Mechanical spectroscopy study of quaternary cation ionic liquids: effects of different conformational flexibility

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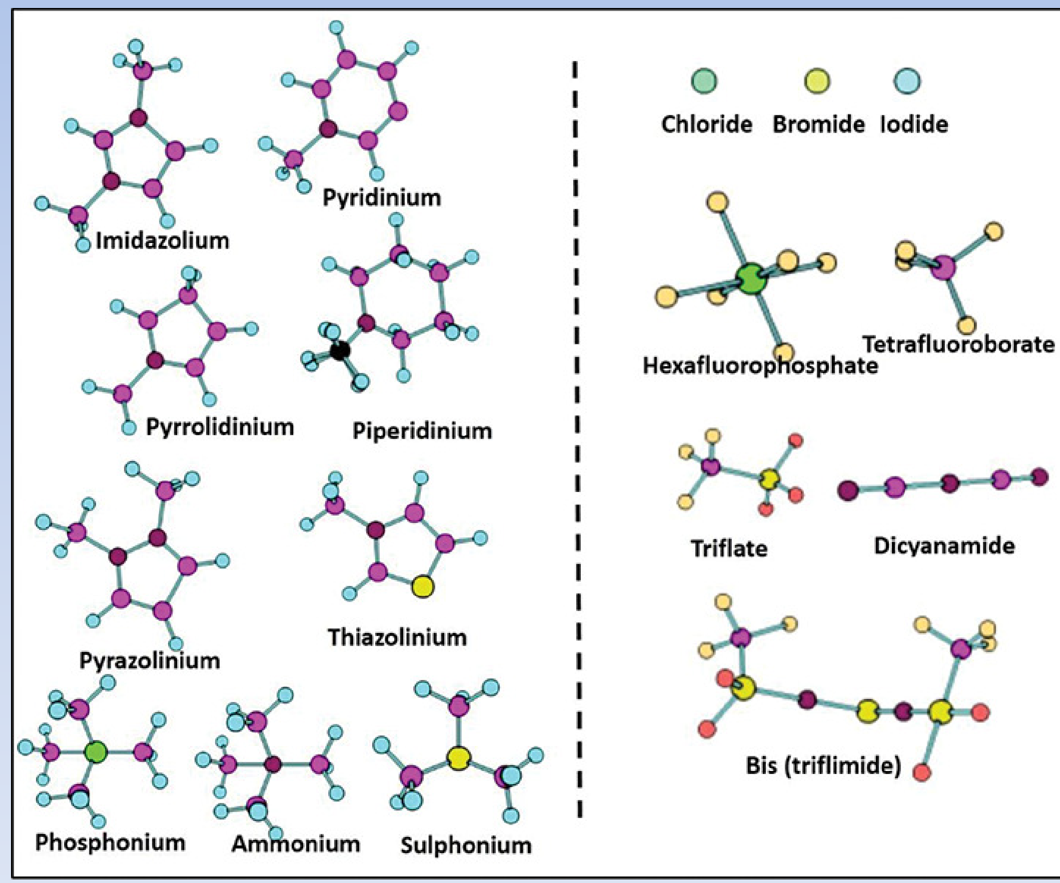
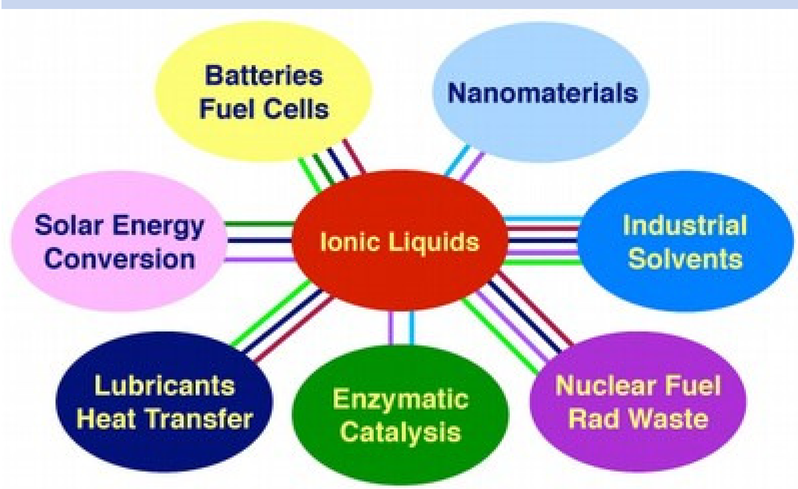
Ionic liquids

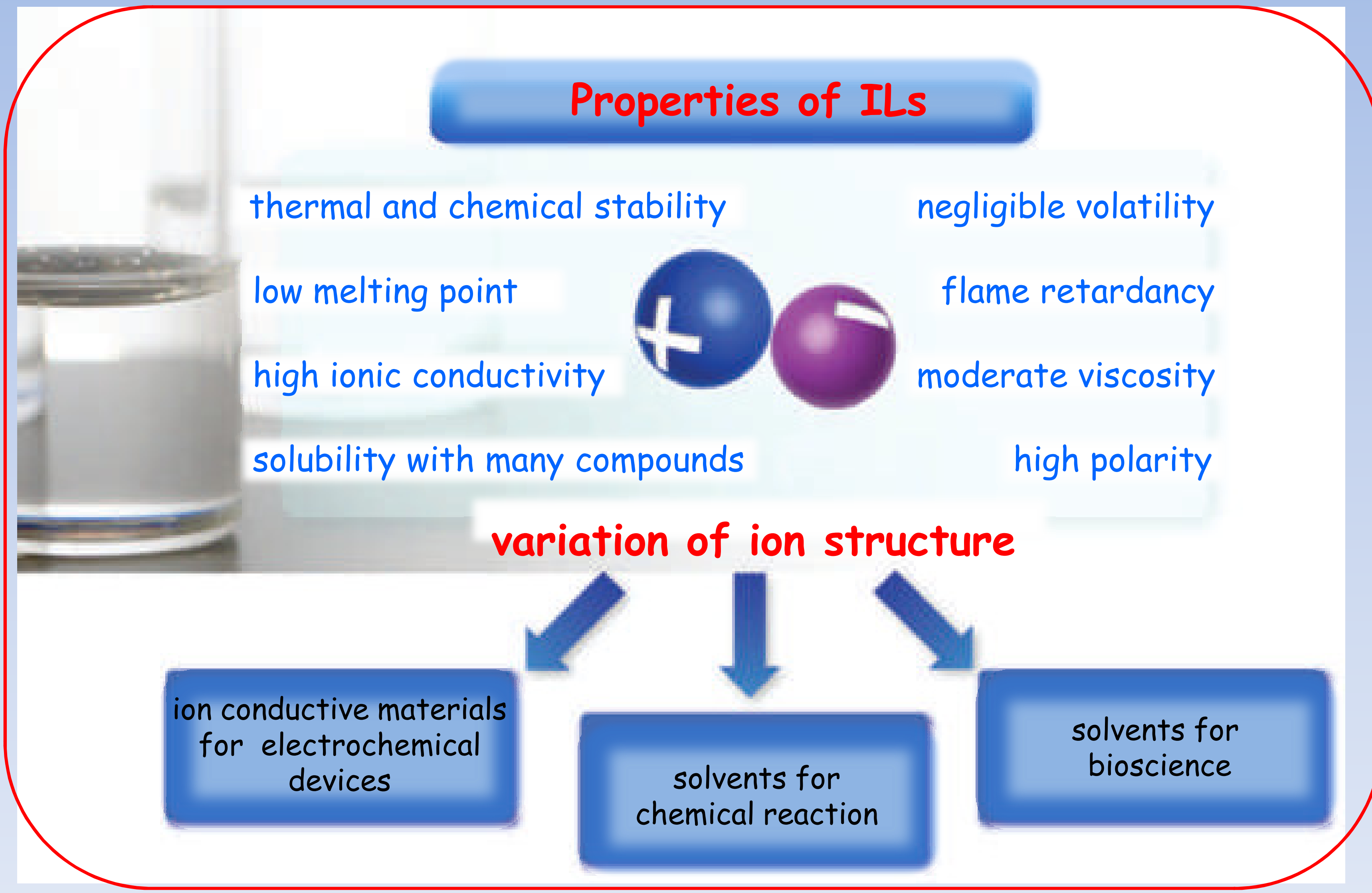
ILs → T_m < 100 °C

(RTILs: liquid phase at ambient conditions)



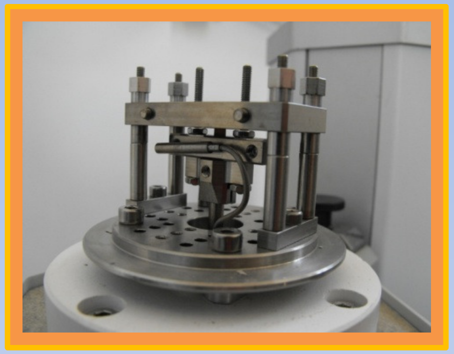


Why ionic liquids?



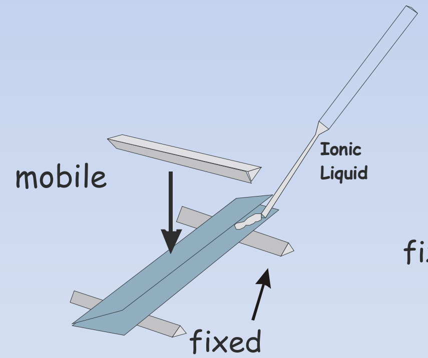
Mechanical spectroscopy on ionic liquids: how can we measure them?

Dynamic Mechanical Analysis

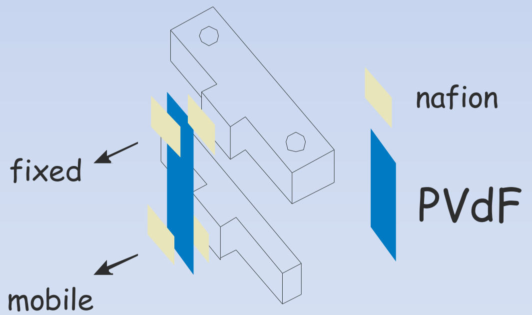


Forced oscillations

100 K – 800 K
0.001 Hz – 200 Hz
PerkinElmer DMA 8000

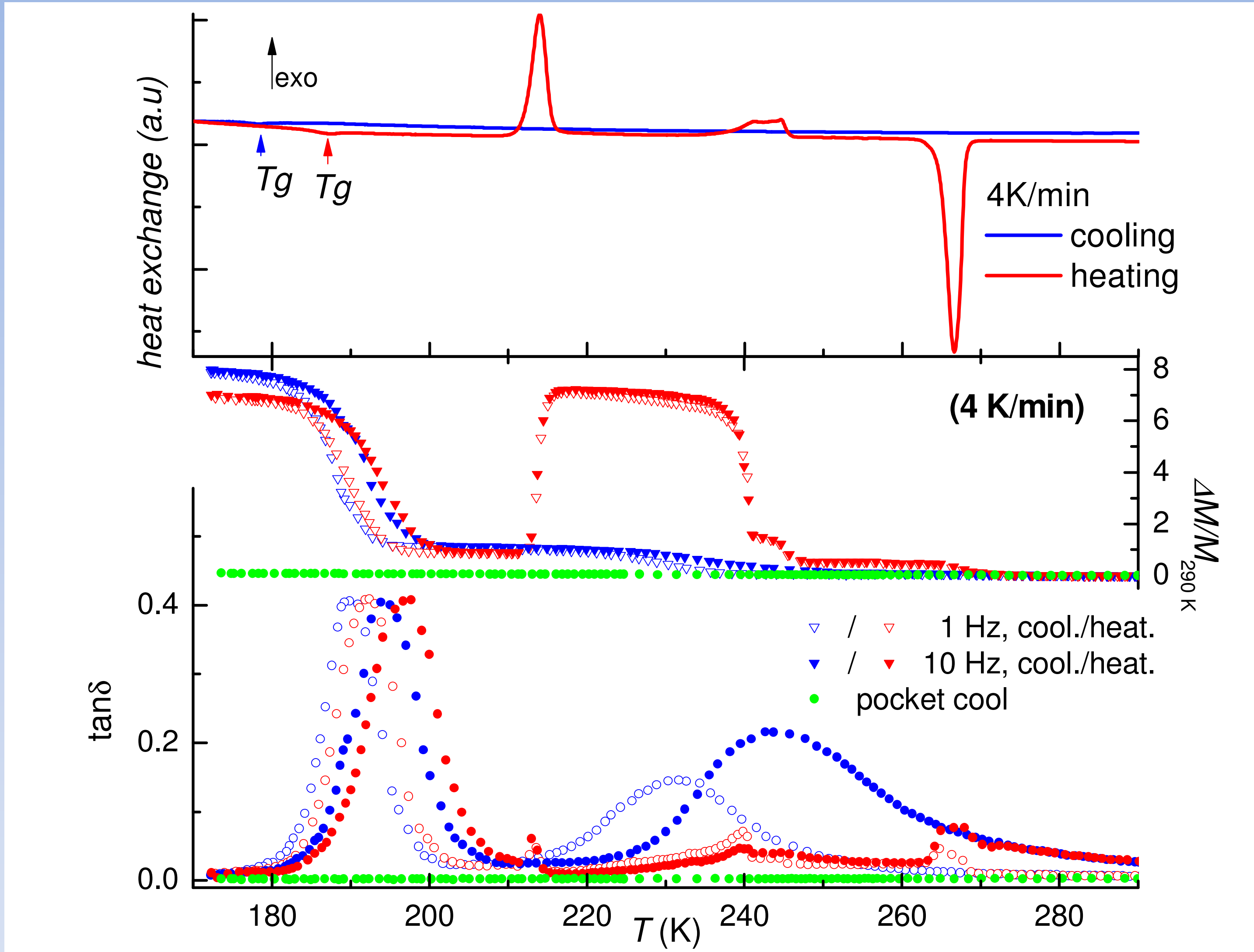


three-point bending



tension

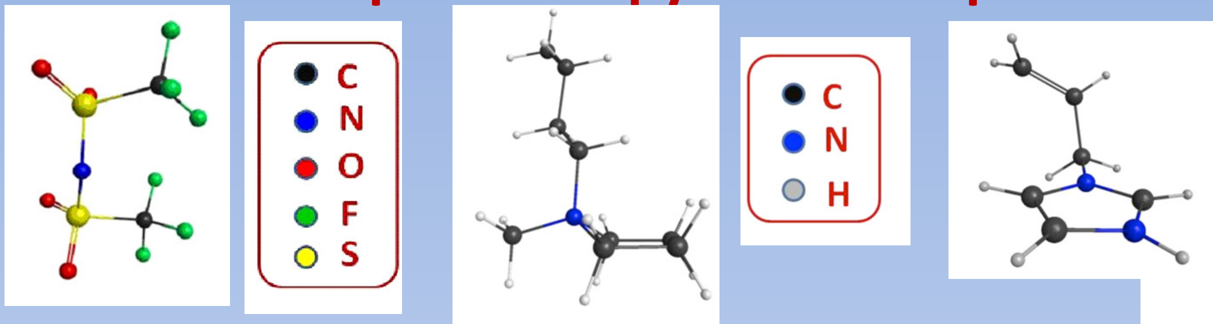
Mechanical spectroscopy of ionic liquids vs. DSC

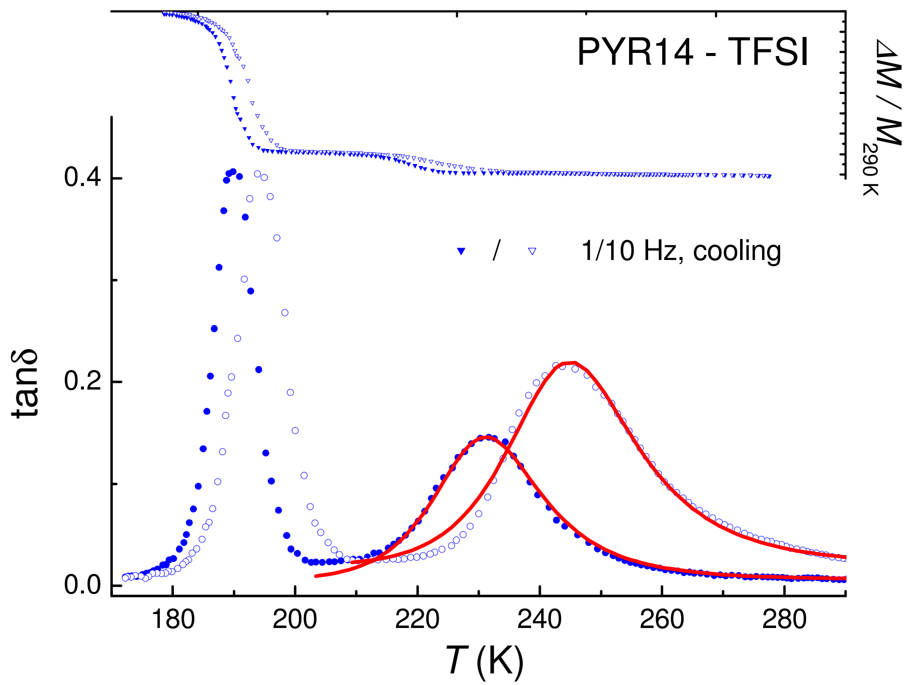


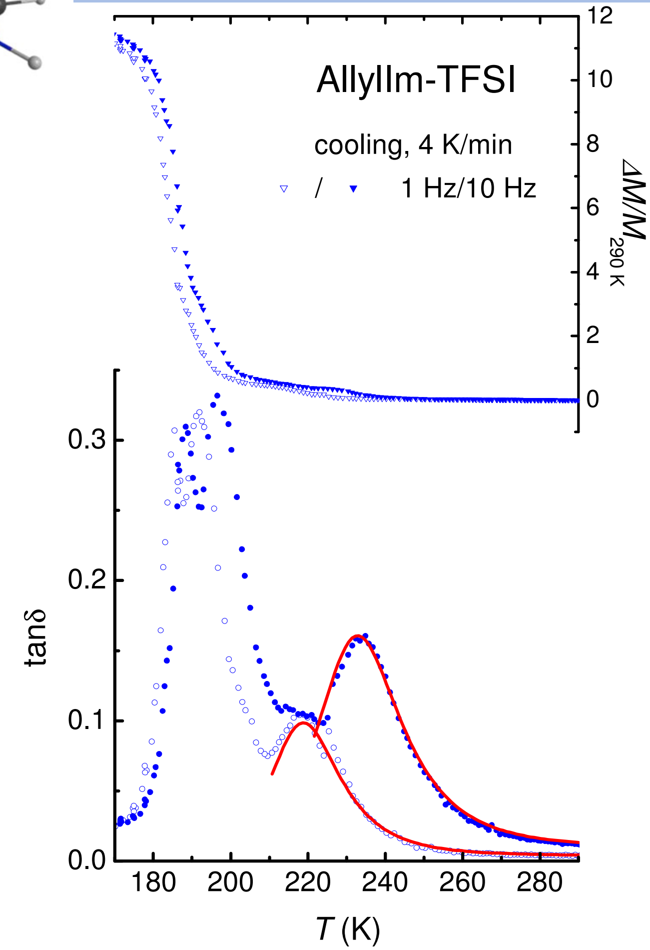
Both techniques can provide information about phase trasitions, but DMA provides also access to relaxations

DOI: 10.1021/acs.jpcb.5b06039
J. Phys. Chem. B 2015, 119, 12905–12911

Mechanical spectroscopy of ionic liquids with the same anion





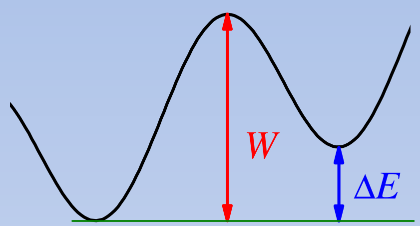


DOI: 10.1021/acs.jpcb.5b06039
J. Phys. Chem. B 2015, 119, 12905−12911

Both ionic liquids display beside the marks of phase transitions, also a thermally actived peak

PYR_{14} -TFSI VFT relaxation time

asymmetric potential wells

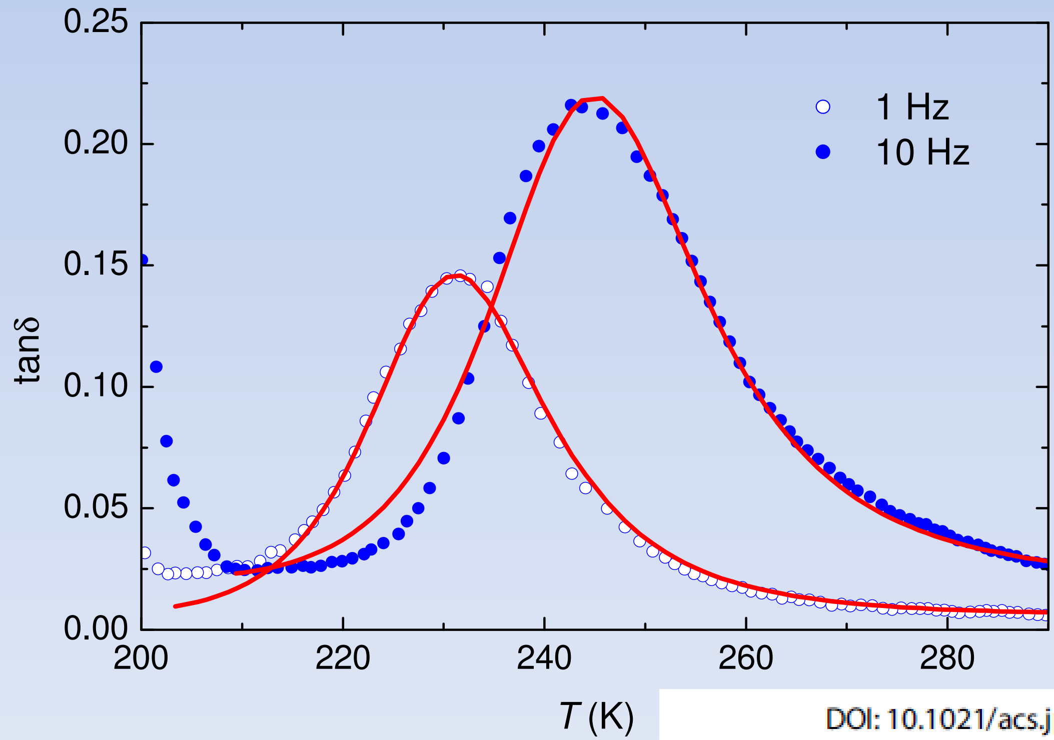


$$\tan\delta = \frac{c}{T}\,\mathrm{sech}^2\left(\frac{\Delta E}{2kT}\right)\frac{1}{(\omega\tau)^{\alpha}+(\omega\tau)^{-\alpha}}$$

relaxation time

$$\tau = \tau_0 \exp\frac{W}{k(T-T_0)}$$

(Vogel-Fulcher-Tamman)



fit parameters

$\tau_0 = 1.7 \cdot 10^{-13}$ s

$W = 0.36$ eV

$\Delta E = 25$ meV

$T_0 = 80$ K

$\alpha = 0.7$

DOI: 10.1021/acs.jpcb.5b06039
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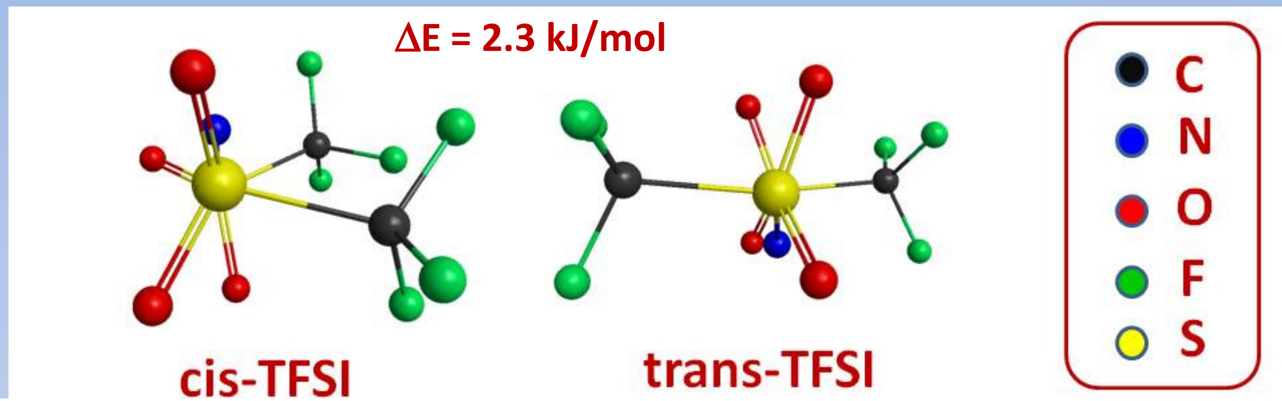
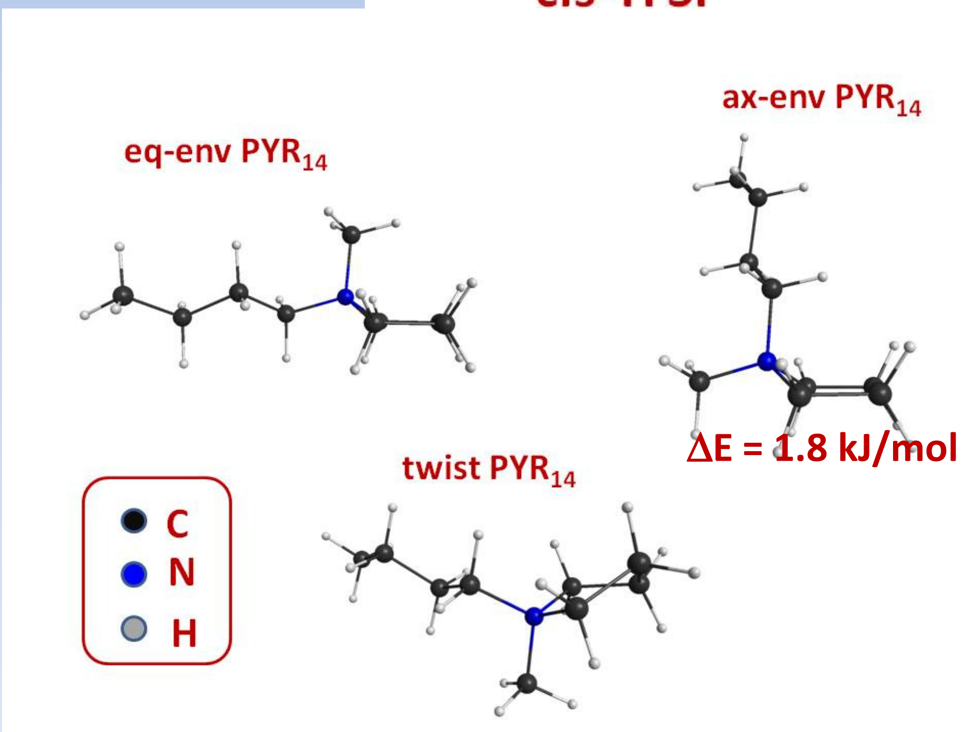
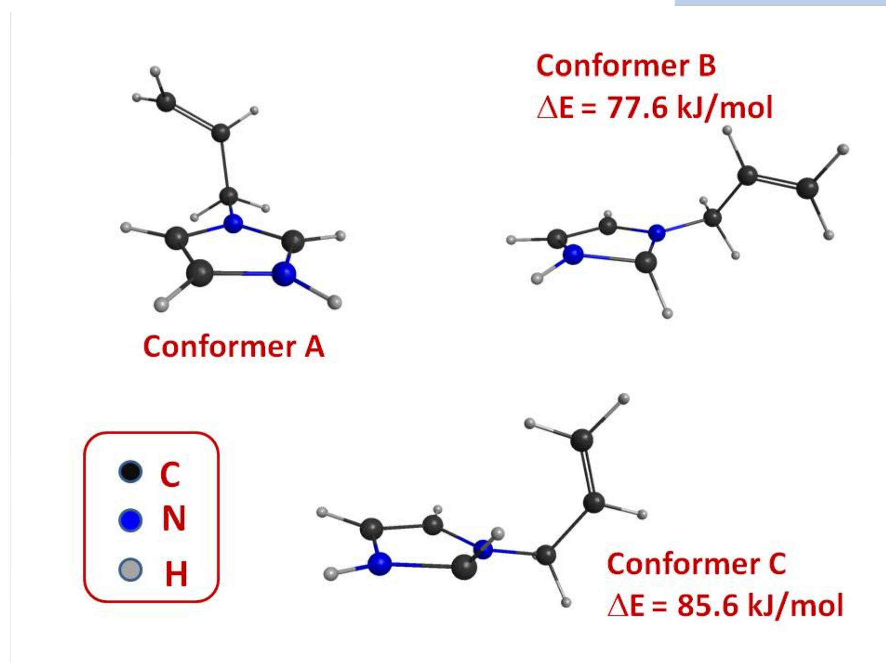
The involvement of anion conformers in the relaxations

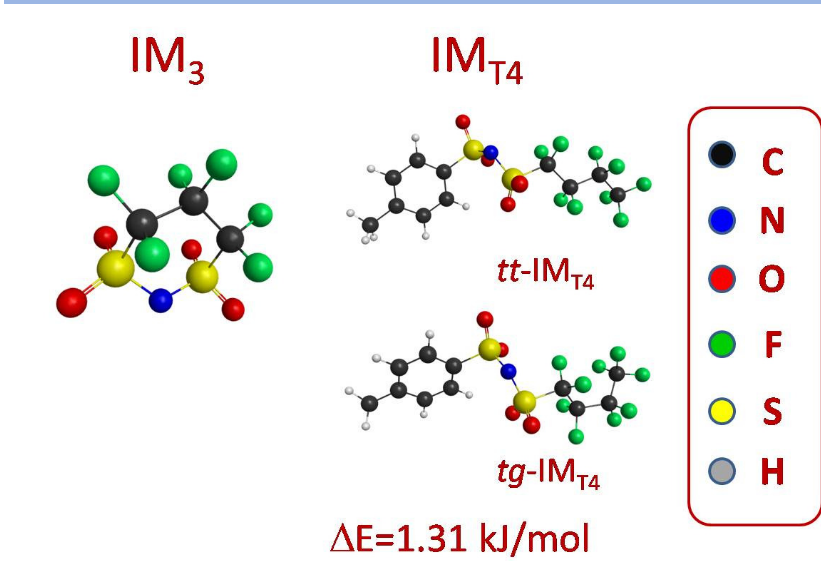


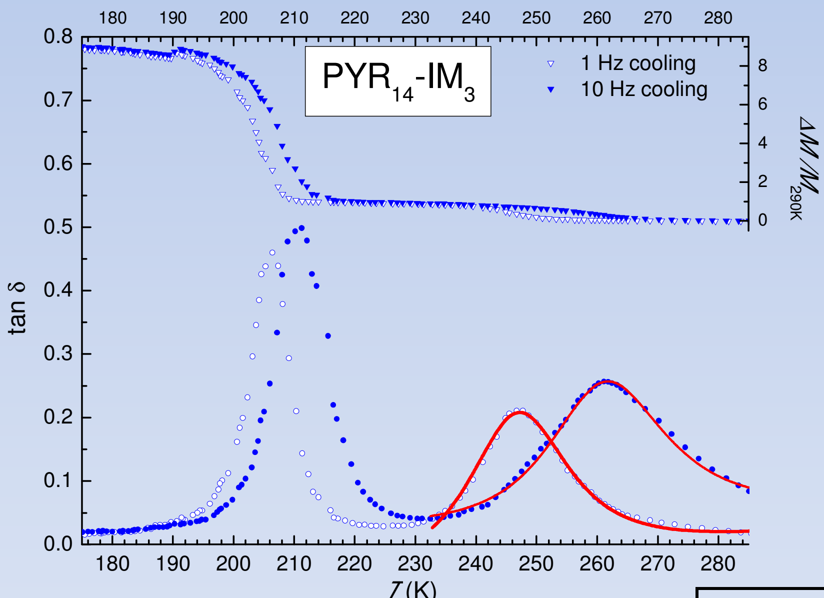


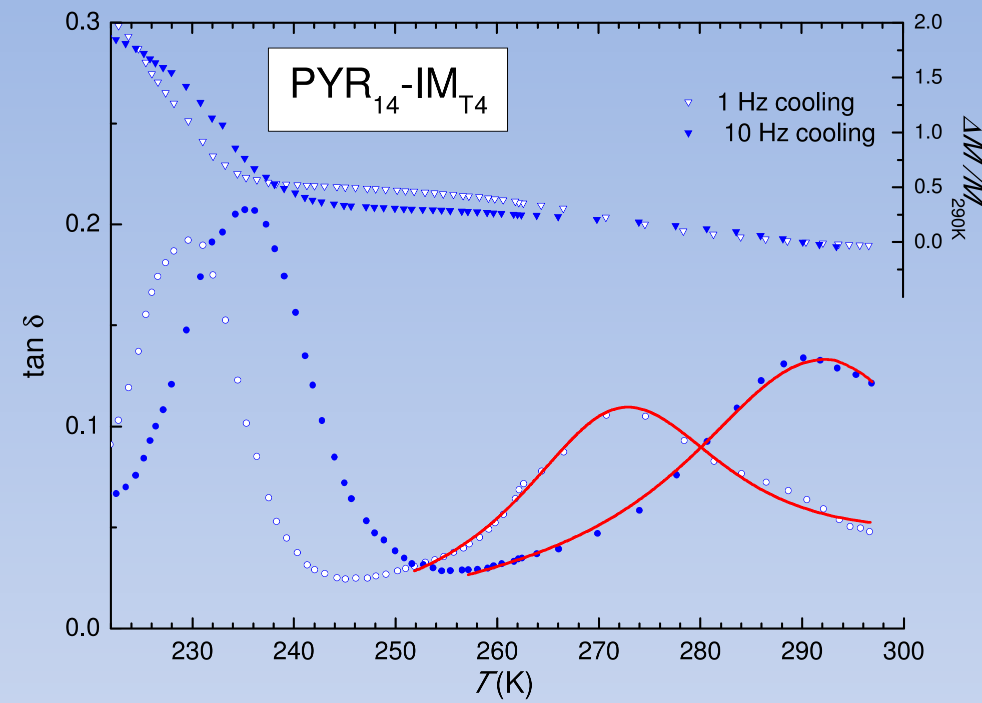
ΔE = 3.0 kJ/mol



allyl-imidazolium conformers







Mechanical spectroscopy of ionic liquids with different anions

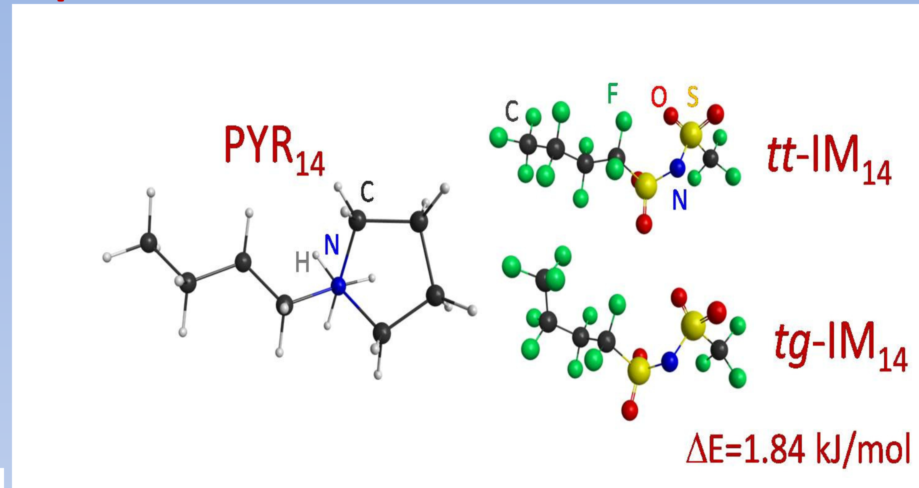
J. Mol. Liq. **243**, 9 (2017)

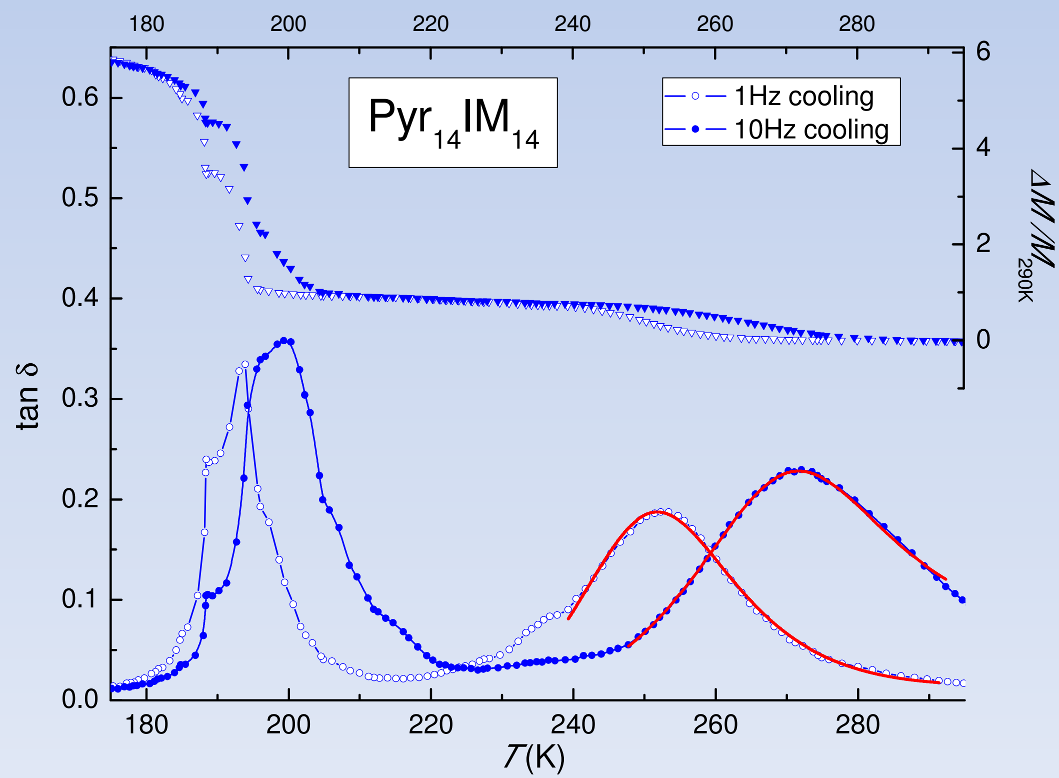
	PYR_{14}-TFSI[10]	PYR_{14}-IM_{T4}	PYR_{14}-IM_3	Allyl-TFSI[10]
τ_0 [s]	(1.7 ± 0.4) 10^{-13}	(8±1) 10^{-14}	(2.7±0.7) 10^{-14}	(9.3 ± 4.5) 10^{-14}
E [eV]	0.36 ± 0.01	0.51±0.02	0.43±0.01	0.37 ± 0.01
T_0 [K]	80± 3	61±6	76±2	67± 2
ΔE [meV]	26± 2	15± 3	2±2	30± 4
α	0.7 ± 0. 4	0.88±0.32	0.95±0.45	0.7 ± 0.5

Mechanical spectroscopy of ionic liquids with different anions

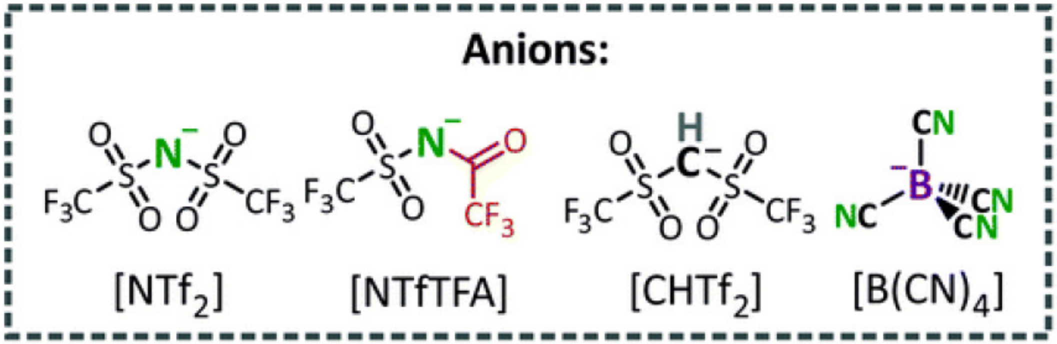
	PYR_{14}-TFSI[DMA1]	PYR_{14}-IM_{14}	PYR_{14}-IM_{T4}
τ0 [s]	(1.7 ± 0.4) 10^{-13}	(7.5±0.4) 10^{-13}	(8±X) 10^{-14}
E [eV]	0.36 ± 0.01	0.45±0.04	0.51±0.02
T_0 [K]	80±3	48±2	61±6
ΔE [meV]	26±2	29±1	15± 3
α	0.7±0.4	0.75±0.35	0.88±0.32

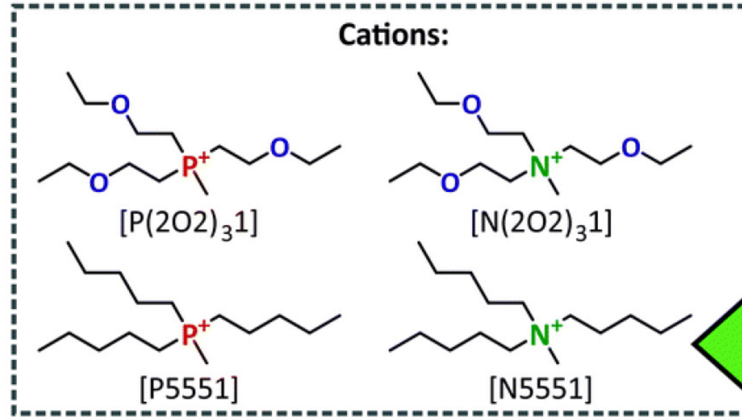
Materials Research. 2018; 21(suppl. 2): e20170870

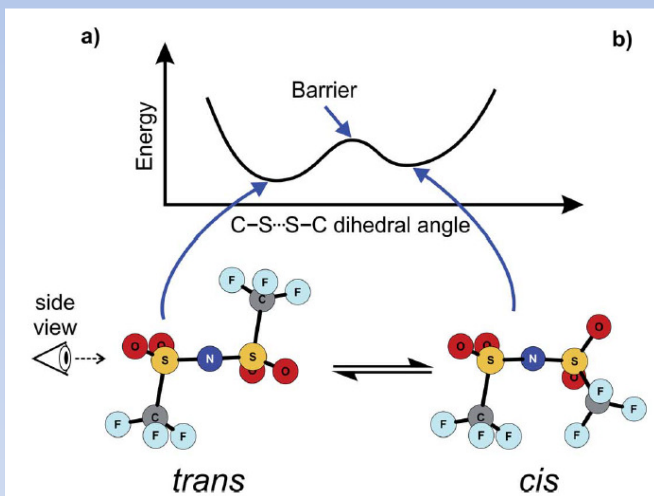




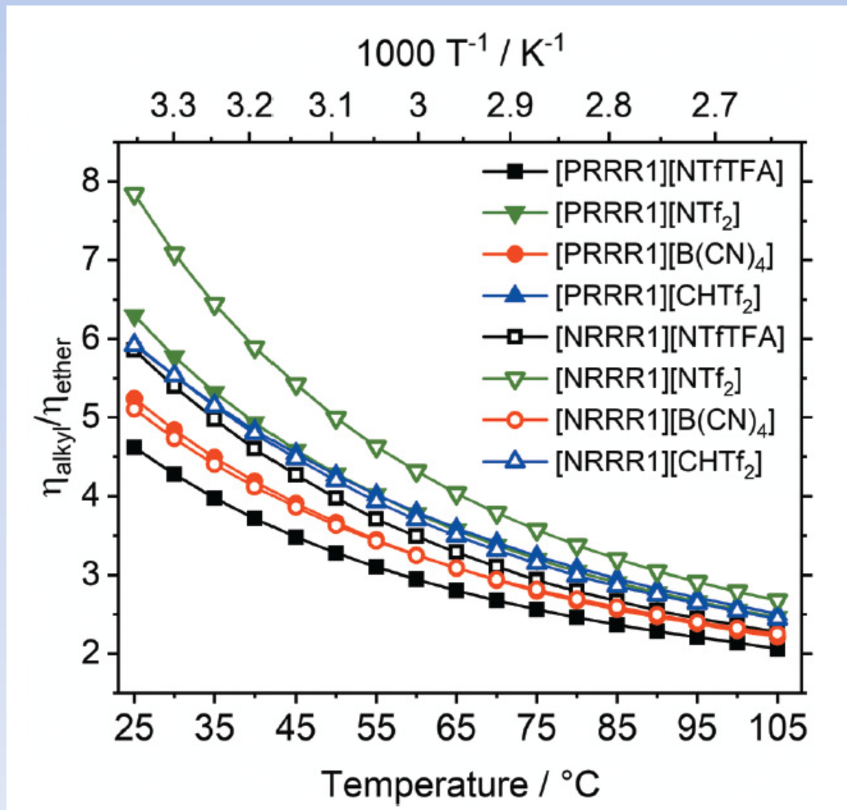
Viscosity and fluidity of ionic liquids: the role of the flexibility of ions







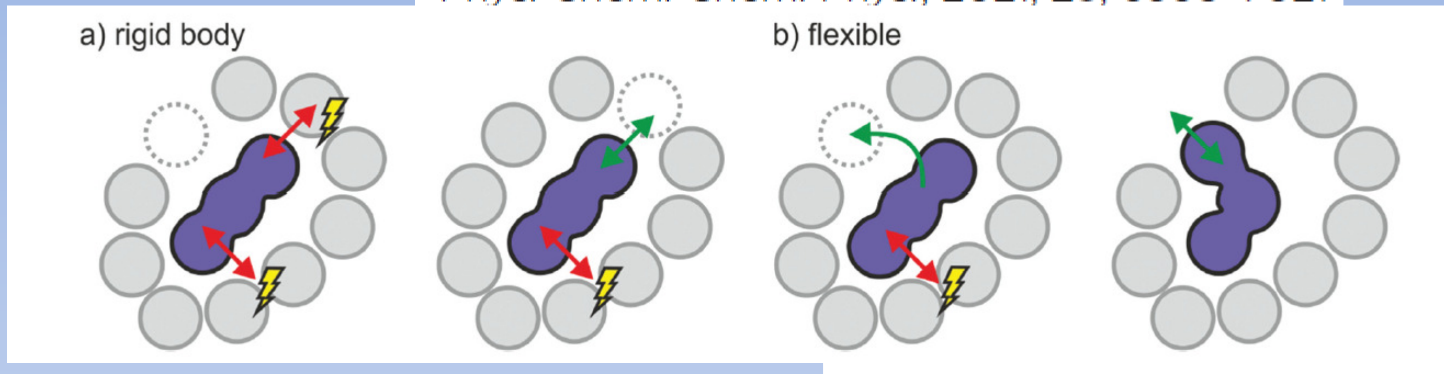
Phys. Chem. Chem. Phys., 2020, **22**, 23038–23056

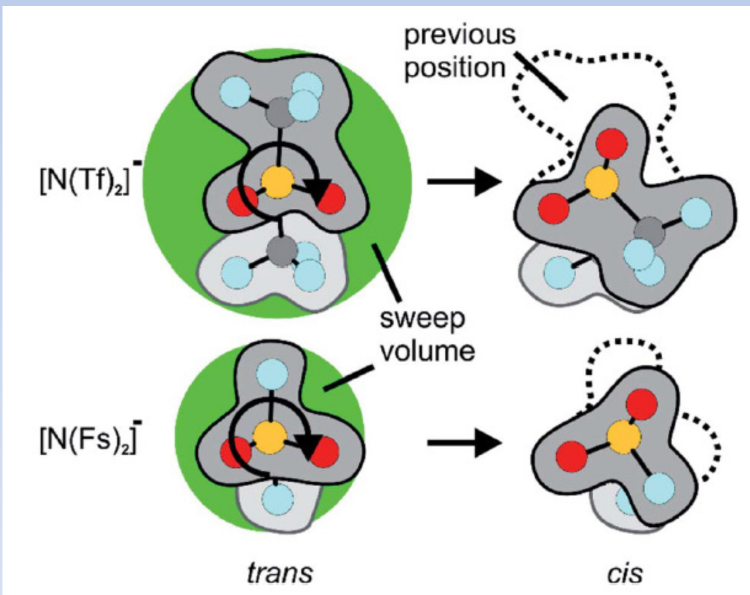


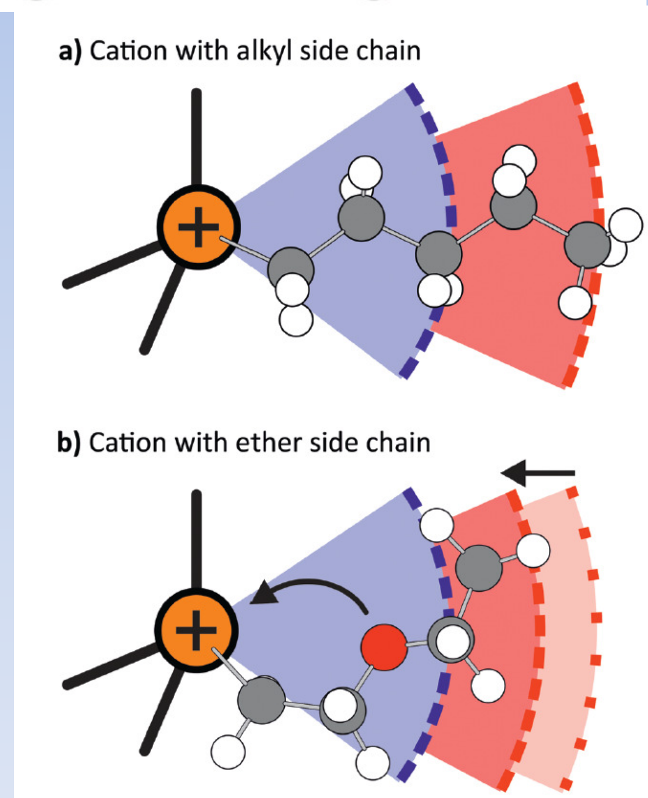
Ionic liquids with more flexible ions tend to have lower viscosity

Viscosity and fluidity of ionic liquids: the role of the flexibility of ions

Phys. Chem. Chem. Phys., 2021, **23**, 6993–7021

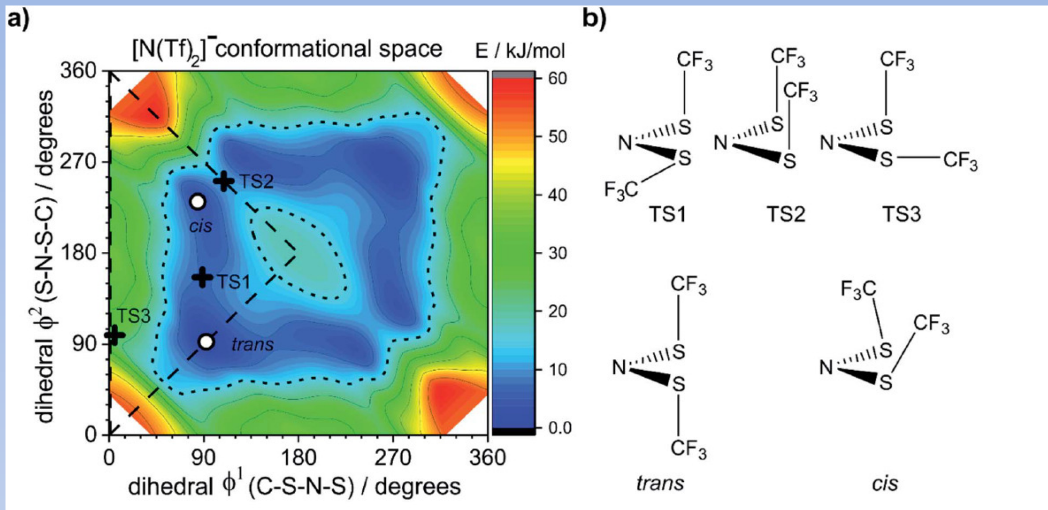




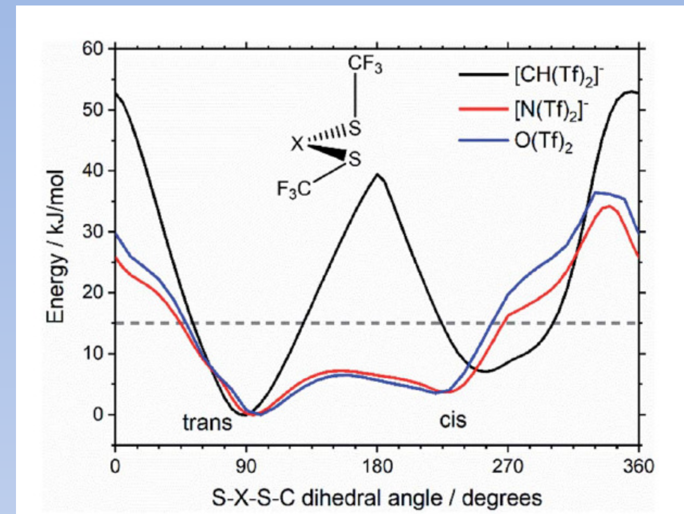


Phys. Chem. Chem. Phys., 2020, **22**, 23038–23056

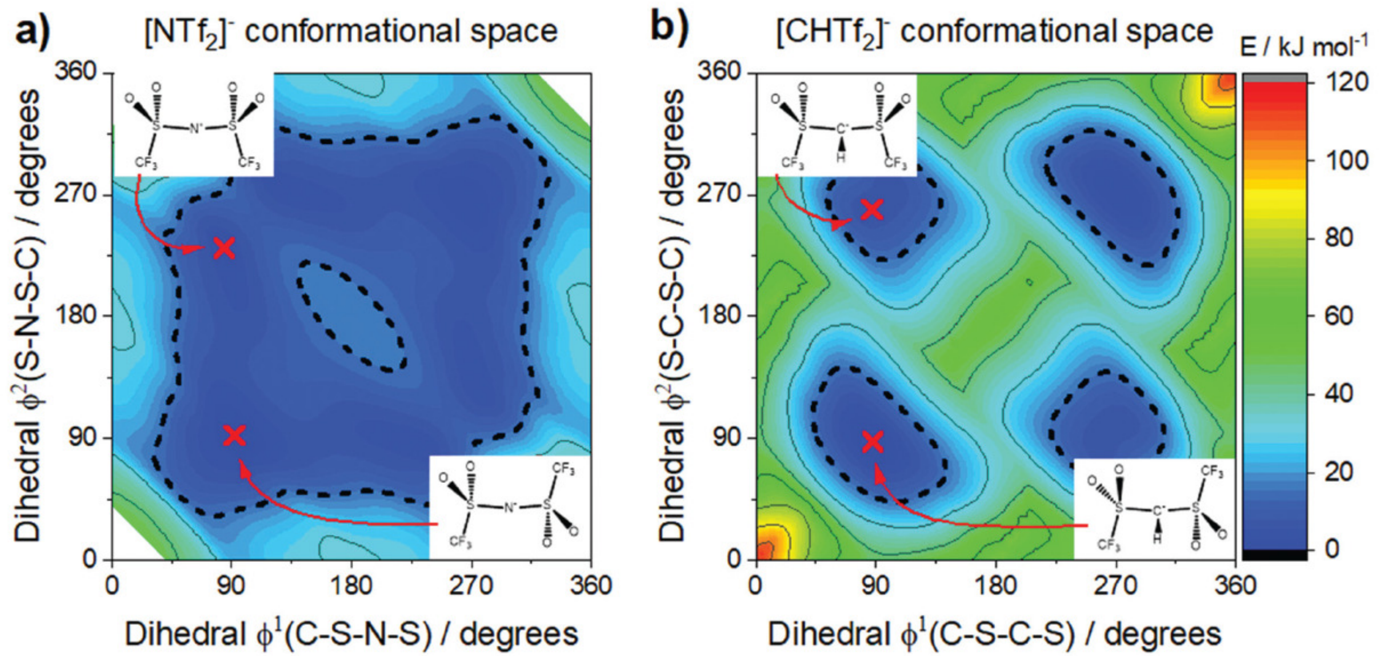
How much energy do we need to change conformations?



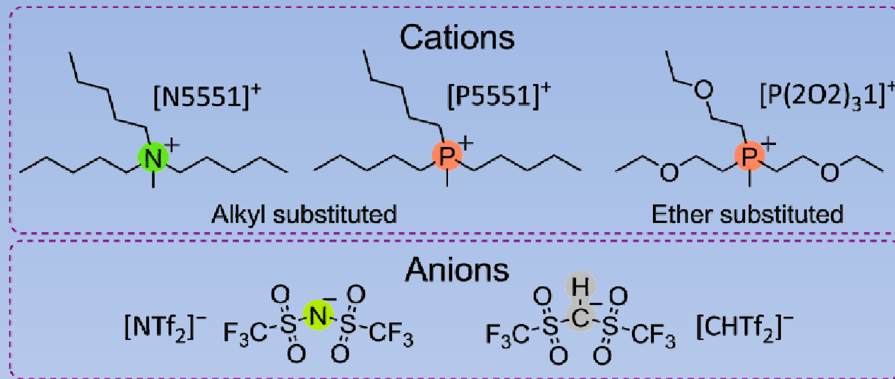
Chem. Sci., 2020, **11**, 6405–6422



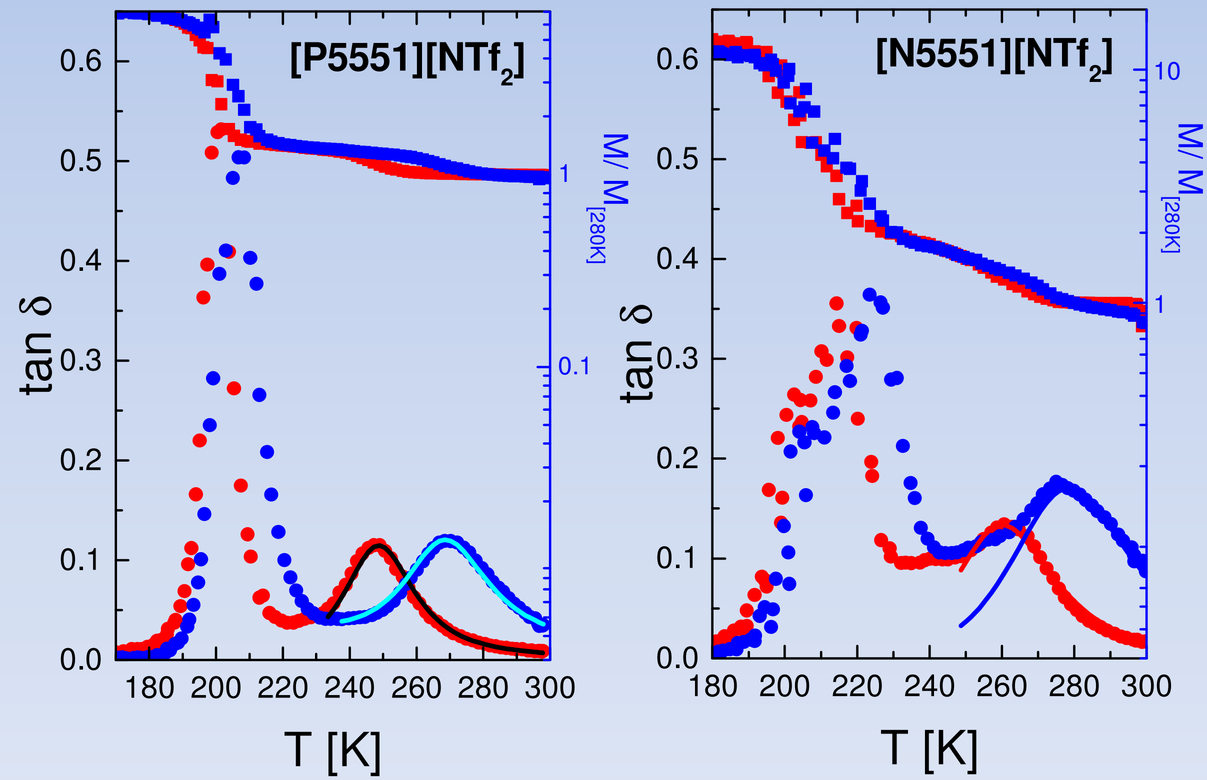
$$\frac{k^{\mathrm{NTf_2}}}{k^{\mathrm{CHTf_2}}} = \exp\left(\frac{E_A^{\mathrm{CHTf_2}} - E_A^{\mathrm{NTf_2}}}{RT}\right) \approx 9 \times 10^5$$



DMA measurements on ionic liquids with a more flexible anion



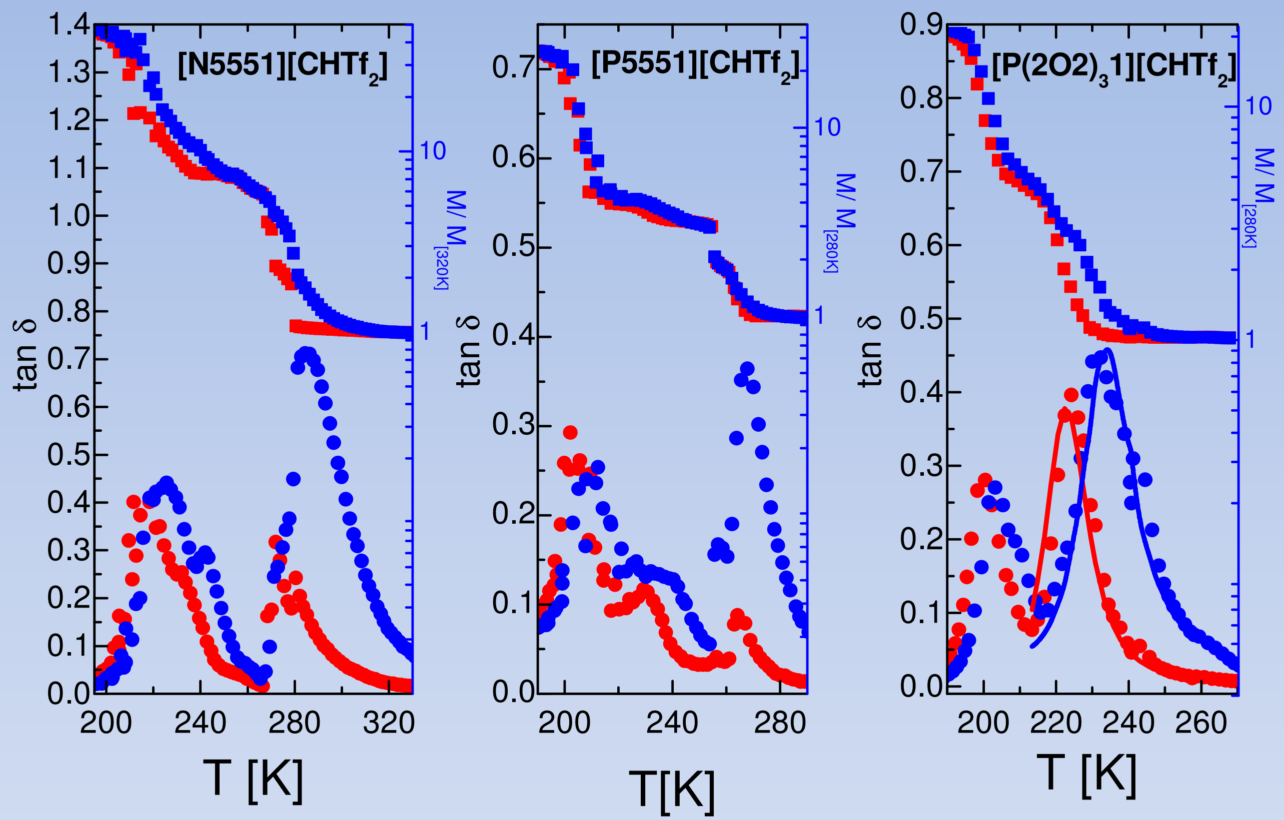
The ionic liquids with a more flexible anion display relaxation dynamics



Journal of Alloys and Compounds 919 (2022) 165860

DMA measurements on ionic liquids with a less flexible anion

The ionic liquids with a less flexible anion tend to crystallize and display no relaxation, except that with a very flexible cation.



	τ_o [s]	T_0 [K]	α	E [eV]	ΔE [meV]
[P5551][NTf$_2$]	(4.1±0.1)10^{-13}	35 ±5	0.9 ±0.1	0.49±0.02	27±3
[N5551][NTf$_2$]	(1.5±0.2)10^{-13}	56±5	0.6±0.2	0.49±0.02	27±7
[P(2O2)$_3$1][CHTf$_2$]	(1.0±0.1)10^{-13}	88±8	0.95±0.02	0.32±0.01	52±8

Journal of Alloys and Compounds 919 (2022) 165860

Conclusions

- A method to investigate ionic liquids by mechanical spectroscpy was developed.

-Dynamical mechanical analysis can provide information about both phase transitions and relaxation processes in ionic liquids.

- Ionic liquids with more flexible ions give rise to relaxation processes with loer activation energy and asymmetry

- Ionic liquids with more rigid ions tend to crystallize more easily

Acknowledgements

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