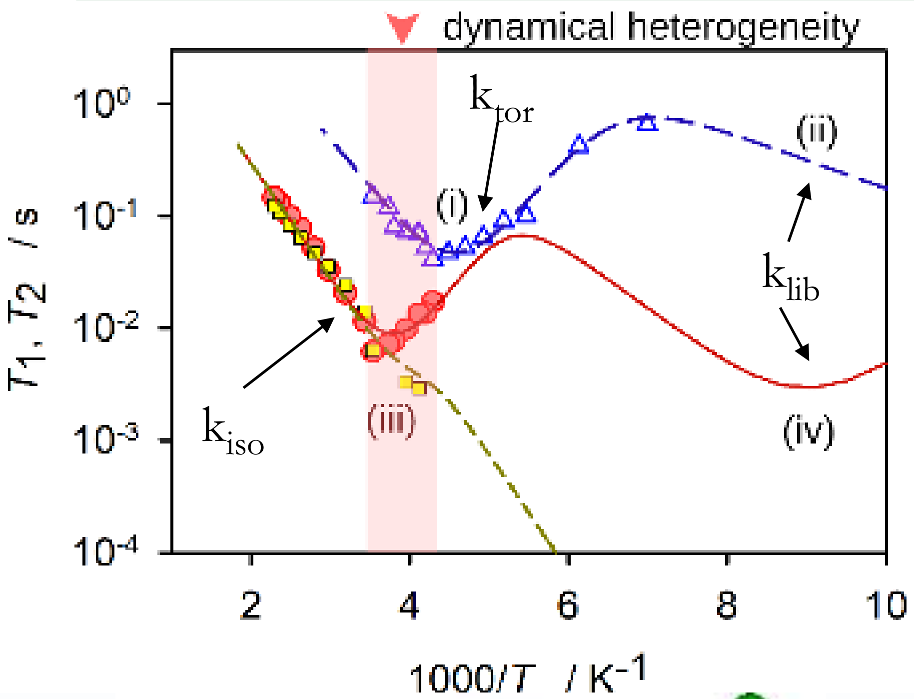


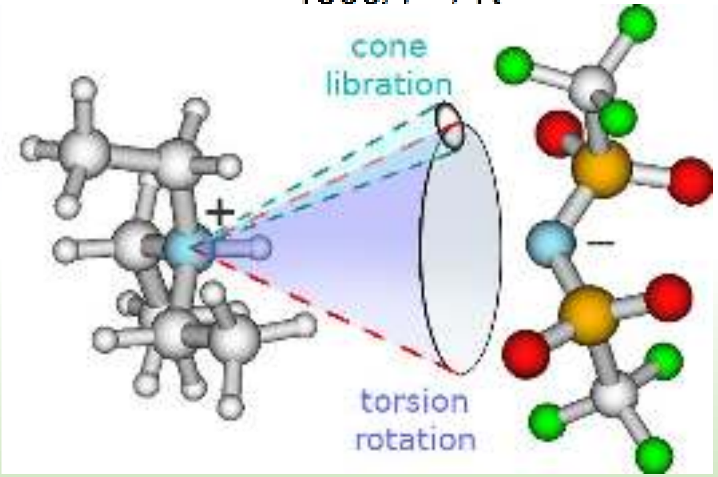
Spin relaxation analysis

	Solid State I	Liquid State II
E_{tor}, kJ mol^{-1}	17	–
k_{tor0}, Hz	1×10^{12}	–
ϕ_{tor}	30°	–
E_{lib}, kJ mol^{-1}	5	10
k_{lib0}, Hz	0.5×10^{12}	5×10^{12}
ϑ_{lib}	10°	42°
E_{iso}, kJ mol^{-1}	–	20
k_{iso0}, Hz	–	9×10^{11}

C_Q^{I} = 173 kHz is taken from spectrum line shape

C_Q^{II} = 203 kHz estimated theoretically with Wendt–Farrar approach

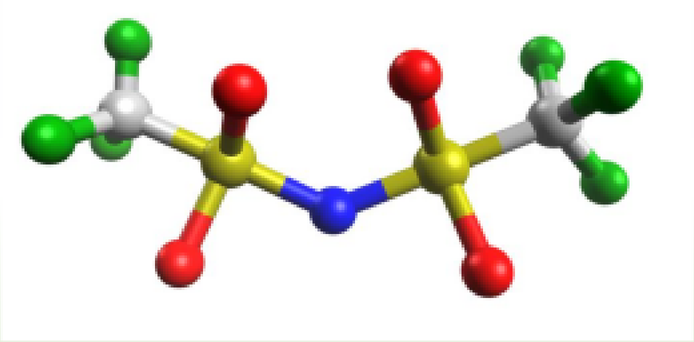




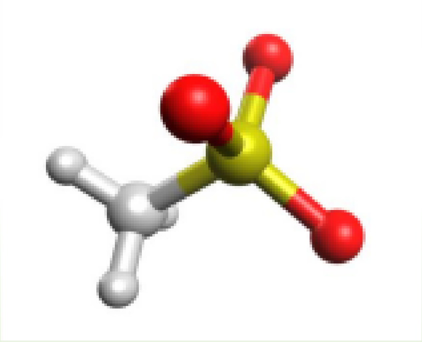
Influence of the anion strength

C_Q^{II} = 203 kHz	C_Q^{II} = 190 kHz	C_Q^{II} = 152 kHz
E_{iso} = 20 kJ mol^{-1}	E_{iso} = 20 kJ mol^{-1}	E_{iso} = 25 kJ mol^{-1}
E_{tor} = 17 kJ mol^{-1}	E_{tor} = 21 kJ mol^{-1}	E_{tor} = 30 kJ mol^{-1}
θ_{lib} = 42°	θ_{lib} = 35°	θ_{lib} = 23°

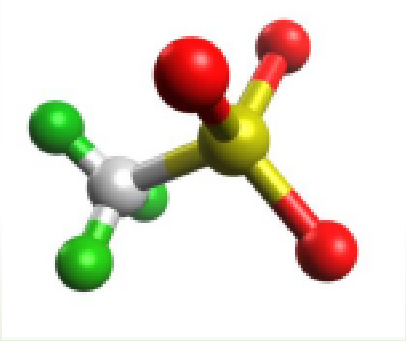
Anion strength



$[NTf_2]^-$



$[OTf]^-$



$[OMs]^-$

Conclusion

- Molecular mobility and melting transition are characterized for [TEA][NTf2], [TEA][OTf] and [TEA][OMs] ionic liquids
- Melting occurs through the dynamically heterogeneous state in two stages with different enthalpies
- Molecular mobility is investigated both below and above melting point
- Influence of anion strength on the molecular mobility and the melting transition is illustrated

Thank you for attention

Wendt–Farrar approach

- DFT calculations prove the linear correlation between proton chemical shift and deuteron quadrupole constant

$$C_Q[kHz] = 285.06 - 14.92 * \delta^1 H[ppm]$$