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Wir schaffen Wissen – heute für morgen

Jan P. Embs

Laboratory for Neutron Scattering & Imaging

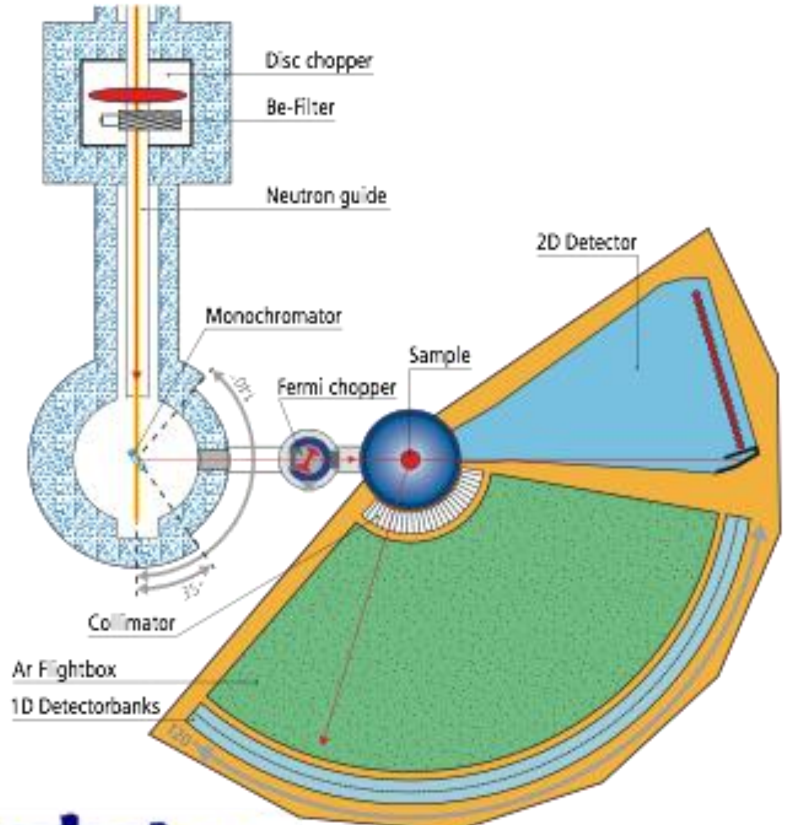
Cation Dynamics in Ionic Liquids (ILs) as Seen by QuasiElastic Neutron Scattering (QENS)

5th Swiss-Sino Workshop, 4th-5th May 2015

outline

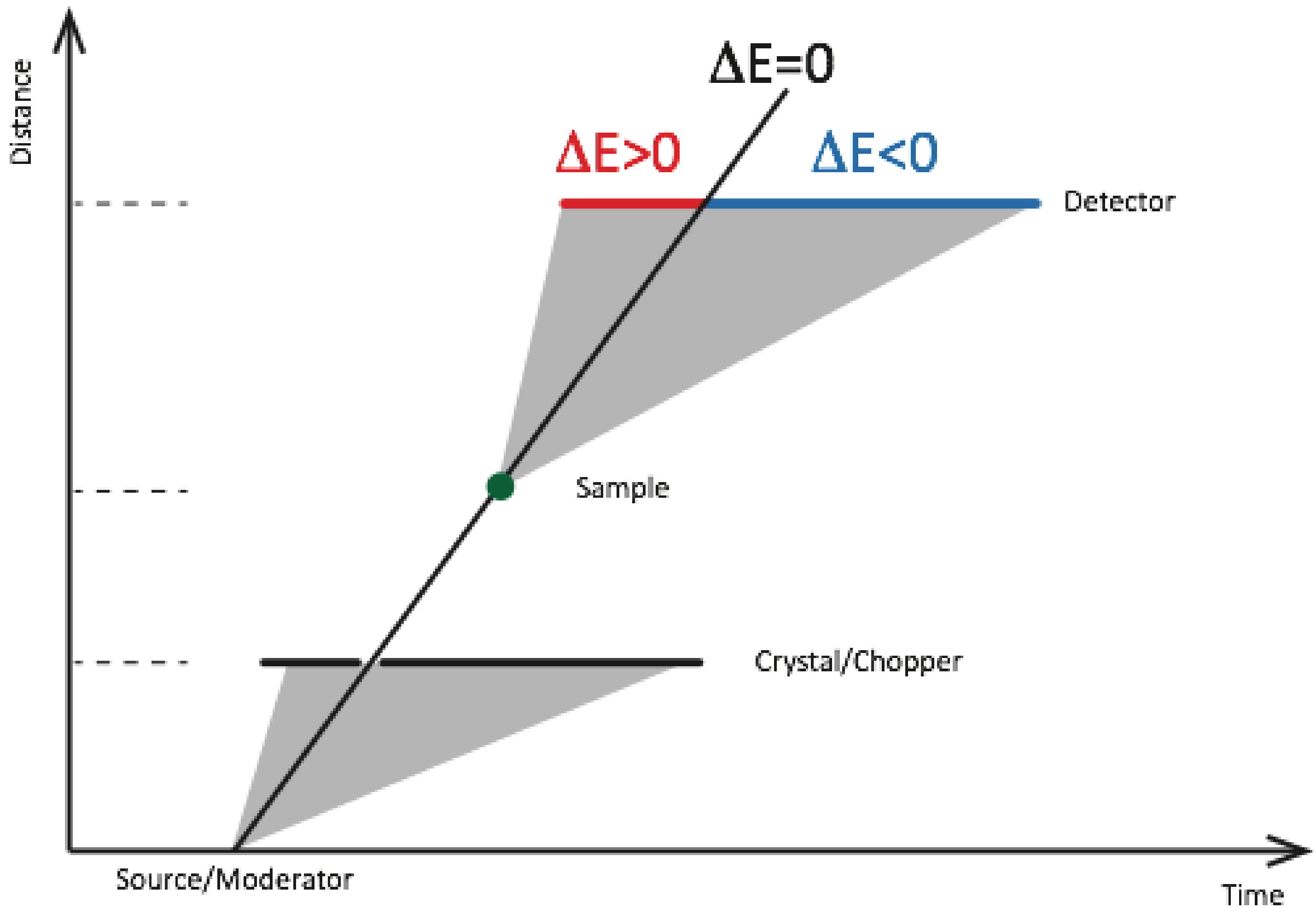
- FOCUS
- QENS
- ILs
- QENS results
- INS on ILs
- Outlook

- 2 Å ≤ λ ≤ 6 Å (PG)
- 6 Å ≤ λ ≤ 16 Å (MICA)
- energy range: 20 – 0.3 meV
- 20 mK ≤ T ≤ 1400 K
- p ≤ 1.2 GPa
- H ≤ 9T



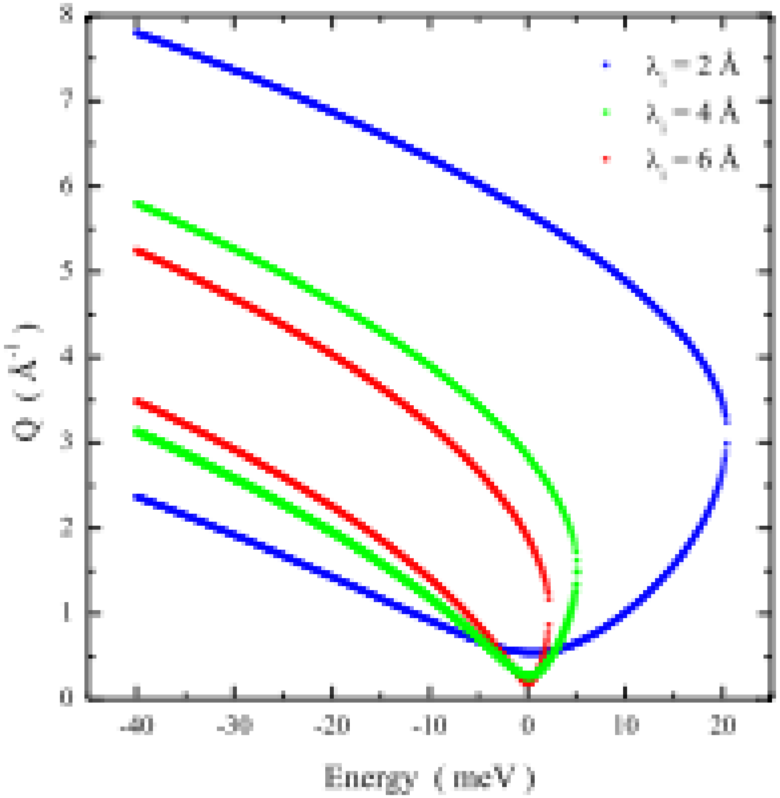
QENS (diffusion, librations, …)
INS (VDOS, magnetic excitations)

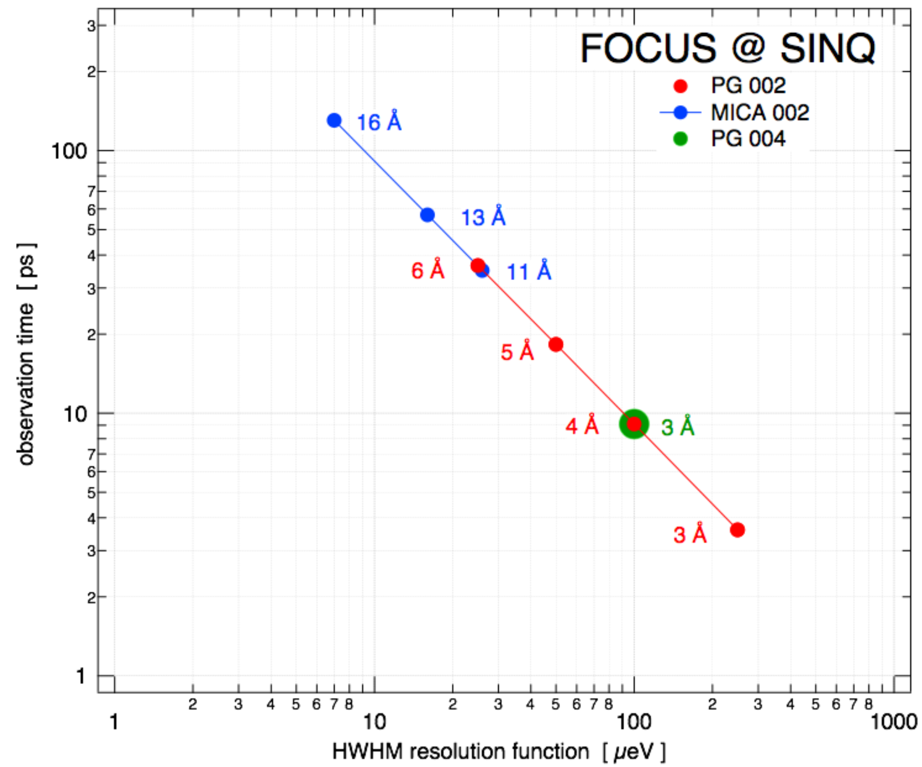
time-of-flight (tof) method



$$I(\mathrm{tof}, 2\theta) \Rightarrow I(Q, \omega) \propto S(Q, \omega)$$

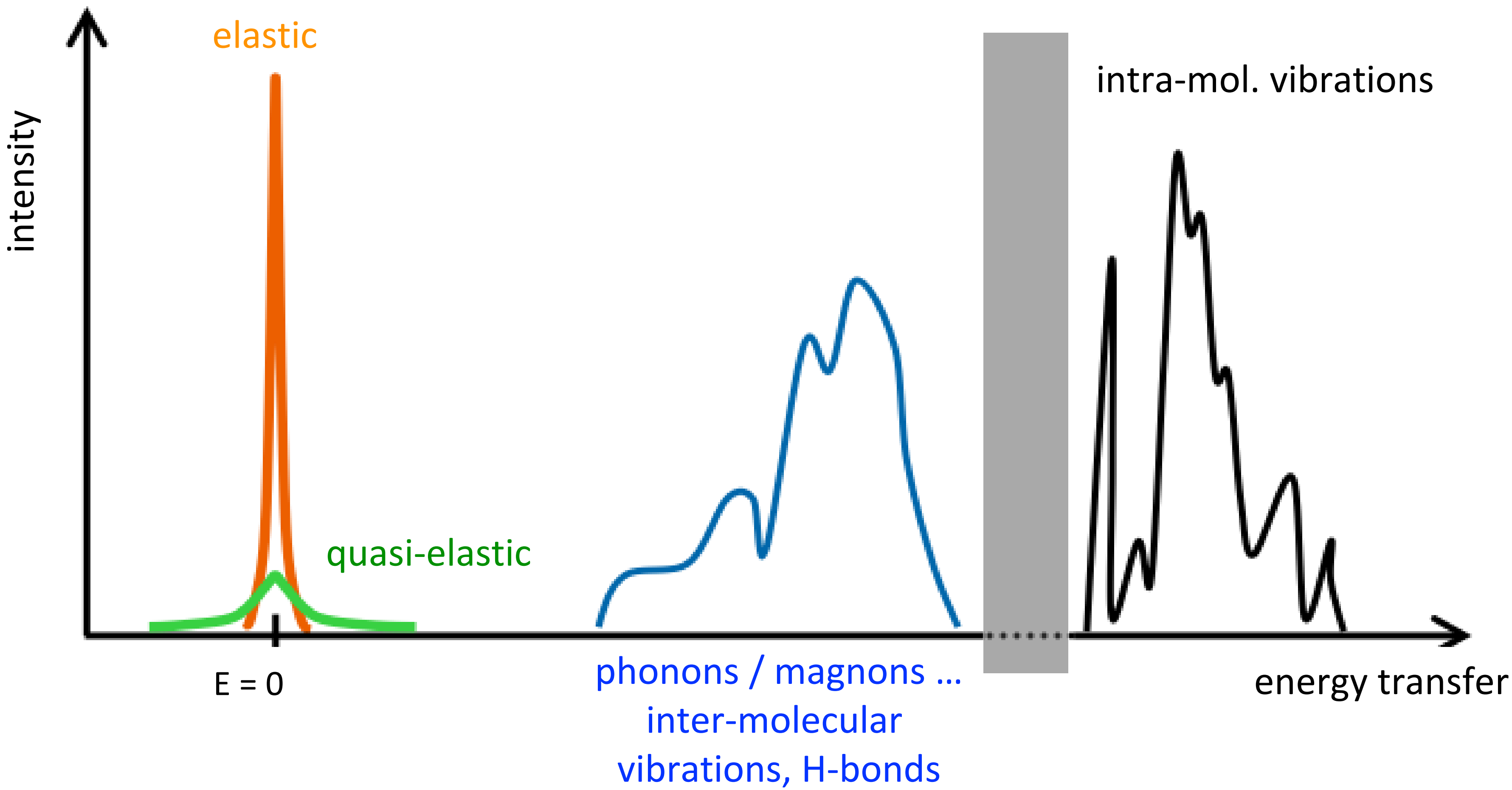
Q-E landscape





$$\Delta t_{\mathrm{obs}} = \frac{2\hbar\sqrt{\ln 2}}{\Delta E}$$

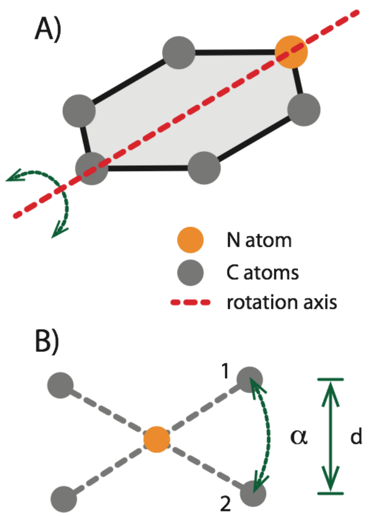
what can be measured?

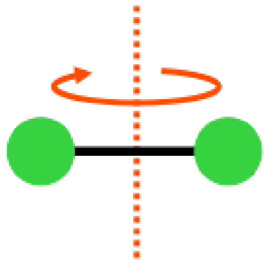


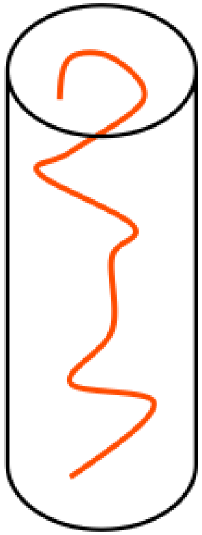
- far-IR / Raman
- dielectric relax spectroscopy
- NO selection rules for neutrons

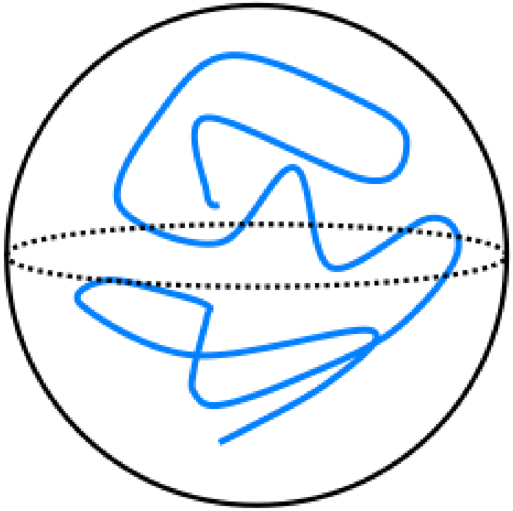
quasielastic neutron scattering = QENS

- stochastic atomic motions on ps time scale
- reveals spatial details of the dynamic process (jump distances, rot. angles etc.)
- discerns between localised (e.g., rotational) & translational types of motions
- well suited for samples containing protons
- masking via deuteration









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IL applications

10^{18}

Separation
- gas separation
- extraction
- membranes

Lubricants & Additives
- lubricants
- fuel additives

Electroelastic Materials
- artificial muscles
- robotics

Electrolytes
- fuel cells
- sensors
- batteries
- supercaps
- metal finishing
- coating

Ionic Liquids

✴ thermal stability
✴ (very) low vapor pressure
✴ electric conductivity
✴ interesting solvent properties
✴ liquid crystalline structures
✴ high heat capacity
✴ high electroelasticity
✴ non flammability
⇔ **designer solvents**

Solvents
- bio-catalysis
- organic reactions & catalysis
- synthesis of nano-particles
- polymerization
- protein-crystallisation

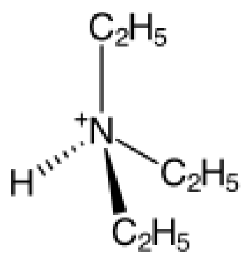
Heat Storage
- thermal fluids

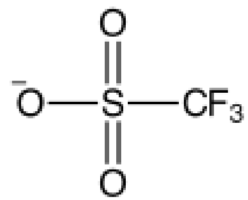
Liquid Crystals
- displays

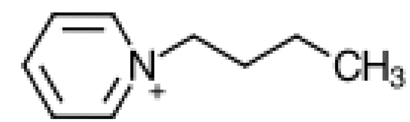
scattering cross sections

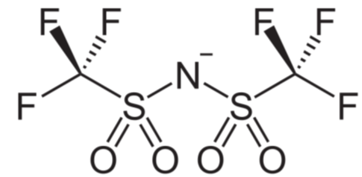
element	σ_{coh}	σ_{inc}	σ_{scatt}	σ_{abs}
H	1.7568	80.26	82.02	0.3326
D	5.592	2.05	7.64	0.000519
C	5.559	0	5.559	0.00353
O	4.232	0	4.232	0.0001
N	11.03	0.5	11.53	1.91
F	4.017	0.0008	4.018	0.0096
S	0.988	0	0.988	0.54

$\sigma_{\text{scatt}} = \sigma_{\text{coh}} + \sigma_{\text{inc}}$





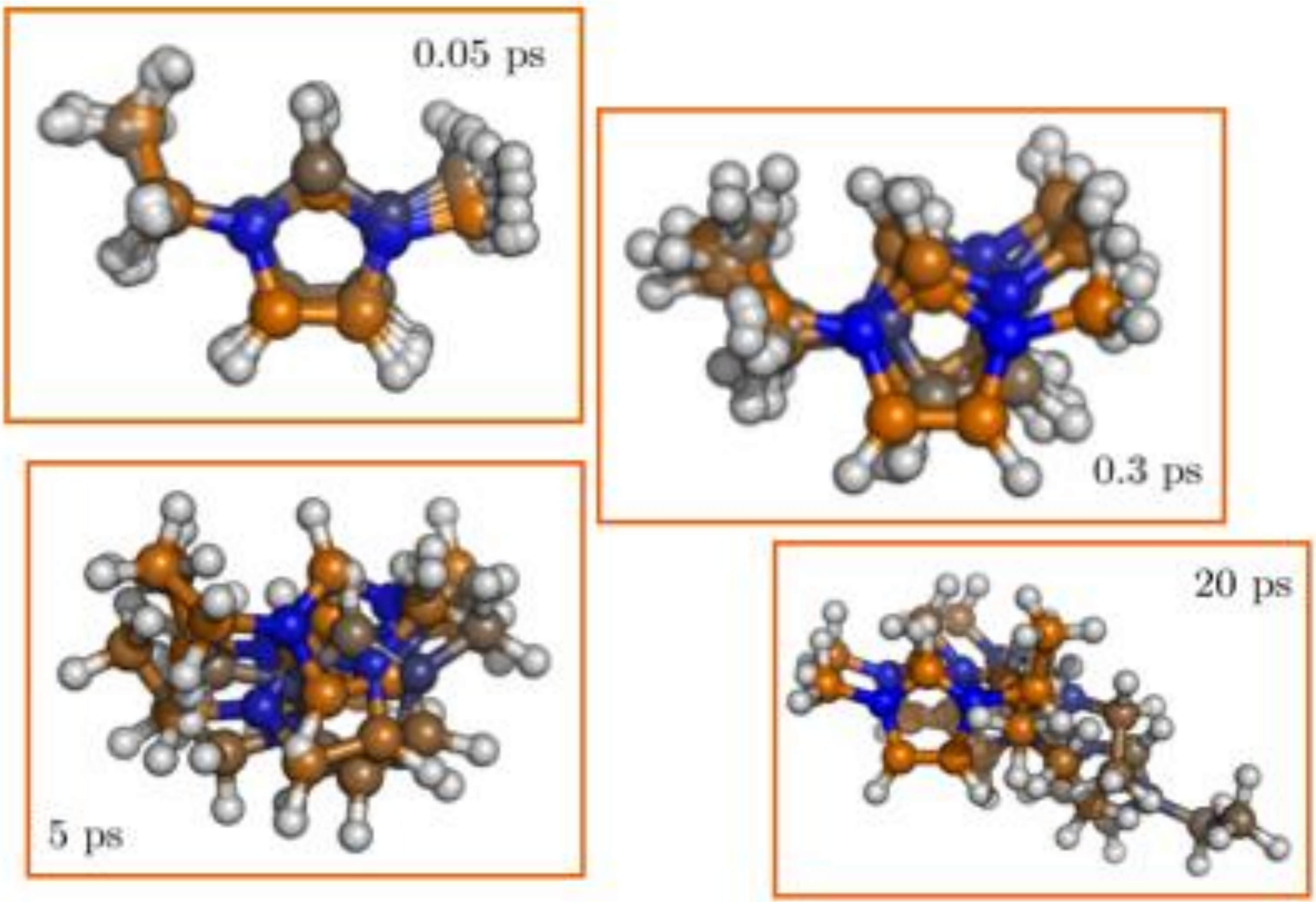




system	σ_{scatt} [b]	σ_{inc} [b]	σ_{abs} @ 5.75 Å	$\sigma_{\text{inc}}/\sigma_{\text{scatt}}$ [%]
BuPy–Tf_2N	1275.6	1124.8	30.7	88.2
Bu_DPy–Tf_2N	606.1	420.8	21.2	69.4
$BuPy_D$–Tf_2N	901.6	731.7	25.4	81.2
C_{12}Py–Tf_2N	2632.5	2409.1	47.9	91.5
TEA–TF	1388.6	1284.8	25.0	92.5
TEA_D–TF	272.8	130.0	9.0	47.6

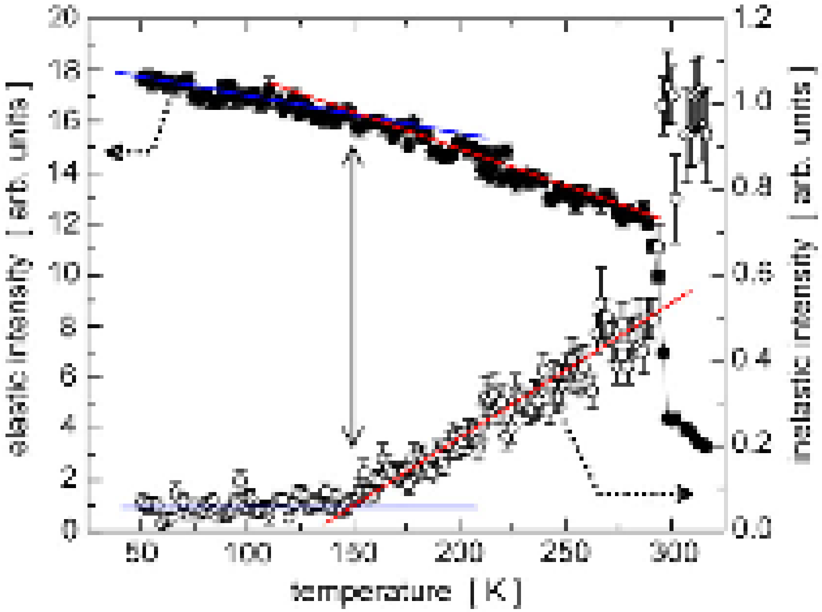
$1\text{b} = 1\text{barn} = 10^{-24}\ \text{cm}^2$

cation dynamics on different time scales

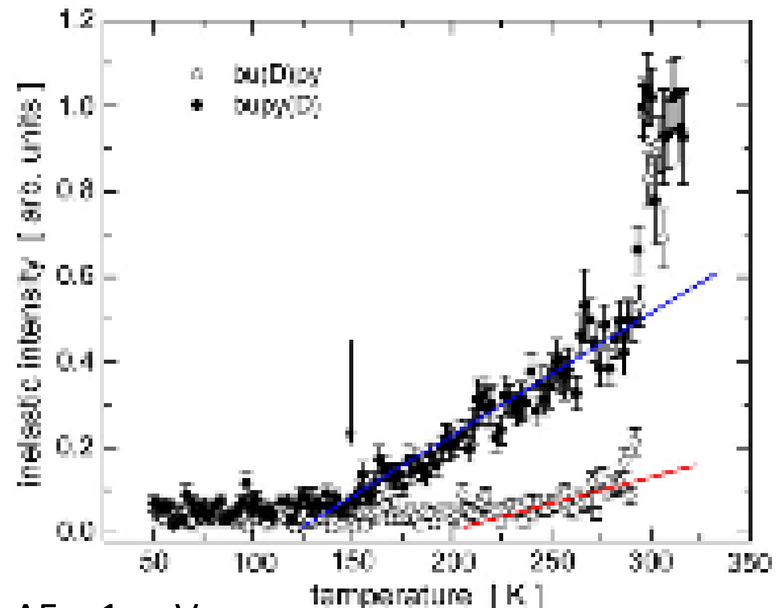


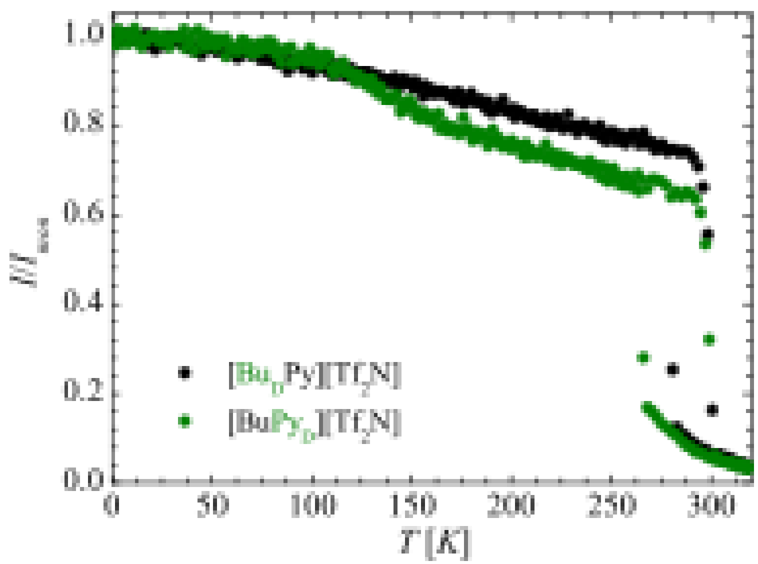
courtesy, B. Kirchner, U Bonn

chain & ring melting, FEW experiments (elastic & inelastic)



data from MARS@SINQ/PSI, ΔE ≈ 14 μeV





IN10 data, ΔE ≈ 1 μeV

Contents lists available at ScienceDirect
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journal homepage: www.elsevier.com/locate/molliq

The dynamics of cations in pyridinium-based ionic liquids by means of quasielastic- and inelastic neutron scattering

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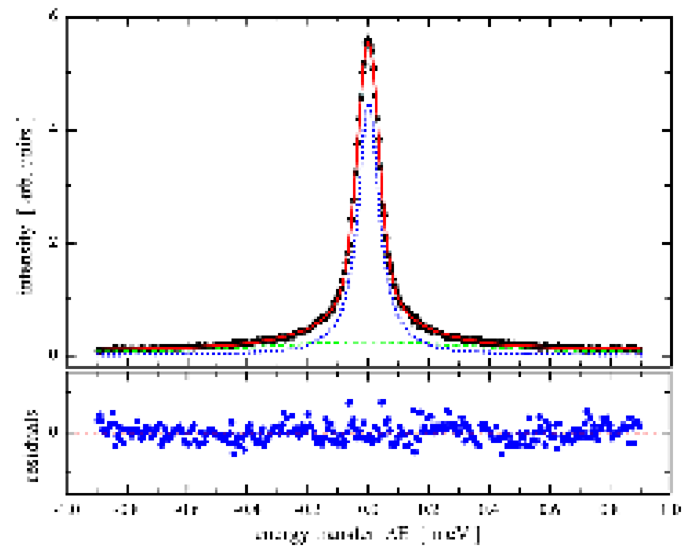
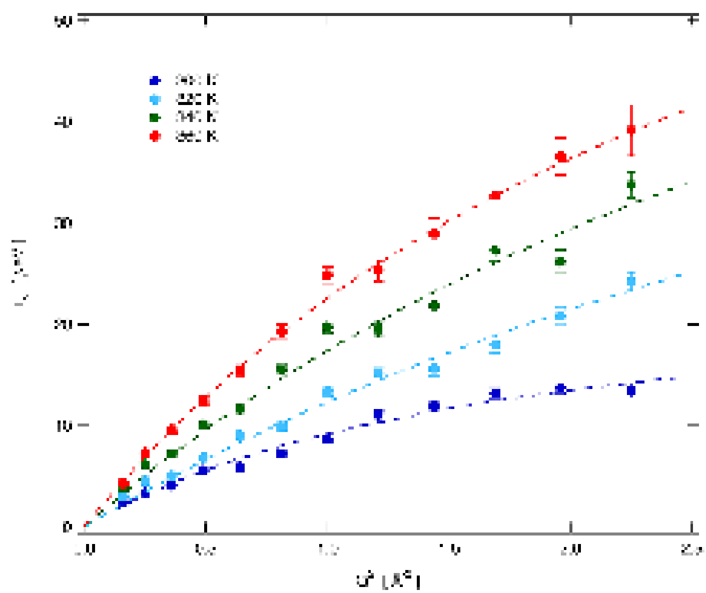
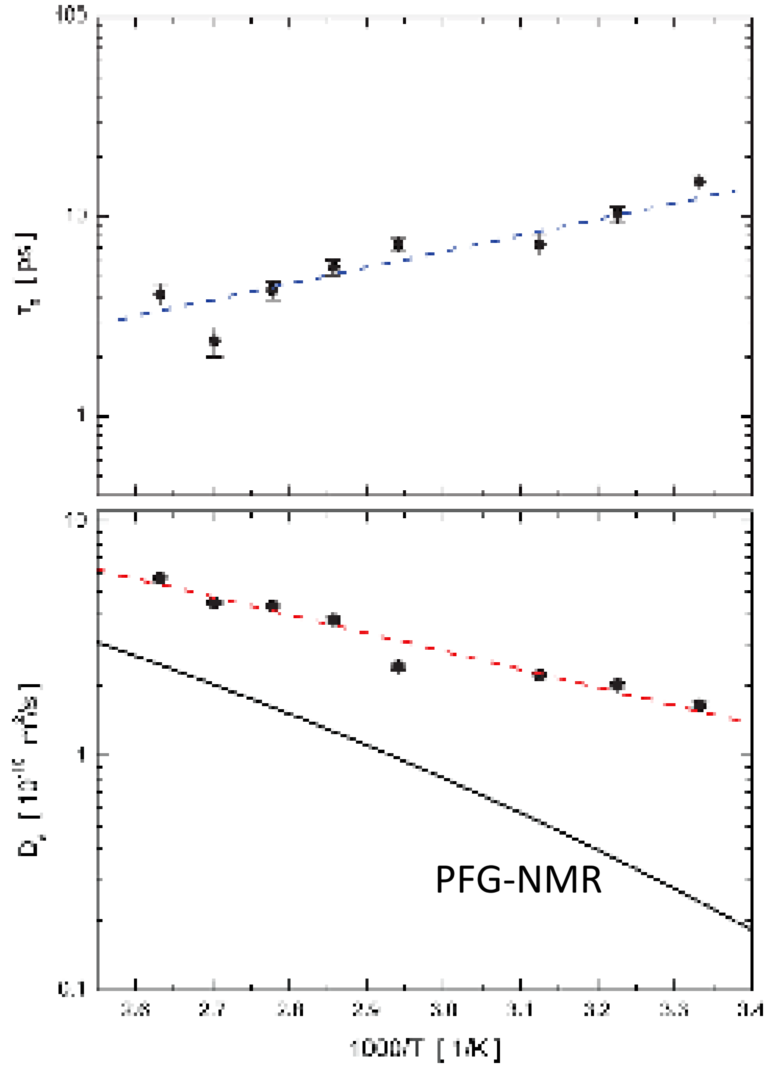
model independent analysis, T > T_m







$$\Gamma_2(Q) = \frac{\hbar D_s Q^2}{1 + D_s Q^2 \tau_0}$$

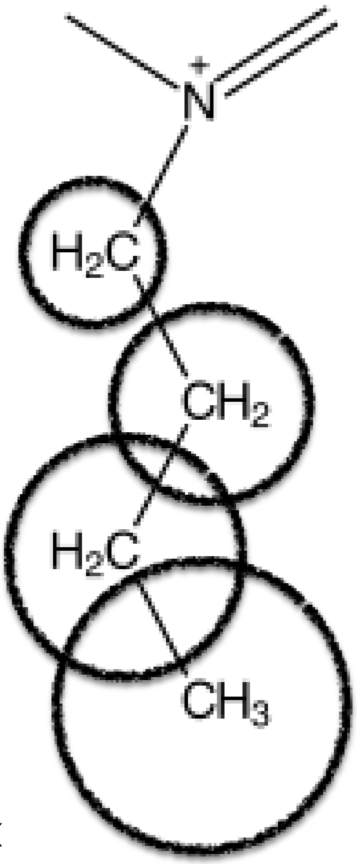
Embs, Burankova et al.
J.Phys.Chem. B **116** (2012), 13265

chain dynamics ⇒ diff. inside spherical confin. / ring deut.

Embs,Burankova et al.
J. Phys. Soc. Jpn. **82** (2013) SA003

$$S_I(Q,E) = I_0(Q) \cdot \frac{1}{\pi}\frac{\Gamma_{\rm glob}}{\Gamma_{\rm glob}^2 + E^2} \otimes \left\{ \int_0^\infty f(r_\sigma; a, \sigma_{\rm lgn}) S_G(Q,E;r_\sigma) dr_\sigma \right\} \otimes R(Q) + a + bE$$

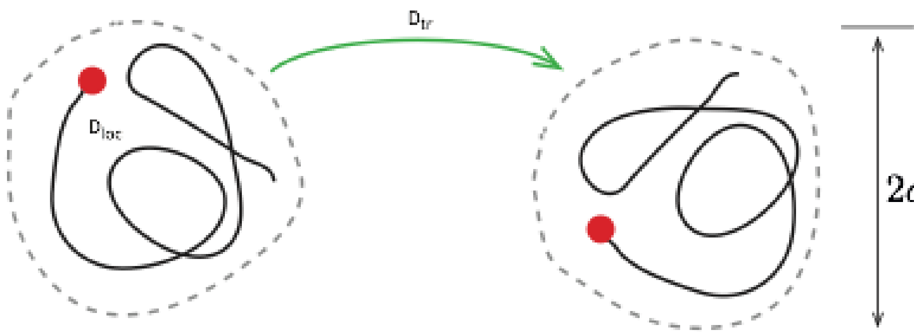
σmin

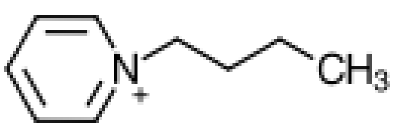


σmax

$$S_G(Q,E) = e^{-Q^2\sigma^2}\left[\delta(E) + \sum_{k=1}^{\infty}\frac{(Q^2\sigma^2)^n}{n!}\mathcal{L}(n\hbar D_{\rm loc}/\sigma^2, E)\right]$$

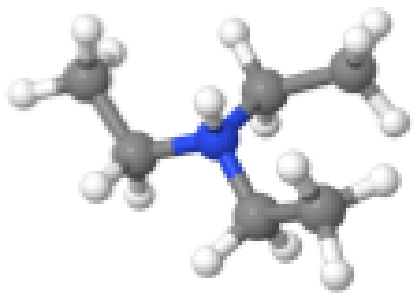
$$f(r;a,\beta) = \frac{\exp(-(\ln^2(r/a) - \beta^2)^2/2\beta^2)}{r\beta\sqrt{2\pi}}$$



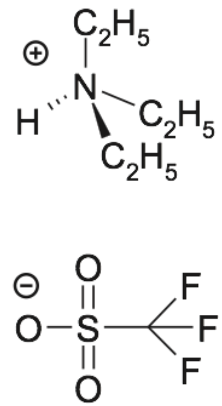


Kneller, PCCP **7** (2005), 2641
Volino et al., J Phys Chem B **110** (2006), 11217

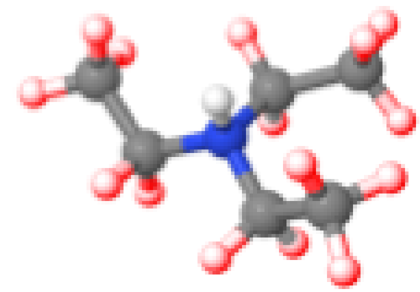
TEA



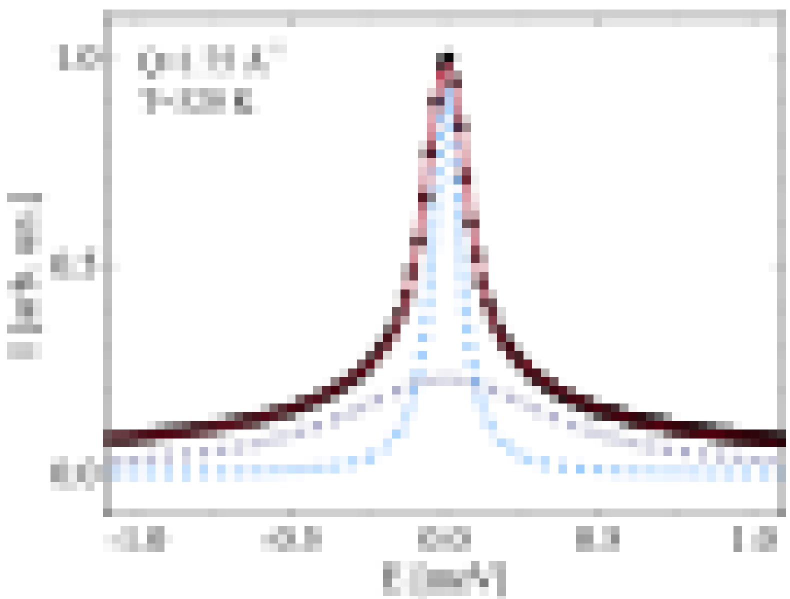
$NH(C_2H_5)_3$

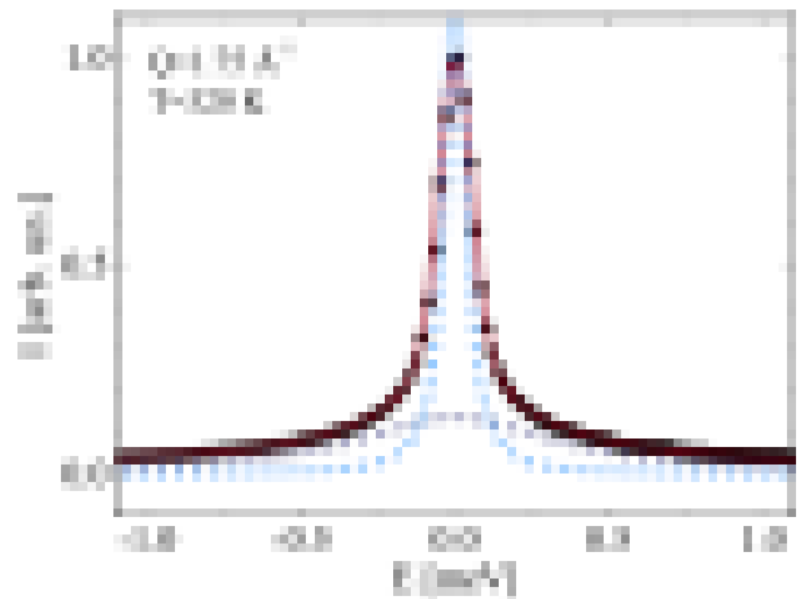


TEA_D



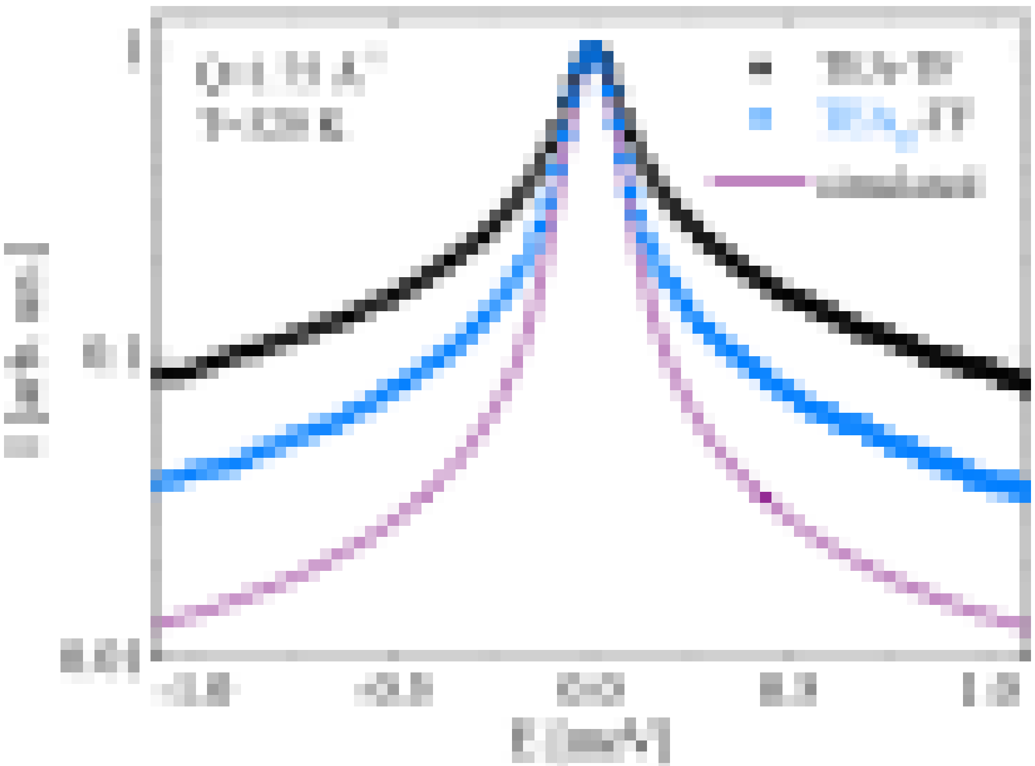
$NH(C_2D_5)_3$



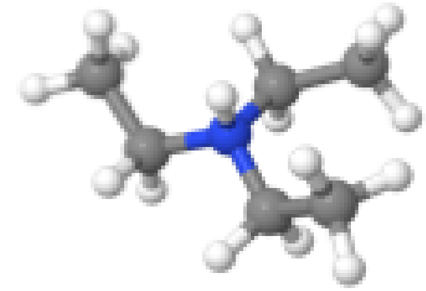


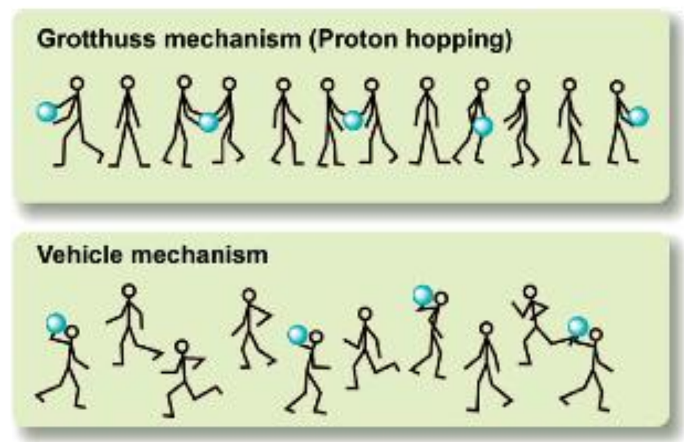
$$S(Q,E) = S_{\mathrm{local}}(Q,E) \otimes S_{\mathrm{global}}(Q,E)$$

origin of the extra component?



TEA

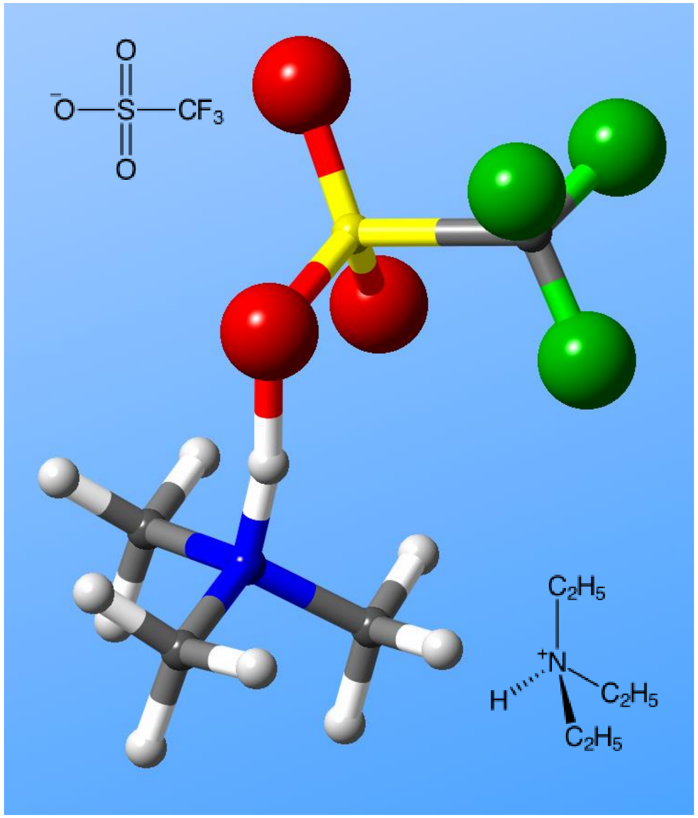




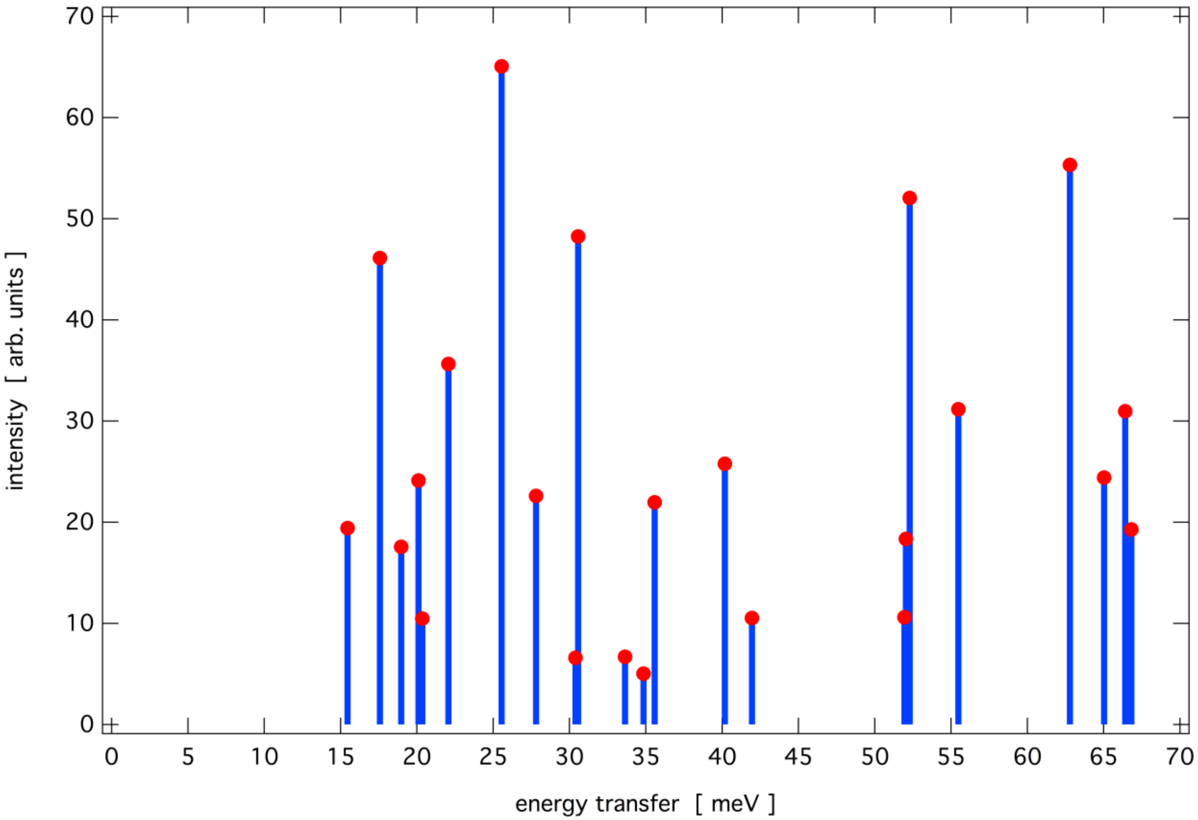
broad component in TEA_D-TF

⇒ H-bond dynamics?!?

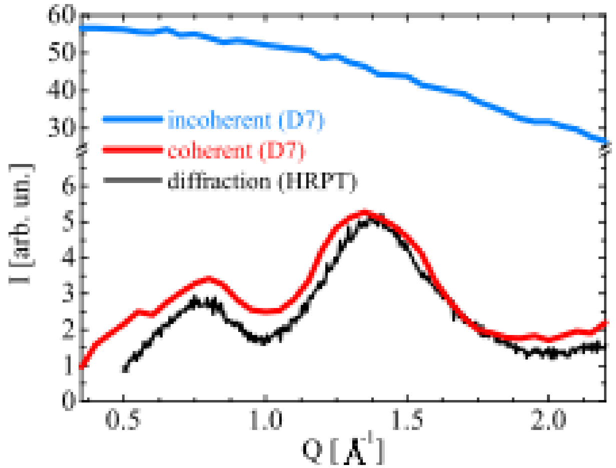
1st ab-initio MD results on TMA-TF

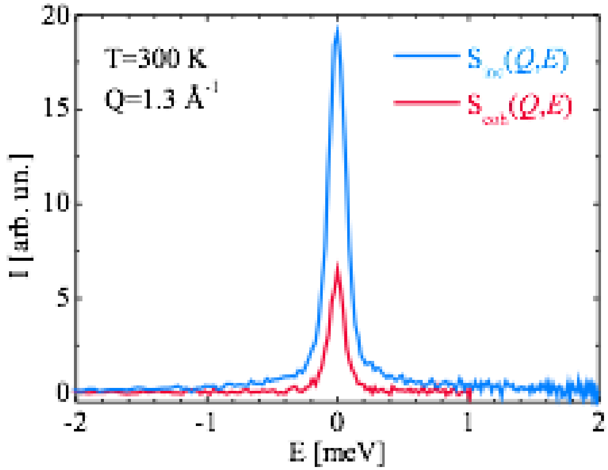


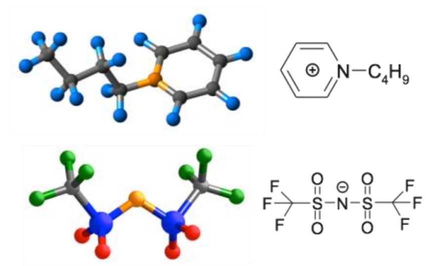
- **Coulomb, dipole-dipole, H-bonding …**
- **force field generation**
- **S(Q,ω), …**



polarized neutrons ⇒ coherent/incoherent



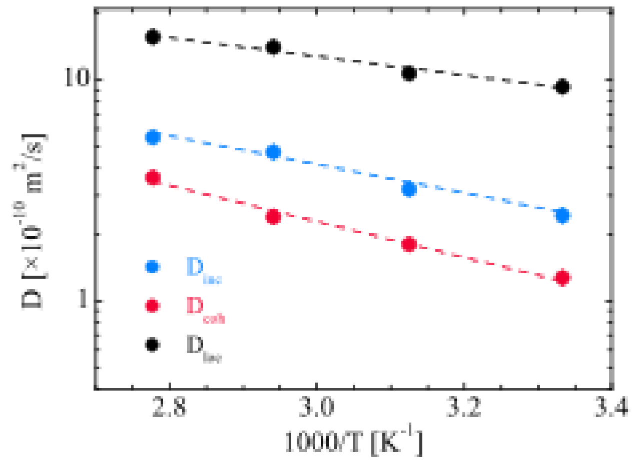


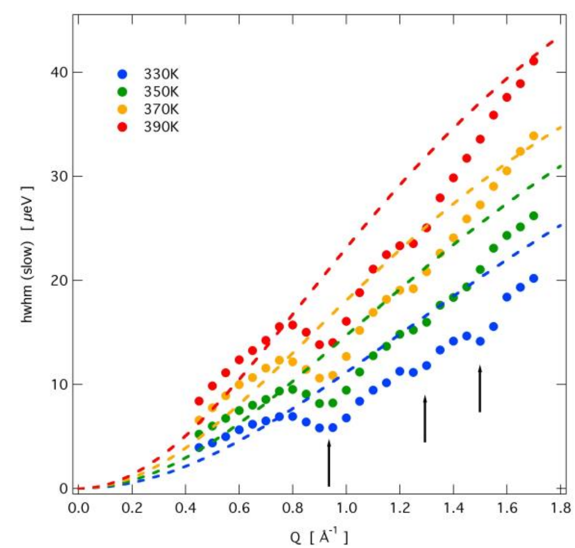


$$I_{\text{coh}} = I_{\text{corr}}^{\uparrow\uparrow} - \frac{1}{2} I_{\text{corr}}^{\uparrow\downarrow}$$

$$I_{\text{inc}} = \frac{3}{2} I_{\text{corr}}^{\uparrow\downarrow}$$

coherent/collective dynamics cannot be neglected (incoherent approx. fails), but clear picture of it still missing ⇒ MD-simulations + neutron results





outlook

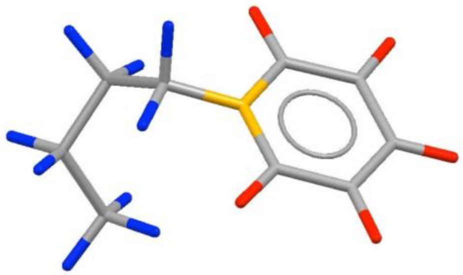
- study of collective dynamics in ILs (using deuteration & polarized neutrons)
- H-bond dynamics in protic ILs ➞ PhD project, SNF funded
- interaction of ILs with prototypical bio-structures, i.e. influence on properties and functions ➞ PSI-Fellow/COFUND in collab. with University College Dublin/School of Physics

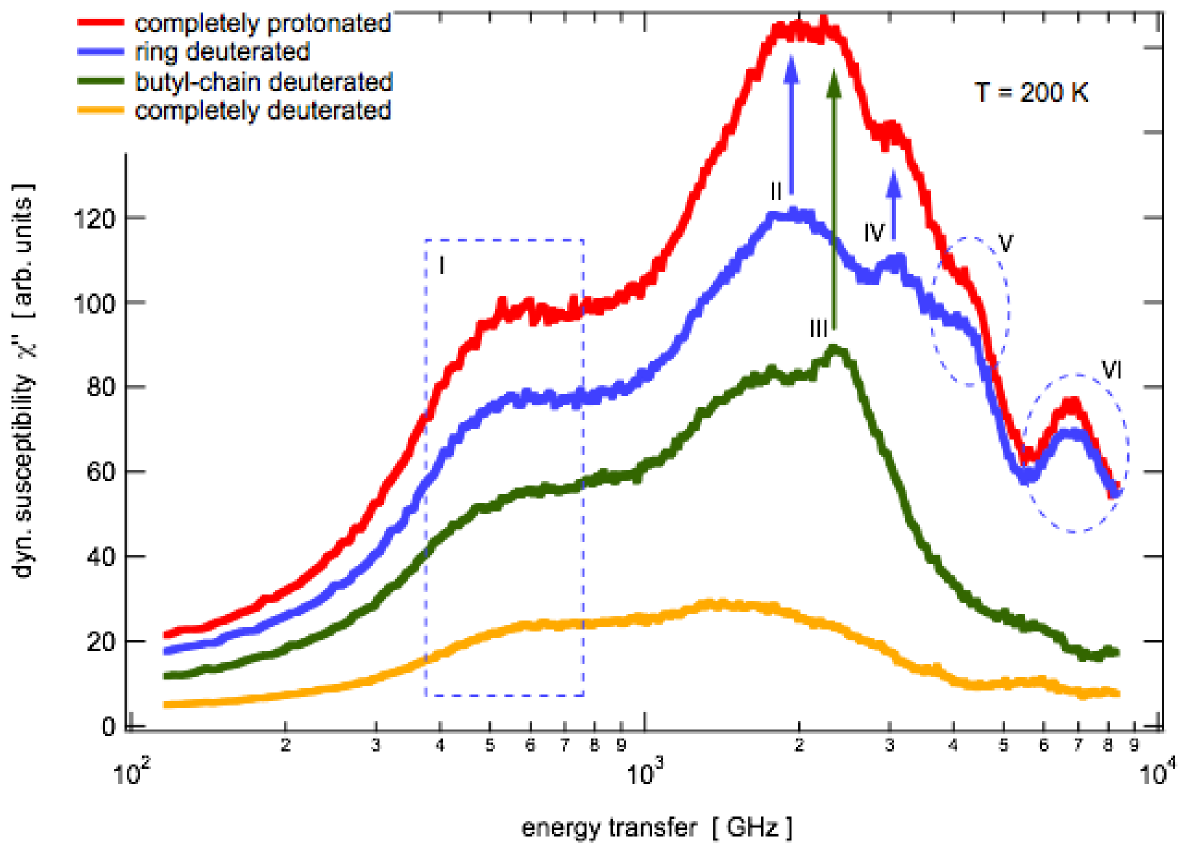
inelastic neutron scattering ⇒ DOS

QENS ⇒ time scale of molecular rotations, reorientations
diffusion mechanisms

- proton hopping (breaking/creating H-bonds) vs. vehicle mech.
- single-particle **&** collective dynamics ➞ polarized neutrons!
- comparison to MD-results

Inelastic Neutron Scattering ⇒ studies of ion interactions (H-bond dynamics)





$$\chi''(E,T) = \frac{S(E)}{n_{\mathrm{B}}(E,T)}$$

$$n_{\mathrm{B}}(E,T) = (\exp(E/k_B T) - 1)^{-1}$$

$$S(E) = \sum_{2\theta} S(2\theta, E)$$

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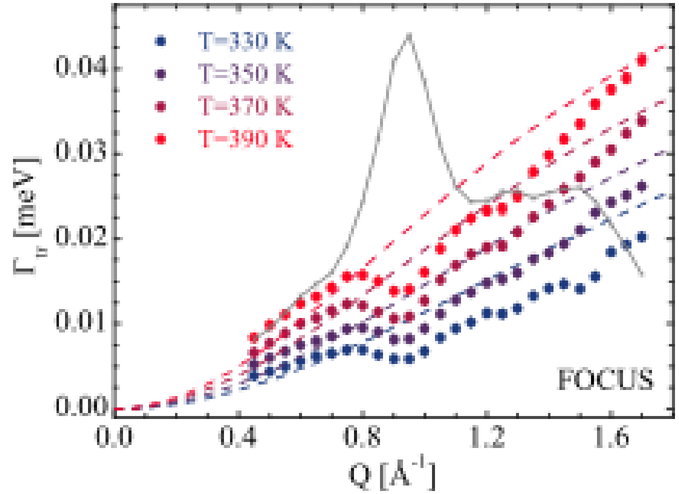
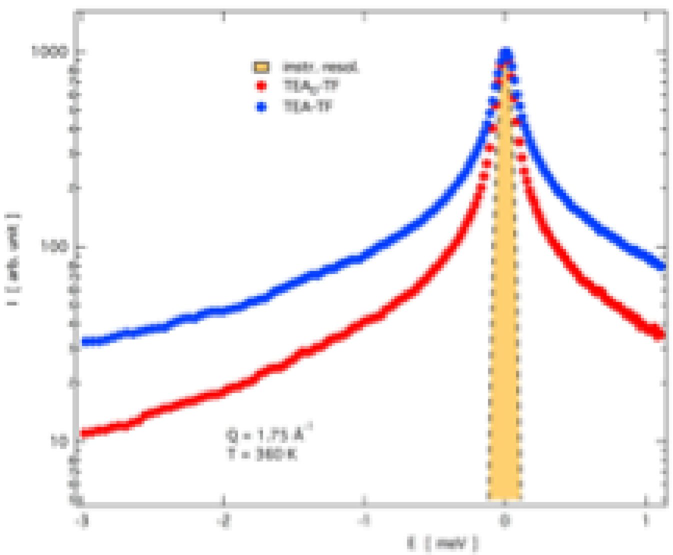
ionic liquids

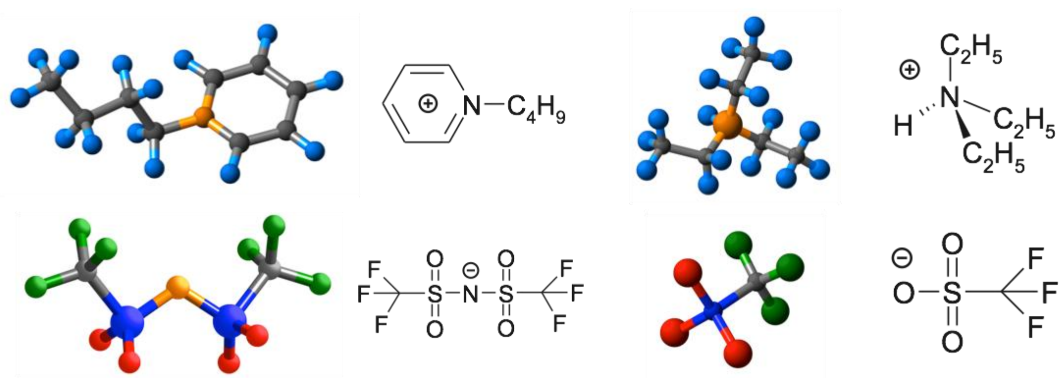
Ionic Liquids ⇒
- tunable physico-chemical properties ⇒ **designer solvents**
- high thermal & electrochemical stability / wide liquid range
- **applications:** potential electrolytes for fuel cells, batteries, …
- Coulomb, dipole-dipole interactions, H-bonding …

QENS ⇒ time scale of molecular rotations, reorientations diffusion mechanisms
- proton hopping (breaking/creating H-bonds) vs. vehicle mech.
- single-particle **&** collective dynamics ➞ polarized neutrons!
- comparison to MD-results

Inelastic Neutron Scattering ⇒ studies of ion interactions (H-bond dynamics)







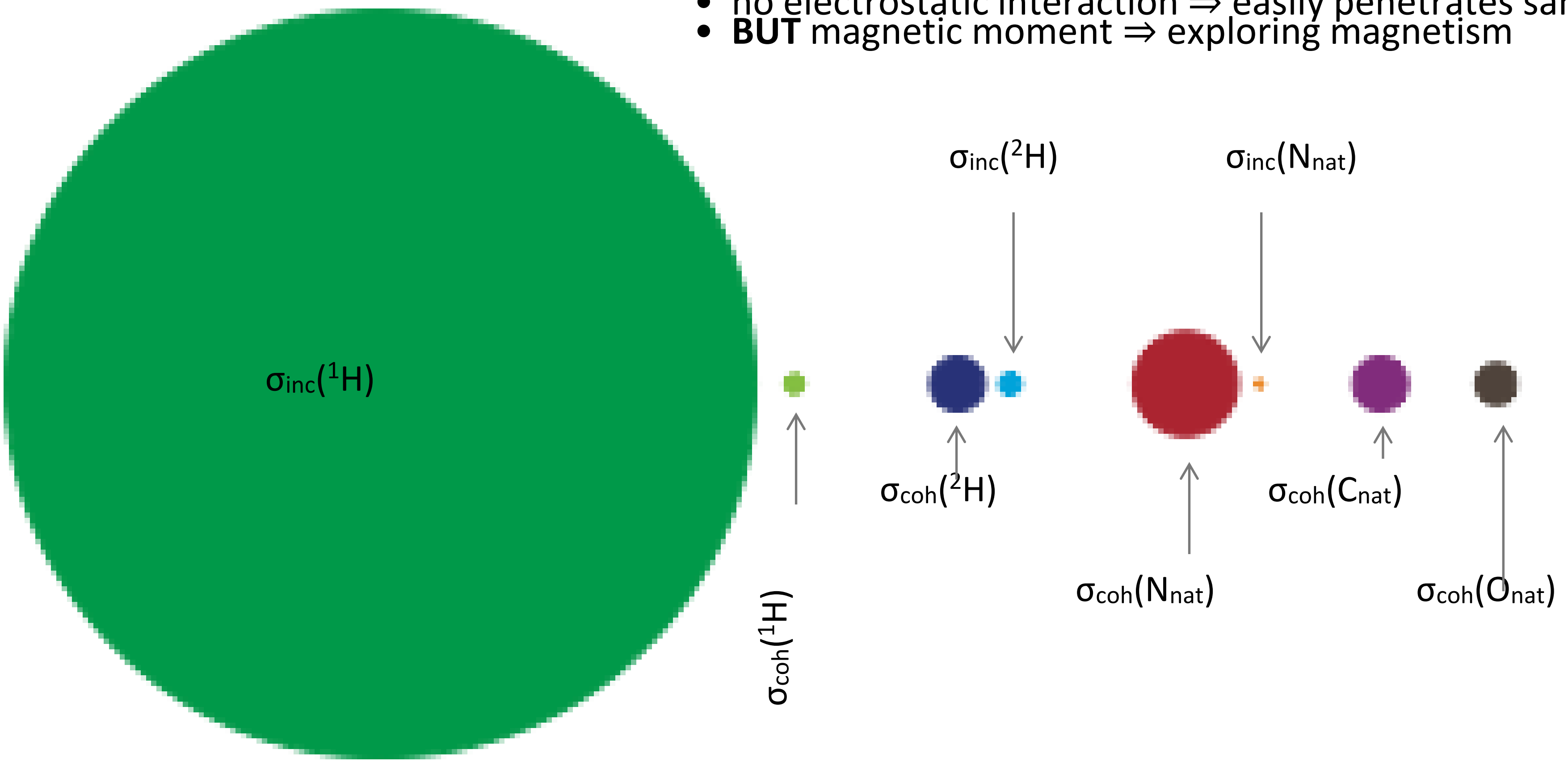
- Z. Phys. Chem. **224** (2010) 5
- J. Phys. Chem. B **116** (2012) 13265
- J. Phys. Soc. Japan **82** (2013) SA003
- J. Mol. Liquids **192** (2014) 199
- J. Phys. Chem. B **118** (2015), 14452–14460
- J.Phys. Chem. B (2015) submitted

scatt cross sections

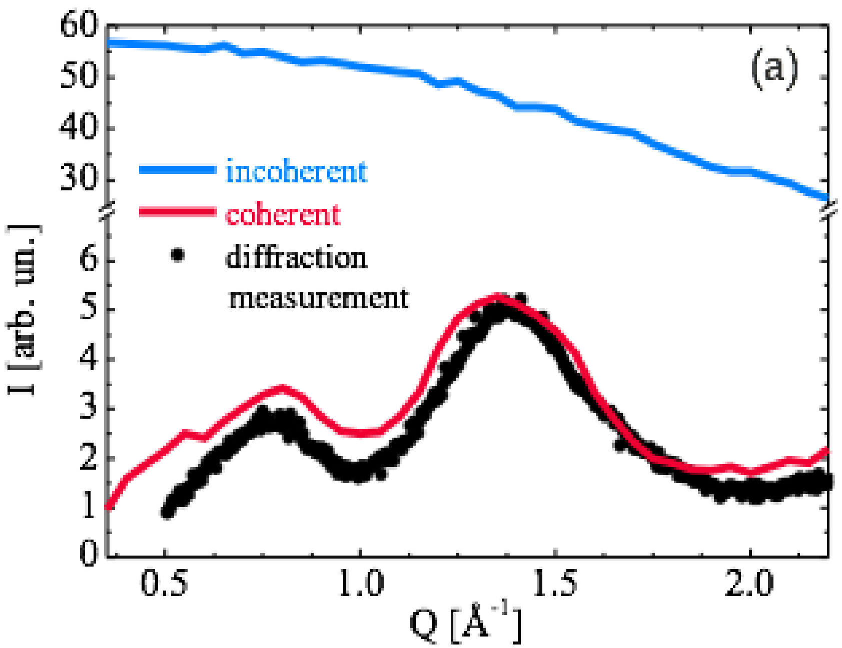
cross section σ (1 b = 1 barn = 10^{-24} cm^2)

area ⇒ prob. that a neutron will interact with a nucleus

- scattering power varies ‘randomly’
- strong but very short ranged interaction
- isotopic labeling
- no electrostatic interaction ⇒ easily penetrates samples
- **BUT** magnetic moment ⇒ exploring magnetism

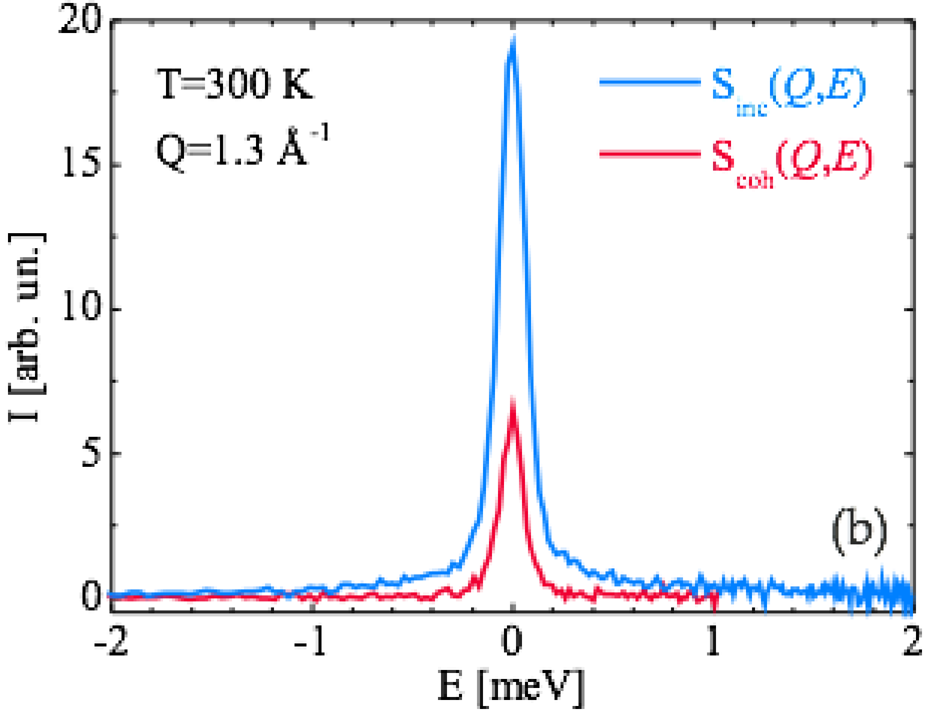


D7 results - I / separation coh & inc contributions



$$I_{\uparrow\uparrow} = I_{\mathrm{coh}} + \frac{1}{3} I_{\mathrm{inc}}$$

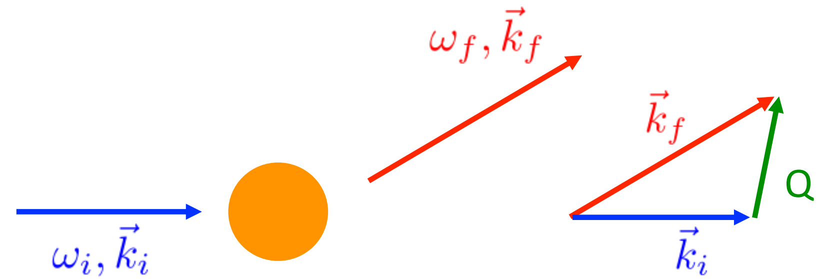
$$I_{\uparrow\downarrow} = \frac{2}{3} I_{\mathrm{inc}}$$

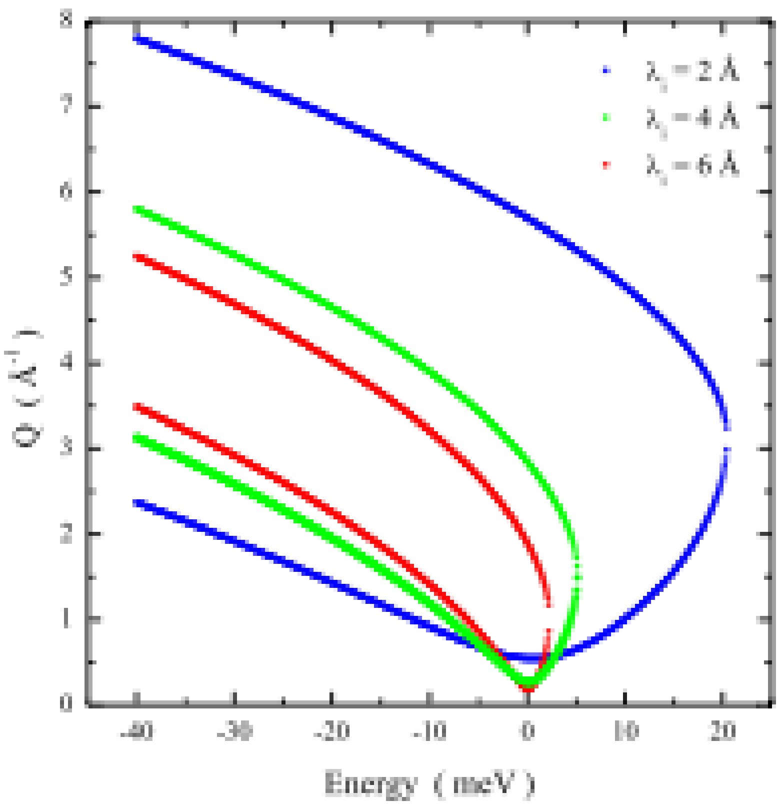


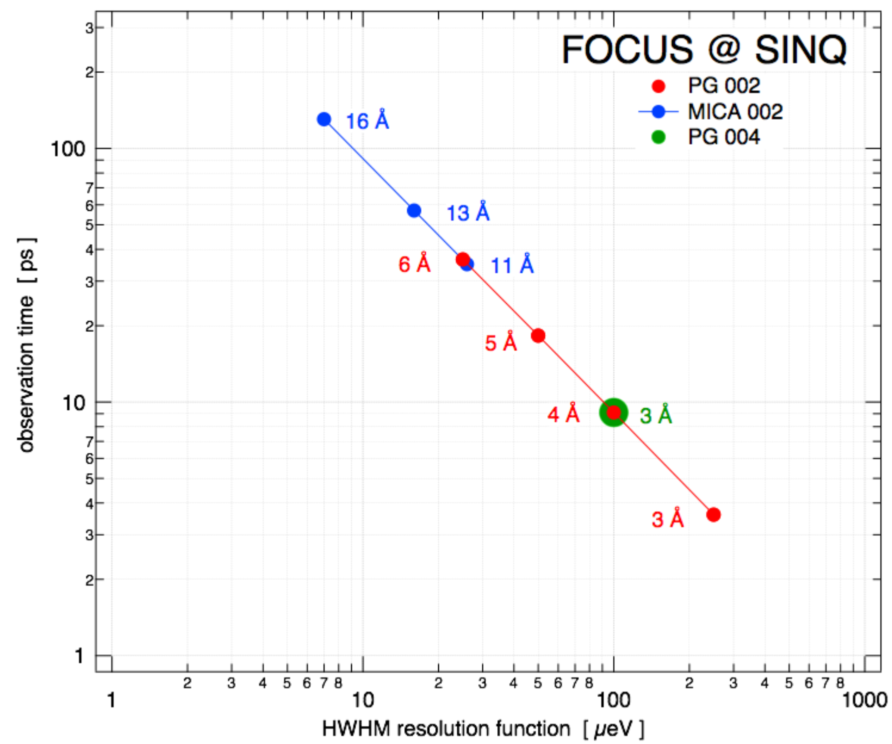
Q-E landscape

$$\hbar\omega = \hbar(\omega_f - \omega_i)$$

$$\hbar\vec{Q} = \hbar(\vec{k}_f - \vec{k}_i)$$







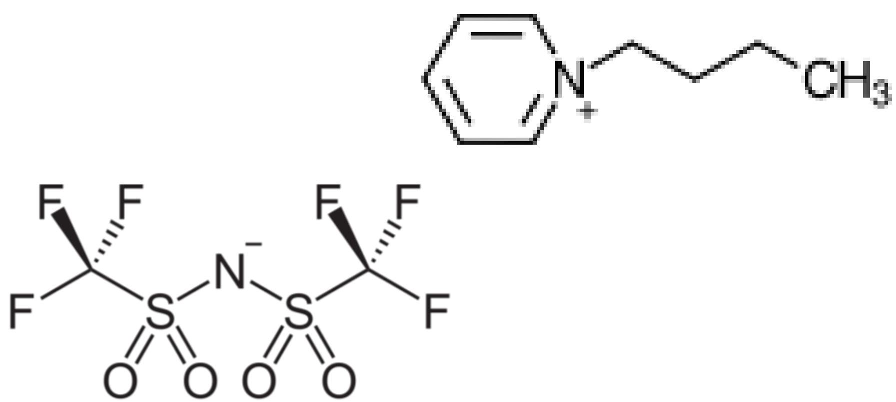
$$\Delta t_{\mathrm{obs}} = \frac{2\hbar\sqrt{\ln 2}}{\Delta E}$$

Ionic Liquids

> molten salts with $T_m \leq 100^{\circ}C$ (ethylammonium nitrate by Paul Walden, 1914)

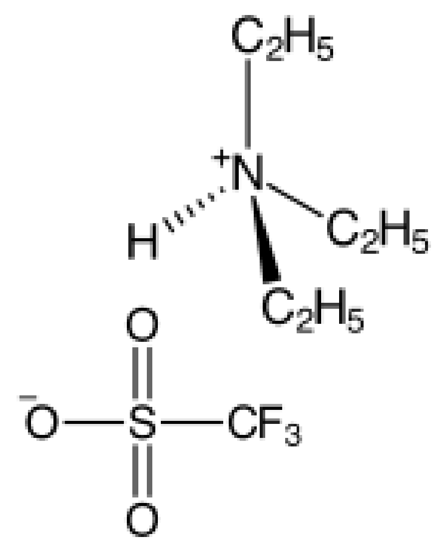
- **ions only**
- **vapor pressure ≃ 0**
- **wide liquid range**
- **high thermal & electrochemical stability**
- **designer solvents (i.e. tuneable physicochemical properties)**
- **Coulomb, dipole-dipole, H-bonding …**

> electrolytes in fuel cells, batteries …



1-butylpyridinium (BuPy)

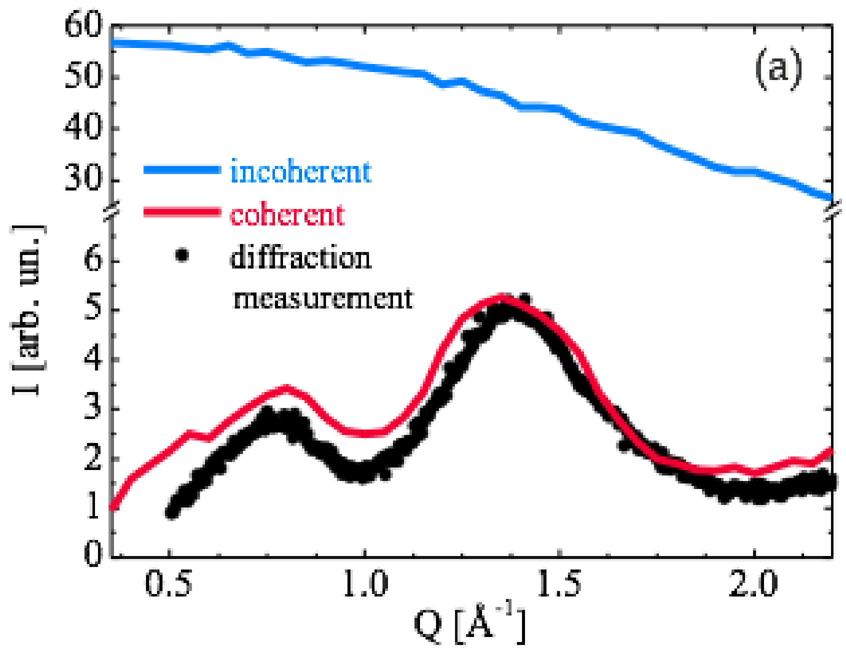
bis(trifluoromathylsulfonyl)imide (Tf_2N)



triethylammonium (TEA)

trifluoromethanesulfonate (TF)

D7 results - I / separation coh & inc contributions



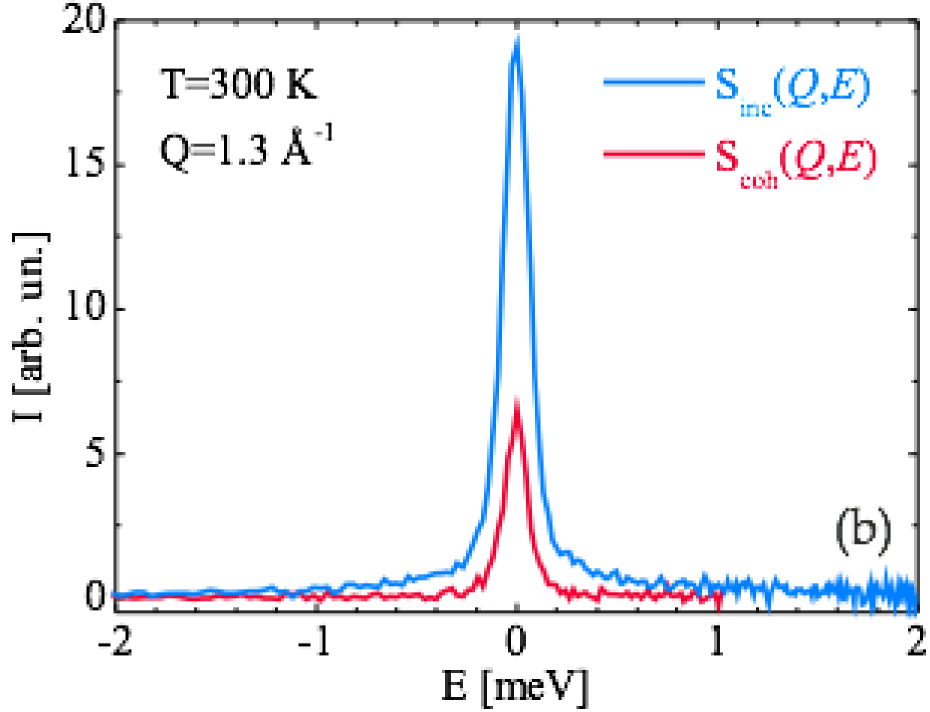
$$I_{\uparrow\uparrow} = I_{\text{coh}} + \frac{1}{3} I_{\text{inc}}$$

$$I_{\uparrow\downarrow} = \frac{2}{3} I_{\text{inc}}$$

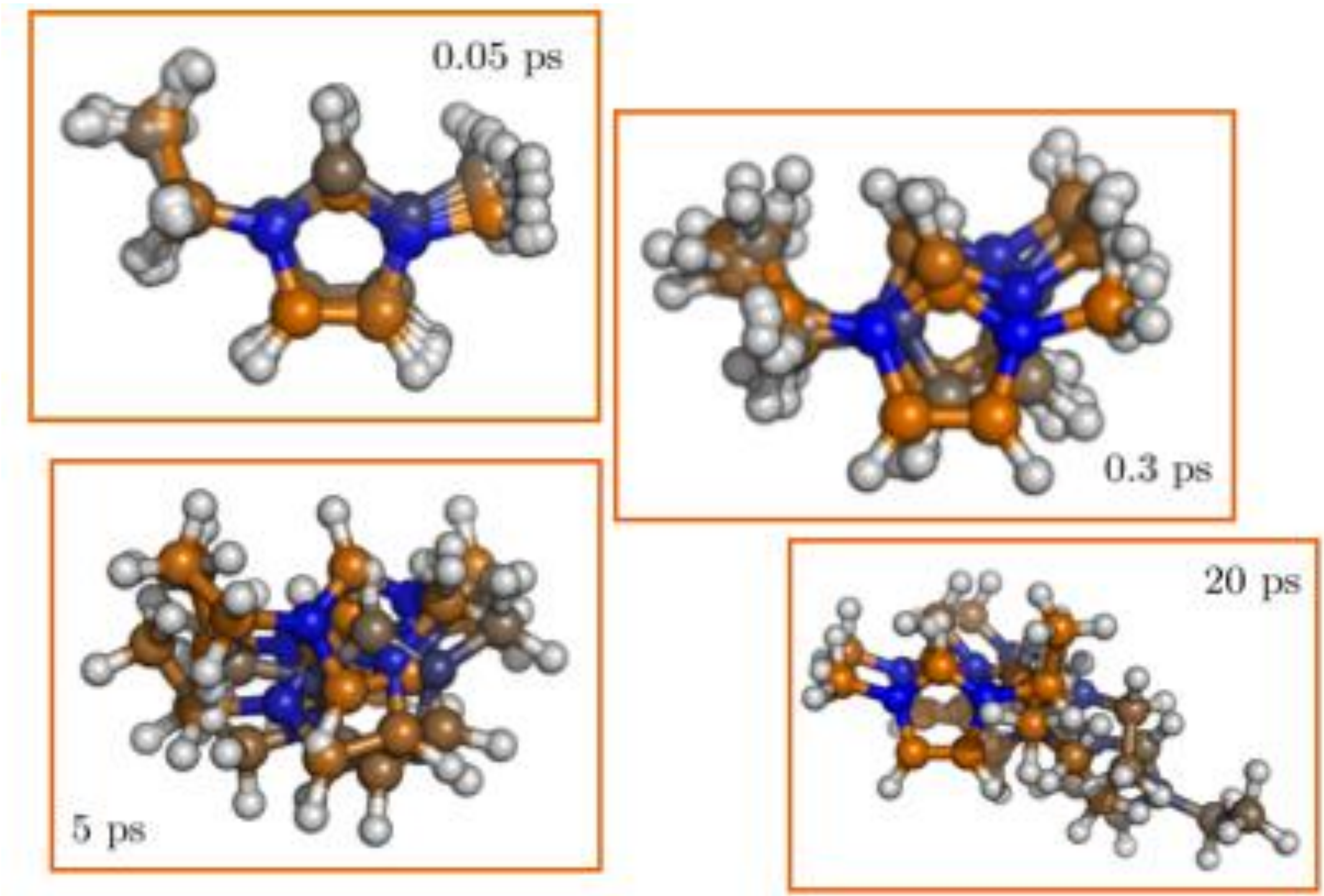
$$I_{corr}^{\uparrow\uparrow} = I^{\uparrow\uparrow} + \frac{1}{R-1}\left[I^{\uparrow\uparrow} - I^{\uparrow\downarrow}\right]$$

$$I_{corr}^{\uparrow\downarrow} = I^{\uparrow\downarrow} - \frac{1}{R-1}\left[I^{\uparrow\uparrow} - I^{\uparrow\downarrow}\right]$$

R = flipping ratio



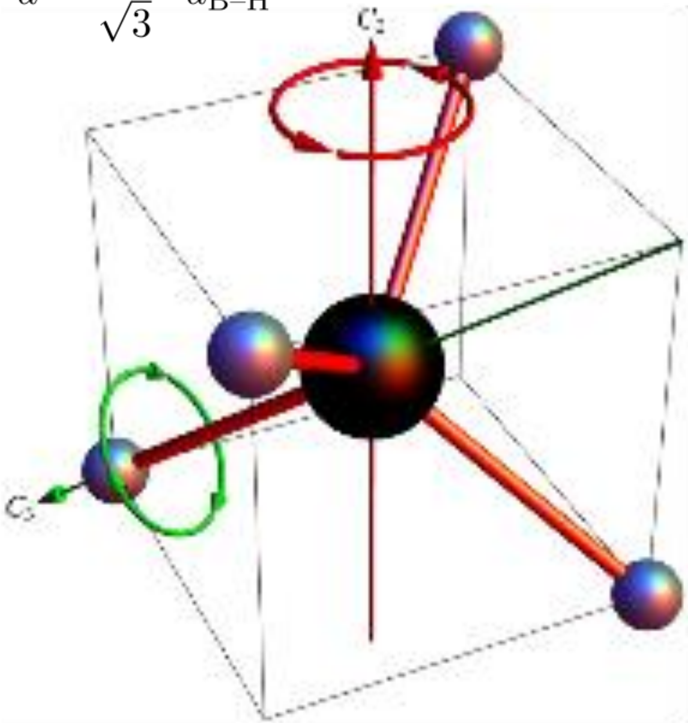
cation dynamics on ps time-scale - MD results



$[BH_4]^-$ subunit rot. motions

from J. Phys. B **45** (2012), 194003

$$a = \frac{2}{\sqrt{3}} \cdot d_{\mathrm{B-H}}$$



PHYSICAL REVIEW B 81, 214304 (2010)

Rotational motion of BH_4 units in MBH_4 (M=Li,Na,K) from quasielastic neutron scattering and density functional calculations

Arndt Remhof,[1,*] Zbigniew Łodziana,[1,2] Pascal Martelli,[1] Oliver Friedrichs,[1] Andreas Züttel,[1] Alexander V. Skripov,[3] Jan Peter Embs,[4,†] and Thierry Strässle[4]

$LiBH_4$ / $NaBH_4$ outstanding volumetric & gravimetric hydrogen density ⇒ possible H_2 storage materials

$$S_{\mathrm{inc}}^{\text{2-site}} = A_0(Q)\delta(E) + [1 - A_0(Q)] \cdot \frac{1}{\pi} \frac{2\hbar/\tau_2}{(2\hbar/\tau_2)^2 + E^2}$$

$$A_0(Q) = \frac{1}{2}[1 + j_0(Qd)] \qquad d = d_{\mathrm{B-H}} \cdot 2\sqrt{\frac{2}{3}}$$

$$B_0(Q) = \frac{1}{3}[1 + 2j_0(Qd)]$$

$$S_{\mathrm{inc}}^{\text{3-site}} = \frac{1}{4}\delta(E) + \frac{3}{4}\left[B_0(Q)\delta(E) + [1 - B_0(Q)] \cdot \frac{1}{\pi}\frac{3\hbar/2\tau_2}{(3\hbar/2\tau_2)^2 + E^2}\right]$$

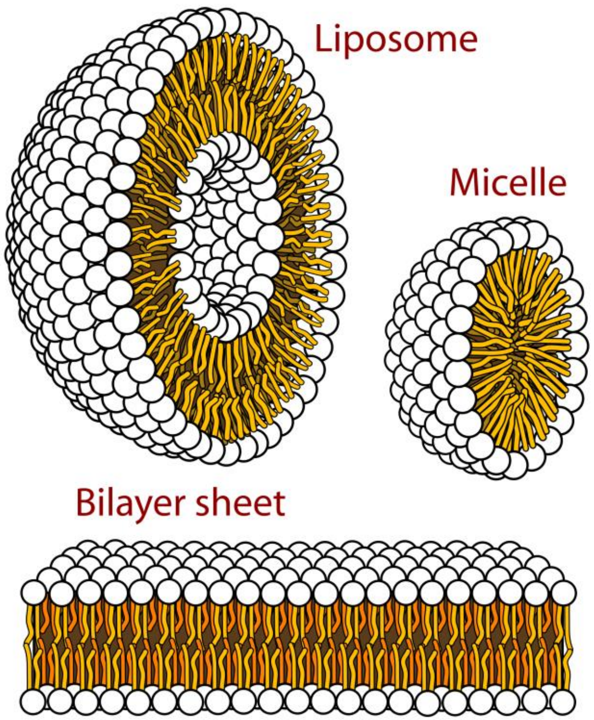
$$S_\Sigma(Q,E) = S_{\mathrm{inc}}^{\text{2-site}}(Q,E) \otimes S_{\mathrm{inc}}^{\text{3-site}}(Q,E)$$

Molecular Mobility in Solid Sodium Dodecyl Sulfate

S. Mitra,[†] V. K. Sharma,[†] V. Garcia Sakai,[‡] J. Peter Embs,[§] and R. Mukhopadhyay[*,†]

J.Phys.Chem. B **115** (2011) 9732
Soft Matter **8** (2012) 7151

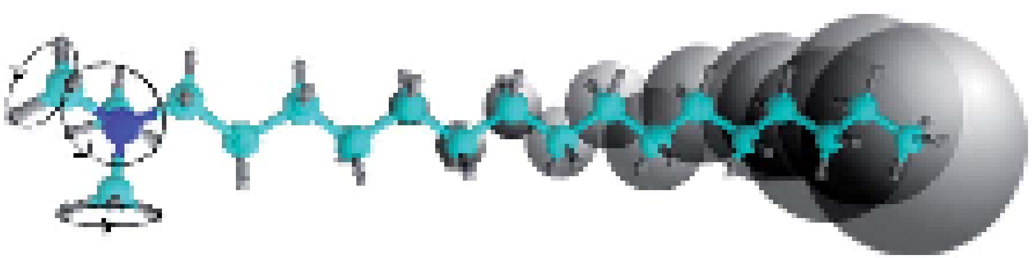
hydrophobic tail

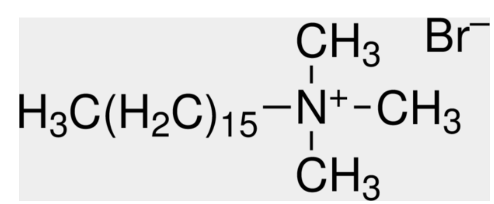


The dynamical landscape in CTAB micelles

V. K. Sharma,[a] S. Mitra,[a] V. Garcia Sakai,[b] P. A. Hassan,[c] J. Peter Embs[d] and R. Mukhopadhyay[*a]

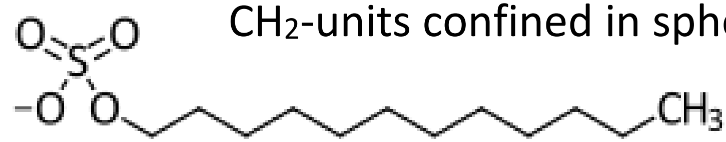
Cetyl**T**rimethyl**A**mmonium **B**romide = CTAB





diffusion in a sphere

$$A_0(Q) \equiv \frac{1}{12}\sum_{k=1}^{12} A_0^0(QR_k) = \frac{1}{12}\sum_{k=1}^{12}\left[\frac{3j_1(QR_k)}{QR_k}\right]^2$$

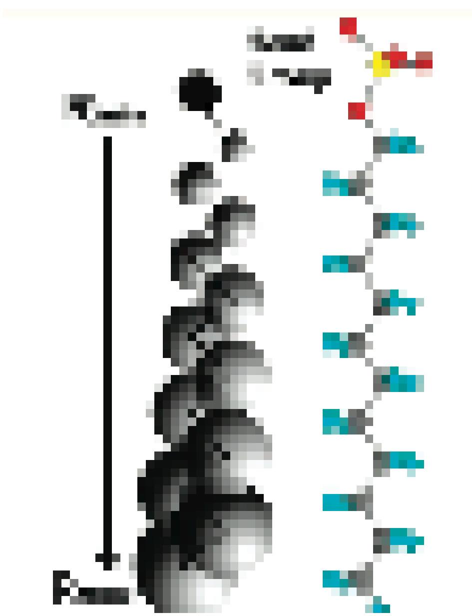


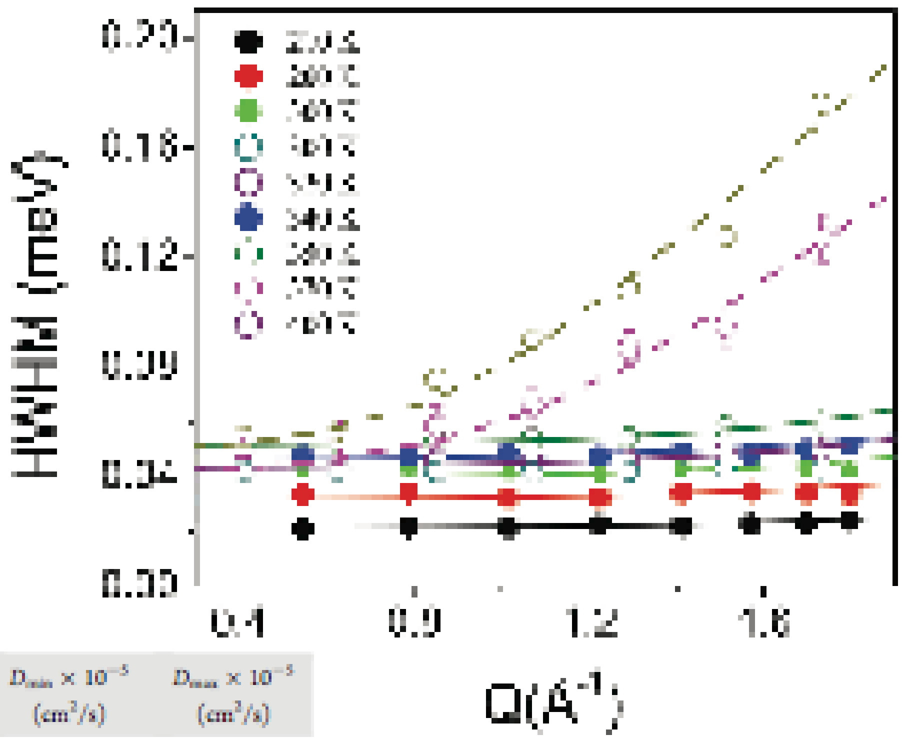
CH_2-units confined in spheres

$$S_{\text{inc}}(Q,\omega) = \frac{1}{N}\sum_{j=1}^{N}\left[A_0^0(QR_j)\delta(\omega) + \frac{1}{\pi}\sum_{(l,n)\neq(0,0)}(2l+1)A_n^l(QR_j)\frac{\hbar(x_n^l)^2 D_j/R_j^2}{(\hbar(x_n^l)^2 D_j/R_j^2)^2+\hbar^2\omega^2}\right]$$

$$R_j \equiv \frac{j-1}{N-1}\left[R_{\max} - R_{\min}\right] + R_{\min}$$

ditto for D_j



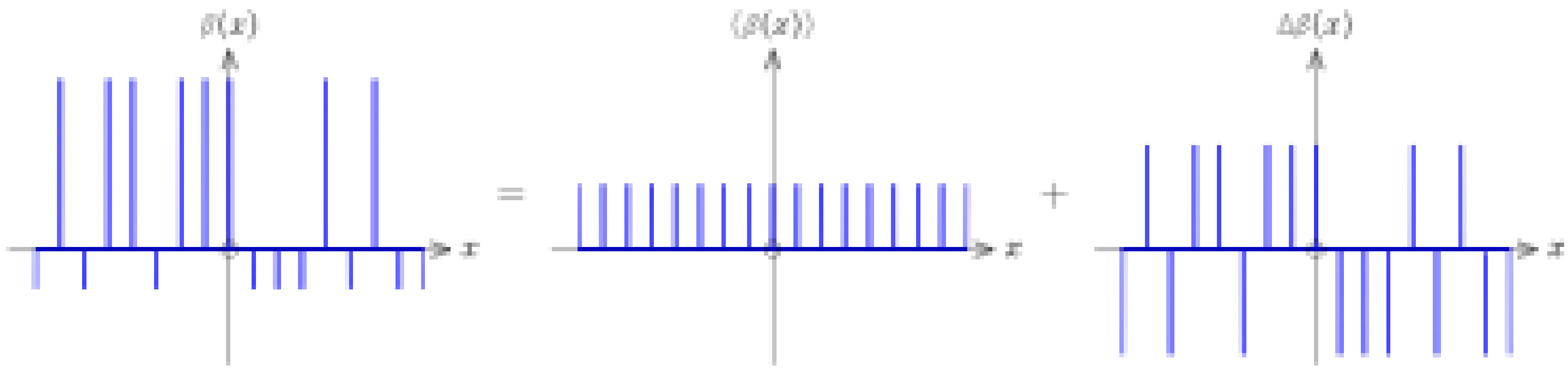


T (K)	R_{min} (Å)	R_{max} (Å)	$D_{min} \times 10^{-5}$ (cm²/s)	$D_{max} \times 10^{-5}$ (cm²/s)
370	0.004 ± 0.003	3.89 ± 0.3	0.015 ± 0.005	1.78 ± 0.3
400	0.002 ± 0.001	4.44 ± 0.3	0.06 ± 0.005	2.77 ± 0.3

coherent & incoherent scatt

due to **isotope & spin effects**, atoms of the same element are not identical!

average | fluctuations



coherent, scatt from average $b_{\text{coh}} = \langle b \rangle$

⇒ correlated dynamics (phonos, magnons, …)

incoherent, scatt from fluctuations $b_{\text{inc}}^2 = \langle b^2 \rangle - \langle b \rangle^2$

⇒ self-correlations, stochastic motions (diffusion, reorientations, …)

$$S_{\mathrm{inc}}(Q,\omega) = A_0(Q)\delta(\omega) + \sum_{j=1}^{N} A_j(Q)\mathcal{L}(\Gamma_j,\omega)$$

$$S_{\mathrm{inc}}(Q,\omega) = A_0(Q)\delta(\omega) + [1 - A_0(Q)]\mathcal{L}(\Gamma,\omega)$$

$$\mathrm{EISF} = \frac{I_{\mathrm{el}}(Q)}{I_{\mathrm{el}}(Q) + I_{\mathrm{qel}}(Q)}$$

space-FT of the particle distribution, taken at $t \Longrightarrow \infty$ and averaged over all its possible initial positions; provides info on the geometry of the molecular motion

localized/rotational motions $\Longrightarrow$ prob of finding a scatterer at infinite time within a small volume ≠ 0 ! ($\not\Rightarrow$ translational diffusion !)

$$S_{\mathrm{inc}}(Q,\omega) = (1-p)\delta(\omega) + p\left[A_0(Q)\delta(\omega) + [1 - A_0(Q)]\mathcal{L}(\Gamma,\omega)\right]$$

p = fraction of mobile particles/scatterers

uniaxial rotational diffusion

particle rotating among N equivalent sites
equally distributed on a circle of radius a

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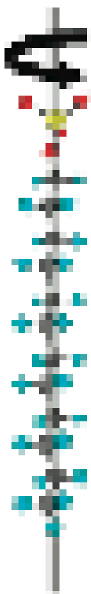
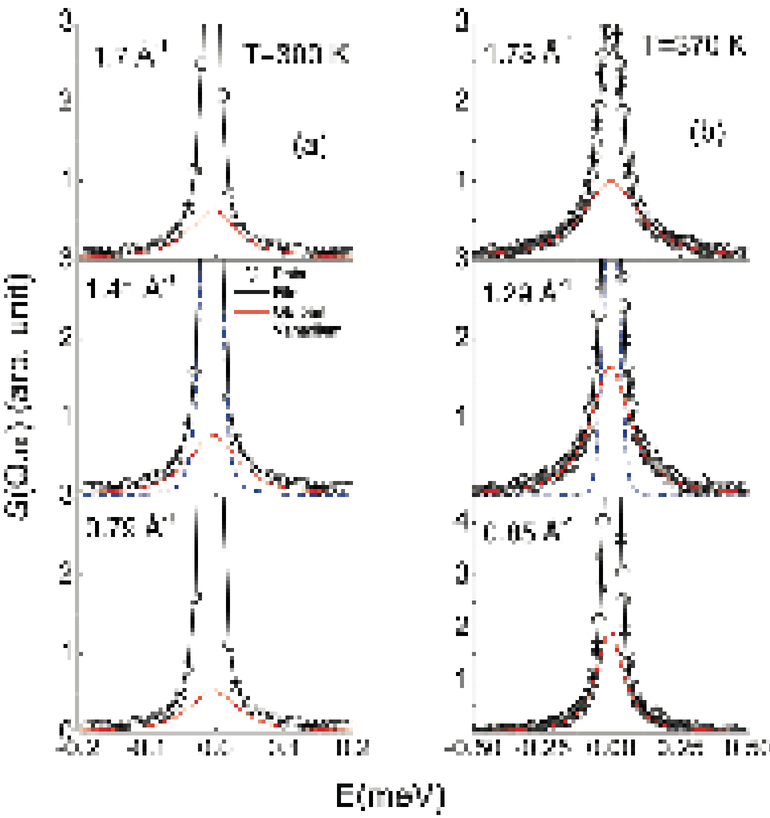
$$S_{\rm inc}(Q,\omega) = B_0(Qa)\delta(\omega) + \sum_{n=1}^{N-1} B_n(Qa)\mathcal{L}_n(\hbar/\tau_n,\omega)$$

$$B_n(Qa) = \frac{1}{N}\sum_{p=1}^{N} j_0(2QA\sin(\pi p/N))\cos(2\pi np/N)$$

$$\frac{1}{\tau_n} = \frac{2}{\tau}\sin^2\left(\frac{n\pi}{N}\right)$$

τ = average time spent on a site between 2 successive jumps





Ionic Liquids & INS

system	σ_{scatt} [b]	σ_{inc} [b]	$\sigma_{inc}/\sigma_{scatt}$ [%]
BuPy–Tf_2N	1275.6	1124.8	88.2
Bu_DPy–Tf_2N	606.1	420.8	69.4
$BuPy_D$–Tf_2N	901.6	731.7	81.2