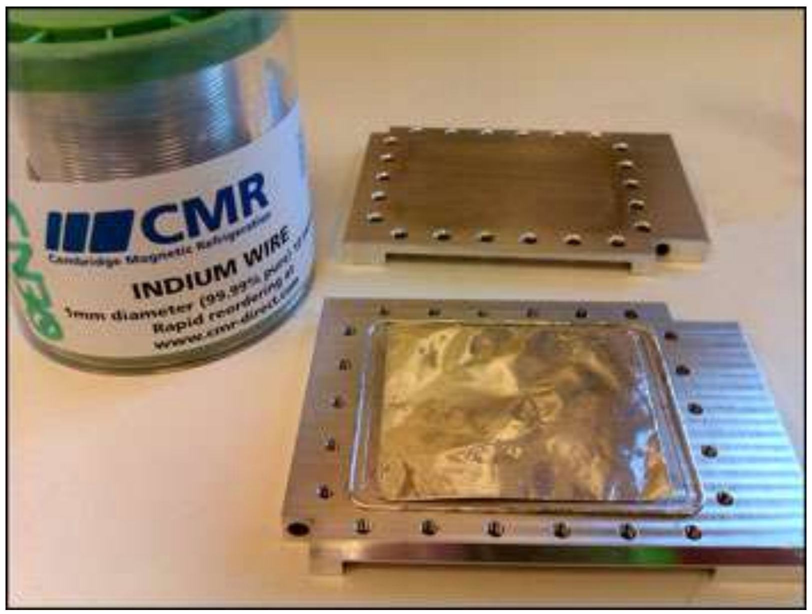
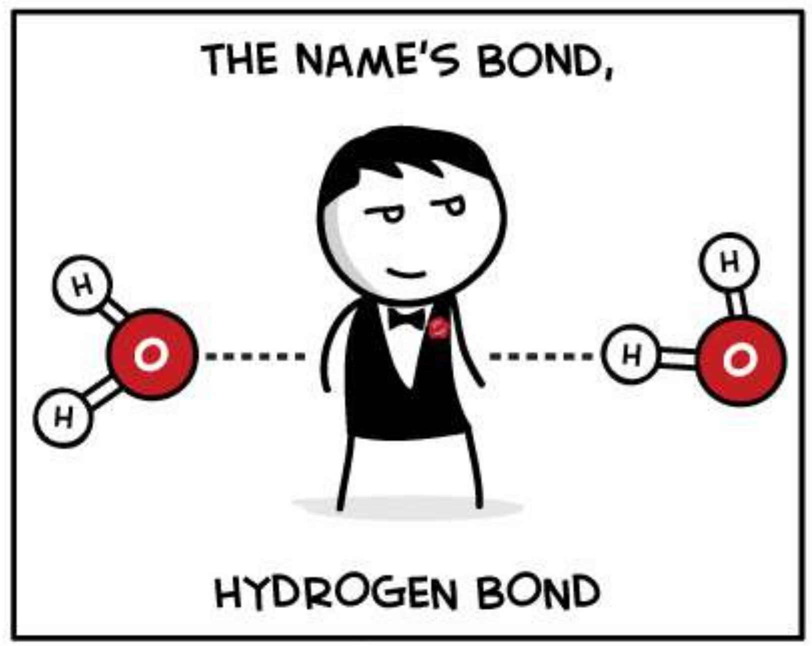
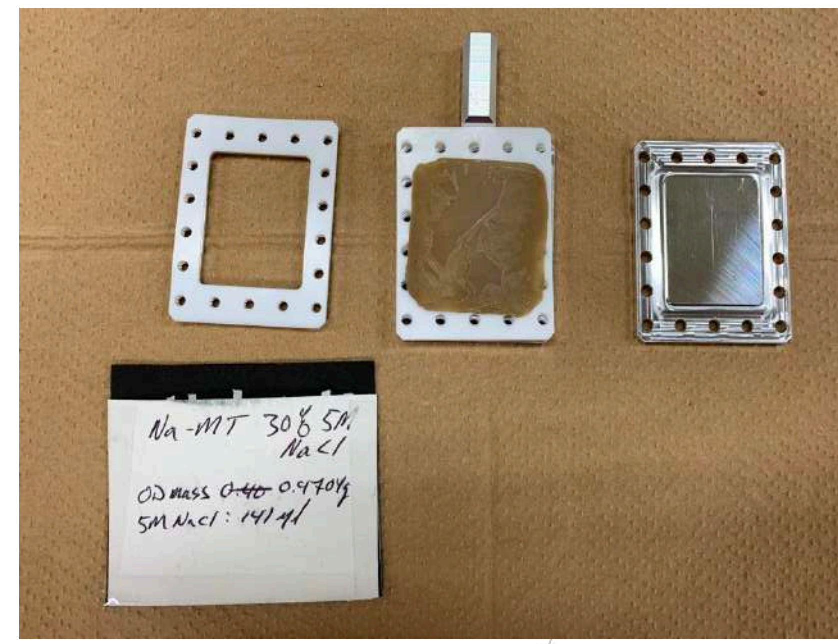
Shedding light on the Muddy World of Clays with Neutrons: Water Dynamics in a Broad Time Scale





VICTIMS OF CIRCUMSOLAR



Heloisa N. Bordallo
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ISRD-RCN Workshop: Exploring Dynamic Properties of Earth and Planetary Materials Using Neutron Scattering and Imaging -
The Hotel UMD, July 25-27, 2023

The brilliant minds behind all this

Will P. Gates

Laurie P. Aldridge

Deakin University - Australia

Simon R. Larsen
MSc, now at NIMS Japan

Rosanna Ignazzi
MSc, now at Weibel DK

Martin H. Petersen
MSc, now PhD student at DTU, DK

Jon Otto Fossum
NTNU, Norway

Funding agencies and large scale facilities

HZB Helmholtz Zentrum Berlin

ANSTO

Science & Technology Facilities Council ISIS

ILL NEUTRONS FOR SCIENCE

SNS SPALLATION NEUTRON SOURCE

J-PARC

Niels Bohr Institutet

ESS EUROPEAN SPALLATION SOURCE

DanScatt

The Research Council of Norway

NTNU Norwegian University of Science and Technology

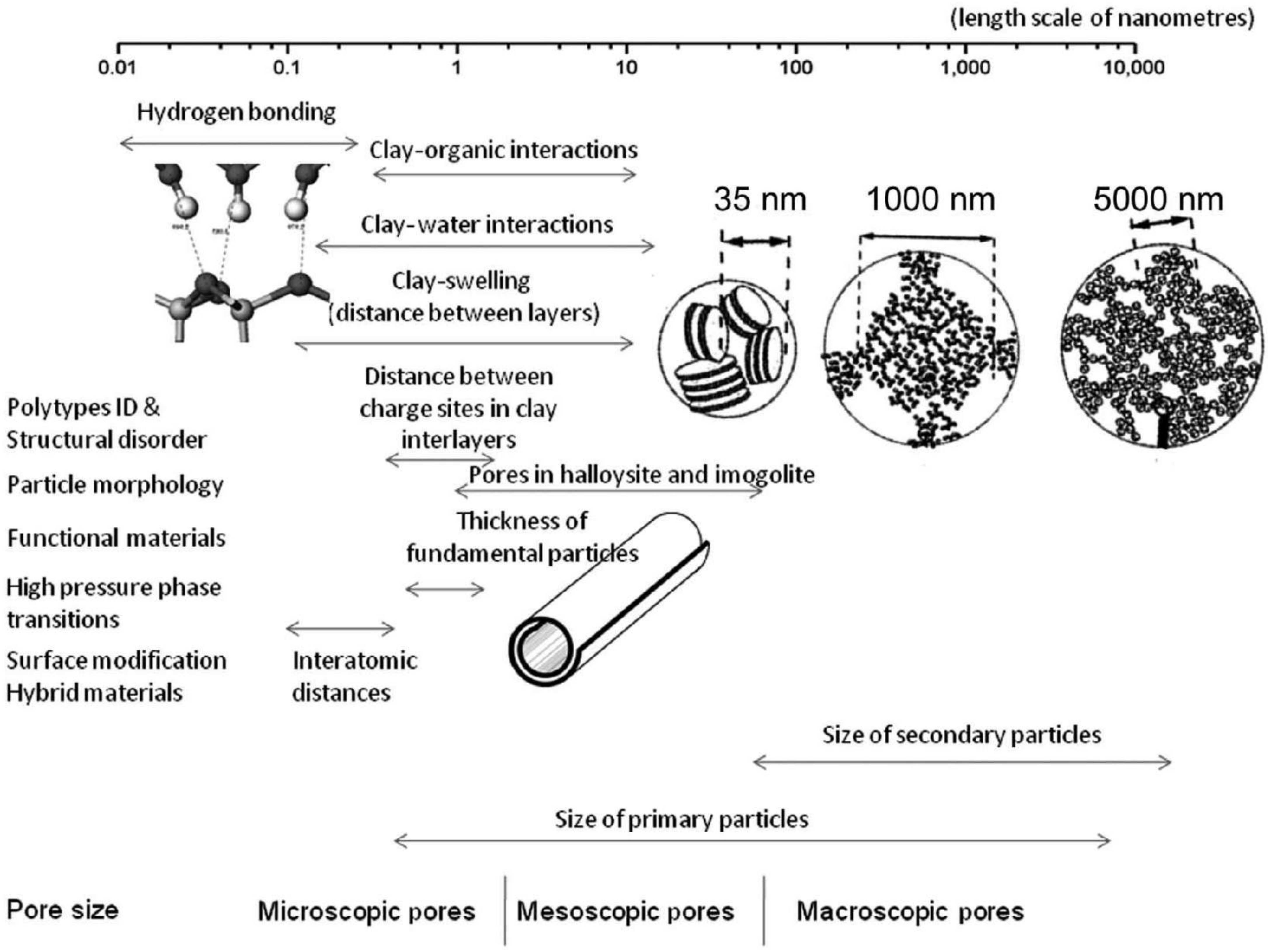
CARLSBERGFONDET

Danish Agency for Science Technology and Innovation
Ministry of Science Technology and Innovation

Understanding the Interactions of Water at Clay Mineral Surfaces are Key to Optimising Applications – Particularly Environmental Applications

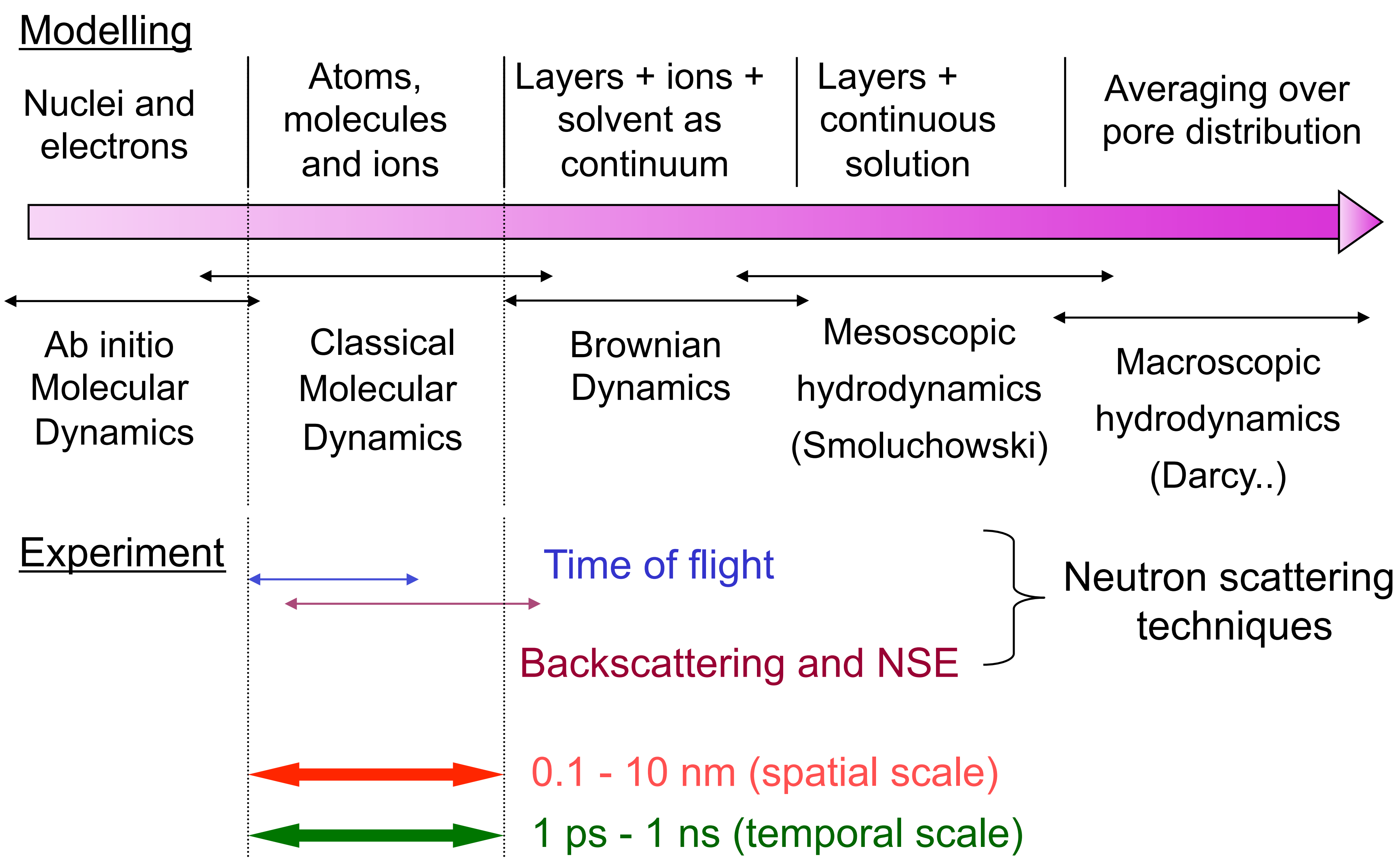
Understanding the Interactions of Water at Clay Mineral Surfaces are Key to Optimising Applications – Particularly Environmental Applications

Length scales associated with the structure and surface chemistry of clay minerals



C. T. Johnston, Clay Minerals, **45** (2010) 245–279.

To understand functionality we need to know the structure and understand the motions in a very broad time scale.

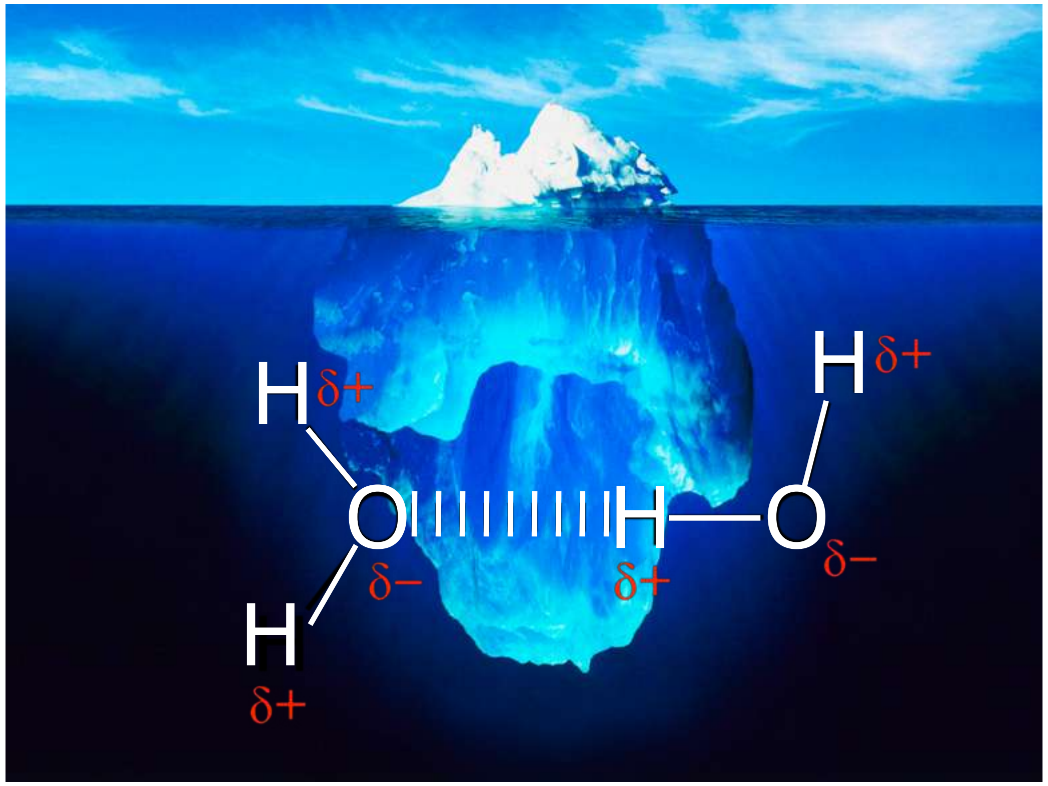


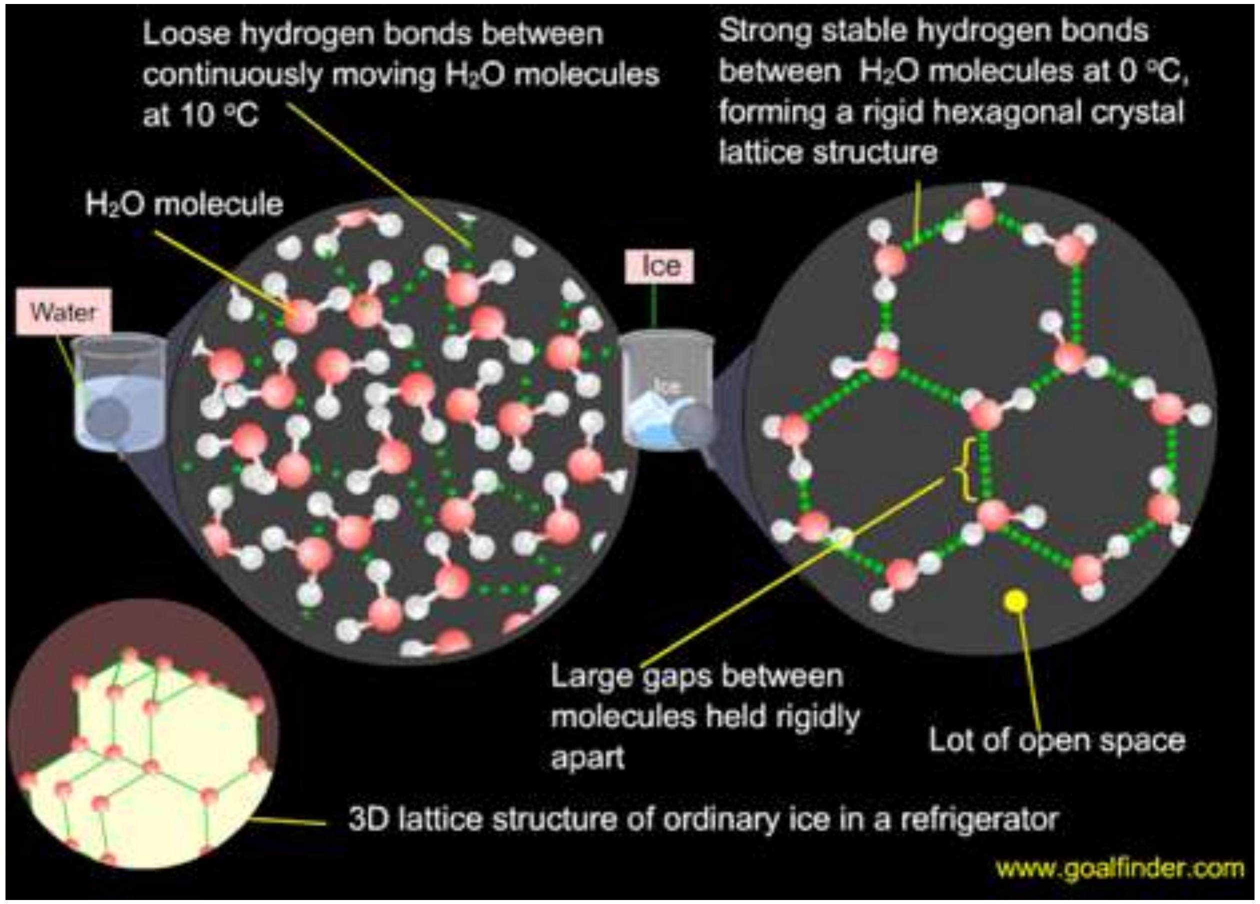
Vibrations: identification of the forms of water/ice confined in the clay layers

Diffusion and Rotational diffusion: water stochastic motions, indicating long-range diffusion or localized dynamical process and*random* changes of orientation

Based on Natalie Malikova presentation

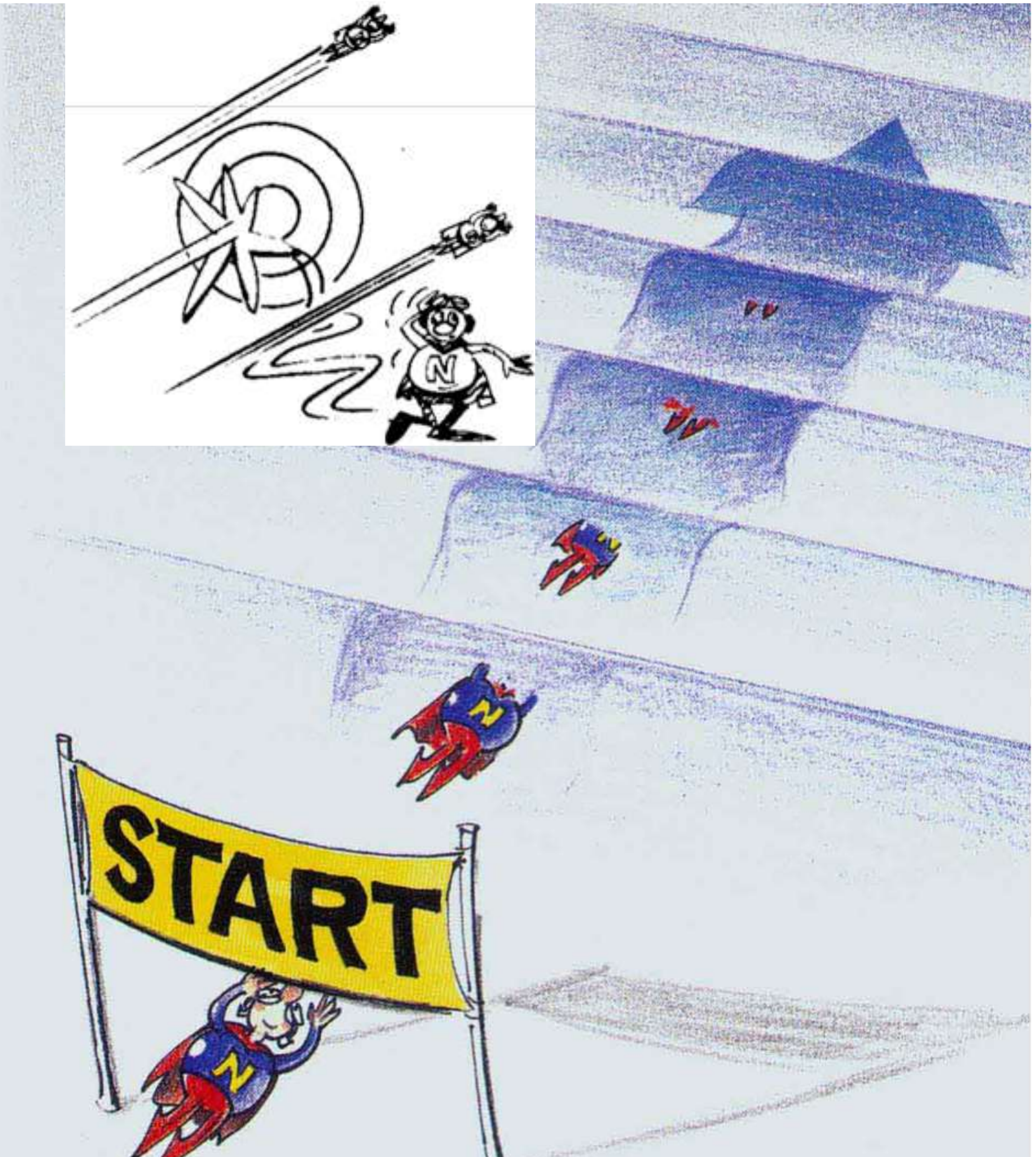
Water (hydrogen bonding) controls the system



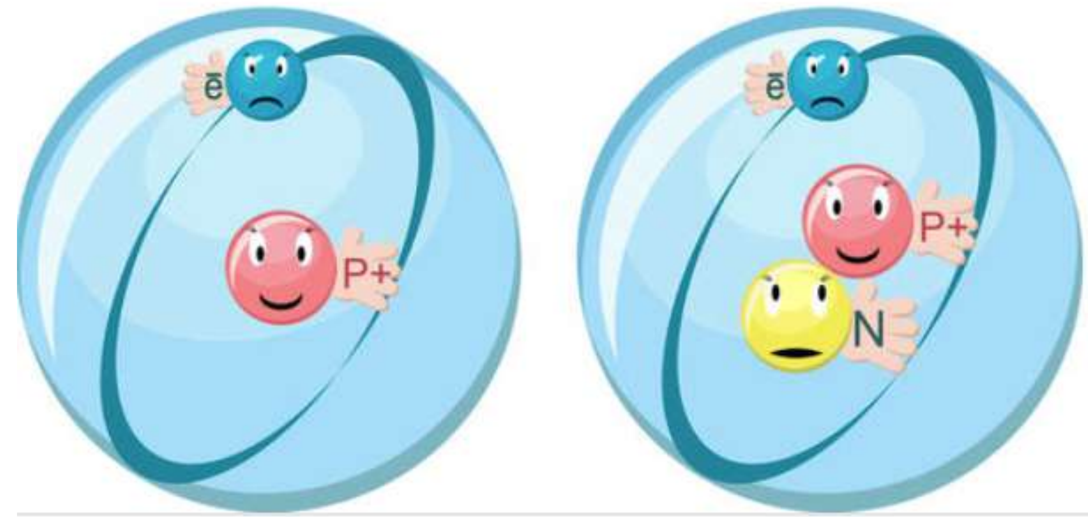


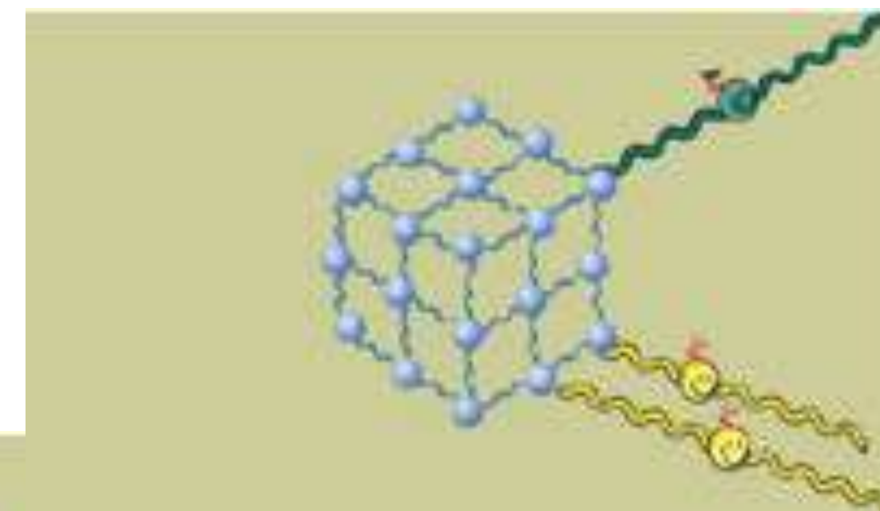
http://xns.nbi.ku.dk/research/dynamics/

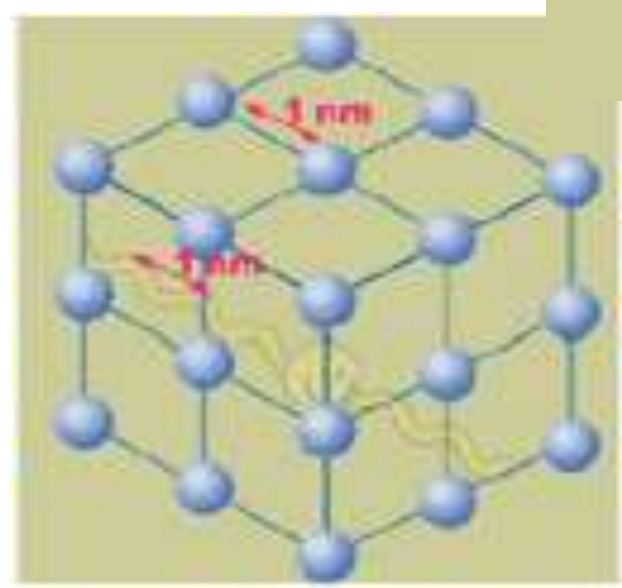
… and neutrons can give unique insight!



Neutron scattering a PRIMER by Roger Pynn.







neutron wave :

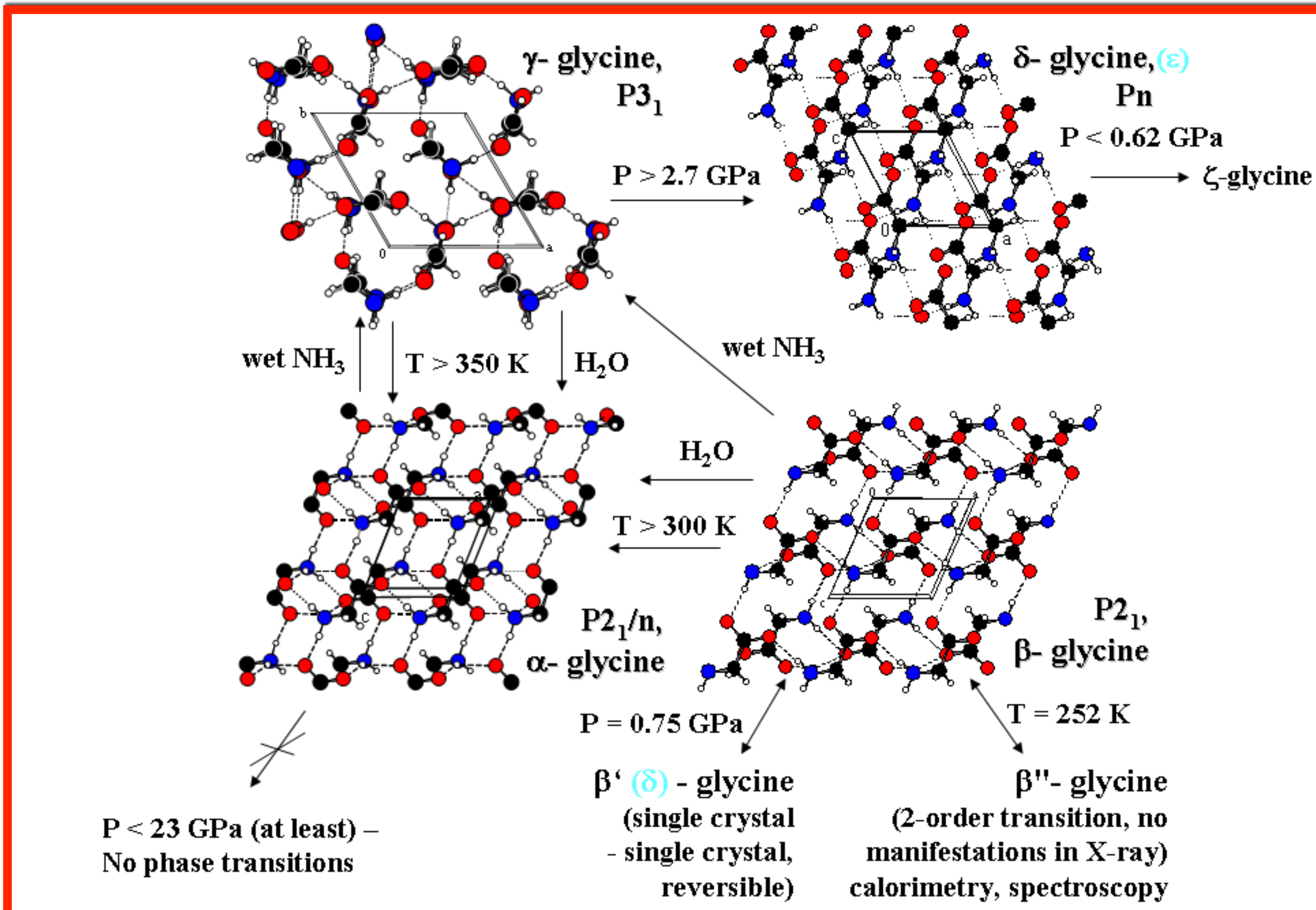
- direction
- length
- amplitude

$\lambda_{\text{neutron}} \leq$ atomic spacing

(

McWhan Type variable pressure in a press between 0.2 and 1.0 GPa

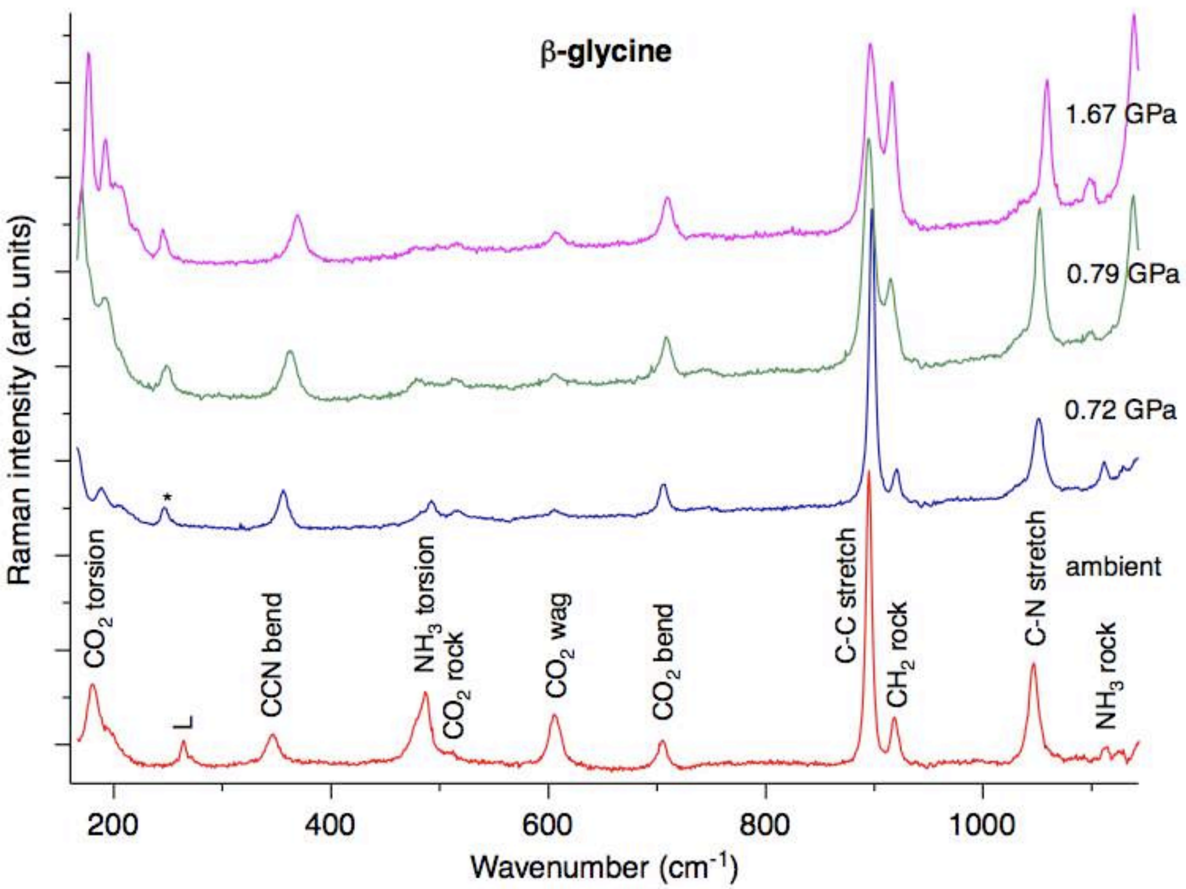
Internal organisation and mobility of hydrogen bonds (HBs)

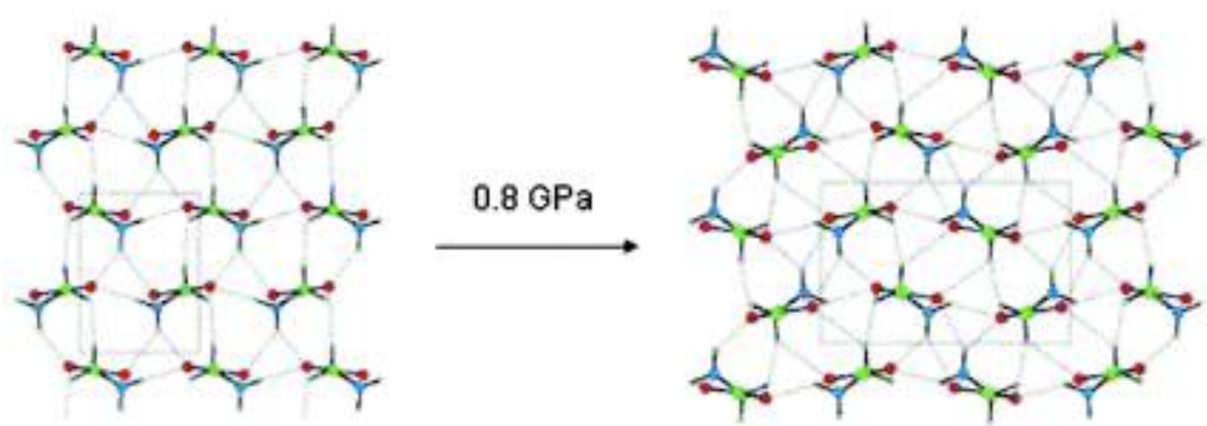


E: V. Boldyreva , S: N. Ivashevskaya , H: Sowa and H. Ahsbahs and H.—P. Weber Effect of hydrostatic pressure on the γ-polymorph of glycine. 1. A polymorphic transition into a new δ-form (2005) Z. fur Krist. - Cryst. Mater. **220**, 50-57.

β-Glycine as a function of pressure

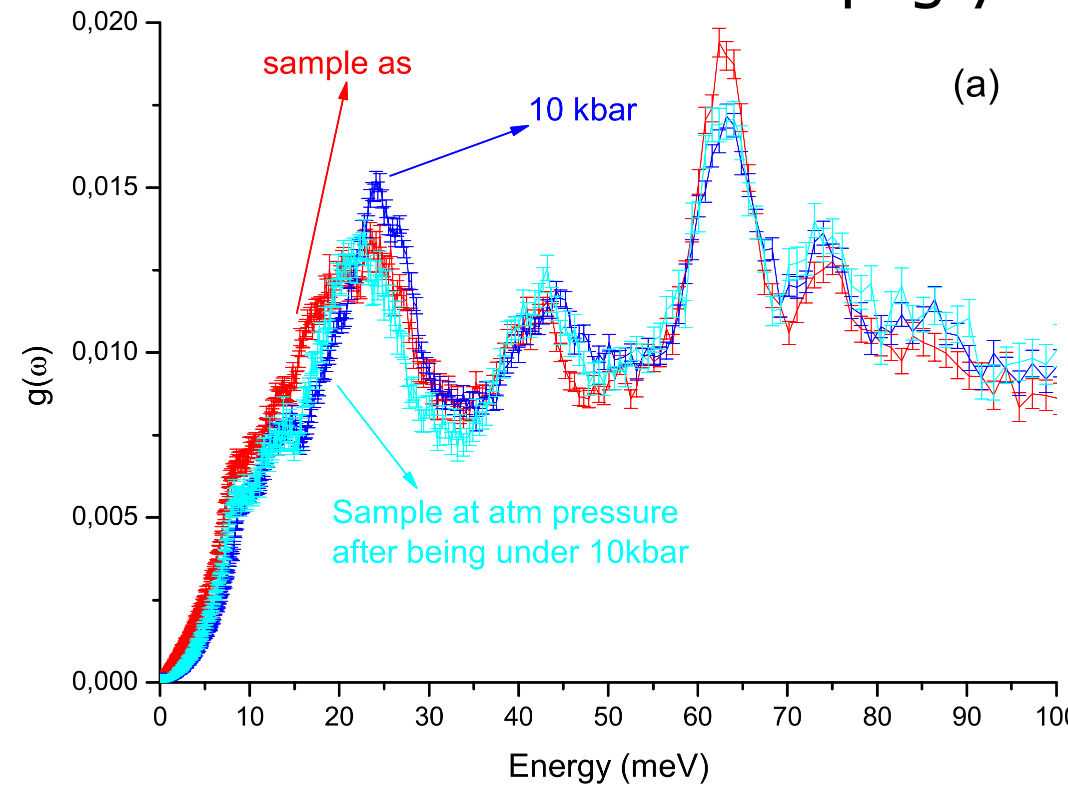
β(P2₁) → β' (P2₁/a)

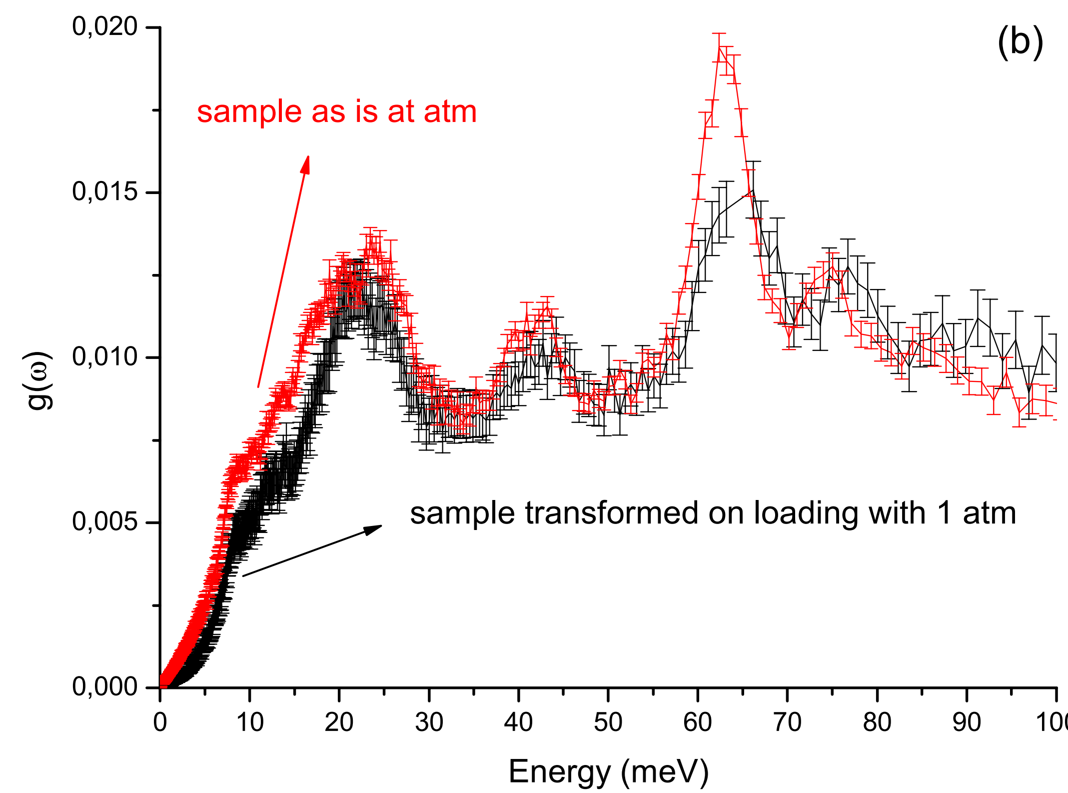




N. Tumanov, E.V . Boldyreva, E., & H. Ahsbahs, (2008). Structure solution and refinement from powder or single-crystal diffraction data? Pros and cons: An example of the high-pressure β′-polymorph of glycine. Powder Diffr., **23**, 307-316.

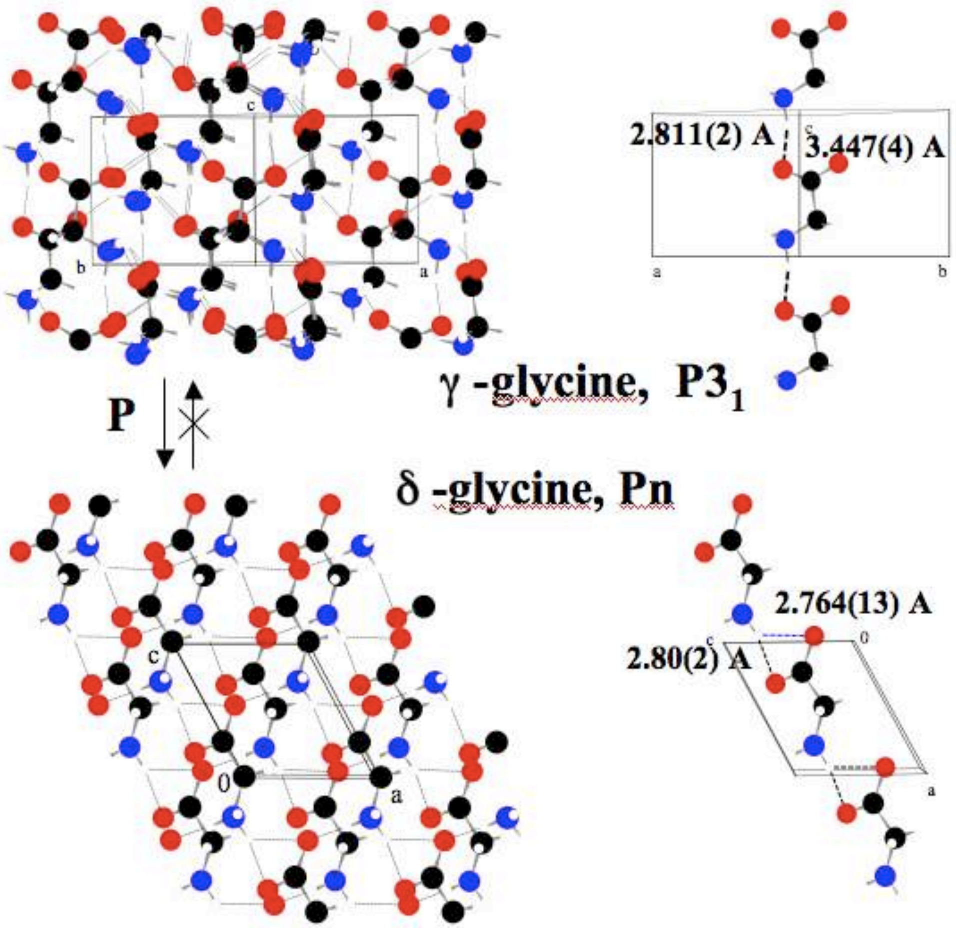
β-glycine



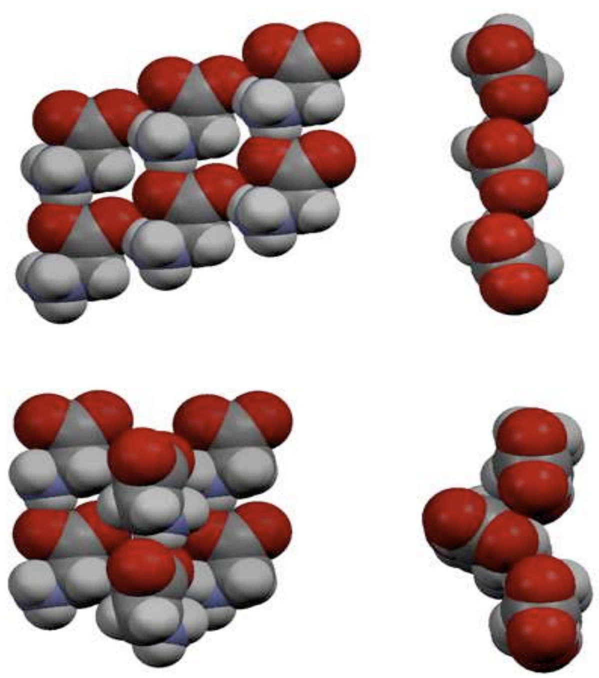


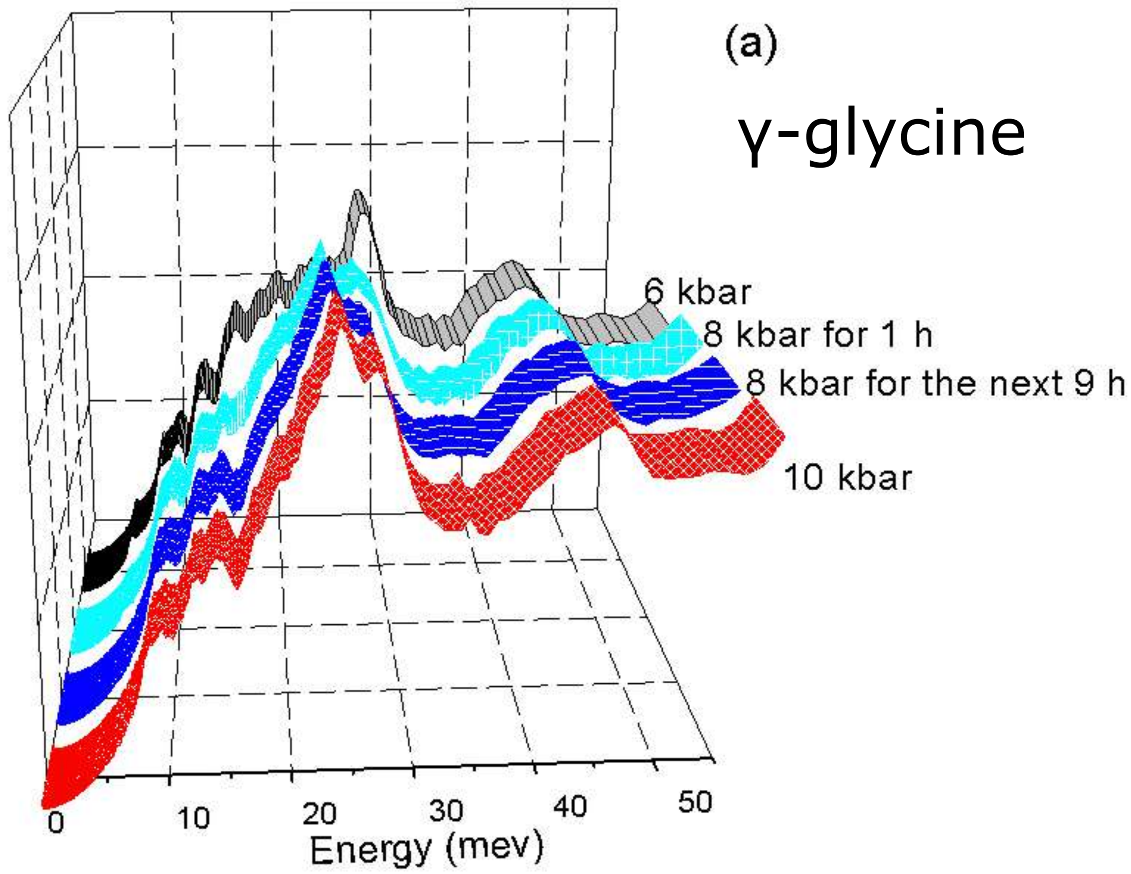
HNB, E.V. Boldyreva, A. Buchsteiner, M. M. Koza and S. Landsgesell (2008) Structure-property relationships in the crystals of the smallest amino acid: an incoherent inelastic neutron scattering study of the glycine polymorphs. J Phys Chem B. **112,** 8748-59.

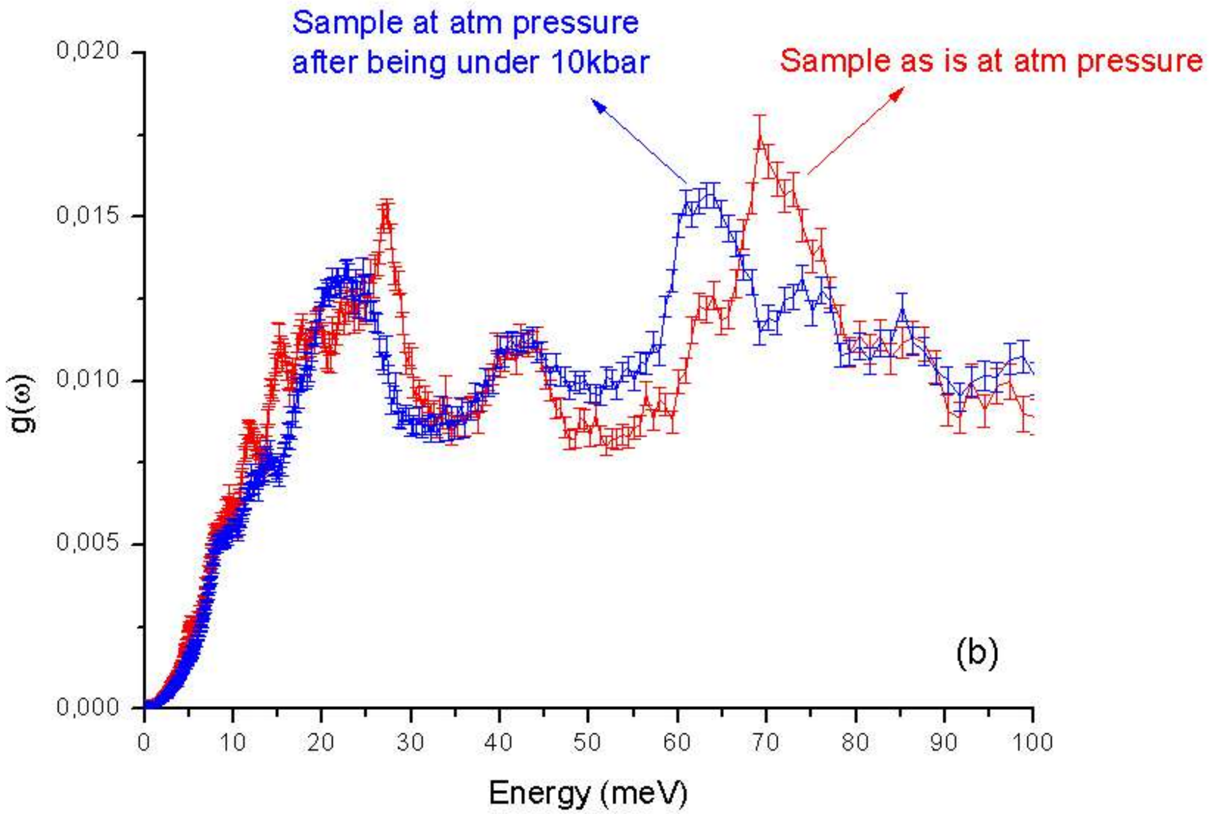
γ-Glycine as a function of pressure



S.V. Goryainov, E.V. Boldyreva and E.N. Kolesnik (2006) Raman observation of a new (ζ) polymorph of glycine? Chem. Phys. Lett. **419** 496-500,







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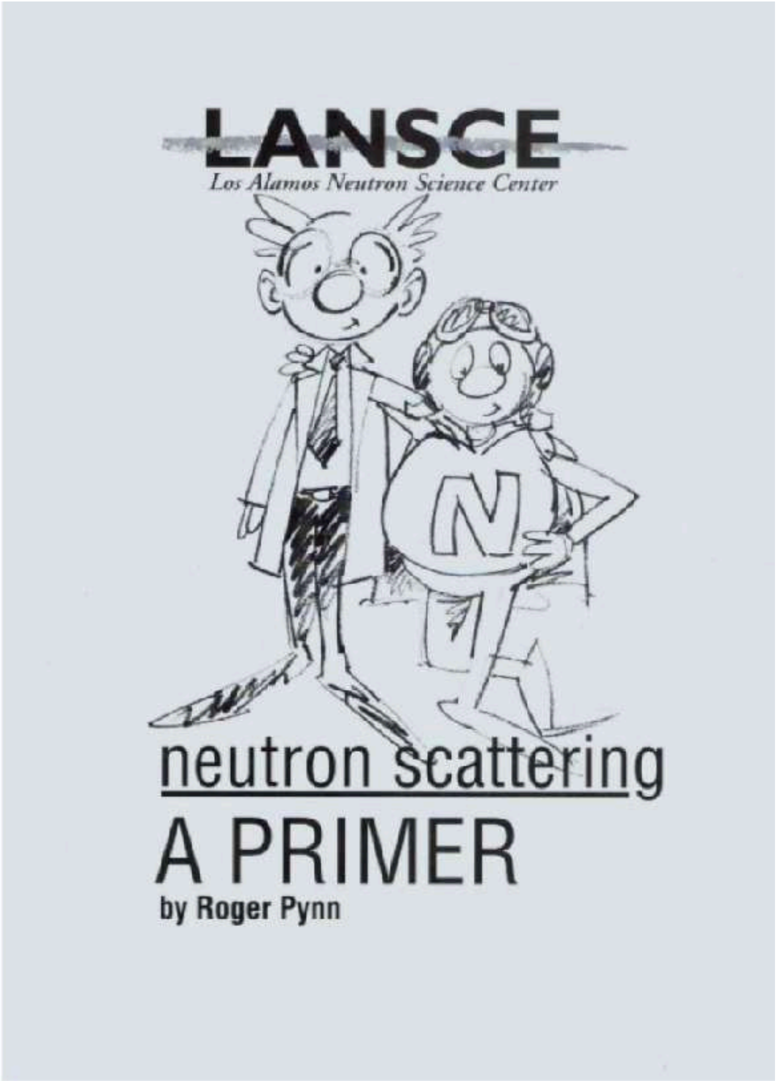
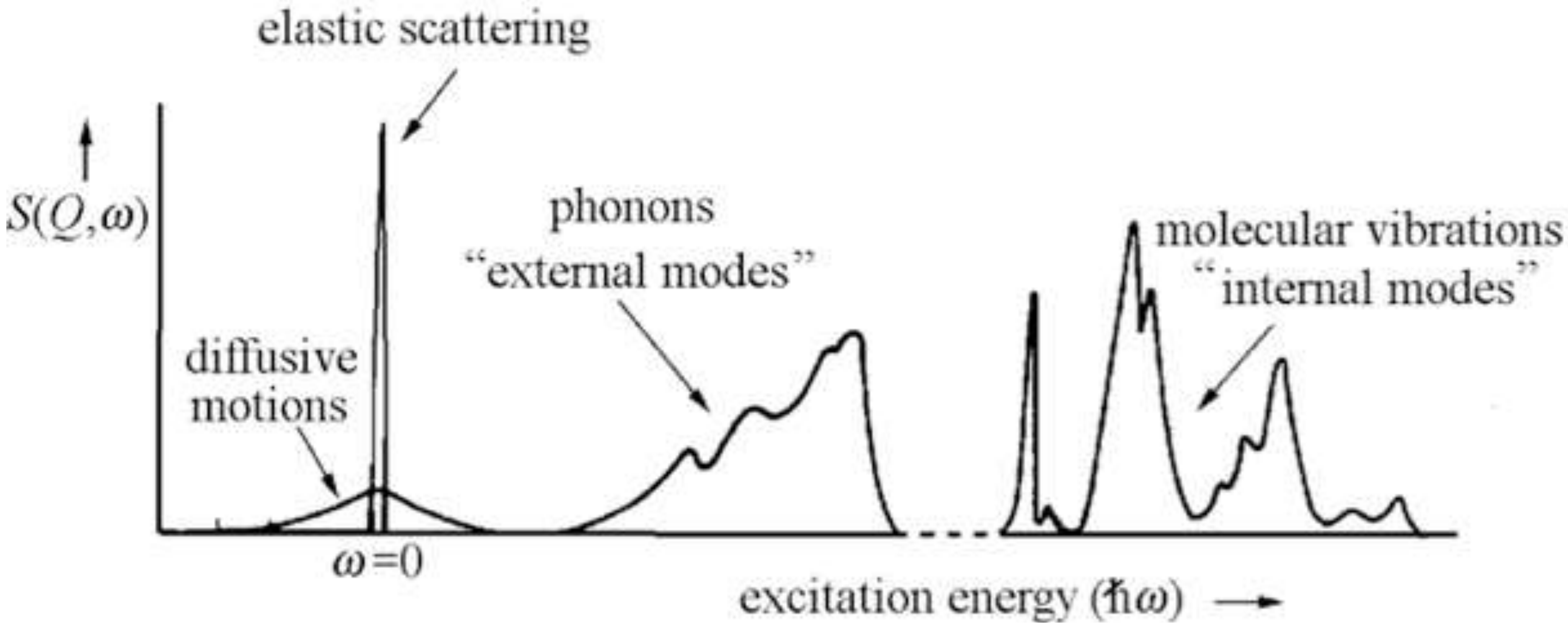


Neutrons are unique!

)

Neutron spectroscopy: Different dynamical



well behaved
molecules

elastic: structural information

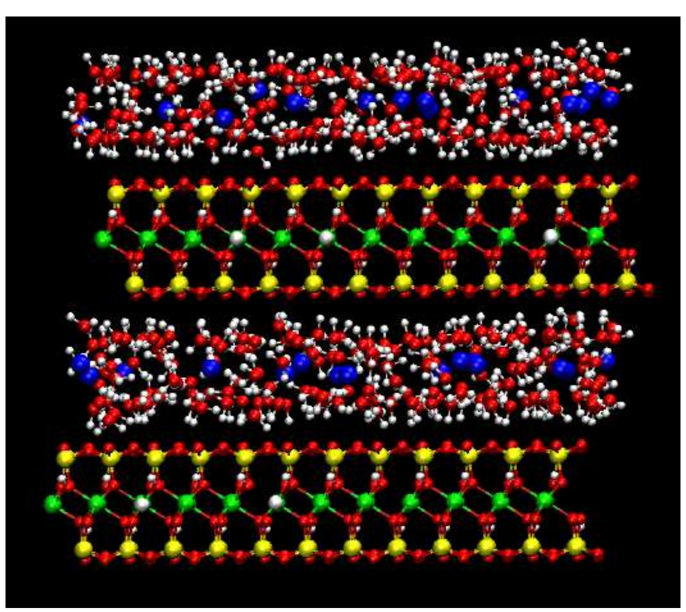
quasielastic scattering:

diffusive motions (rotational, translational, transport)

external modes:

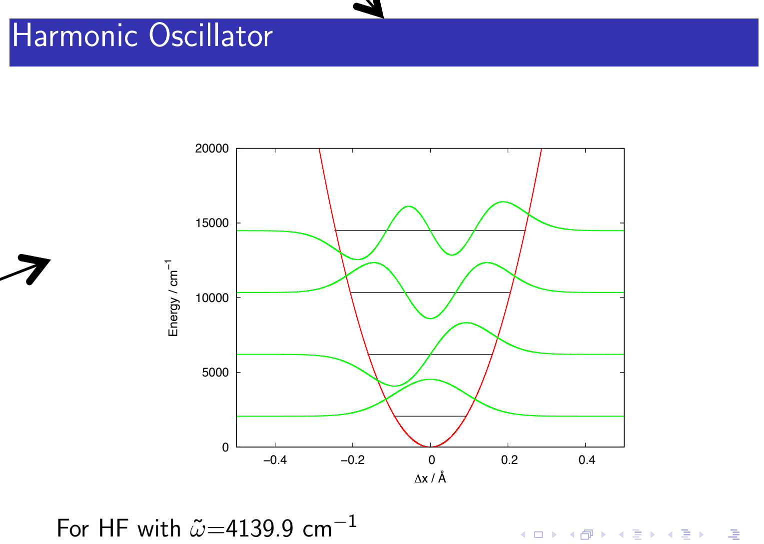
whole-body librations, translations

(internal) molecular vibrations:

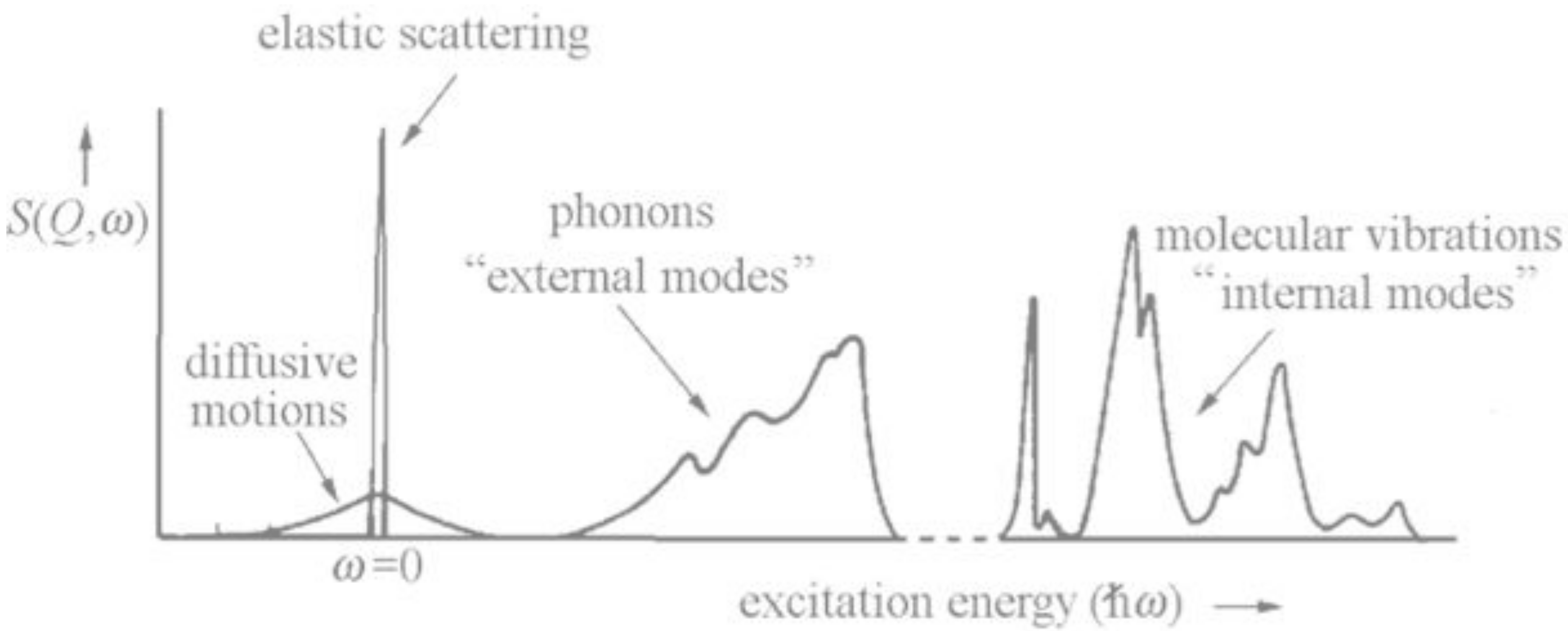


Badly behaved
water molecules

some of the time



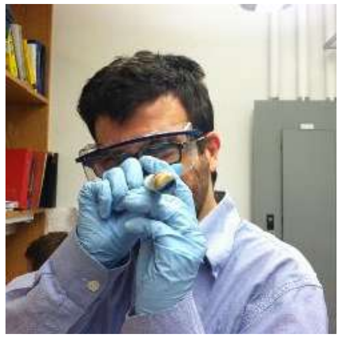
Neutron spectroscopy: Different dynamical

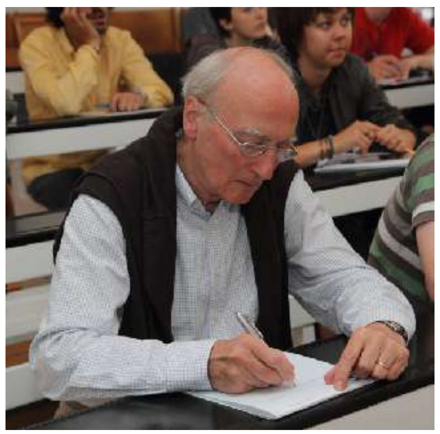


No holy grail!

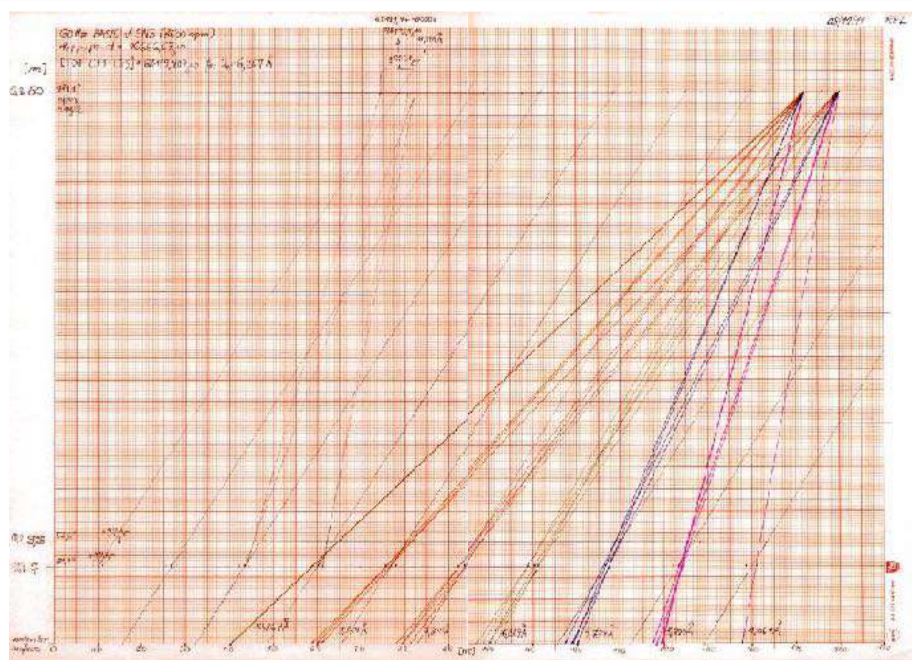
No single experiment can measure all processes in the best possible way.

MIRACLES DO happen!*



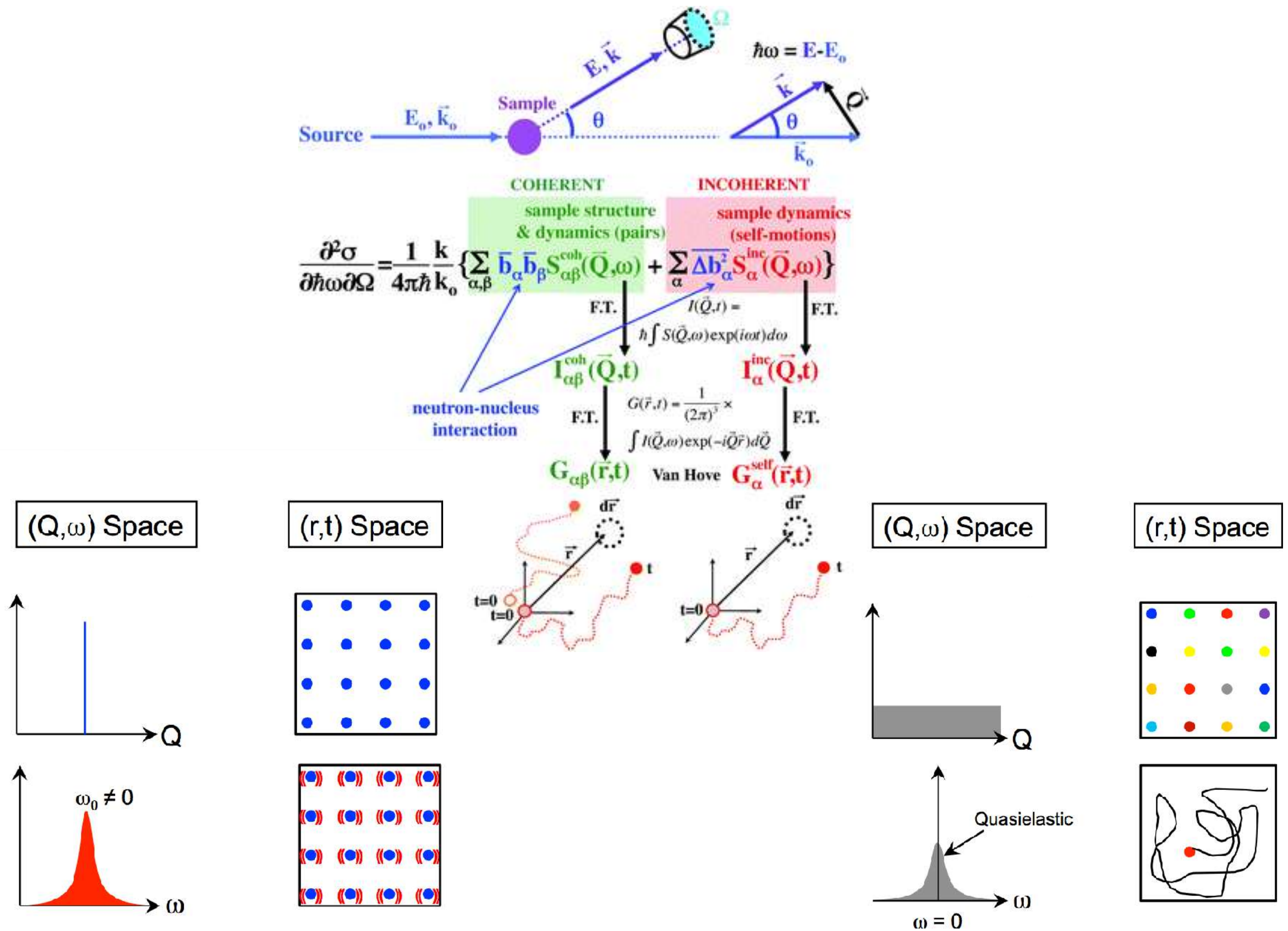


† April, 2nd 2019



F. J. Villacorta et al (2022) Quantum Beam Sci. 6, 3 (17 pages).
F. J. Villacorta et al (2021) Quantum Beam Sci. **5**, 2 (13 pages).
P. Luna et al (2019) Physica B 564, 64–69.
N. Tsapatsaris et al (2016) Rev. Sci. Instrum. **87**, 085118.
N. Tsapatsaris et al (2015) EPJ Web of Conferences, **83**, 03015.
The instrument suite of the European Spallation Source. (2020) Nucl. Instrum. Methods Phys. Res A **957**, 163402 (39 pages).

A neutron scattering experiment: How the water molecules move in time and space

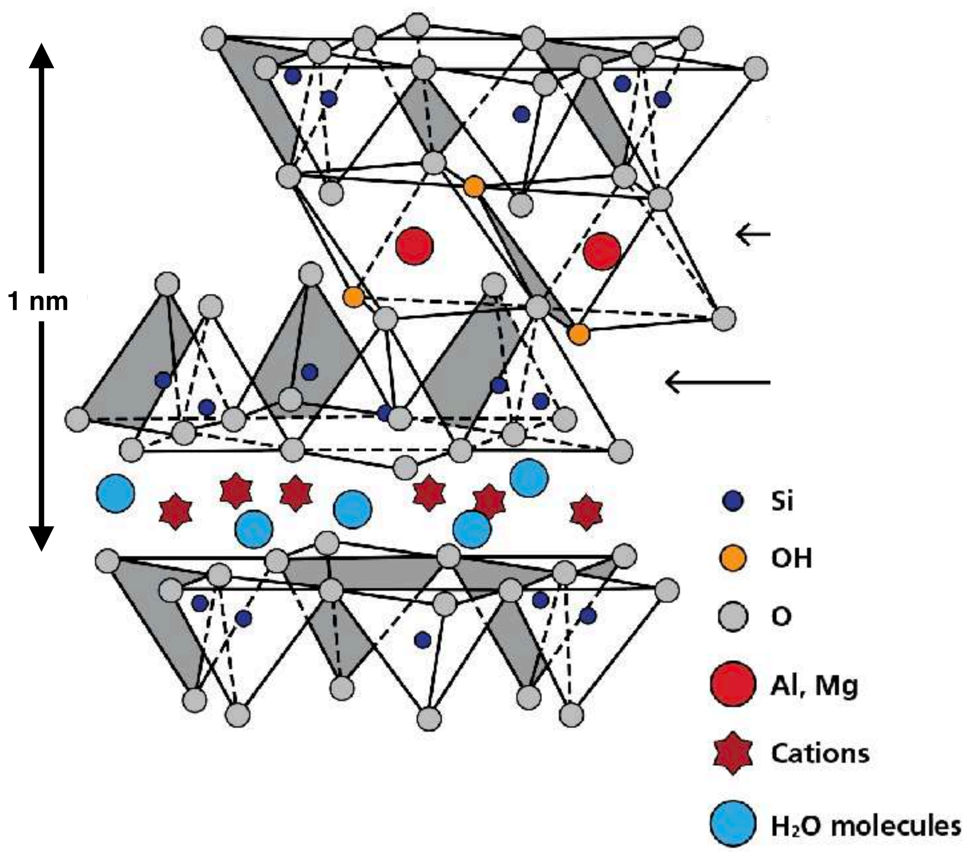


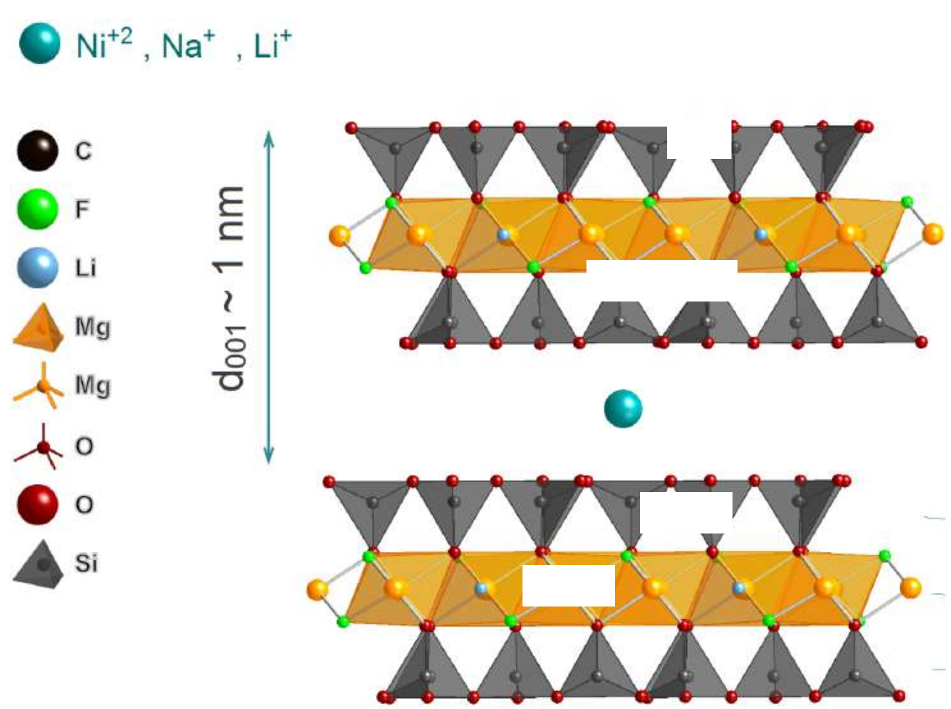
Neutron scattering and molecular dynamics simulations: synergetic tools to unravel structure and dynamics in polymers
A. Arbe, F. Alvarez & Juan Colmenero (2012) Soft Matter **8**, 8257.

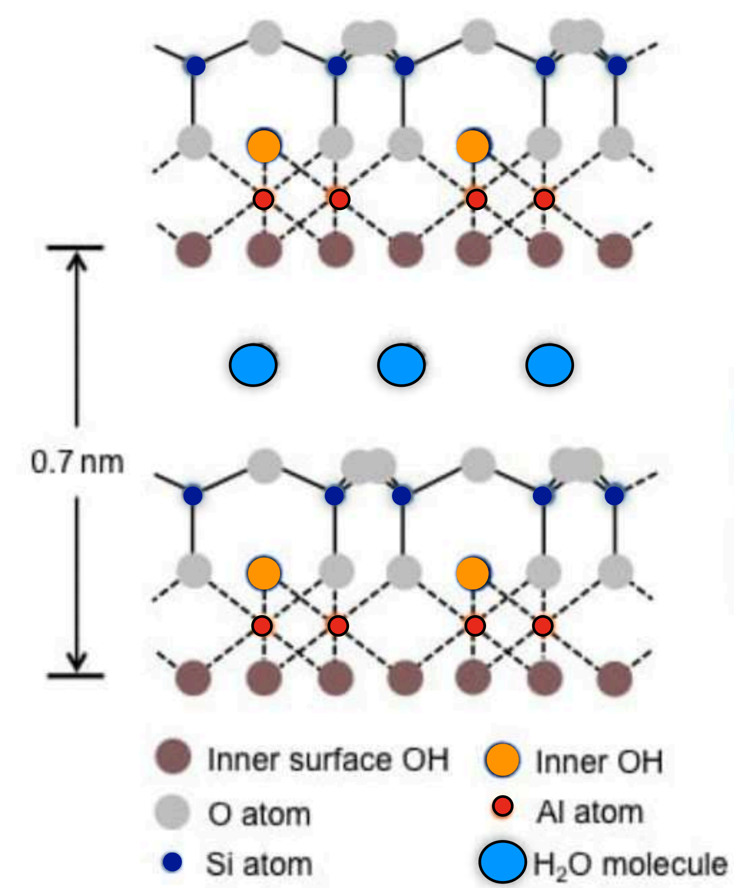
Focusing on 2 questions:

☑ What is the role of the exchange cation in the water dynamics?

☑ How can we get more out of the neutron data?







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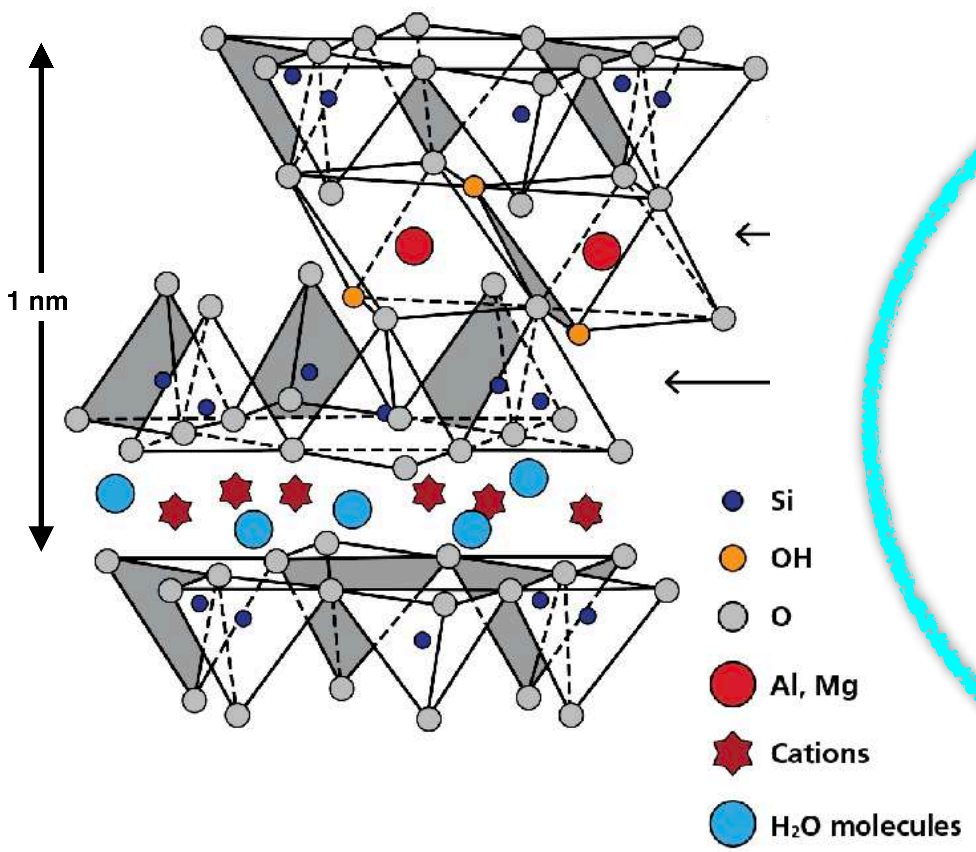
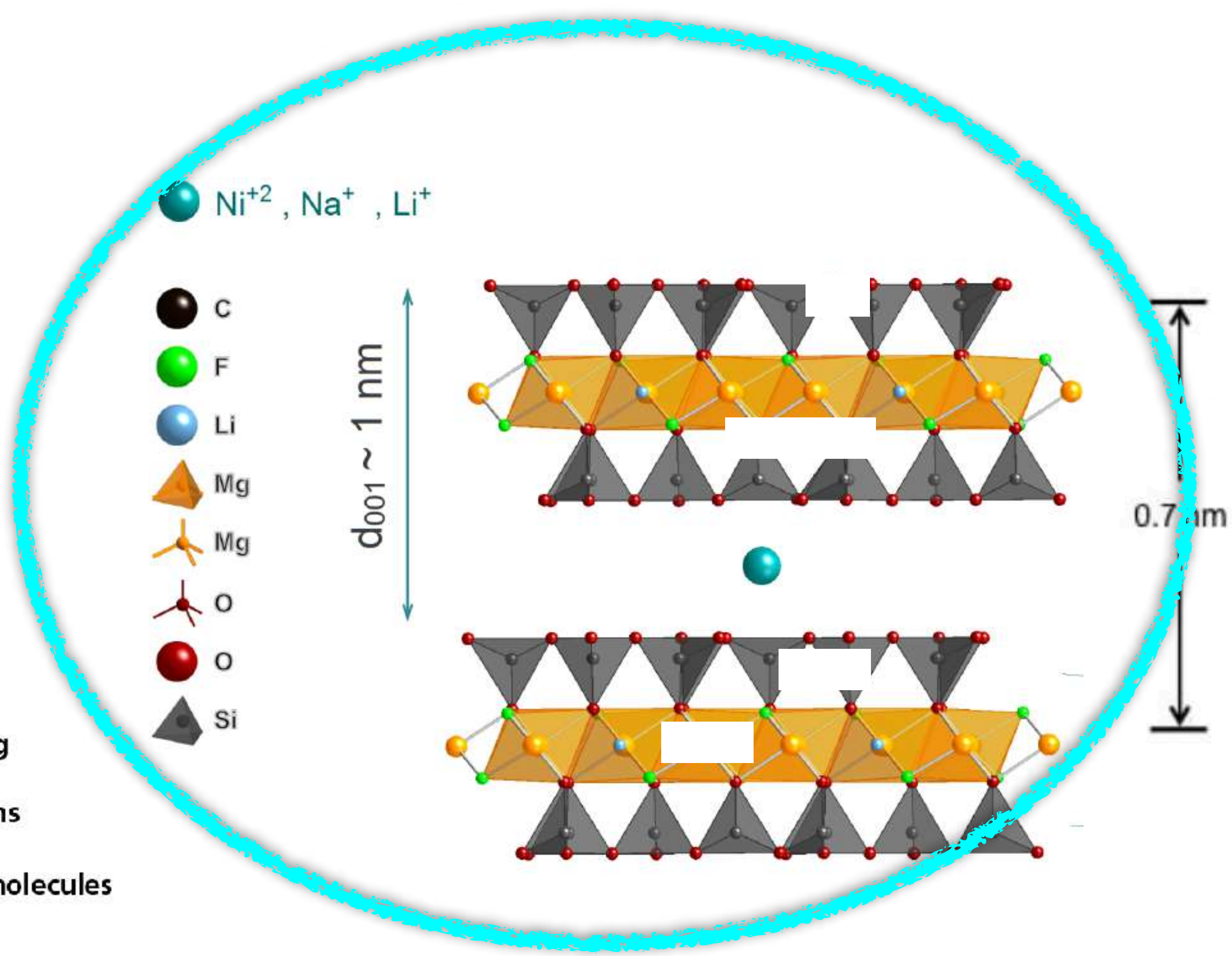
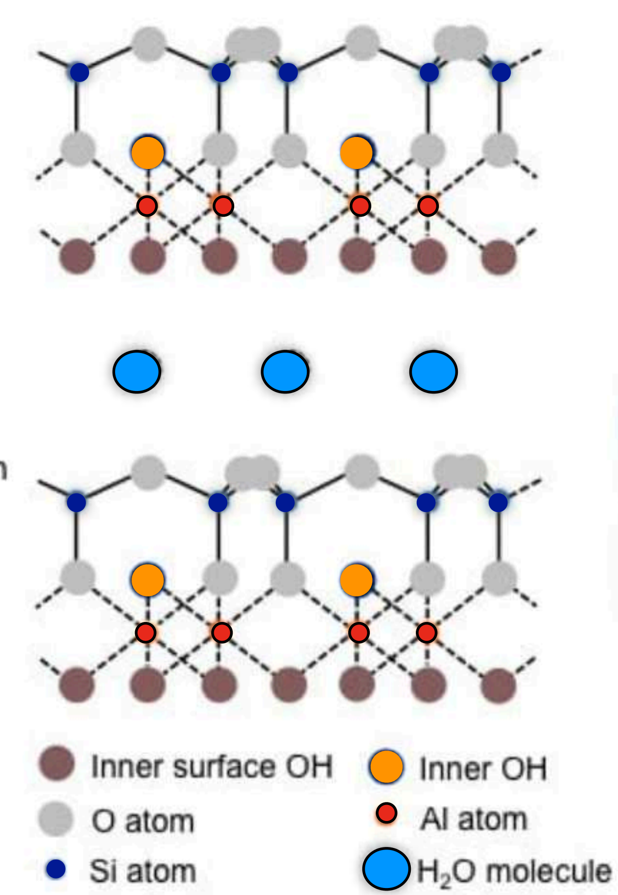


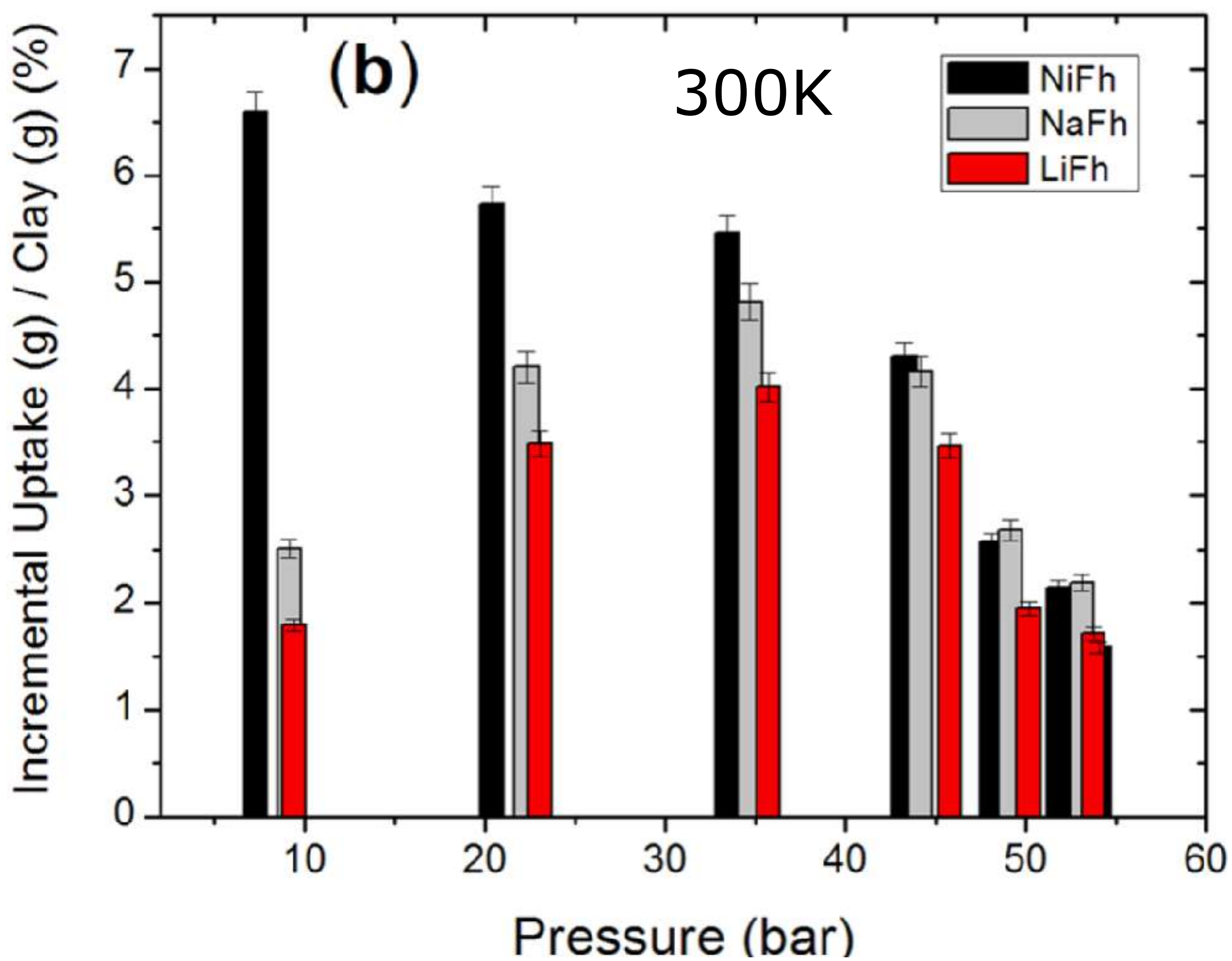




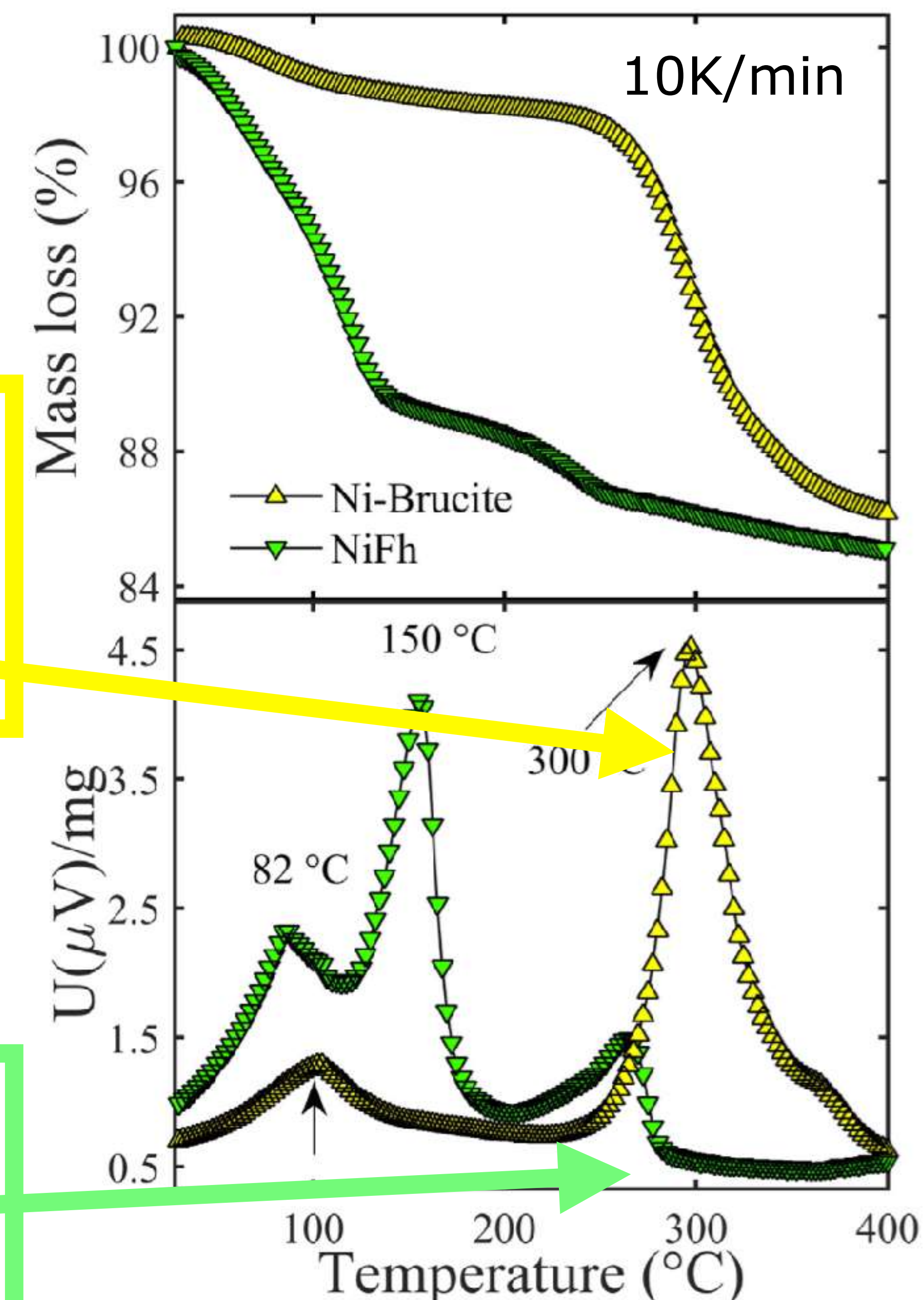
FHt: Different intercalation and retention of CO_2

Hypothesis : Existence of Ni^{2+}-H_2O complexes in the interlayer.

Carbon Capture and Storage (CCS): Possibility for a tailored material



L.P. Cavalcanti, G.N. Kalantzopoulos, J. Eckert, K.D. Knudsen & J.O. Fossum,(2018) A nano-silicate material with exceptional capacity for CO_2 capture and storage at room temperature. Sci. Rep. **8**, 11827.

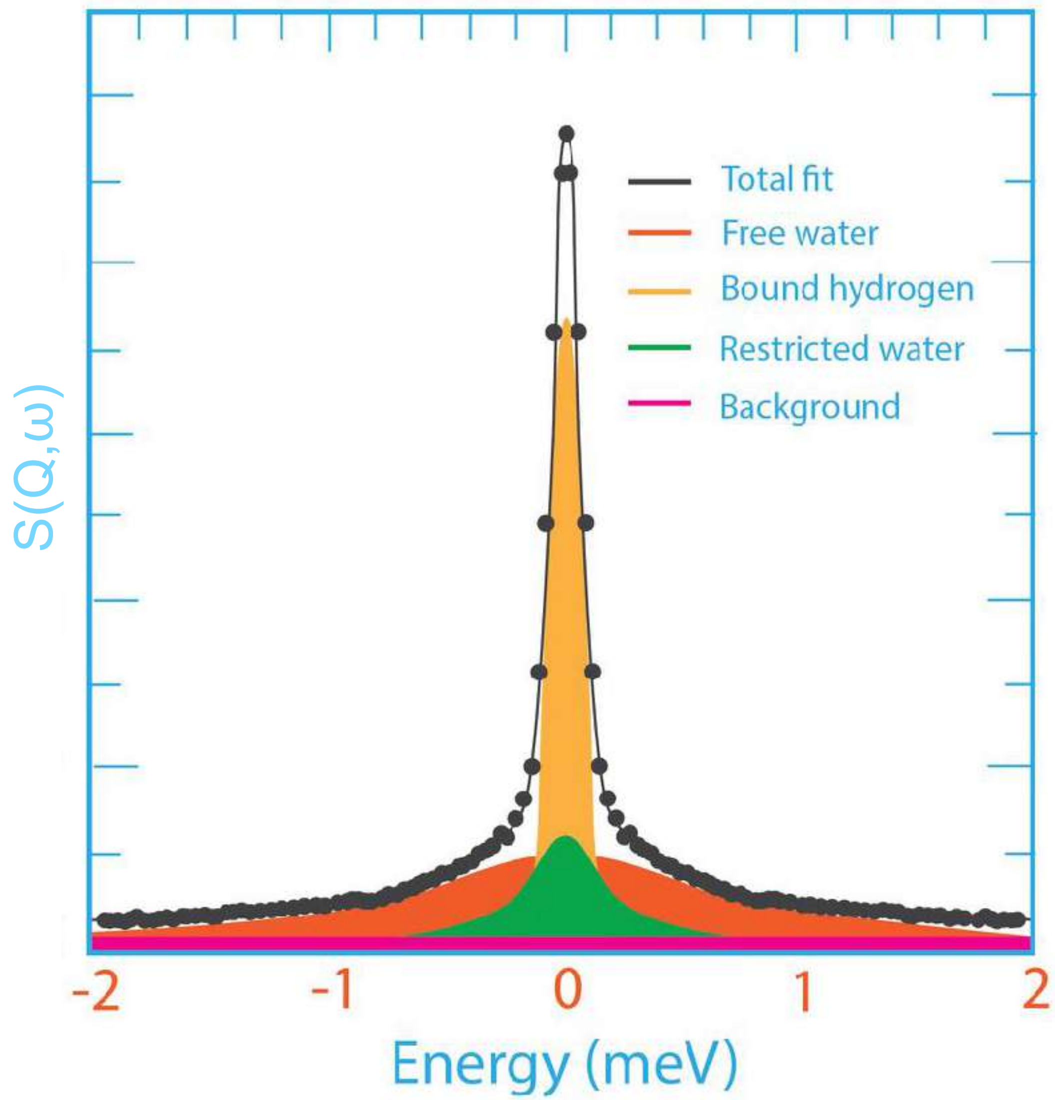


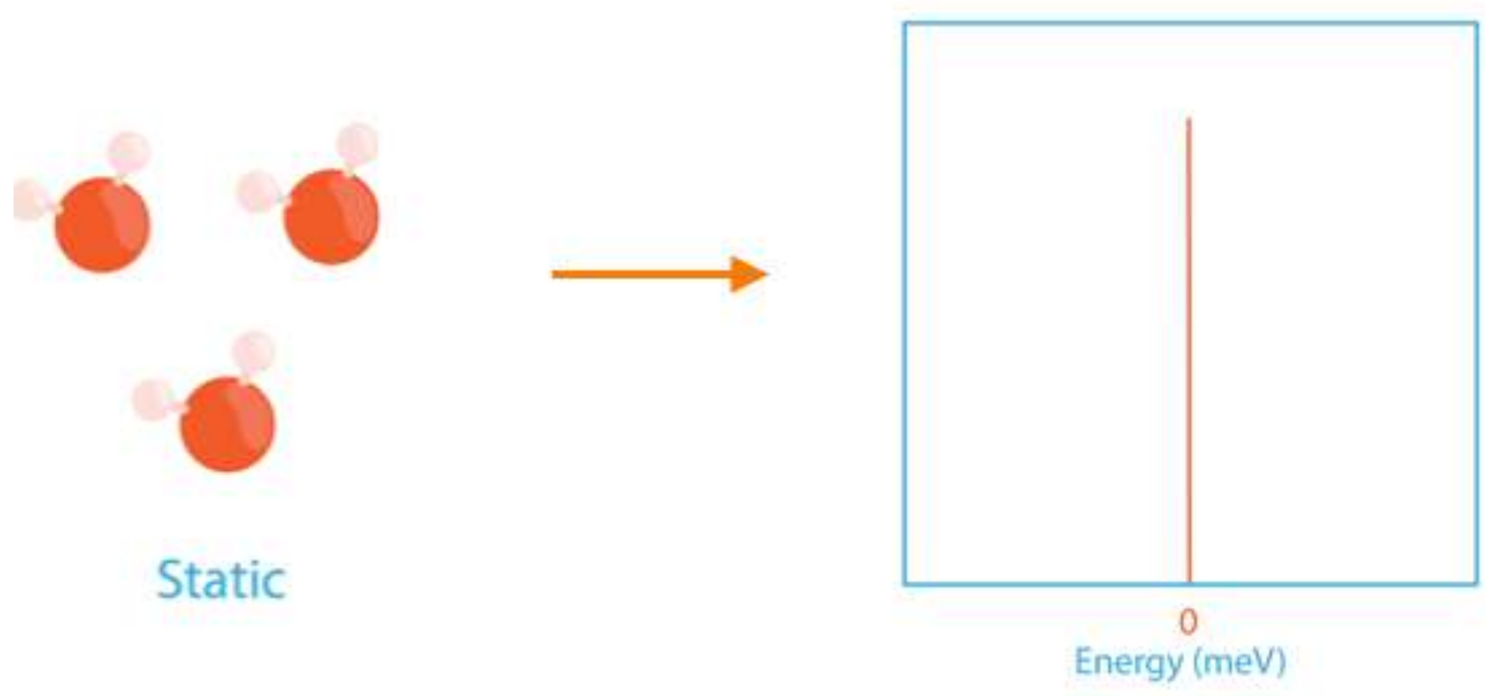
loss of outer OH from the Mg_3-OH

Ni-OH/Ni-H_2O complex: hydrolysis

M. A. S. Altoé, L. Michels, E. C. dos Santos, R. Droppa Jr, G. Grassi, L. Ribeiro, K.D. Knudsen, HNB, J. O. Fossum and G. J. da Silva (2016) Continuous water adsorption states promoted by Ni^{2+} confined in a synthetic smectite. Applied Clays Science, **123**, 83.

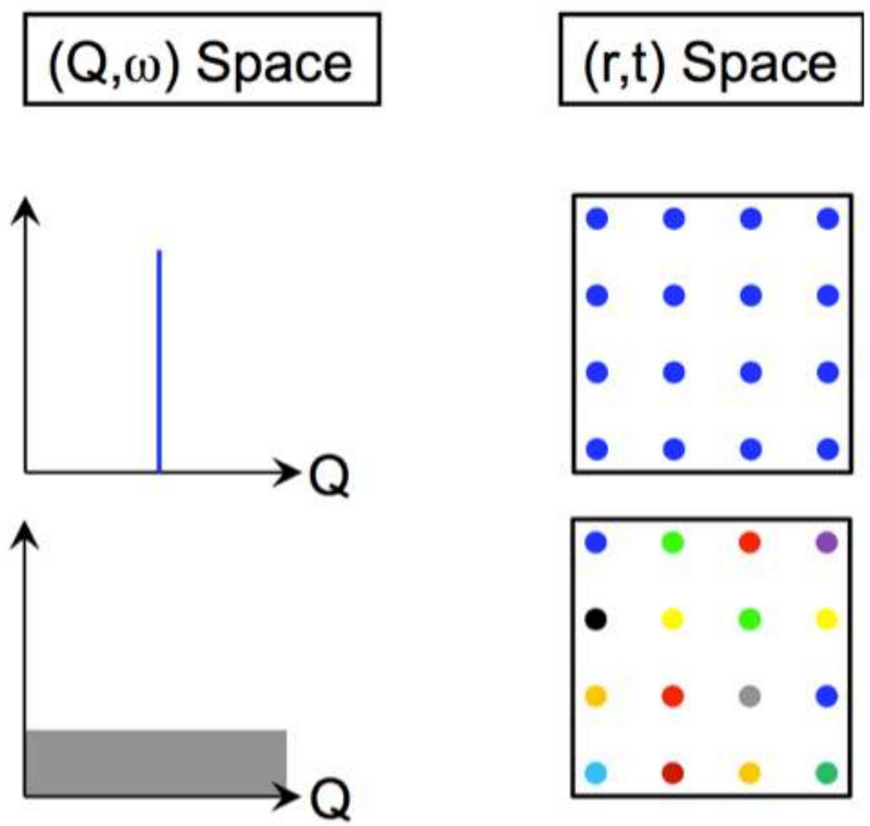
Exploring the full information given by the inelastic neutron scattering data



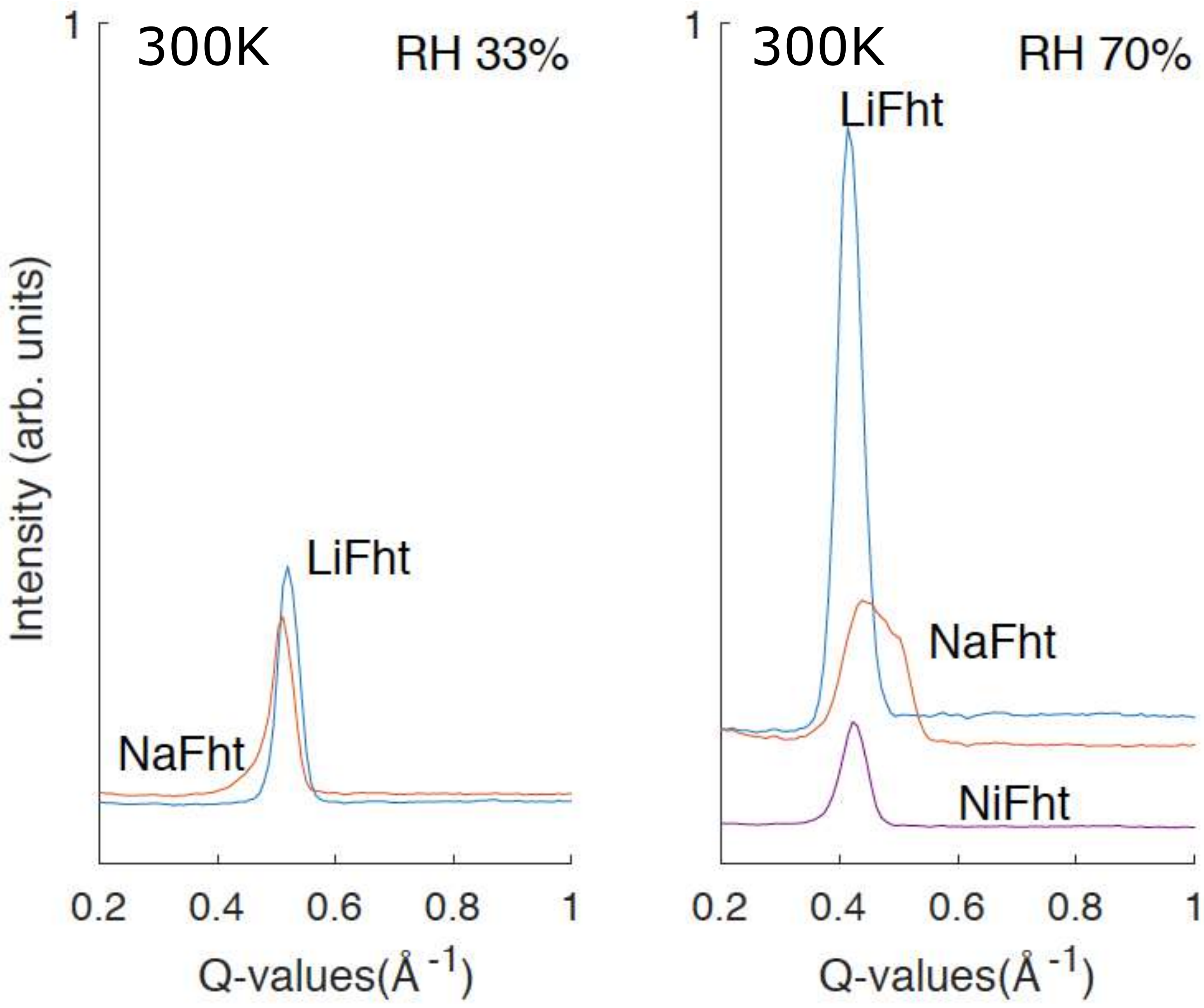


$$\left.\frac{d\sigma}{d\Omega}\right|_{coh} = \frac{\sigma_{coh}}{4\pi} S(Q)$$

$$\left.\frac{d\sigma}{d\Omega}\right|_{inc} = \frac{\sigma_{inc}}{4\pi}$$



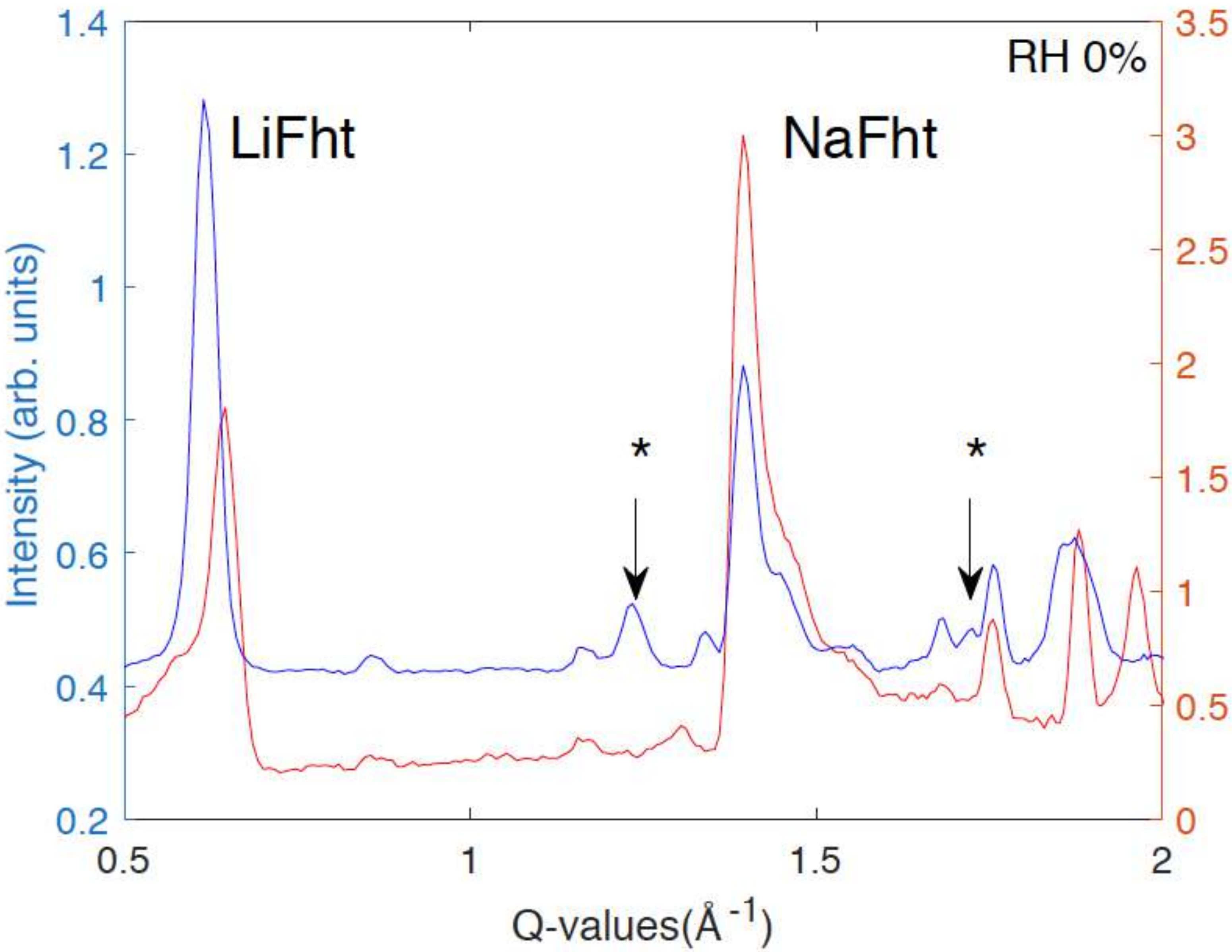
Integrated elastic line: Hydration state of FHt



- LiFHt gives nice symmetric reflections at 1LH (33% RH) and 2LH (70% RH) whereas the NaFHt shows asymmetry in both cases, indicating some interstratification.
- NiFHt (brown) is also equilibrated in a 1WL and 2WL.

S. Larsen, L. Michels, E. C dos Santos, M. C. Berg, W. P Gates, L. P Aldridge, T. Seydel, J. Ollivier, M. T. F. Telling, J. O. Fossum, and HNB (2020) Physicochemical characterisation of fluorohectorite: Water dynamics and nanocarrier properties. Micropor. and Mesopor. Mat. **306**, 110512 (11 pages).

Integrated elastic line: Impurities in the interlayer space

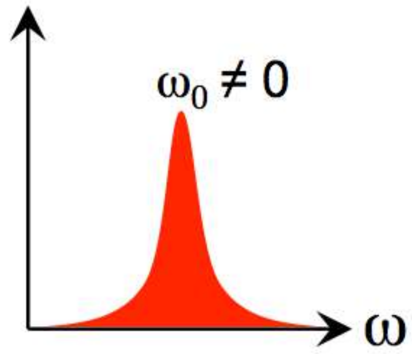


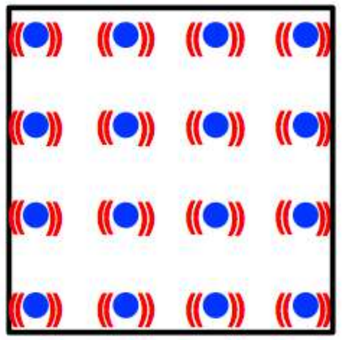
- Diffraction patterns for dried LiFHt, NaFHt. The reflections [001] and [002] are clearly seen.
- Unidentified mineral impurities (*) and the peak at about 1.3 °A^{-1} indicates the presence of brucite in LiFHt which is washed out during the cation exchange process.

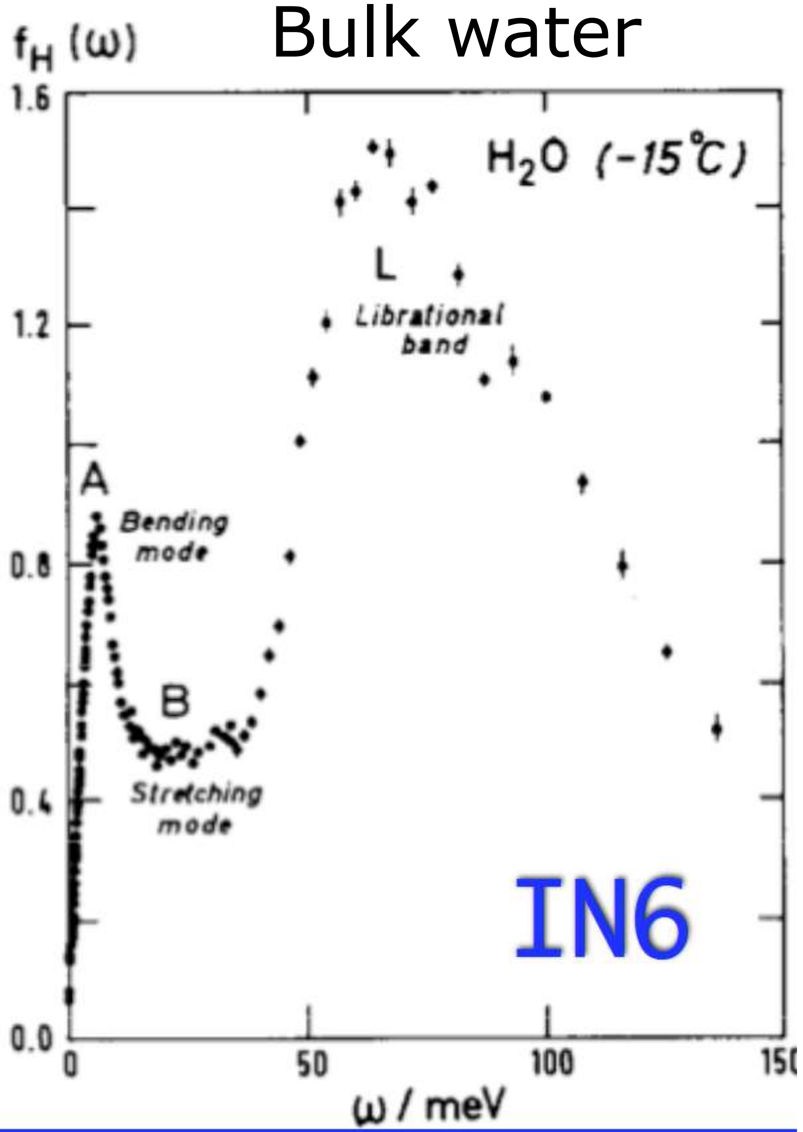
S. Larsen, L. Michels, E. C dos Santos, M. C. Berg, W. P Gates, L. P Aldridge, T. Seydel, J. Ollivier, M. T. F. Telling, J. O. Fossum, and HNB (2020) Physicochemical characterisation of fluorohectorite: Water dynamics and nanocarrier properties. Micropor. and Mesopor. Mat. **306**, 110512 (11 pages).

Exploring the full information given by the inelastic neutron scattering

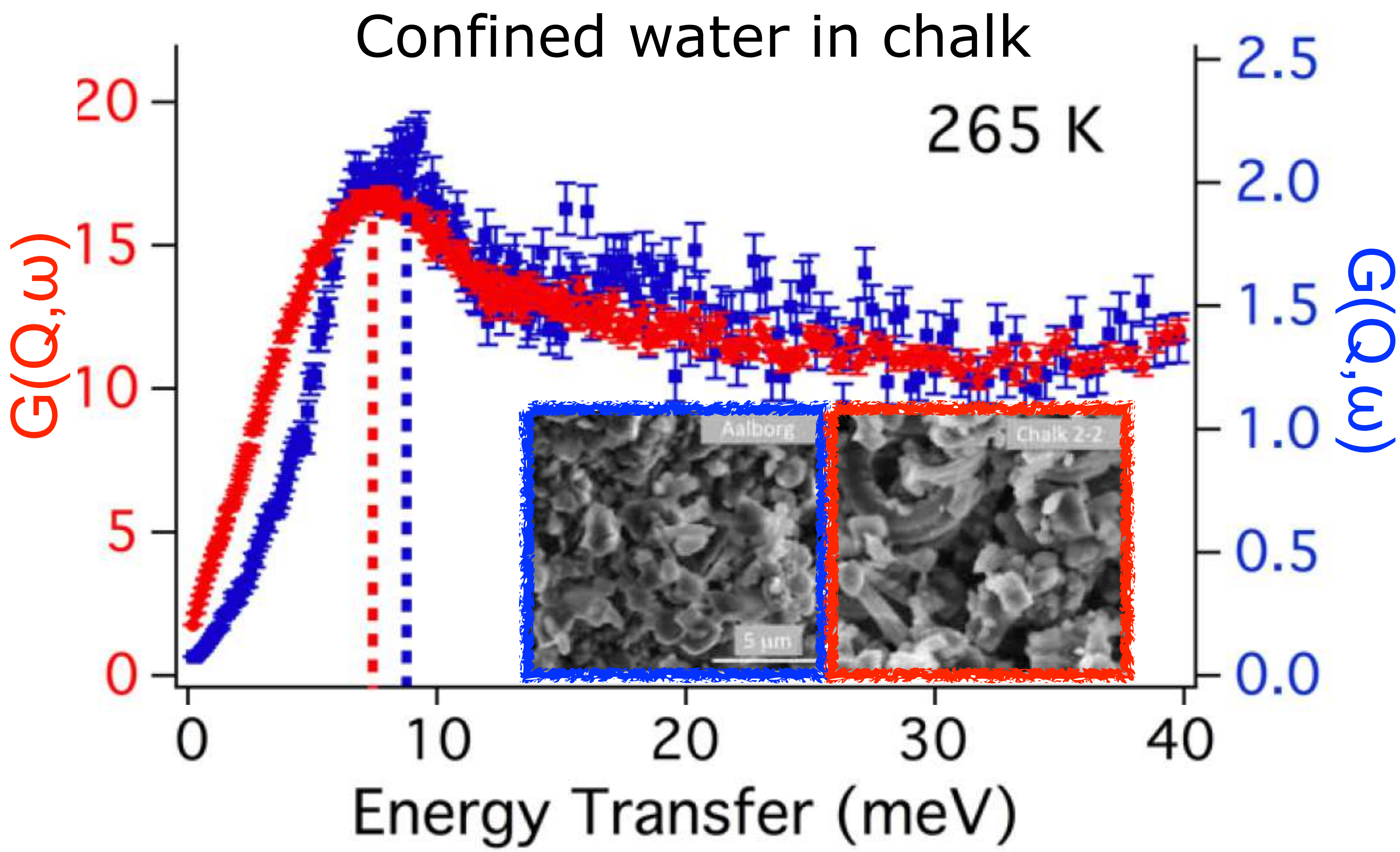
$$\left.\frac{d^2\sigma}{d\Omega dE_f}\right|_{coh} = \frac{k_f}{k_i}\frac{\sigma_{coh}}{4\pi} S_{coh}(Q,\omega)$$





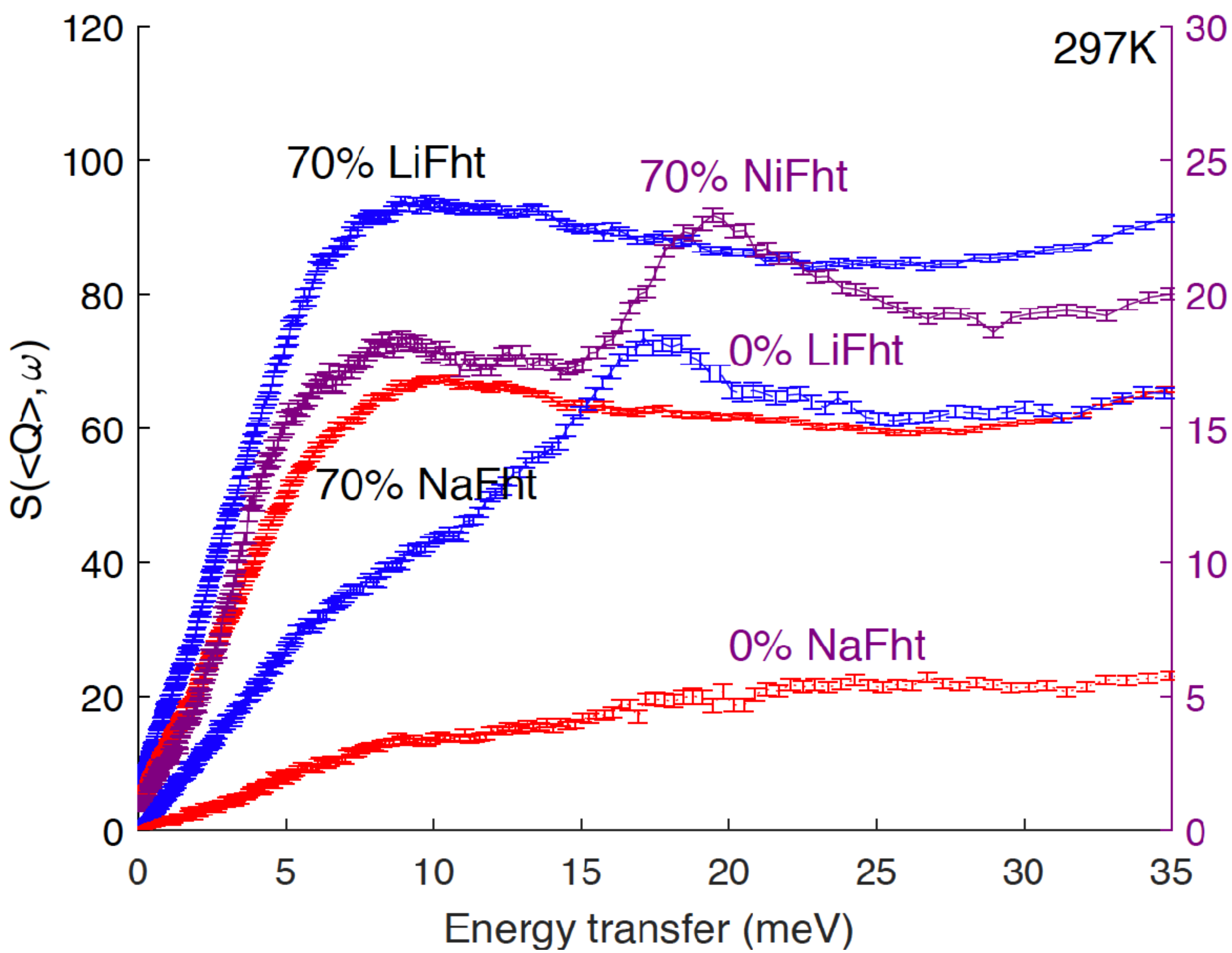


M.-C. Bellissent-Funel & J. Teixeira (1991) J. of Mol. Struct., 250 213.



M. C. Berg, K. N. Dalby, N. Tsapatsaris, D. V. Okhrimenko, H. O. Sørensen, D. Jha, J. P. Embs, S. L. S. Stipp & HNB (2017) Water Mobility in Chalk: A Quasielastic Neutron Scattering Study. Journal of Physical Chemistry C, 121, 14088.

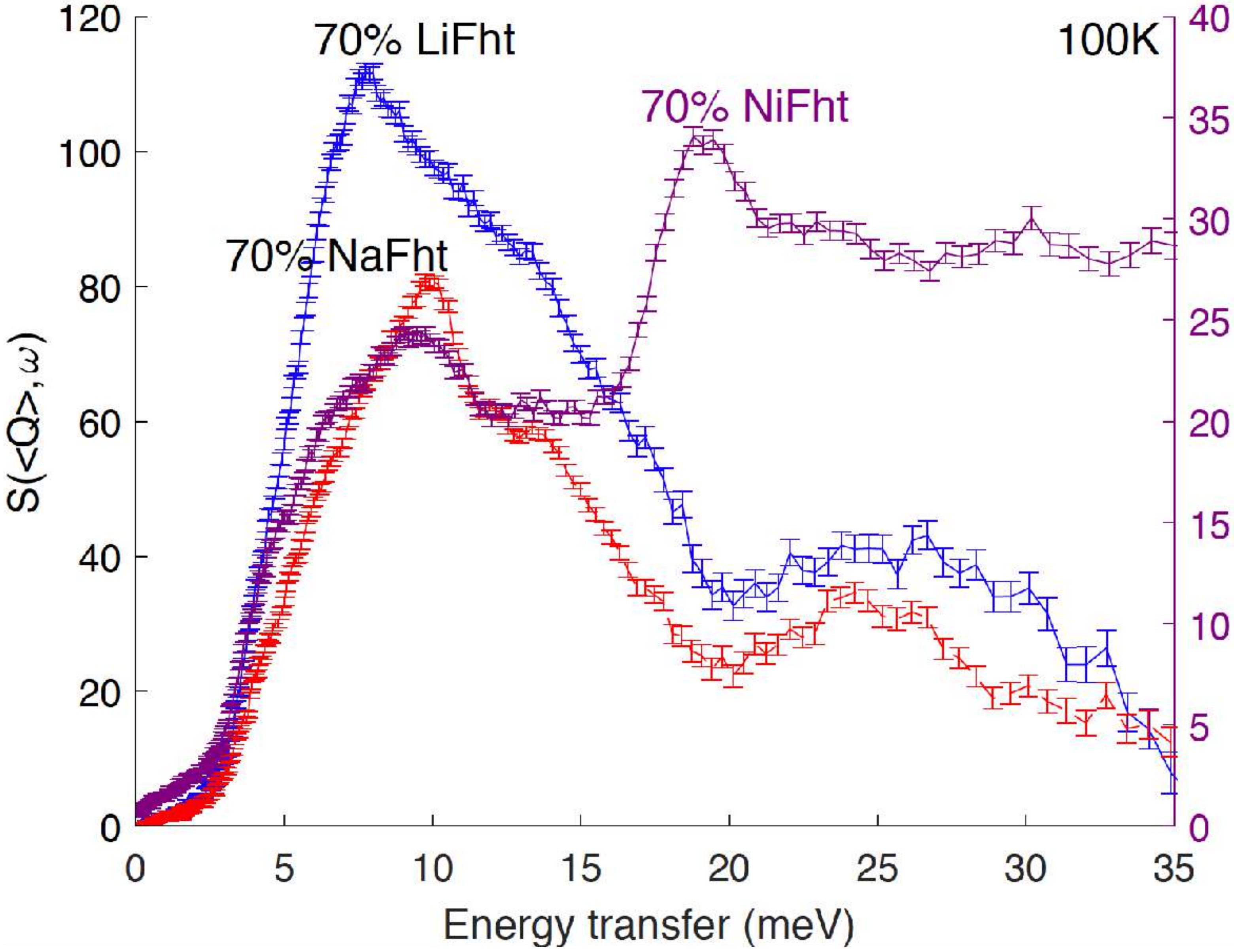
Density of States: Indirect insight on the FHt structure



- Lower signal in NiFht is a consequence of smaller water content.
- A clear vibration is observed in the dried LiFHt and in the NiFHt at nominal 70% RH: Mg_3OH in LiFHt and $Ni(OH)_x$-H_2O phase within the interlayer space ("pillared clay?).

M. A. S. Altoé, L. Michels, E. C. dos Santos, R. Droppa Jr, G. Grassi, L. Ribeiro, K.D. Knudsen, HNB, J. O. Fossum and G. J. da Silva (2016) Continuous water adsorption states promoted by Ni2+ confined in a synthetic smectite. Applied Clays Science, **123**, 83-91.
S. Larsen, L. Michels, E. C dos Santos, M. C. Berg, W. P Gates, L. P Aldridge, T. Seydel, J. Ollivier, M. T. F. Telling, J. O. Fossum and HNB (2020) Physicochemical characterisation of fluorohectorite: Water dynamics and nanocarrier properties. Micropor. and Mesopor. Mat. **306**, 110512 (11 pages).

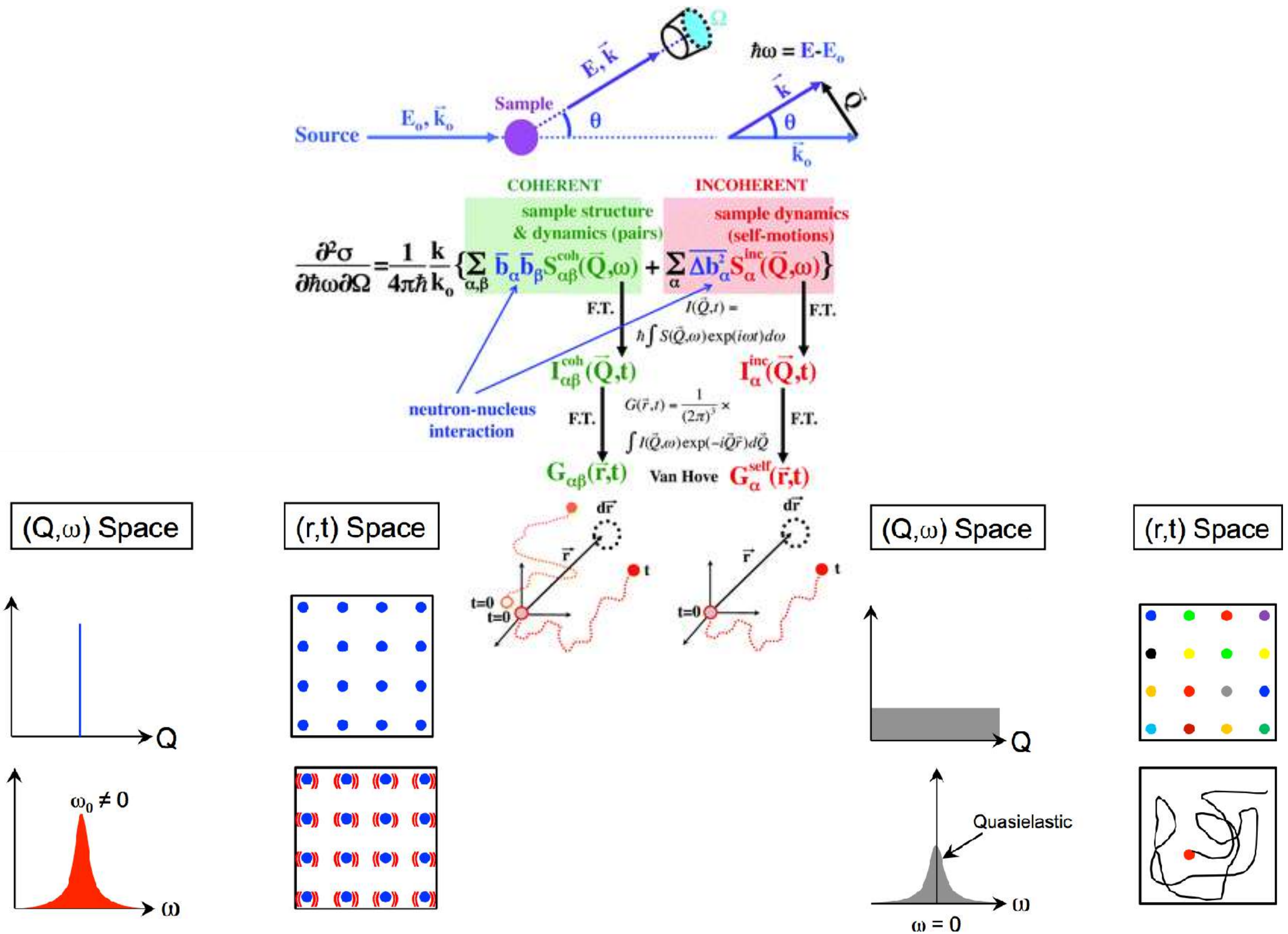
Density of States at 100K: Different water-cation strength



- On cooling, the water molecules became more structured and the vibrations have narrowed.
- The first vibration - attributed to confined water - is at a slighter higher frequency in NaFHt, around 10meV. This is an indication that water is more strongly bonded in NaFHt than in LiFHt.
- In NiFHt, the NiOH-H_2O vibration is clearly observed.

S. Larsen, L. Michels, E. C dos Santos, M. C. Berg, W. P Gates, L. P Aldridge, T. Seydel, J. Ollivier, M. T. F. Telling, J. O. Fossum and HNB (2020) Physicochemical characterisation of fluorohectorite: Water dynamics and nanocarrier properties. Micropor. and Mesopor. Mat. **306**, 110512 (11 pages).

Single-molecule dynamics using quasi-elastic neutron scattering (QENS)
How the water molecules move in time and space?



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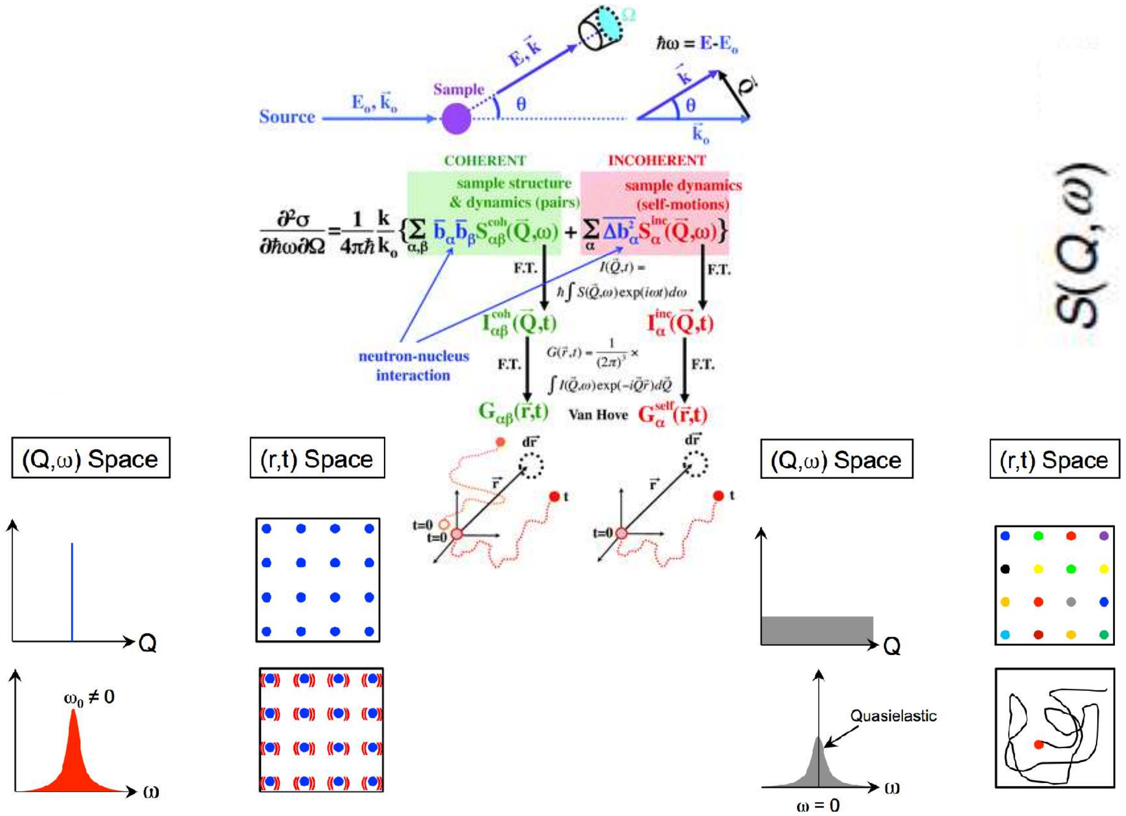
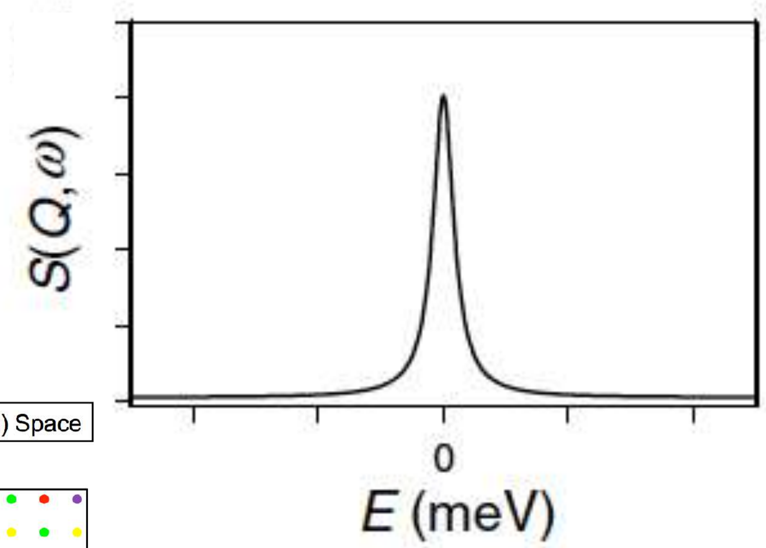
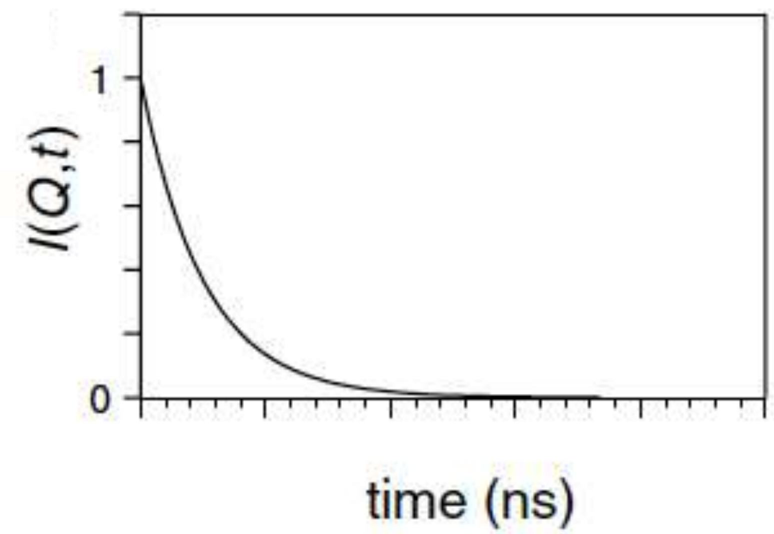
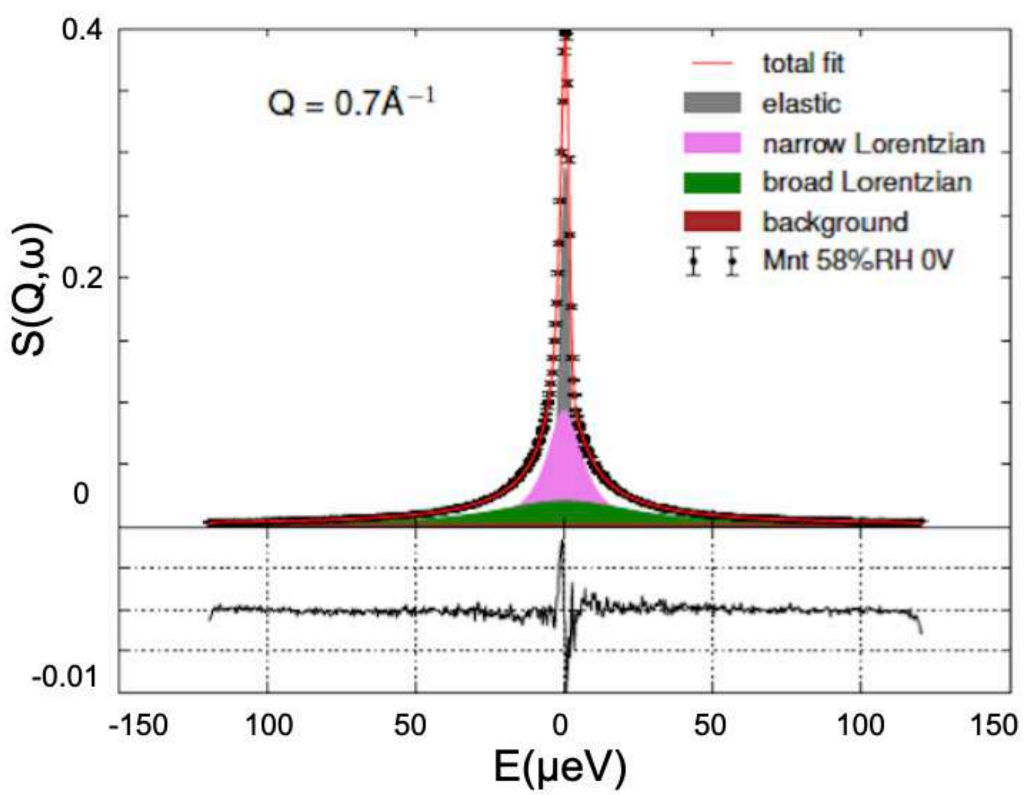
How the water molecules move in time and space?

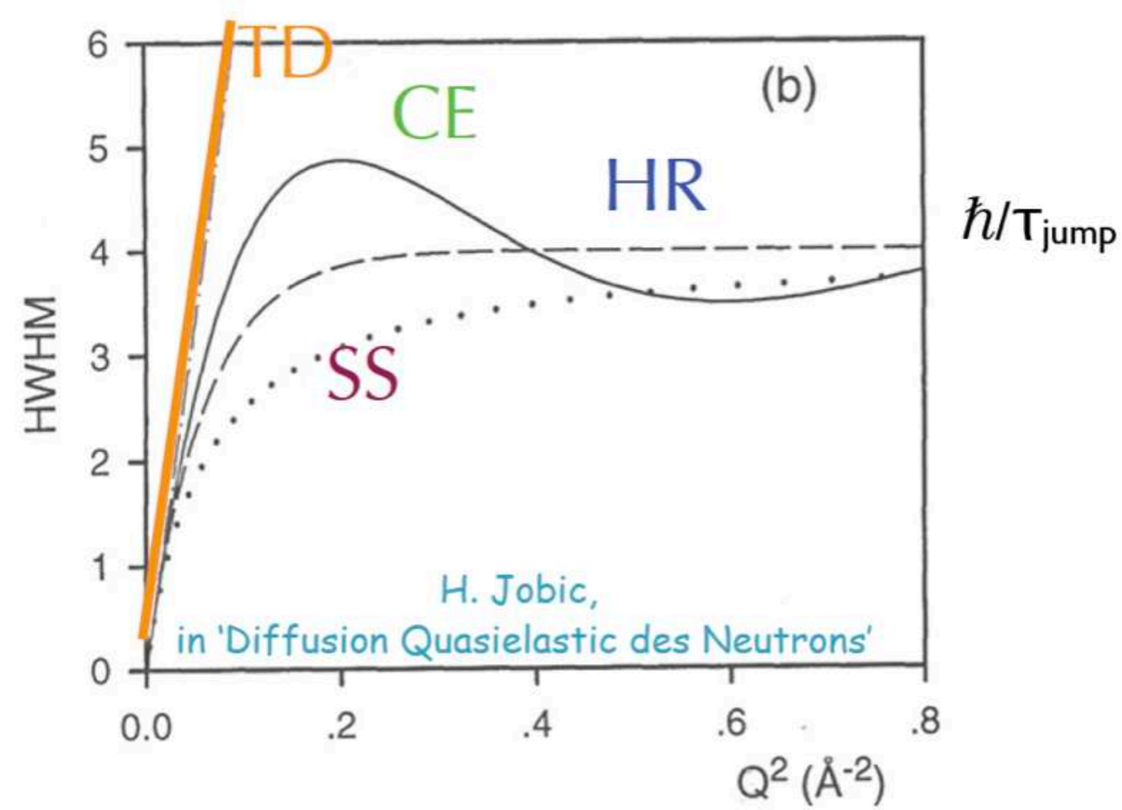






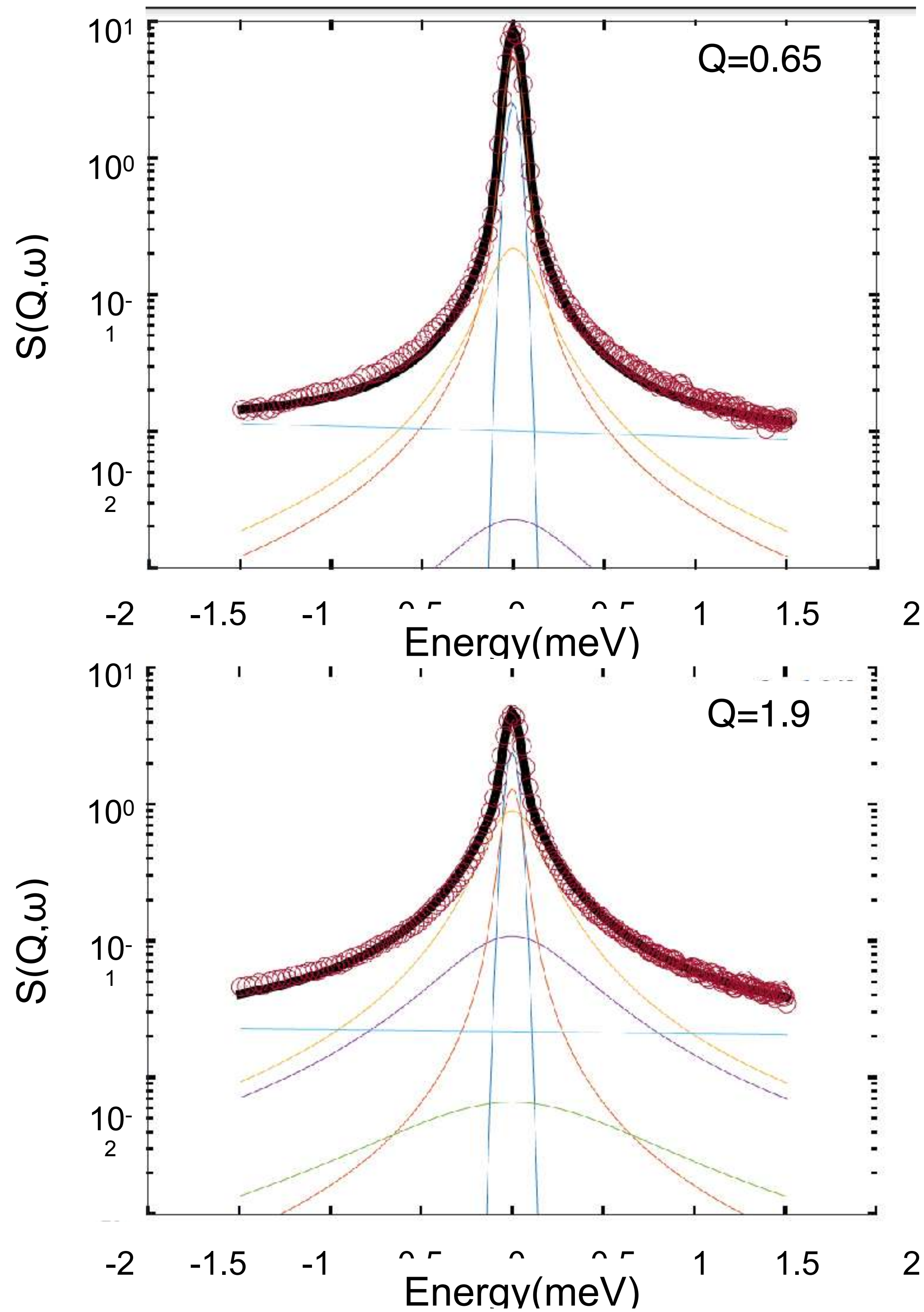
Quasi-elastic neutron scattering and molecular dynamics simulation as complementary techniques for studying diffusion in zeolites
H. Jobic & D.N. Theodorou (2007) Micropor Mesopor Mat **102**, 21–50.

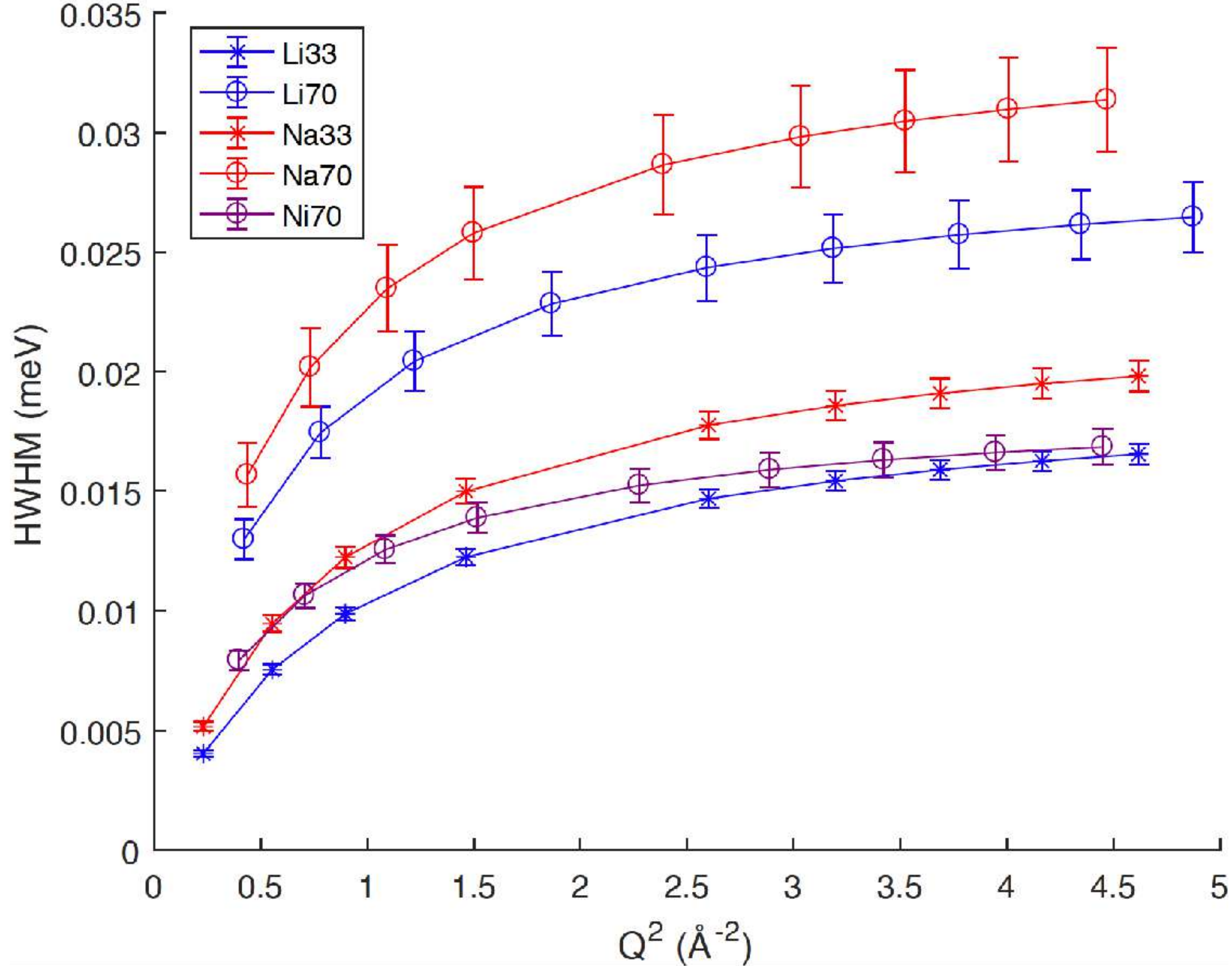




Neutron scattering and molecular dynamics simulations: synergetic tools to unravel structure and dynamics in polymers
A. Arbe, F. Alvarez & Juan Colmenero (2012) Soft Matter **8**, 8257.

QENS shows that the interlayer cation influences water diffusion





S. Larsen, L. Michels, E. C dos Santos, M. C. Berg, W. P Gates, L. P Aldridge, T. Seydel, J. Ollivier, M. T. F. Telling, J. O. Fossum, HNB (2020) Physicochemical characterisation of fluorohectorite: Water dynamics and nanocarrier properties. Micropor. and Mesopor. Mat. **306**, 110512 (11 pages).
L.P. Aldridge, S.R. Larsen & HNB (2019) Octave Program for Fitting Quasi-Elastic Neutron Scattering Data. Physica B. **561**, 75–78.

QENS shows that the interlayer cation influences water diffusion

Table 1: Parameters obtained from fitting the HWHMs using the random jump diffusion model.

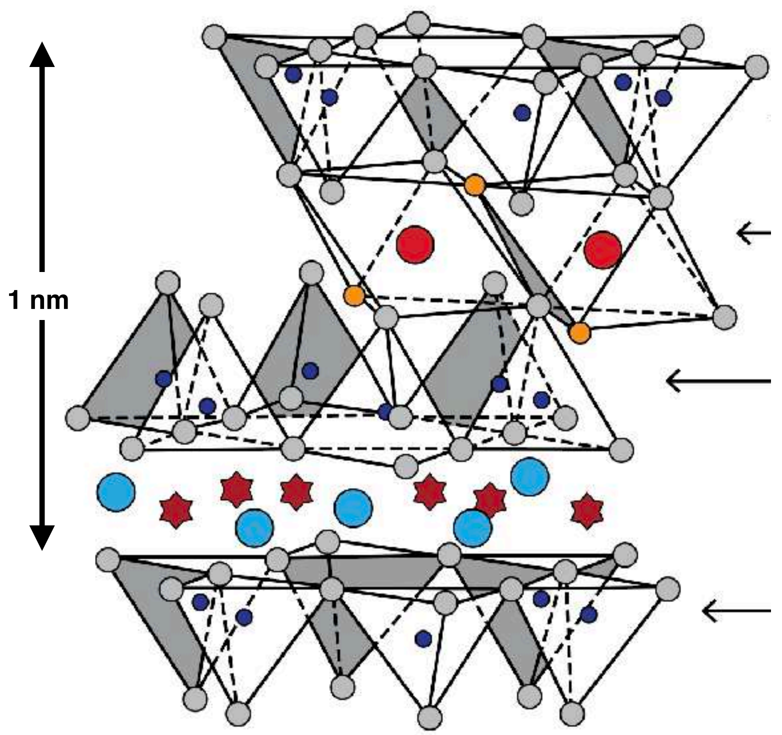
Sample	Water layers	C	D (10^{-9} m^2 s^{-1})	τ_0 (ps)	$u^2(\AA^2)$	τ_R (ps)
bulk water [31]	-	-	2.49 ± 0.07	1.57 ± 0.12	0.23	1.07 ± 0.08
LiFHt33	1WL	0.54	0.33 ± 0.02	33 ± 1	0.005	1.4
NaFh33	1WL	0.57	0.44 ± 0.02	28 ± 1	0.02	2.1
LiFht70	2WL	0.22	0.83 ± 0.04	22.4 ± 0.7	0.02	1.8
NaFht70	1Wl and 2WL	0.36	0.95 ± 0.04	18.9 ± 0.2	0.02	1.4
NiFht70	1WL	0.69	0.47 ± 0.03	34.9 ± 0.6	0.04	3.3

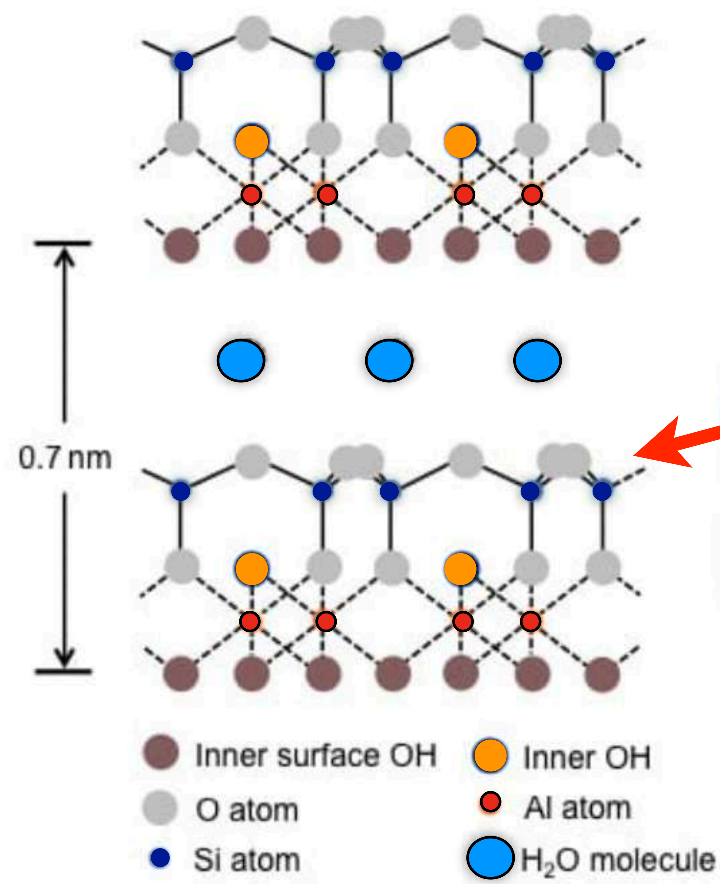
- ☑ Li, Ni and NaFHt samples had water molecules arranged in a single layer (1WL) with highly hindered mobility as reflected by the values of the residence times and diffusion coefficients extracted using the full jump diffusion model.

- ☑ Restricted mobility, most likely related to the presence of other hydrogenous complexes, was also reflected in the LiFHt 70% nominal RH when compared to the mixed state NaFHt.

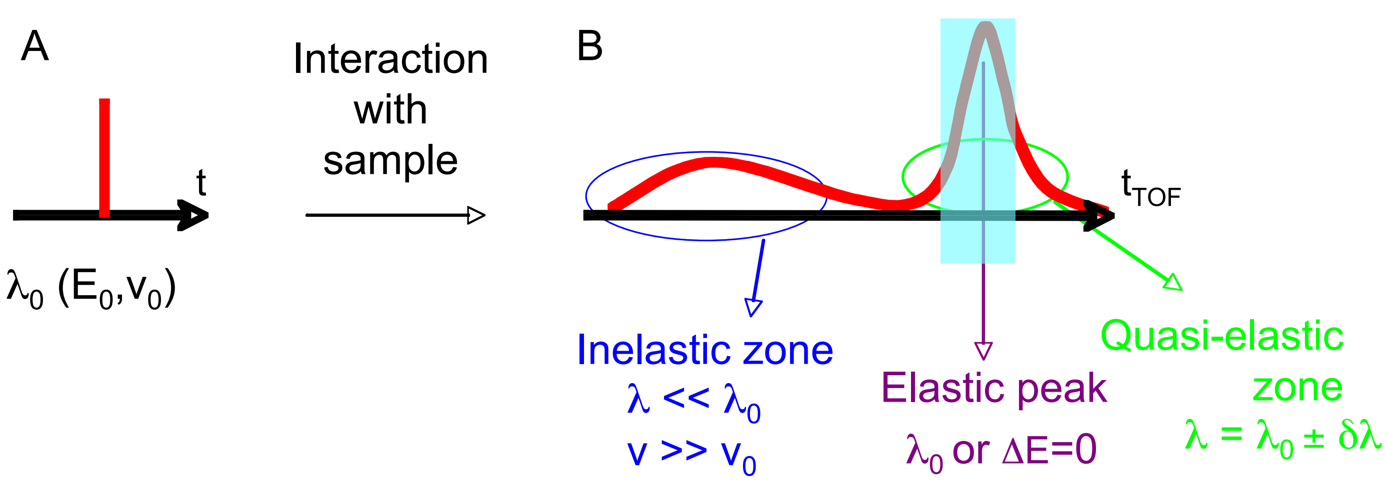
S. Larsen, L. Michels, E. C dos Santos, M. C. Berg, W. P Gates, L. P Aldridge, T. Seydel, J. Ollivier, M. T. F. Telling, J. O. Fossum, HNB (2020) Physicochemical characterisation of fluorohectorite: Water dynamics and nanocarrier properties. Micropor. and Mesopor. Mat. **306**, 110512 (11 pages).
L.P. Aldridge, S.R. Larsen & HNB (2019) Octave Program for Fitting Quasi-Elastic Neutron Scattering Data. Physica B. **561**, 75–78.

What if there are no cations? Does our conclusion still hold?





water can be potentially H-bonded



Heloisa N. Bordallo *et al* Quasi-Elastic Neutron Scattering Studies on Clay Interlayer-Space Highlighting the Effect of the Cation in Confined Water Dynamics. The Journal of Physical Chemistry C (2008) **112**,13982-13991.

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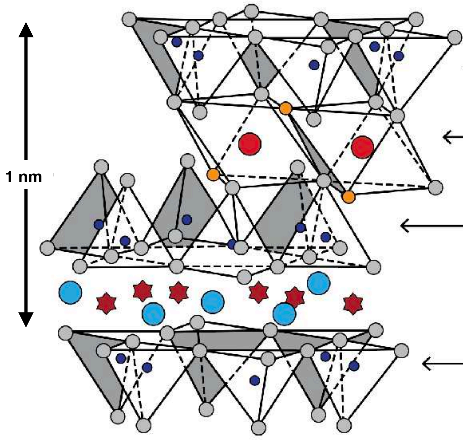
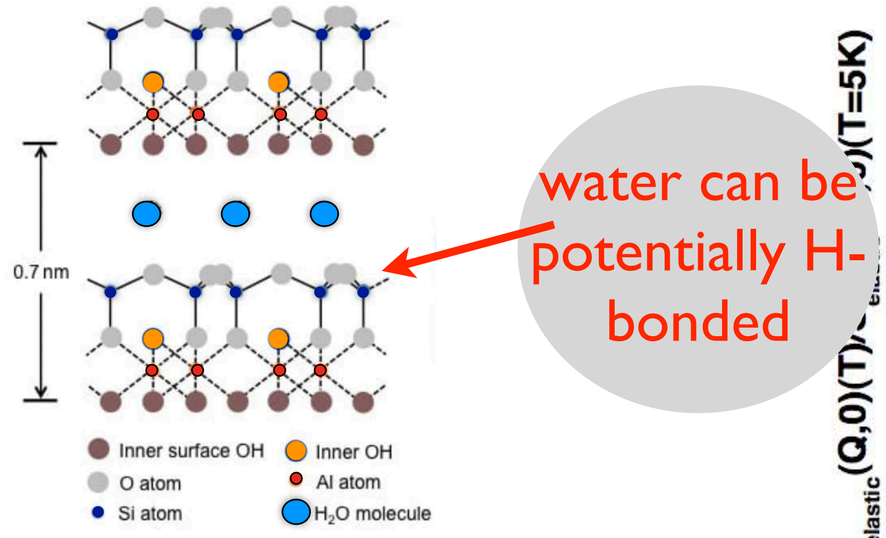
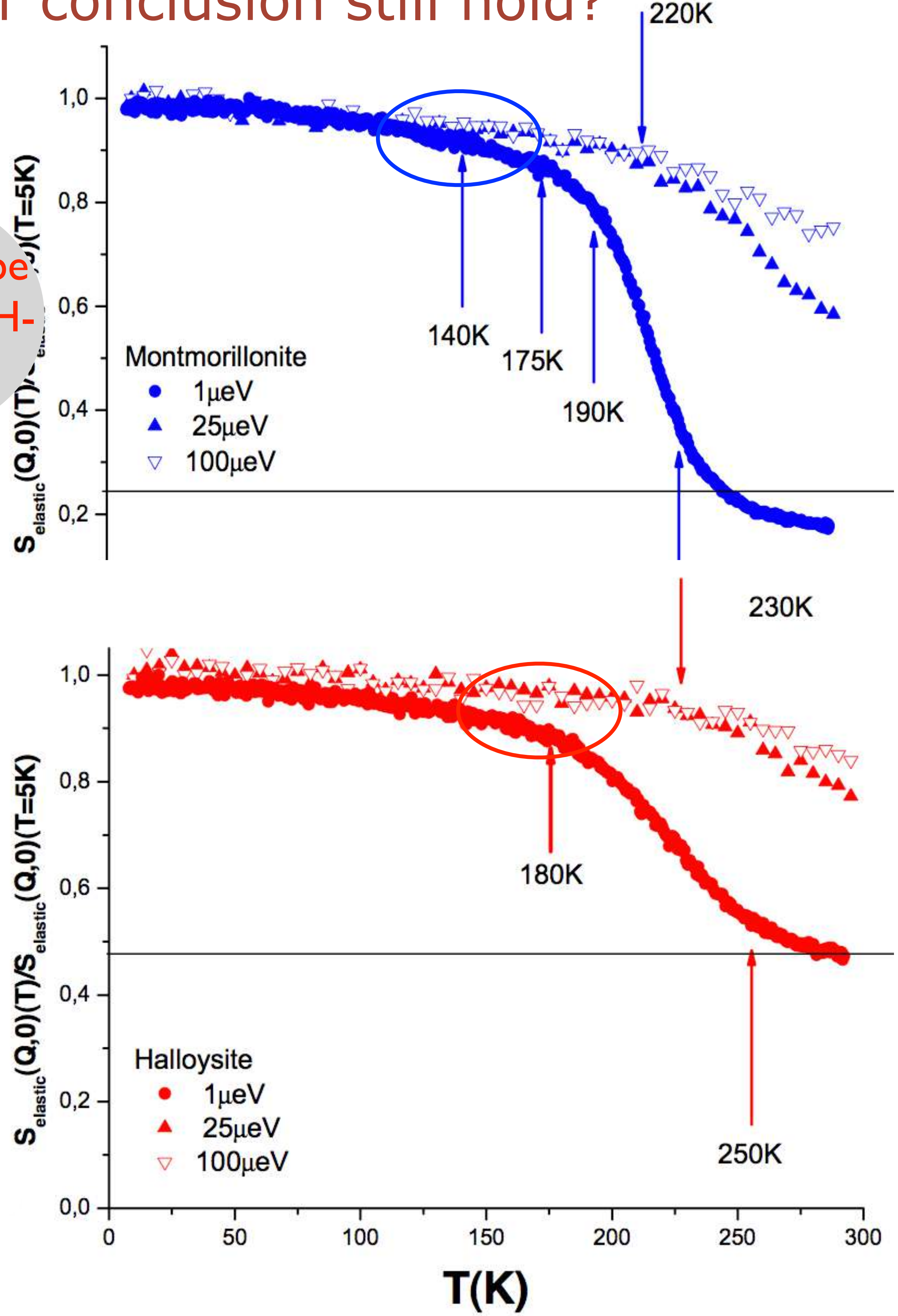
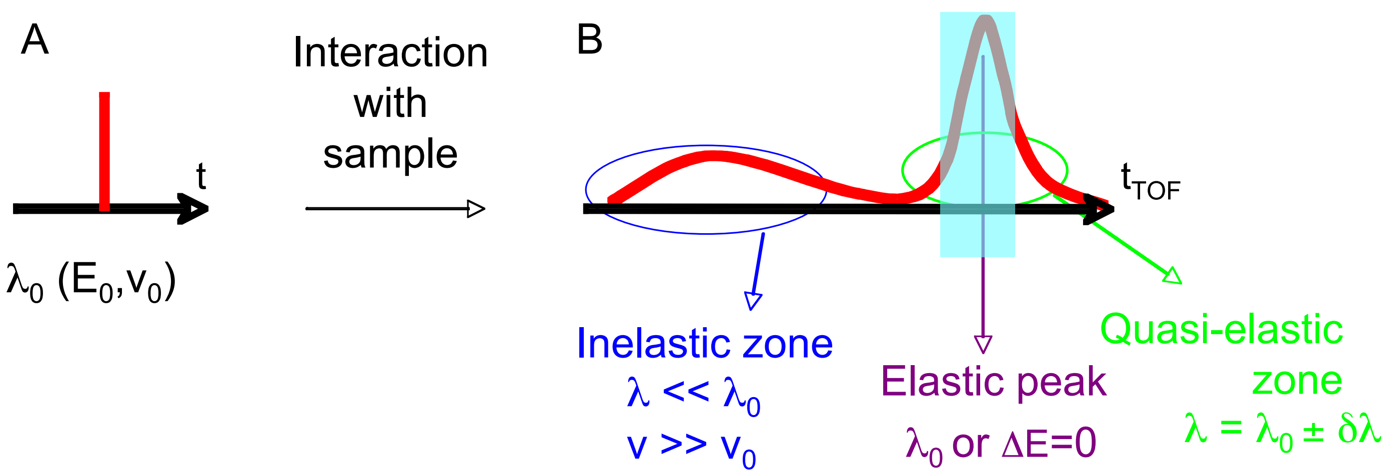






YES! Cations facilitate activation of H_2O motion!



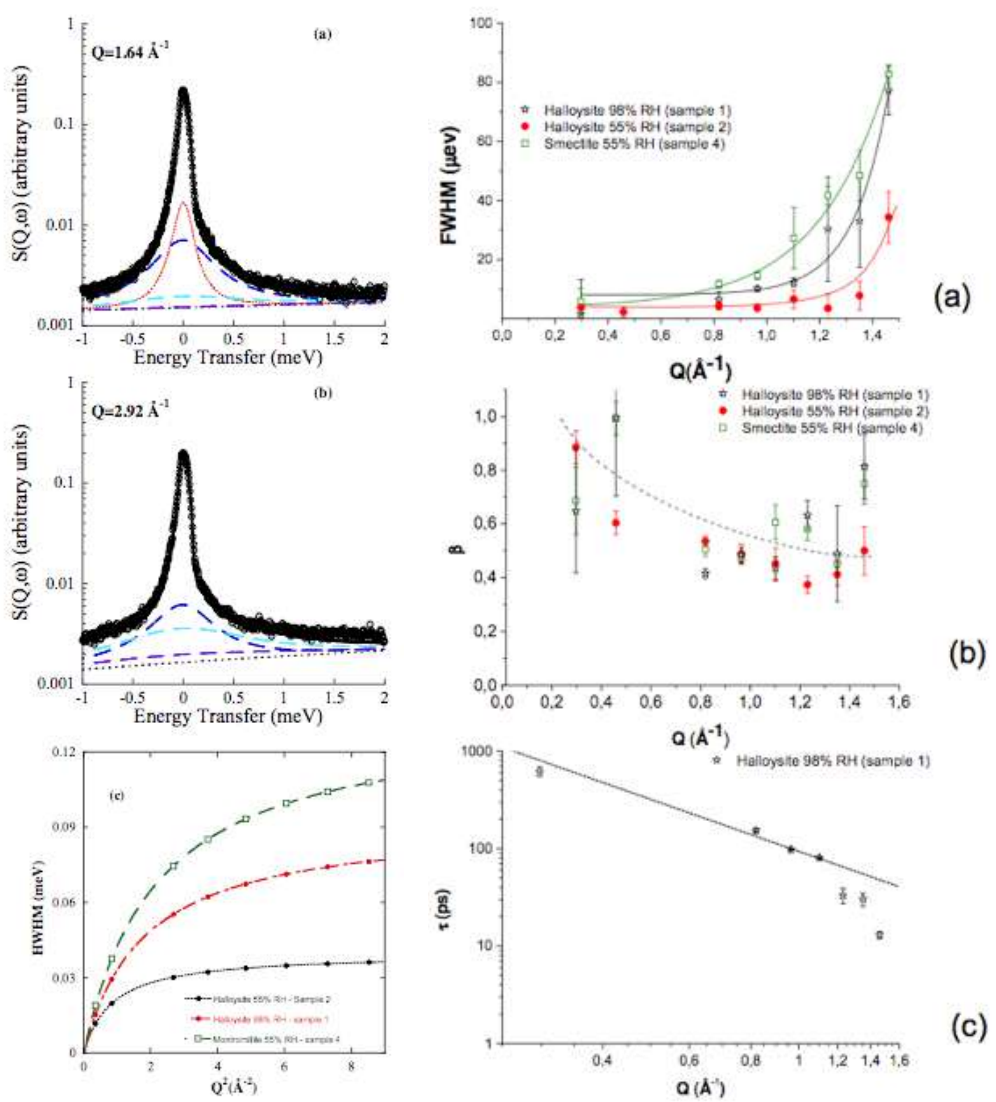
Heloisa N. Bordallo *et al* Quasi-Elastic Neutron Scattering Studies on Clay Interlayer-Space Highlighting the Effect of the Cation in Confined Water Dynamics. The Journal of Physical Chemistry C (2008) **112**,13982-13991.

Cations vs Pore surface geometry

H-bond at the halloysite surface (Al-OH)

if Al-OH...H_2O:

$D_{halloysite} < D_{montmorillonite}$



Sample	$D_{apperant}$ ($10^{-9} m^2/s$)
Bulk water [46,47]	2.49±0.07
Halloysite 55%RH	0.7±0.2
Halloysite 98%RH Fast[1] Slow[2]	 0.8±0.1 ~0.2
Montmorillonite 55%RH	0.9±0.1

H.N. Bordallo *et al.* (2008) Quasi-Elastic Neutron Scattering Studies on Clay Interlayer Space Highlighting the Effect of the Cation in Confined Water Dynamics. Journal of Physical Chemistry C, **112**, 19982-91.

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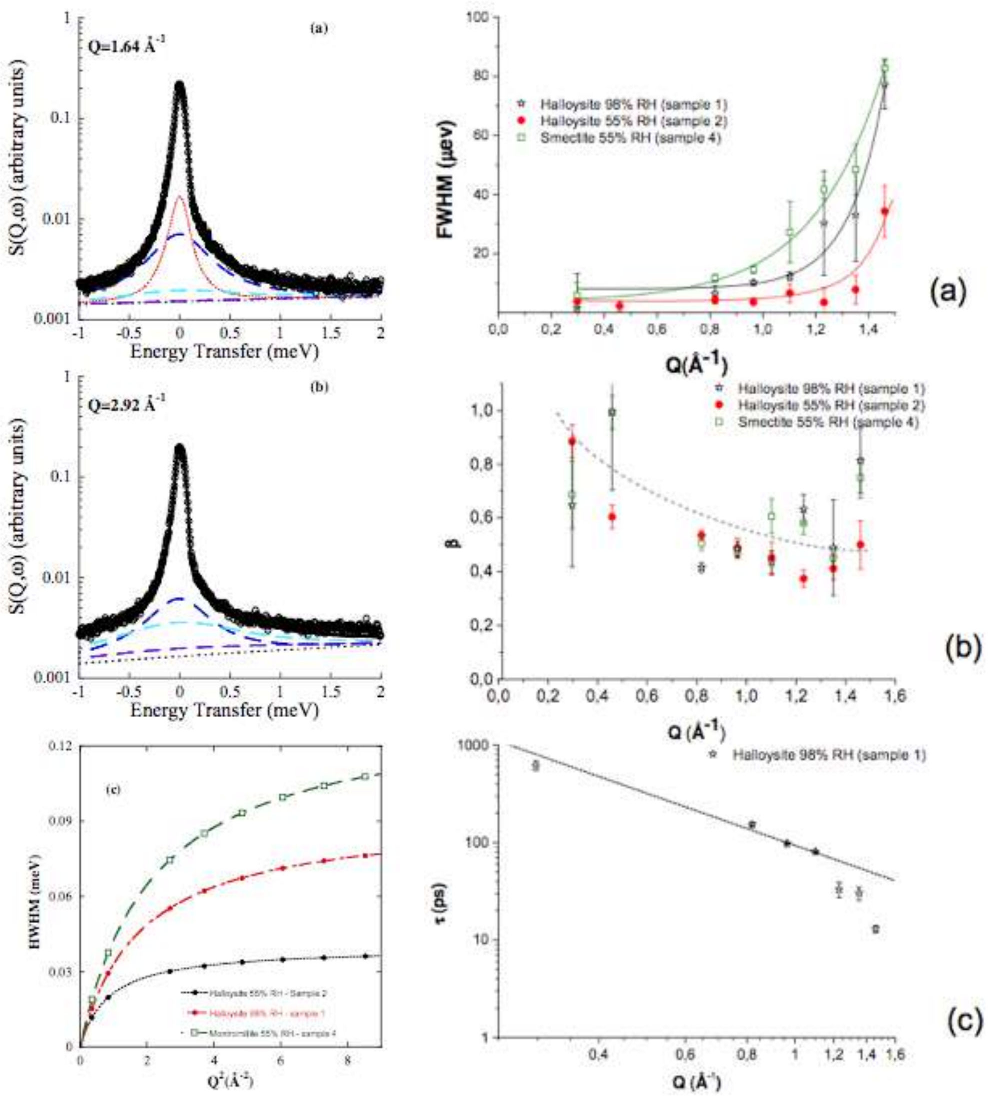

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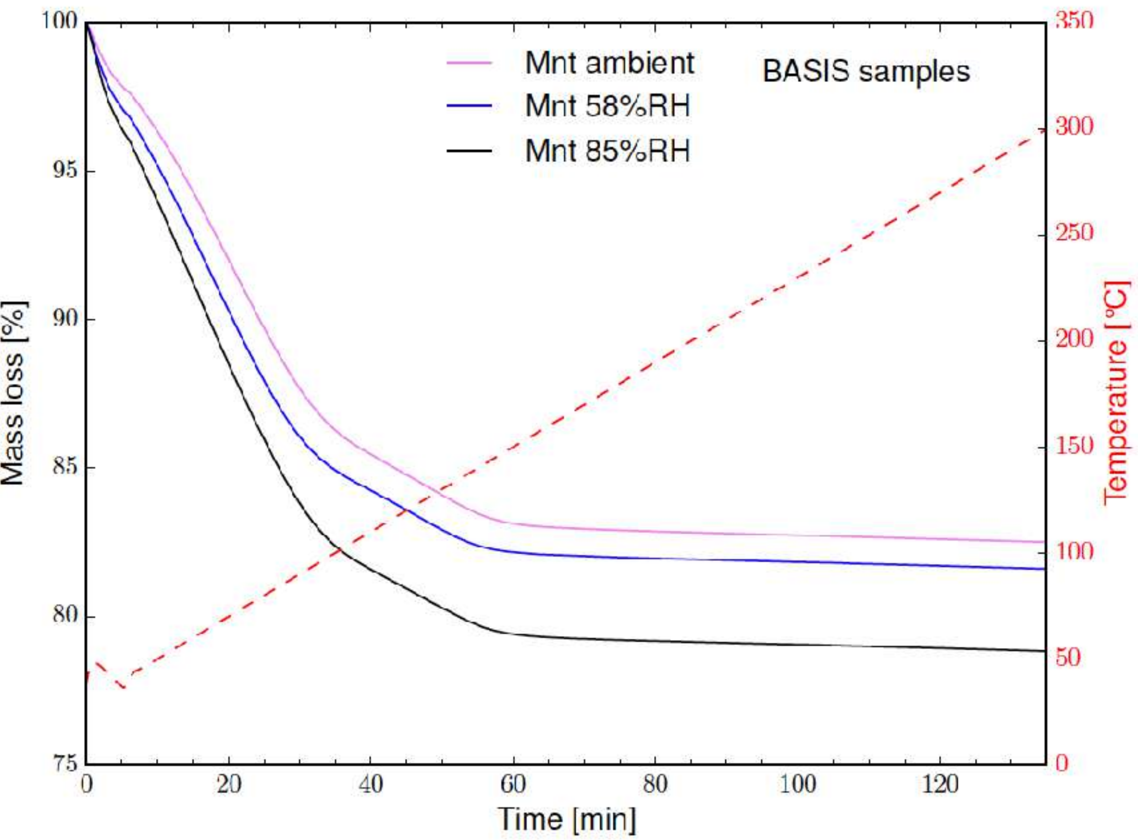
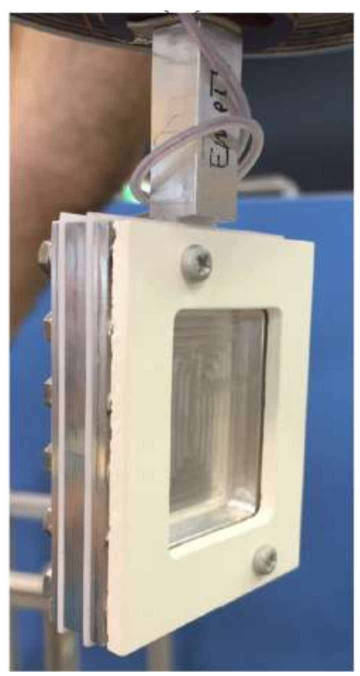
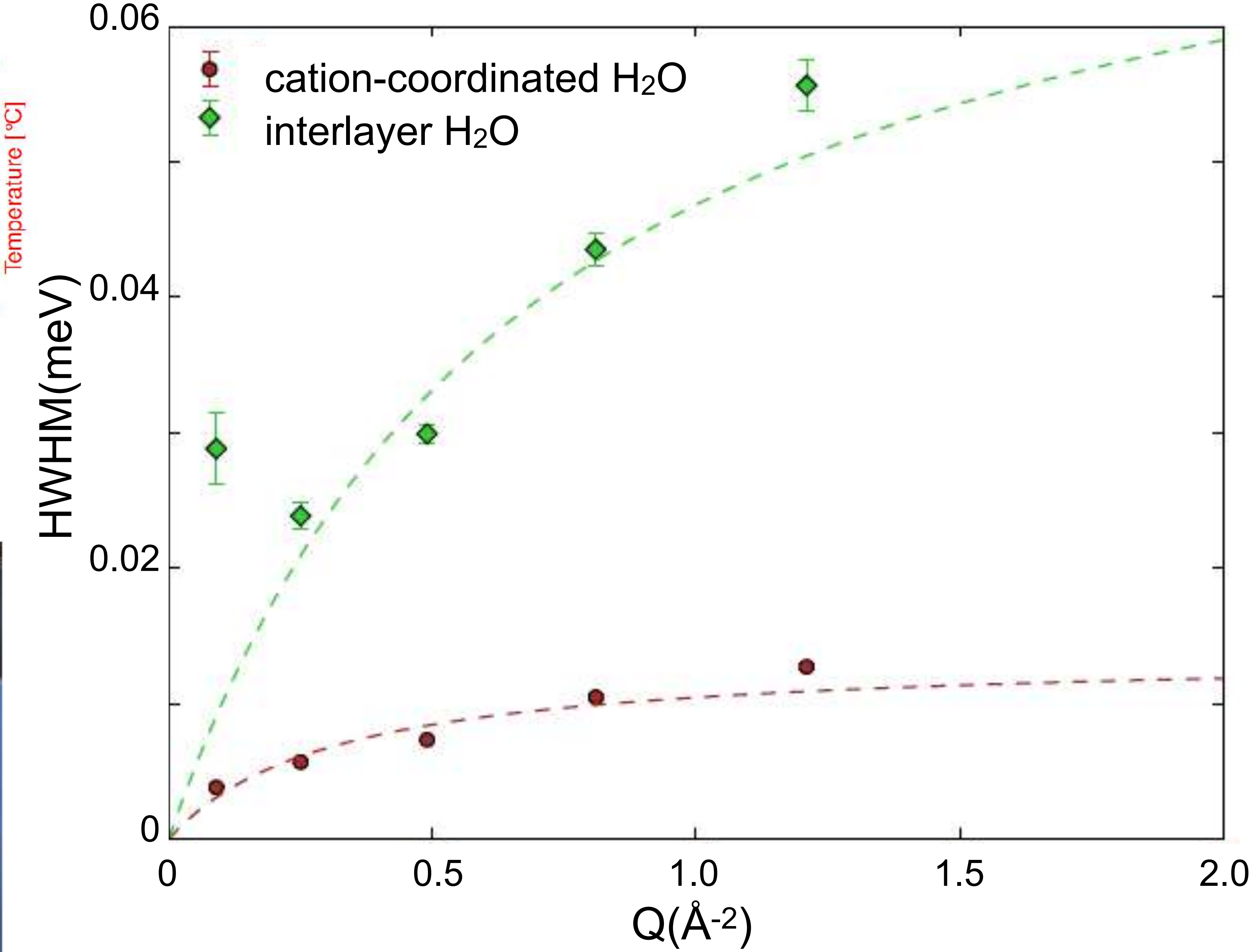
H.N. Bordallo *et al.* (2008) Quasi-Elastic Neutron Scattering Studies on Clay Interlayer Space Highlighting the Effect of the Cation in Confined Water Dynamics. Journal of Physical Chemistry C, **112**, 19982-91.

Ca-Mt: Cation-coordinated water is 5 times slower than bulk water!





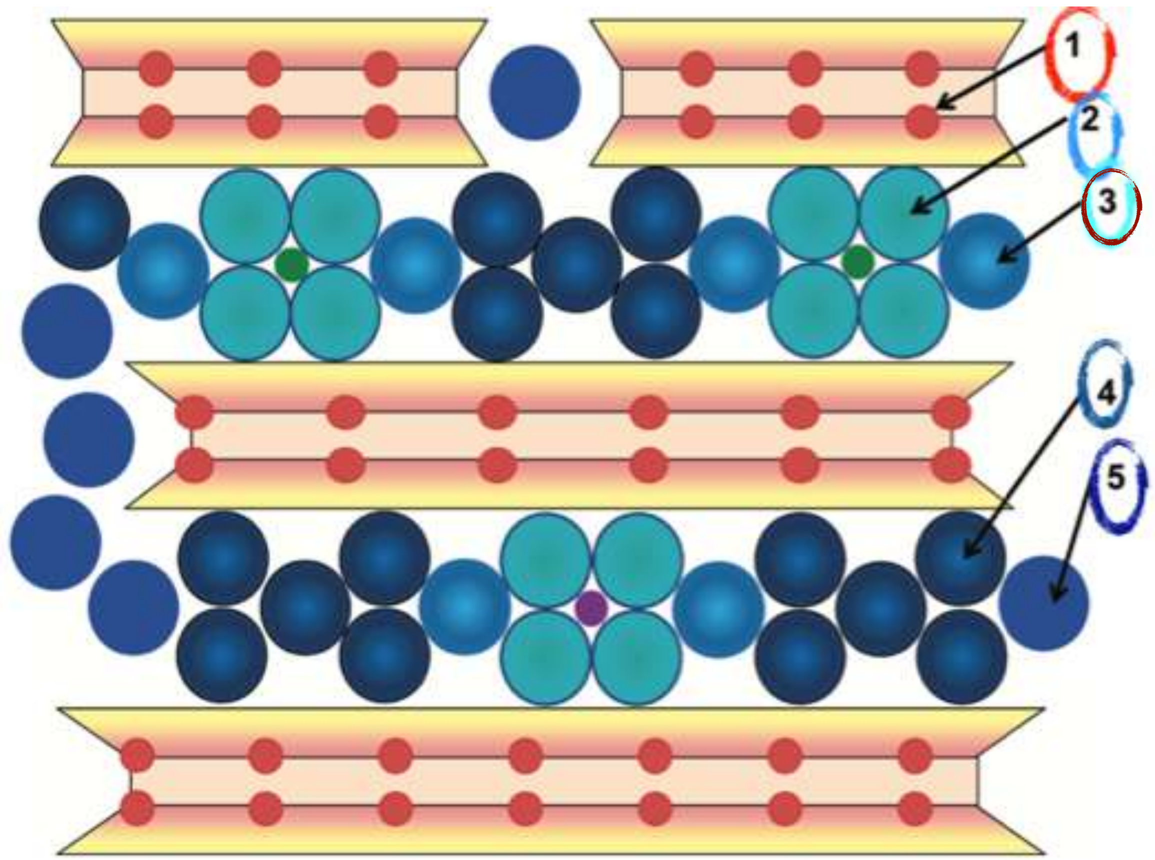


R. Ignazzi, W. P Gates, S. O. Diallo, D. Yu, F. Juranyi, F. Natali, and HNB (2017) Electric Field Induced Polarization Effects Measured by In Situ Neutron Spectroscopy. Journal of Physical Chemistry C, **121**, 23582–91.

QENS: Water-Cation interaction controls the clay properties

2.interlayer H_2O bonded directly to the cations

5. interparticle (surface) H_2O



1. OH or structural H_2O

3. interlayer H_2O that does not directly interact with the cations

4. H_2O loosely HB to the interlayer clay surface

W.P. Gates, HNB *et al.* (2012) Neutron Time-of-Flight Quantification of Water Desorption Isotherms of Montmorillonite. Journal of Physical Chemistry C, **116**, 5558-70.

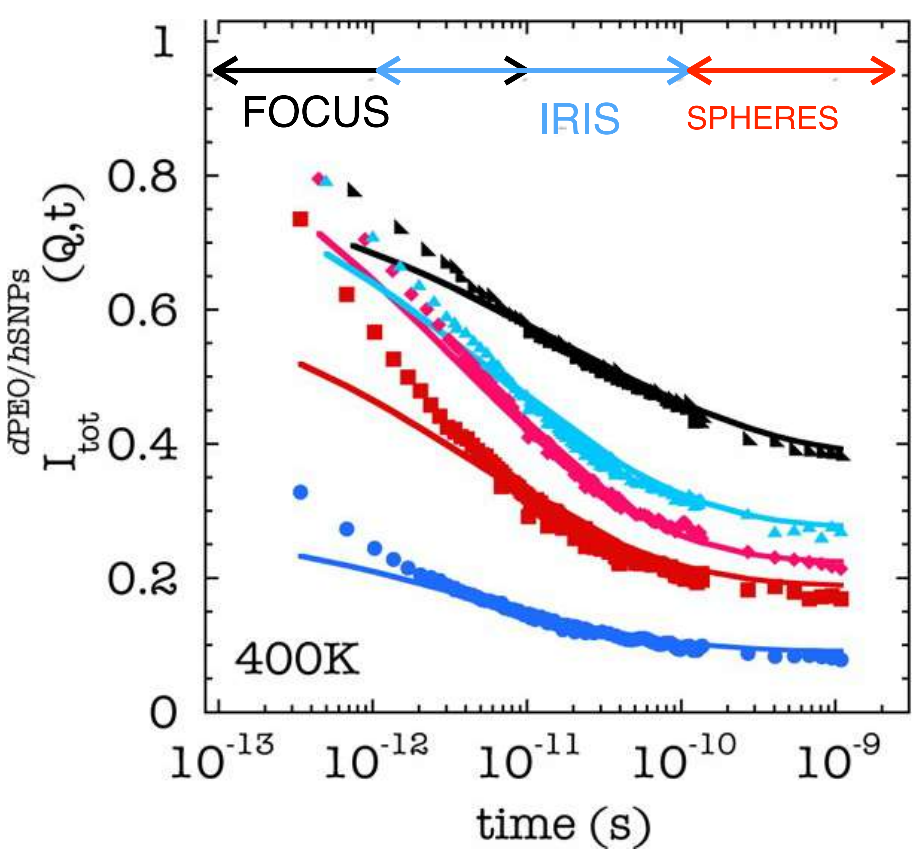
Question 1: Final remarks

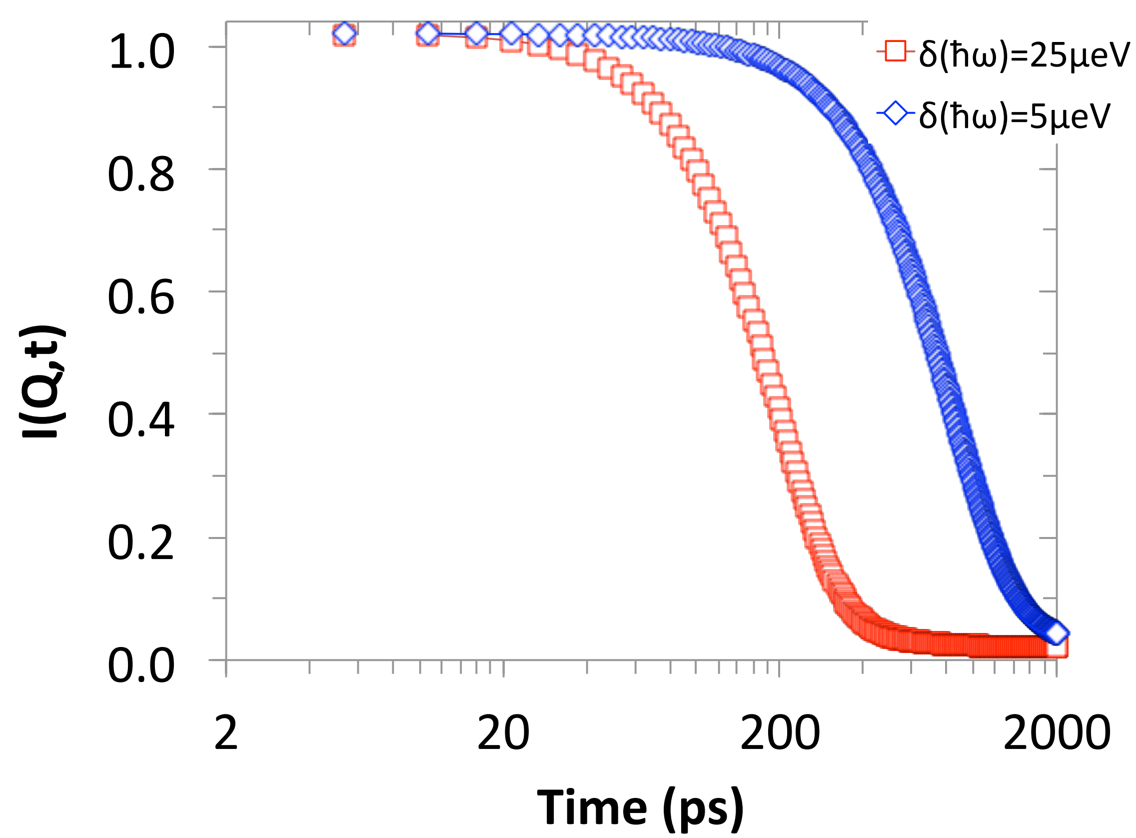
☑Water is held within many different pore environments and the pore environments control the relative ease by which it is released or the strength by which it is held.

☑The presence of exchange cations perturbs this interaction.

☑In Ni-fluorohectorite CO_2 attaches to the edge of nickel hydroxide islands present in the interlayer.

☑Extension of the water behaviour in montmorillonite: cations act as gate keepers.





D. Bhowmik; J. A. Pomposo; F. Juranyi; V. García-Sakai; M. Zamponi; Y. Su; A. Arbe; J. Colmenero (2014) Microscopic Dynamics in Nanocomposites of Poly(ethylene oxide) and Poly(methyl methacrylate) Soft Nanoparticles: A Quasi-Elastic Neutron Scattering Study. Macromolecules **47**, 304-315.

… but we still analysing data as we if we were in the 80s'

Future directions in quasi-elastic neutron scattering

A.J. Dianoux
Institut Laue–Langevin, Grenoble Cedex, France

Physica B 182 (1992) 389–402
North-Holland

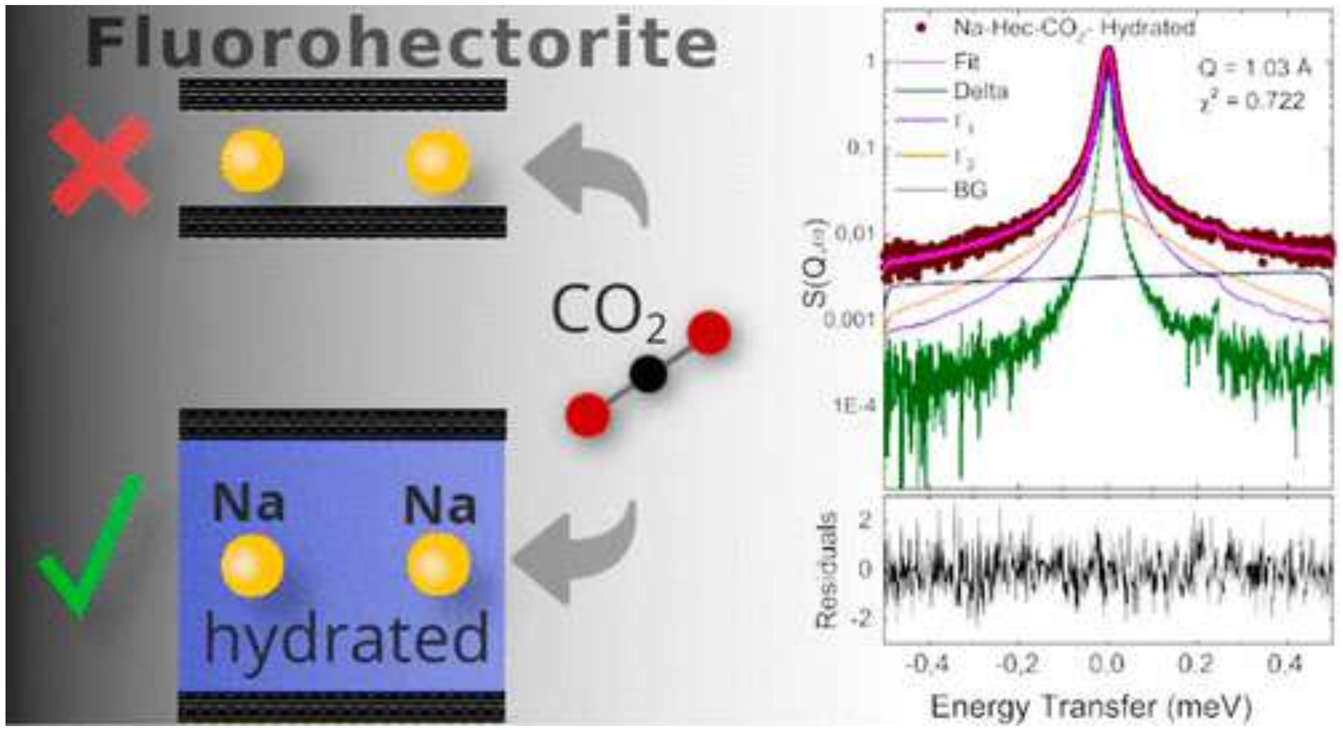
4. Conclusions

We can return to the main purpose of this paper which could be rephrased as: what is the future of QENS? For me this is not a scientific question, but more a political one (if one considers as political the funding of neutron facilities).

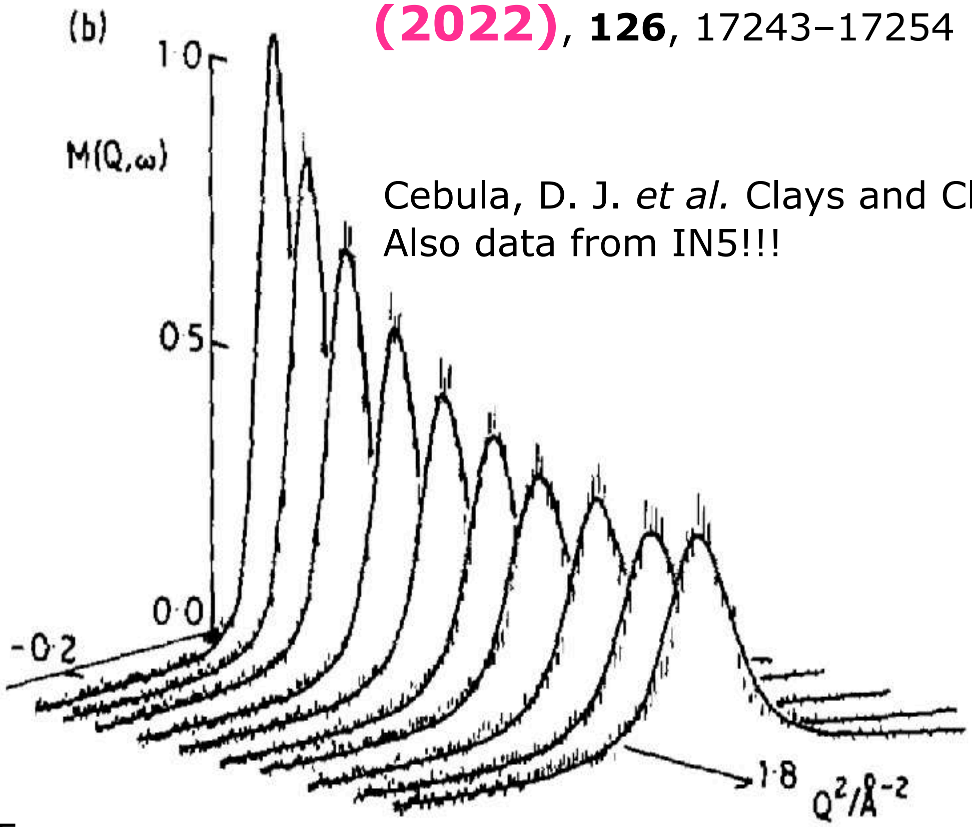
I have shown, using some selected examples, that the information brought by QENS is more *direct*, and sometimes more *detailed* than that obtained by the other spectroscopic techniques

.....

However, the full capabilities of QENS can only be realized if one has access to high intensity neutron sources, either continuous (reactor) or pulsed (spallation source). Furthermore, one needs to have an ongoing development of sophisticated spectrometers.



K. W. B. Hunvik, …. and H. N. Bordallo, J. Phys. Chem. C **(2022)**, **126**, 17243–17254

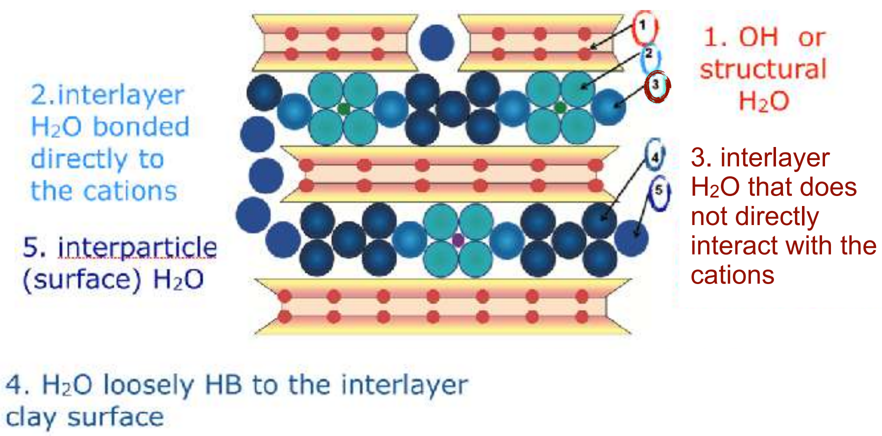


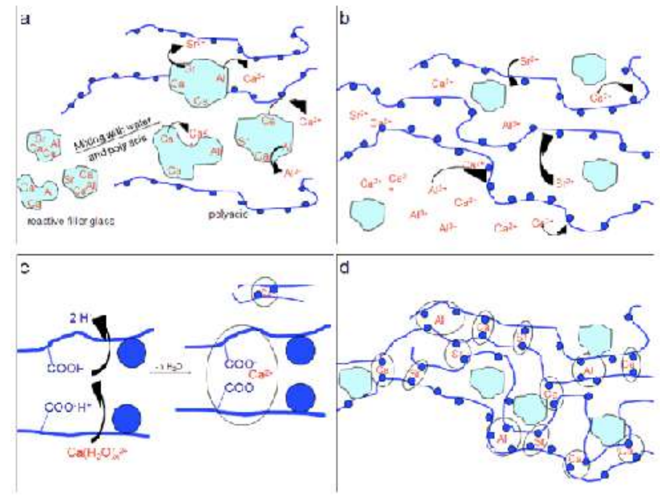
Cebula, D. J. *et al.* Clays and Clay Miner **(1981)** **29**, 241.
Also data from IN5!!!

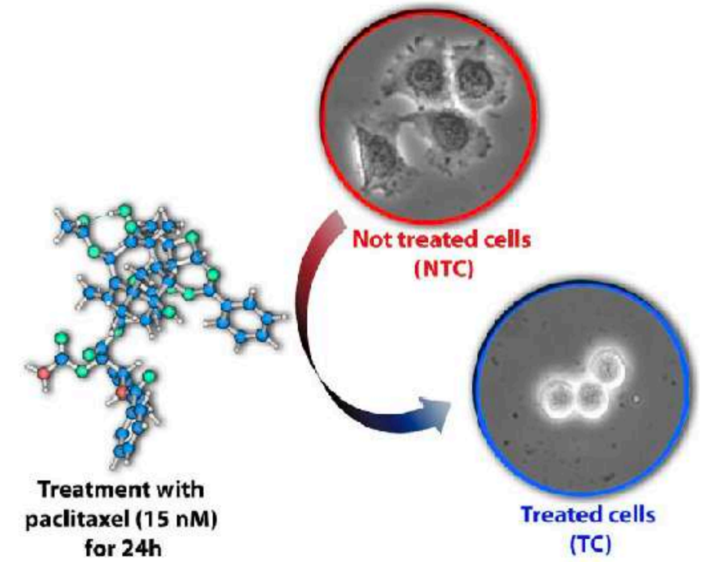
… Remember … at neutron instruments performance have already surpassed our expectative of performance !
And what about analysis?

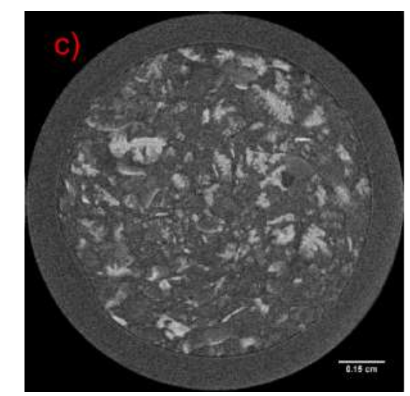
Aldridge, L.P., Larsen, S.R. & HNB Physica B (2019) **561** 75.

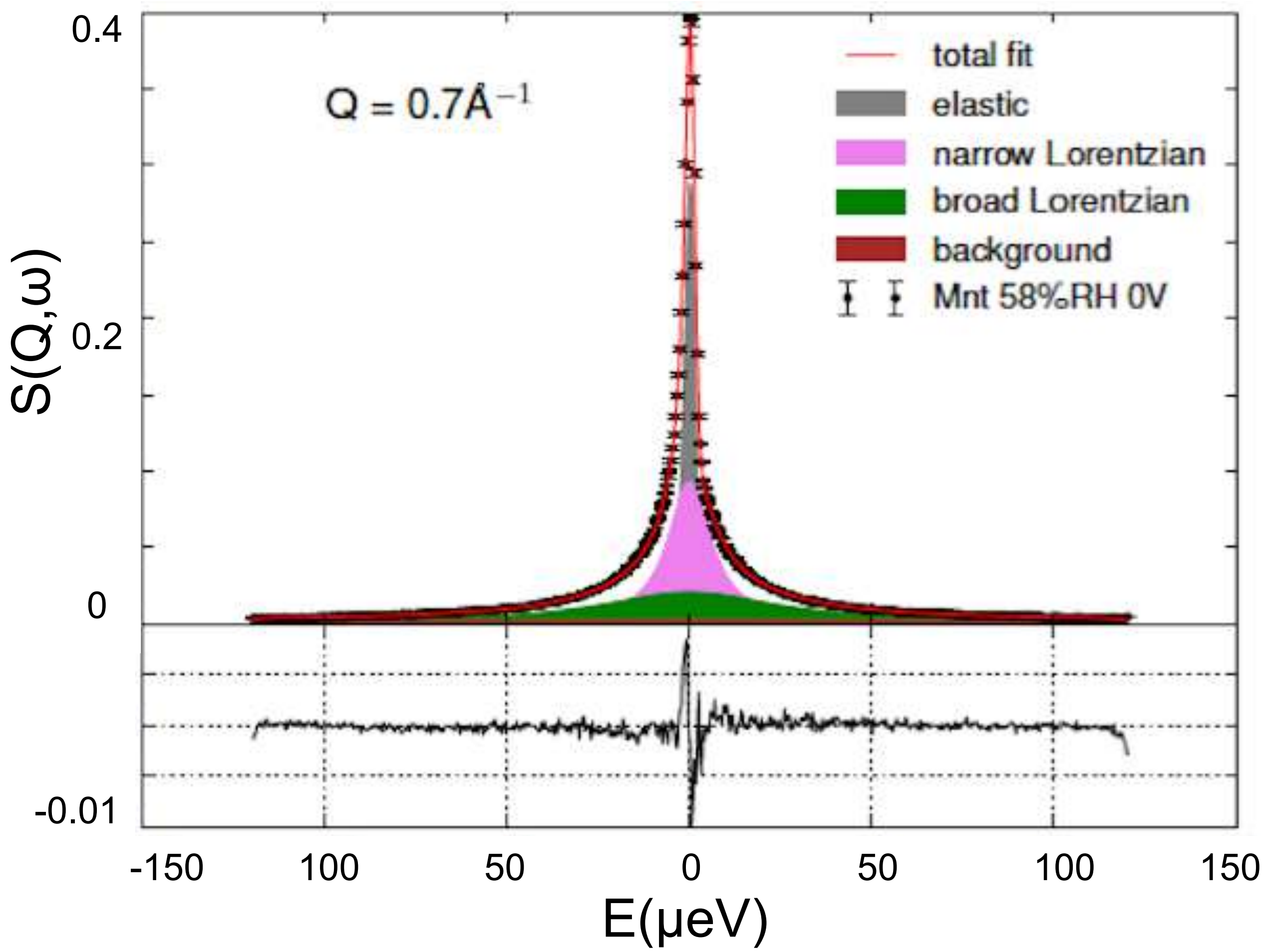
One hammer for all nails!









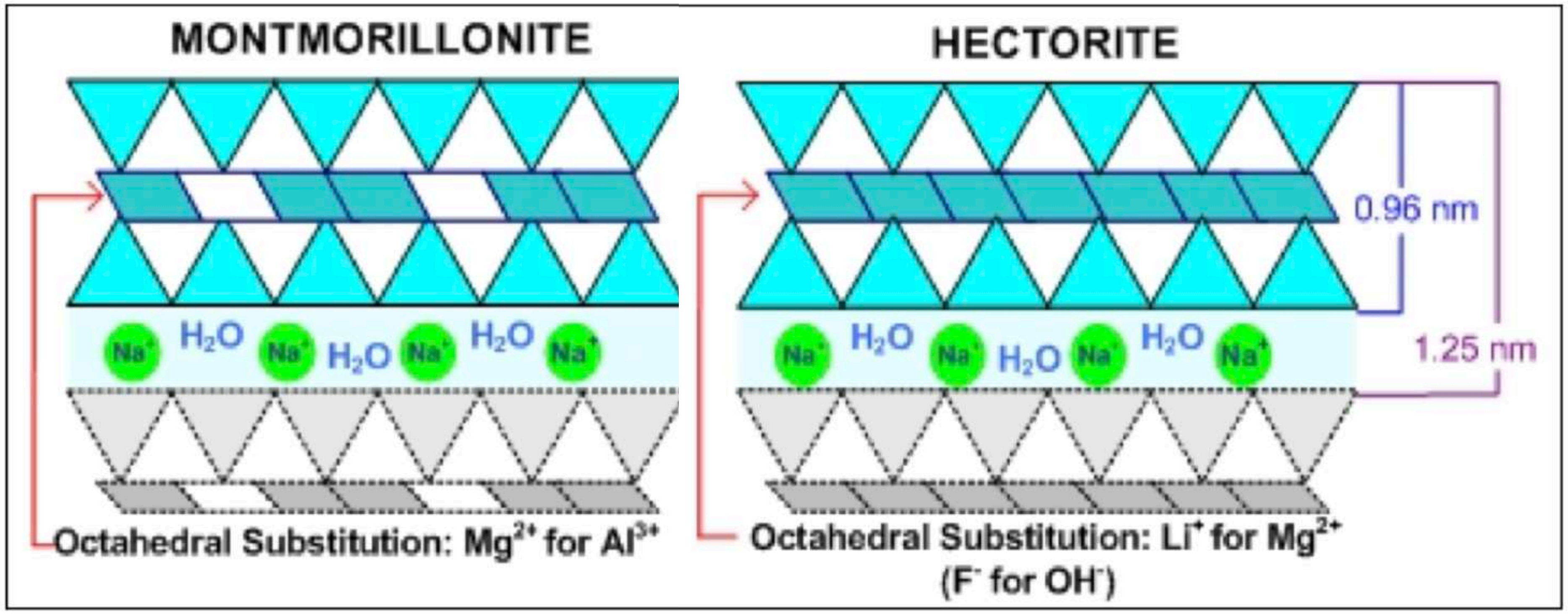


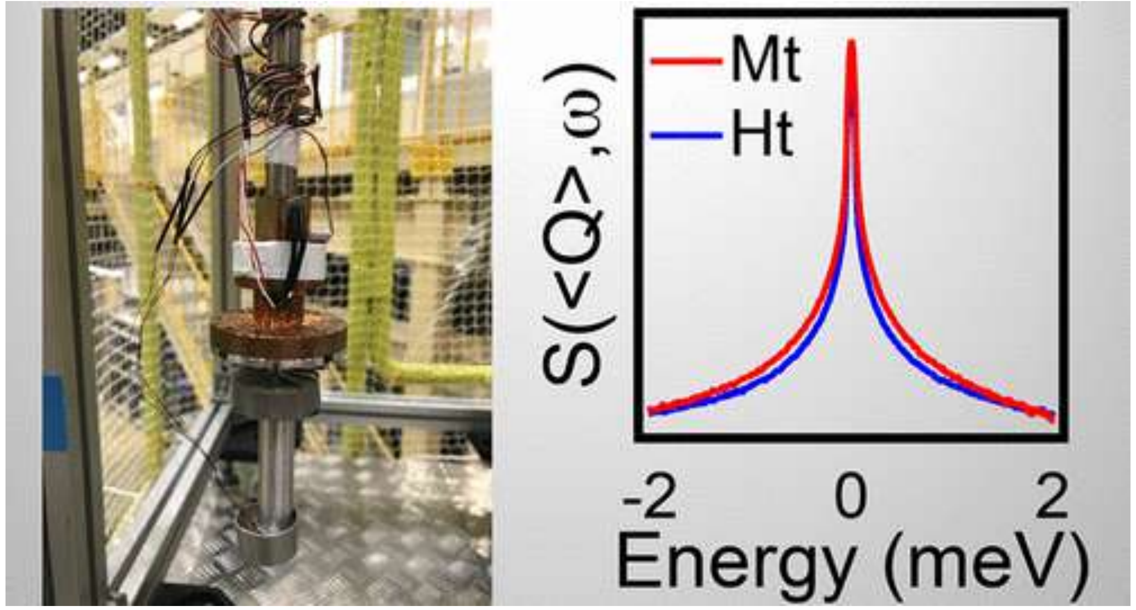
- Quasielastic scattering (a relaxation-like contribution) usually dominates the spectra at higher T.
- It is traditionally approximated by a sum of a few Lorentzians. This approximation assumes a few single exponential relaxation processes.

Bordallo, H.N. *et al.* (2008) J. Phys. Chem. C, **112**, 19982-91.
Peters, J. *et al.* (2016) PCCP, **18**, 12992.
Berg, M.C. *et al.* ACS Applied Mat. & Interf. **10** (2018) 9904.
Martins, M.L. *et al.* Sci. Rep. **9** (2019) 8704.

Focusing on 2 questions:

- What is the role of the exchange cation in the water dynamics?
- How can we get more out of the neutron data?

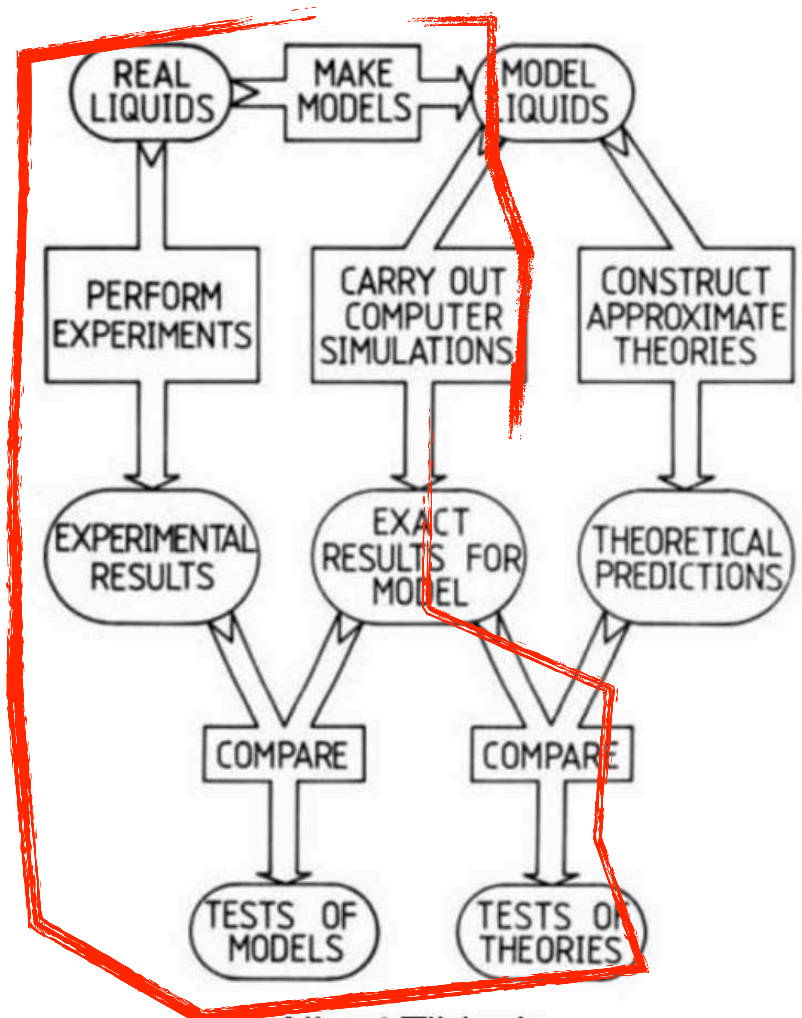




Assessing Diffusion Relaxation of Interlayer Water in Clay Minerals Using a Minimalist Three-Parameter Model. M. H.Petersen, N. Vernet, W. P. Gates, F. J. Villacorta, S. Ohira-Kawamura, Y. Kawakita, M. Arai, G. Kneller and HNB. J. Phys. Chem. C (2021) **125,** 15085−15093.

Way forward: my personal view

With the next-generation neutron spectrometers, such as MIRACLES (ESS, Lund, Sweden), AMATERAS and DNA (J-Parc, Japan) and BWAVES (SNS, ORNL), sophisticated experiments will become possible at different time scales in single instruments. We shall be able to divide the investigations not only into the different water populations but also into portions of time scales.*



Allen&Tildesley

*H. N. Bordallo and Gerald R. Kneller (2022) Front. Phys. **10**, 951028 (6 pages).

*Dynamical Accuracy of Water Models on Supercooling. T. O. Farmer, A. J. Markvardsen, T. H. Rod, HNB and J. Swenson (2020) J. Phys. Chem. Lett. **11**, 7469−7475.

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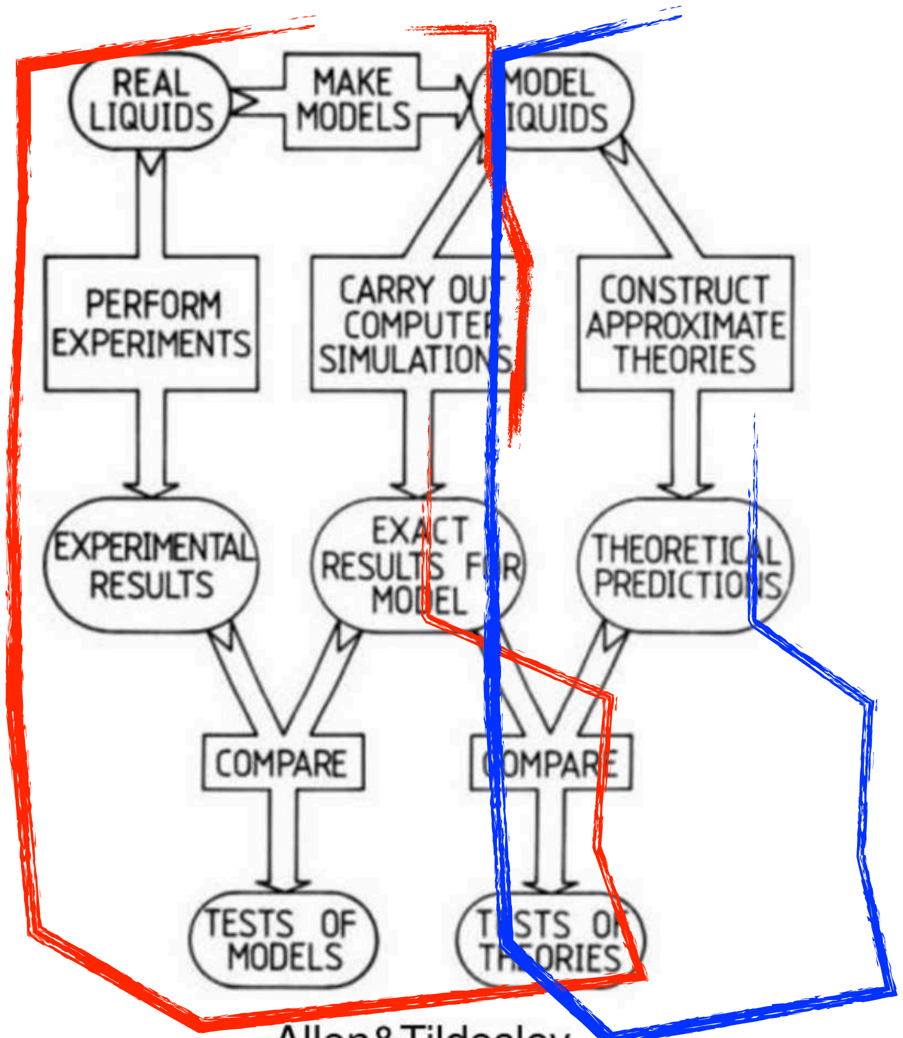

Allen&Tildesley

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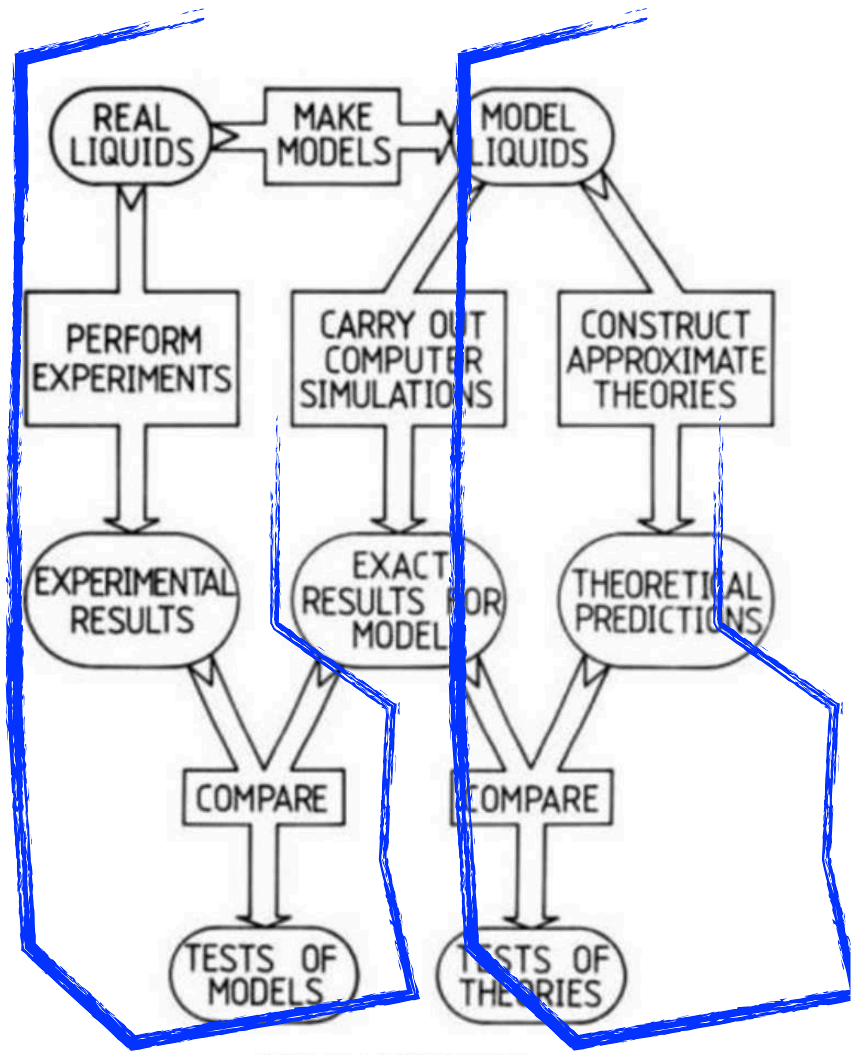
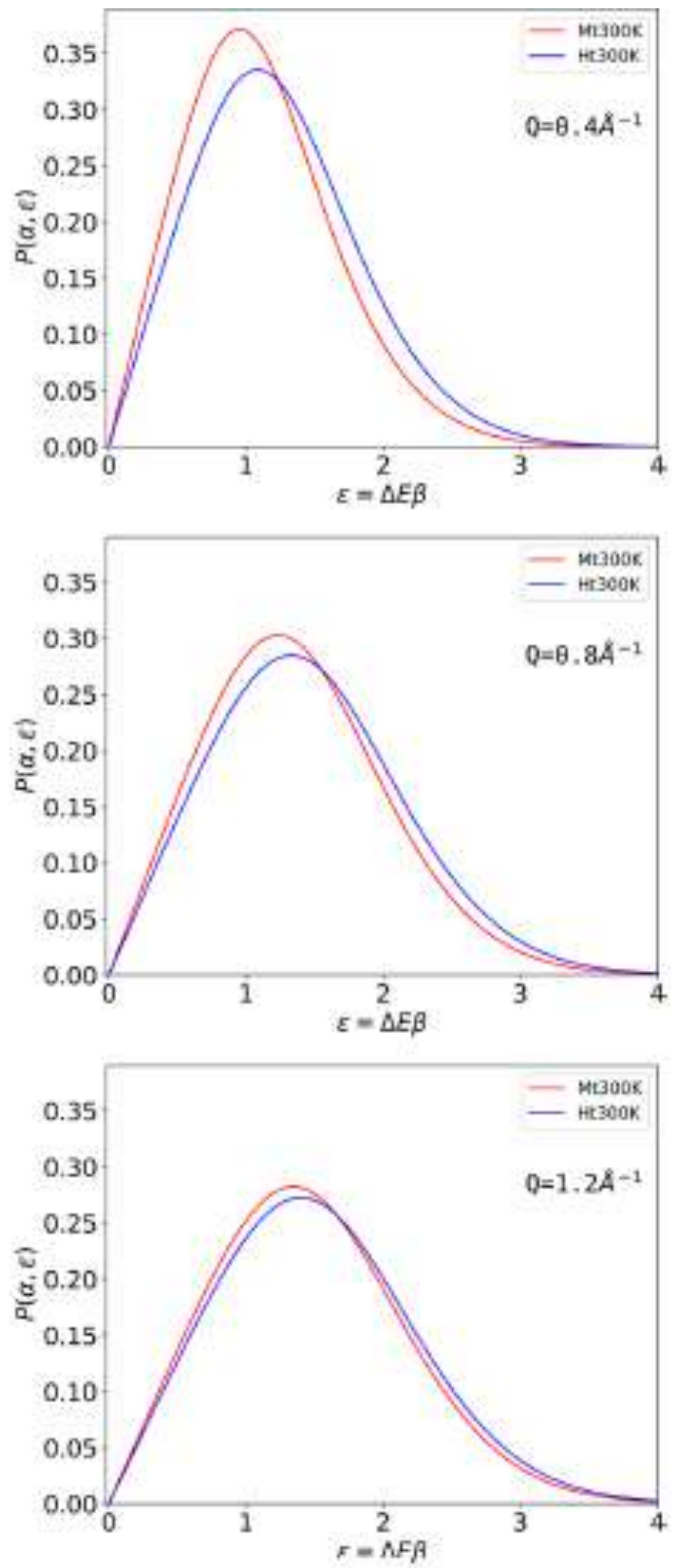
… there are huge opportunities!



Allen&Tildesley

Effective energy landscapes: motional heterogeneity

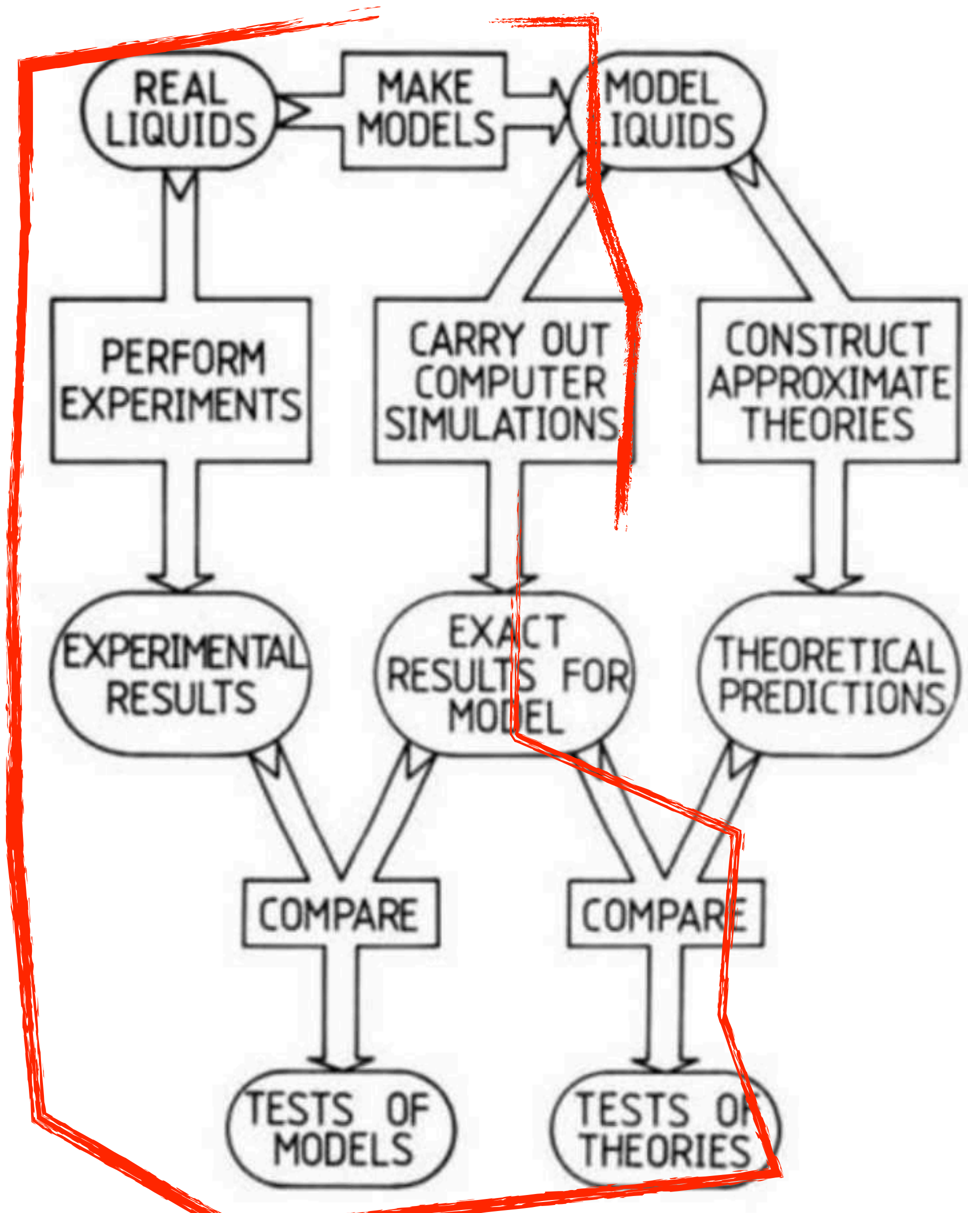


- ☑ As Q increased, the curves became equally broader, indicating coupled long- and short-range motions .
- ☑ On the other hand, at low Q values, the lower energy barrier and narrower distributions observed for Mt reflects that more electrons are shared elsewhere and not in the water molecule. This can be explained by Mt polarizing the ensemble of water molecules in the interlayer space and holding it longer.

*Peters, J. *et al,* (2016) PCCP, **18**, 12992.
*Saouessi M. *et al,* (2019) J. Chem. Phys. **150**, 161104.
Petersen, M. H. *et al* (2021) J. Phys. Chem. C **125, 15085–15093.
Hunvik, K. W. B. *et al* (2022) J. Phys. Chem. C **126, 17243–17254.

MDMC: Moving towards new ways to look at QENS data

Calculate S(Q, ω) using SPC/E, OPC3, TIP3P, TIP3P-FB, OPC, TIP4P-Ew, TIP4P-2005, and TIP4P-FB19 & (coarse-grained) mW model from 300K to supercooled temperatures above NML using LAMMPS.*



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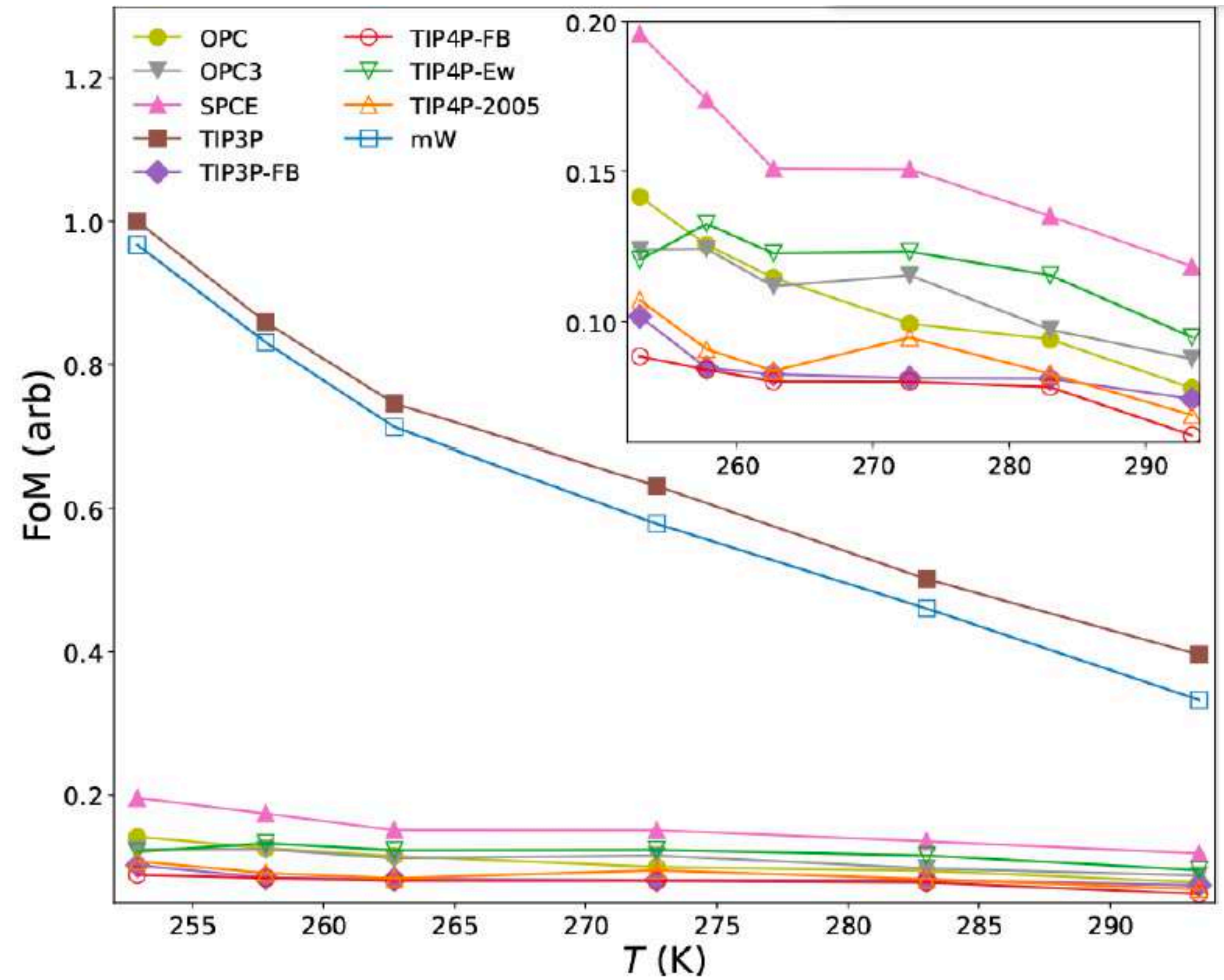


$$\mathrm{FoM} = \sum_{Q} \sum_{\omega} \left(\frac{S_{\mathrm{QENS}}(\mathbf{Q}, \omega) - S_{\mathrm{MD}}(\mathbf{Q}, \omega)}{\sqrt{\sigma_{\mathrm{QENS}}(\mathbf{Q}, \omega)^2 + \sigma_{\mathrm{MD}}(\mathbf{Q}, \omega)^2}} \right)^2$$

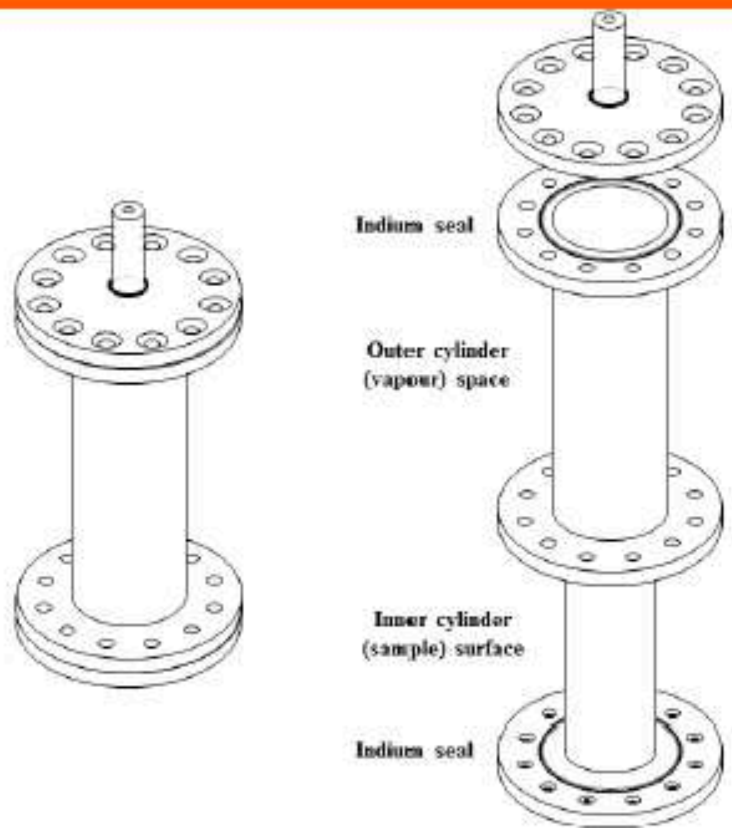
Adapted from Introduction to Molecular Dynamics by Ilian Todorov (STFC, UK) – DL_POLY and Rossen Apostolov (KTH, SWE) – GROMACS.

*Dynamical Accuracy of Water Models on Supercooling. T. O. Farmer, A. J. Markvardsen, T. H. Rod, HNB and J. Swenson (2020) J. Phys. Chem. Lett. **11**, 7469–7475

Getting more out of the data even if unconventional

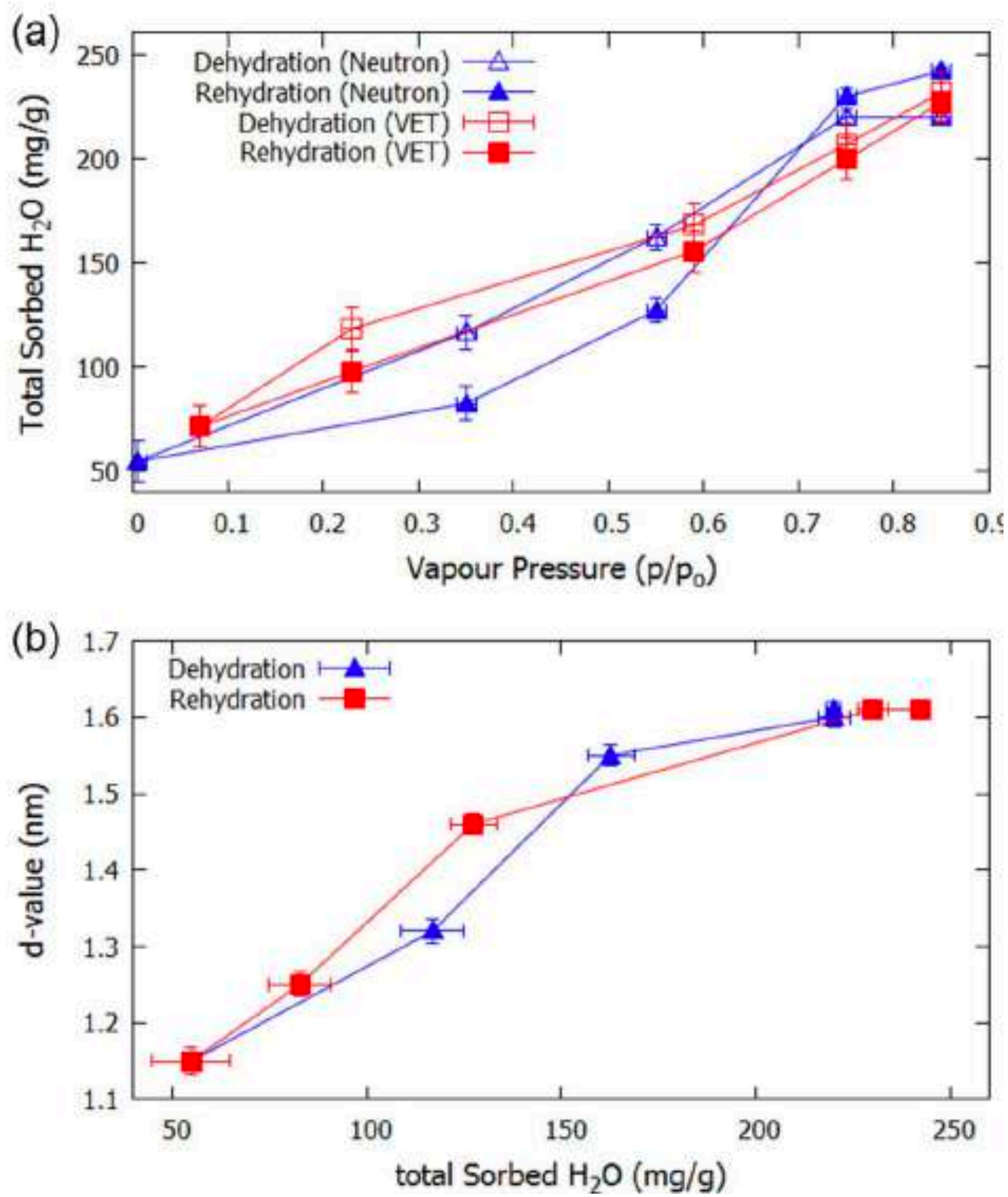
Sample environment

(Gates et al., 2017 QENS study)



W.P. Gates, HNB *et al.* (2012) Neutron Time-of-Flight Quantification of Water Desorption Isotherms of Montmorillonite. Journal of Physical Chemistry C **116** (2012) 5558-70.
W. P. Gates, L. P. Aldridge, G. G. Guzman, R. A. Mole, D. Yu, G. N. Iles, A. Klapproth & HNB (2017) Water desorption and absorption isotherms of sodium montmorillonite: A QENS study. Applied Clay Science **147** 97–104.
G. Guzman, W. P. Gates, A. Bouazza, L. P. Aldridge and HNB (2018) Using neutron spectroscopy to measure soil water retention at high suction values. Can. Geotech. J. **56**, 1999–2003

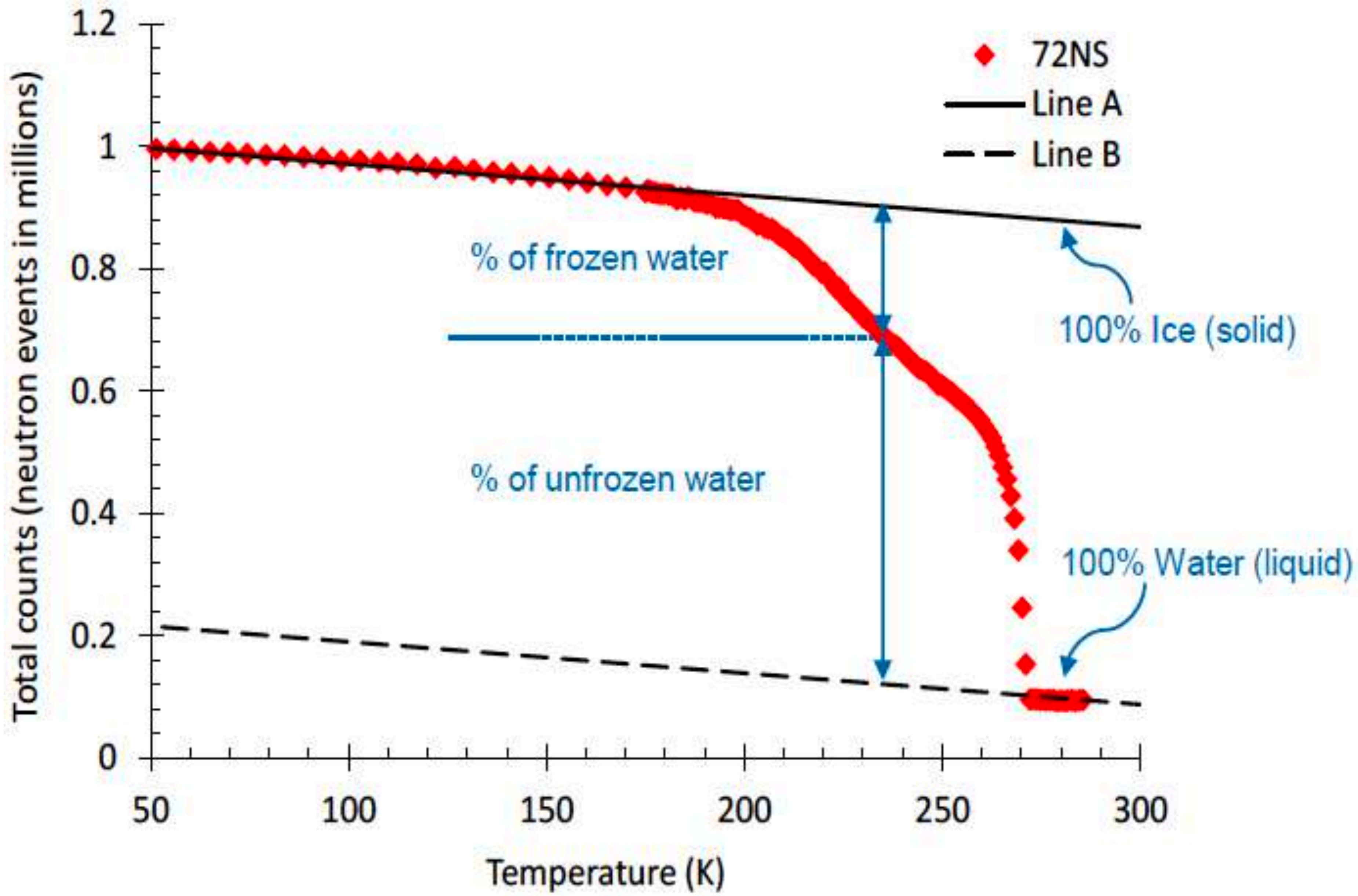
True material equilibrium at intermediate hydration states is a time dependent phenomenon.



- VET (vapour equilibrium technique using desiccators) over-estimates water adsorption at low RH.
- Hysteresis between drying and wetting paths.
- Analysis of the confined water diffusion suggests that on rehydration at low hydration level water initially occupies the external surfaces before entering the interlayer spaces (*not shown*).

W. P. Gates, L. P. Aldridge, G. G. Guzman, R. A. Mole, D. Yu, G. N. Iles, A. Klapproth and HNB (2017) Water desorption and absorption isotherms of sodium montmorillonite: A QENS study. Applied Clay Science **147** 97–104.
G. Guzman, W. P. Gates, A. Bouazza, L. P. Aldridge and HNB (2018) Using neutron spectroscopy to measure soil water retention at high suction values. Can. Geotech. J. **56**, 1999–2003

Determination of Unfrozen Water in Clays: A different approach from the neutron scattering processing routine



W. P. Gates, L. P. Aldridge, G. G. Guzman, R. A. Mole, D. Yu, G. N. Iles, A. Klapproth, and HNB (2017) Water desorption and absorption isotherms of sodium montmorillonite: A QENS study. Applied Clay Science **147** 97–104.

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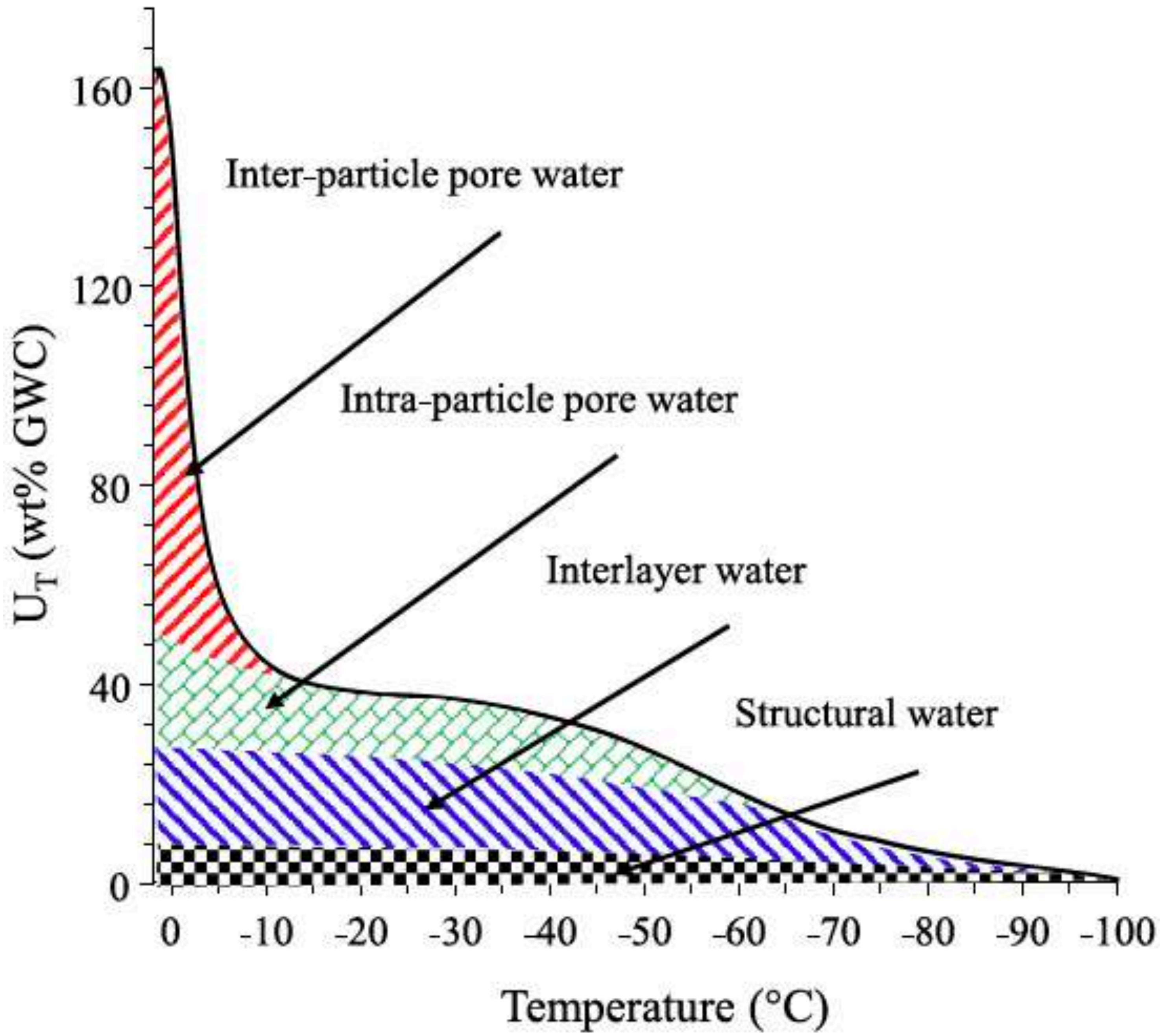

Significant unfrozen interlayer water (U_T) is present in hydrated Na-Mt smectite gels at below 200 K (about 73 ◦C).

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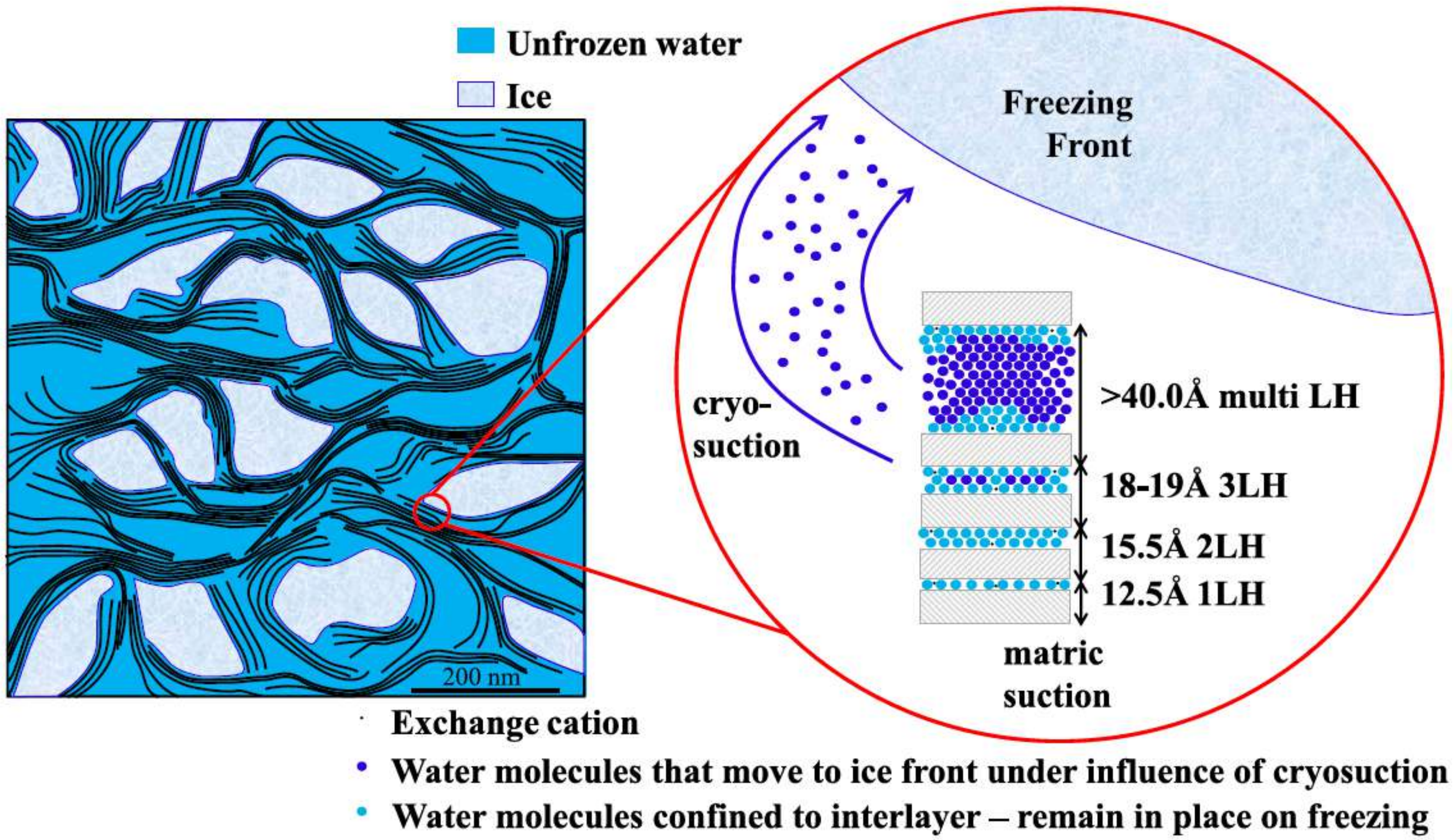
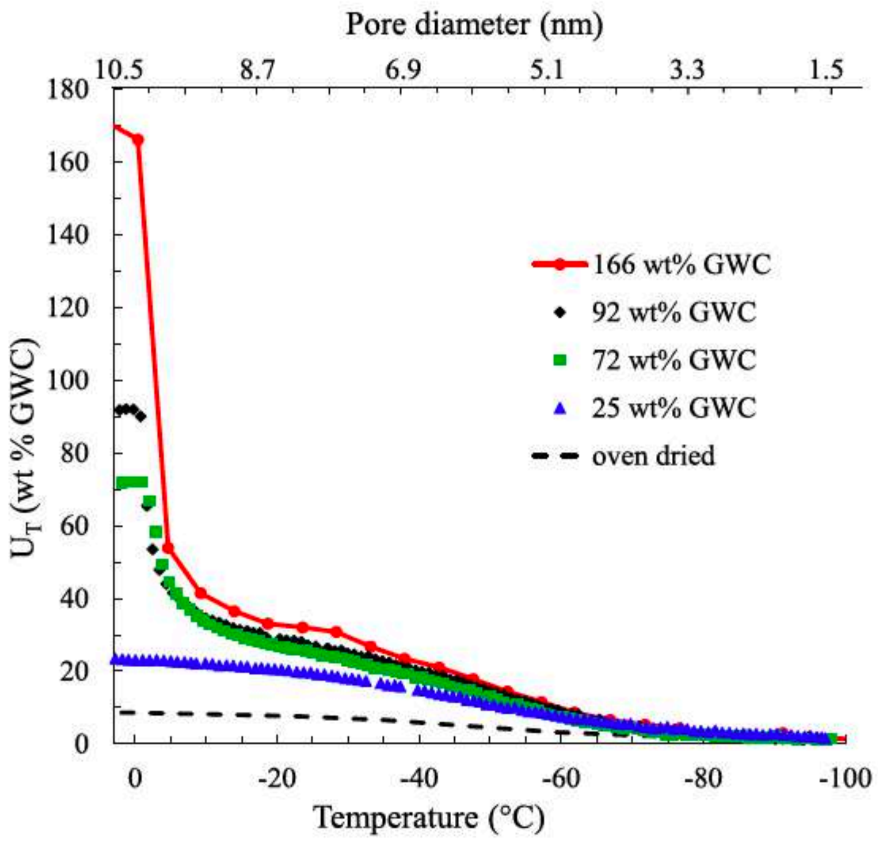
Question 2: Final remarks

☑True material equilibrium at intermediate hydration states is a time dependent phenomenon.

☑The freezing characteristic curves (FCC) depicting the original water content of the sample as a function of cryosuction were developed using a simplified Clapeyron equation, from which the pore water pressure, P_{wp}, can be shown to be proportional to the freezing point depression.





Take home message

☑Neutrons are omnipresent, do not lie and 'see' all.

☑Given the instrumentation at hand, which might exceed expectations in many ways, determines what we are able to observe.

☑ How we interpret the data depends on how we go about looking the obtained info. This night be why some of the unconventional approaches work.

☑Dynamics determined from neutron scattering indicates that water in clay gel pores thaws at much lower temperatures than currently considered. The general poor strength of wet clays can significantly impact infrastructure in cold regions undergoing an increased frequency of freeze-thaw events.