Proton Dynamics in Hydrated Barium Indate Oxides

Studied with neutron vibrational spectroscopy & quasielastic neutron scattering

PRESENTED BY ADRIEN PERRICHON

2024-05-12 SCIENCE AWAY DAYS, SUNDSGÅRDEN

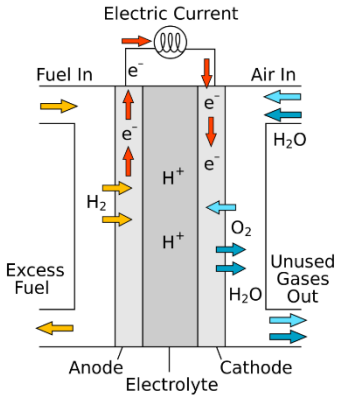
Background

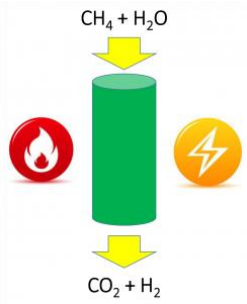
Since March 2024: Instrument scientist for VESPA

Previous 6 years: instrument scientist at ISIS

- Neutron instrumentation for TOSCA & OSIRIS
- Energy materials research using neutron spectroscopy and first-principles calculations

Fuel Cell & Battery Technology





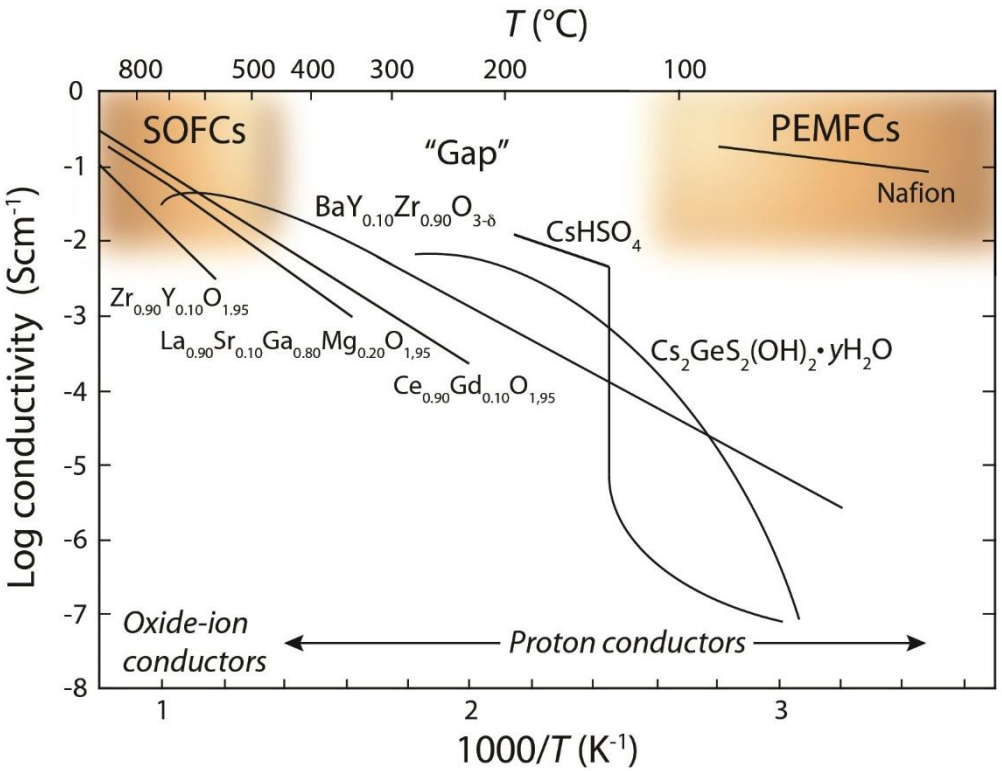
Solar Cell Technology

Hydrogen Technology

H storage, heterogeneous catalysis

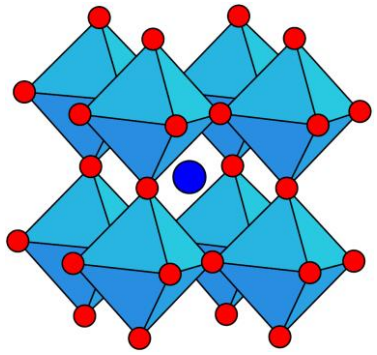
Motivations

Candidate materials as solid state electrolyte for intermediate temperature applications

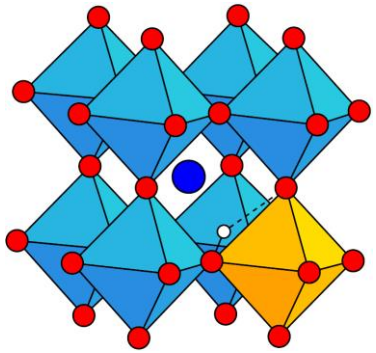


❖ M. Karlsson, A. Perrichon, *Ionic Conductors and Protonics*, Exp. Methods Phys. Sci. **49** (2017) 547

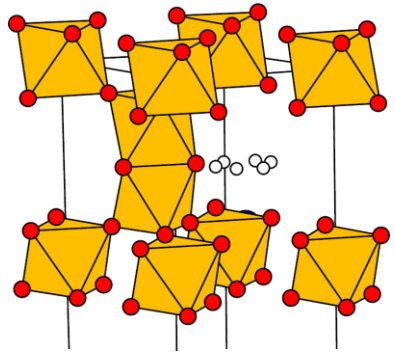
Perovskite



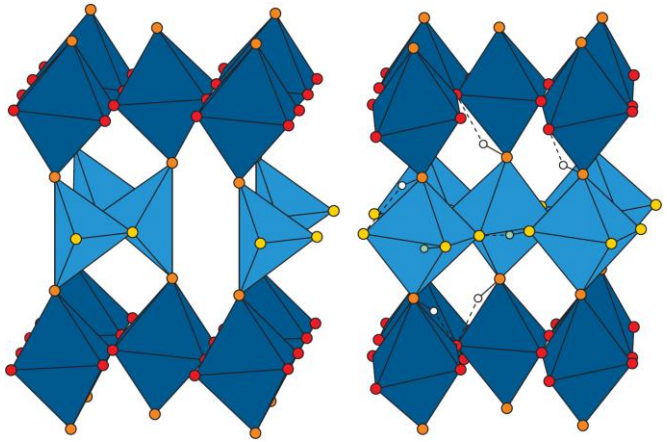
Doped perovskite



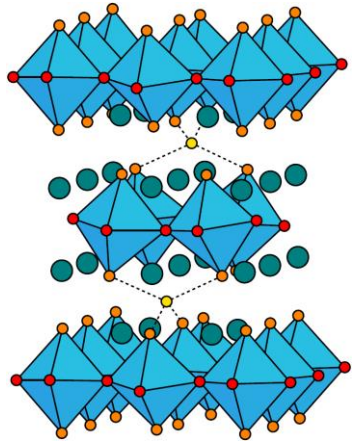
Non-cubic perovskite



Brownmillerite



Ruddlesden-Popper

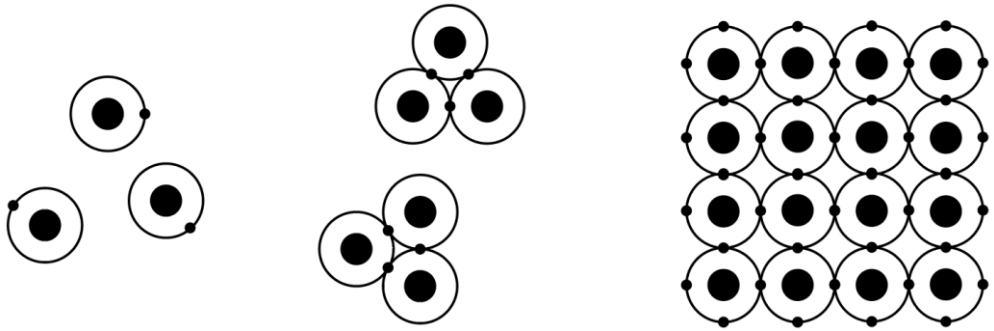


Motivations

Introduction to neutron spectroscopy

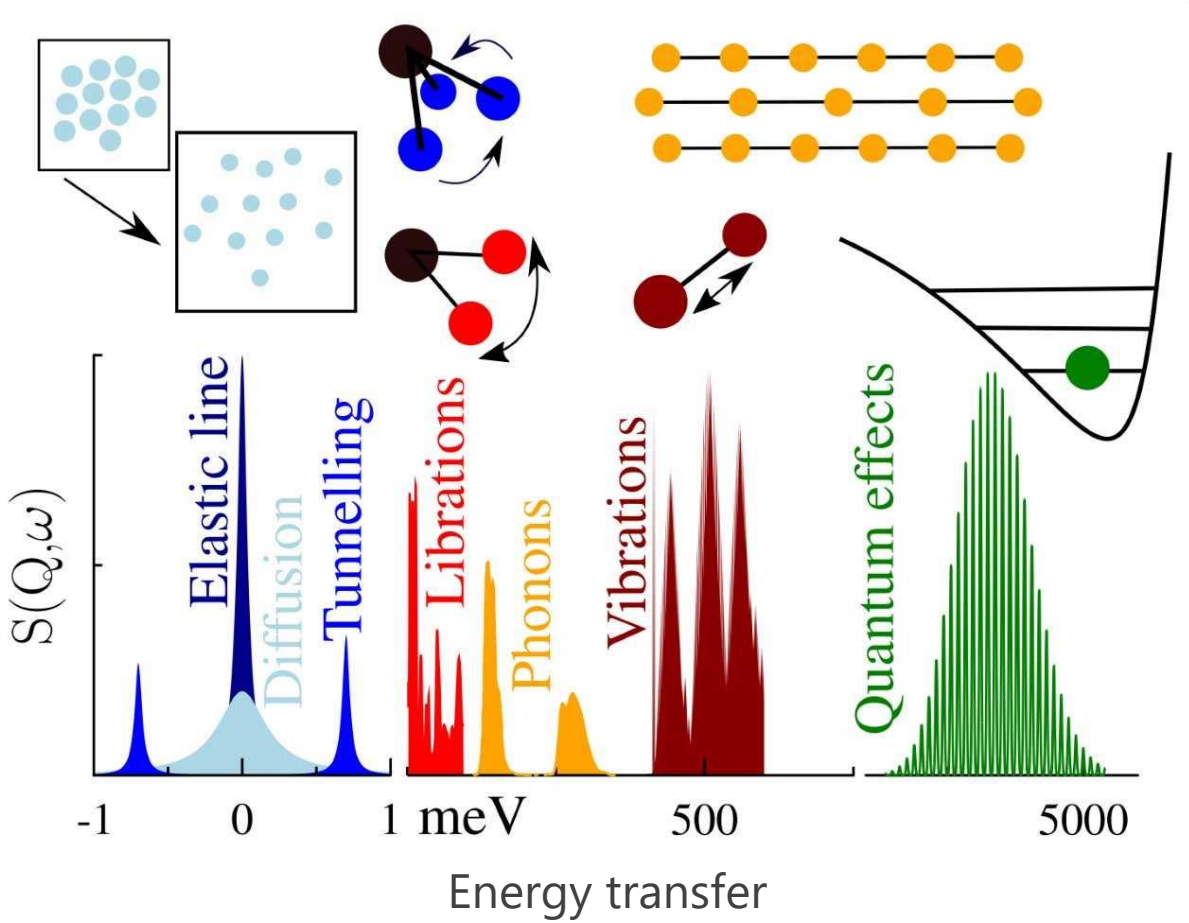
<u>INS to probe dynamics, how atoms move</u>

- Diffusive motions (stochastic, tunnelling)
- Molecular vibrations (bond stretching)
- Lattice dynamics (phonons)



<u>For a system of atoms in motion</u>

- Time-dependent pair correlation function $G(r,t)$
- Intermediate scattering function $I(Q,t)$
- Scattering function $S(Q,\omega)$



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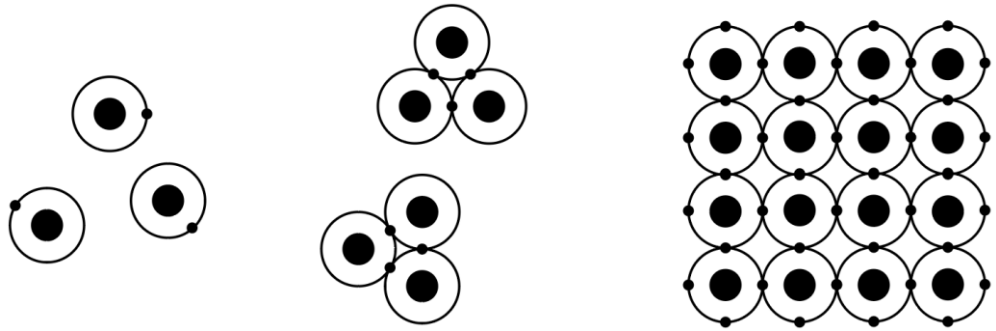

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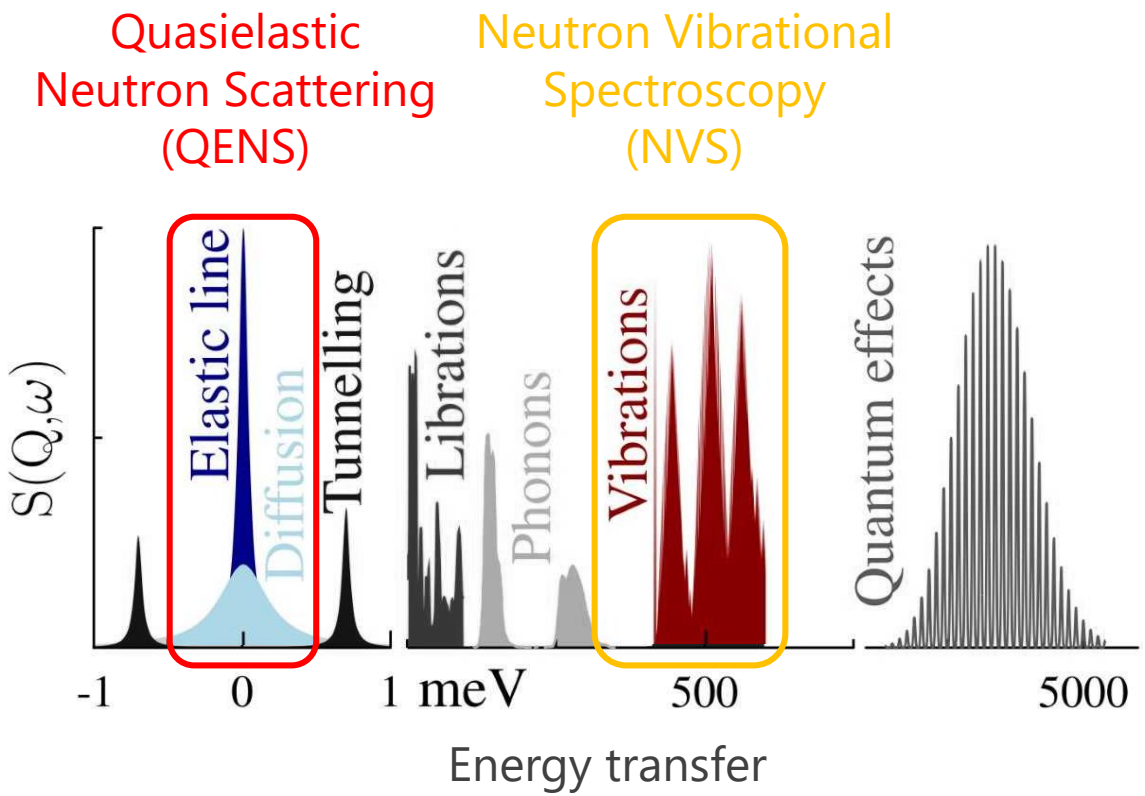


➢ Understanding the microscopic mechanism of proton diffusion in proton-conducting oxides

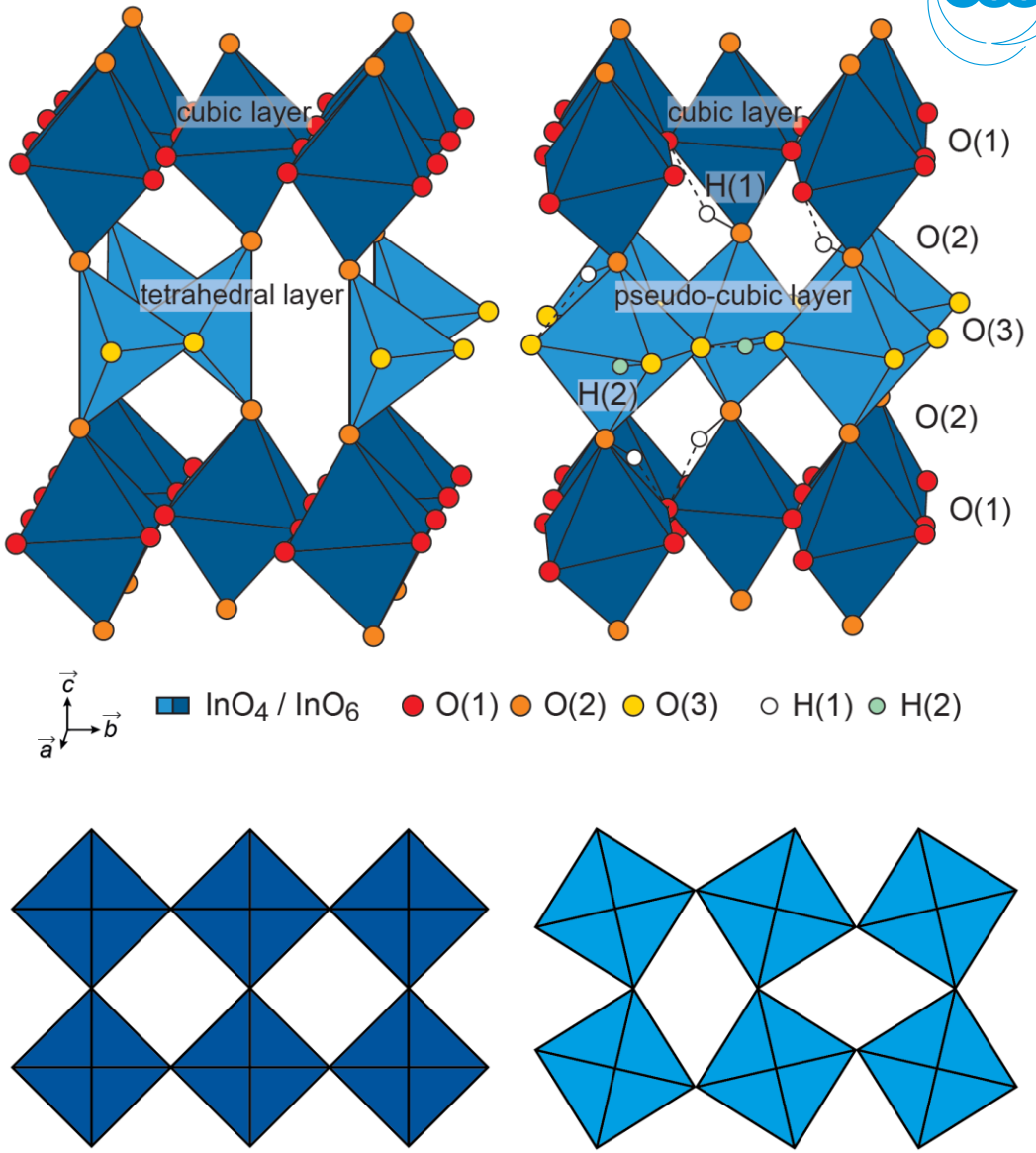
Introduction

Barium indate, $Ba_2In_2O_5(H_2O)_x$

Perovskite-derived structure

Dry form (x = 0)
- Brownmillerite $Ba_2In_2O_5$
- Planes of InO_6 octahedra (cubic)
- Planes of InO_4 tetrahedral chains
- 1D oxygen vacancy channels

Fully-hydrated form (x = 1)
- Pseudo-cubic $BaInO_3H$
- Planes of InO_6 octahedra (cubic)
- Planes of InO_6 octahedra (distorted)



- Fischer et al. Solid State Ionics **116** (1999) 211–215
- Speakman et al. Solid State Ionics **149** (2002) 247–259
- Jayaraman et al. Solid State Ionics **170** (2004) 17–24 & 25–32
- Martinez et al. J. Solid State Chem. **180** (2007) 3388–3392
- Dervişoğlu et al. Chem. Mater. **27** (2015) 3861−3873

Introduction

Protons in $BaInO_3H$

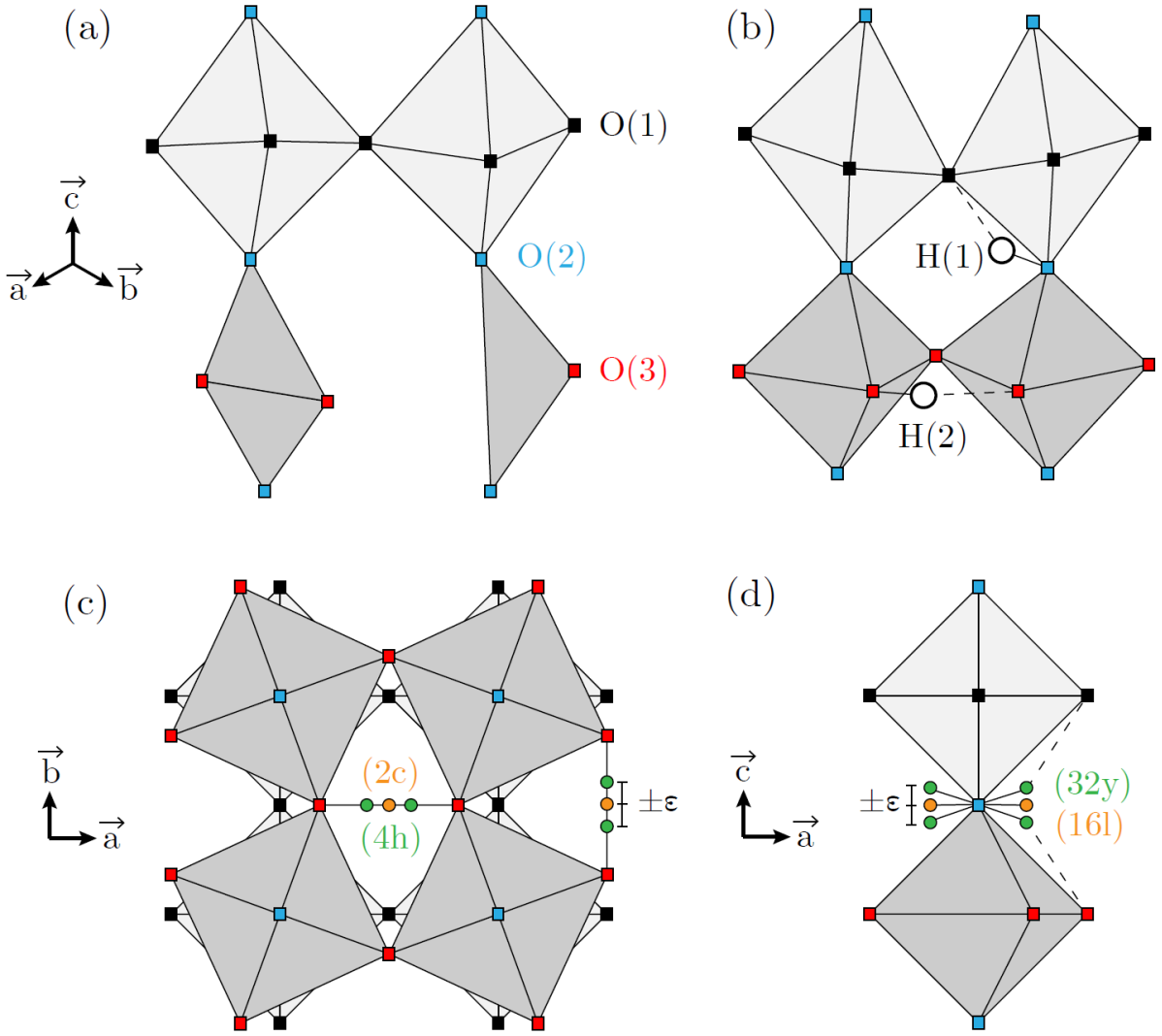
- Water dissociates in H(1) + OH(2)
- Perovskite-like H(1) protons
- H(2) in the pseudo-cubic layer

- Reports of 2 or 3 distinct proton sites
- Complex dehydration behaviour

❖ Dervişoğlu et al. Chem. Mater. **27** (2015) 3861−3873
❖ Bielecki et al. J. Mater. Chem. A **2** (2014) 16915–16924
❖ Bielecki et al. J. Mater. Chem. A **4** (2016) 1224–1232

<u>Research questions</u>

- Exact number & geometry of proton sites?
- Proton local environments?
- Dependency with hydration level *x*?
- Diffusion pathways, activation energies?
- Diffusion mechanism?

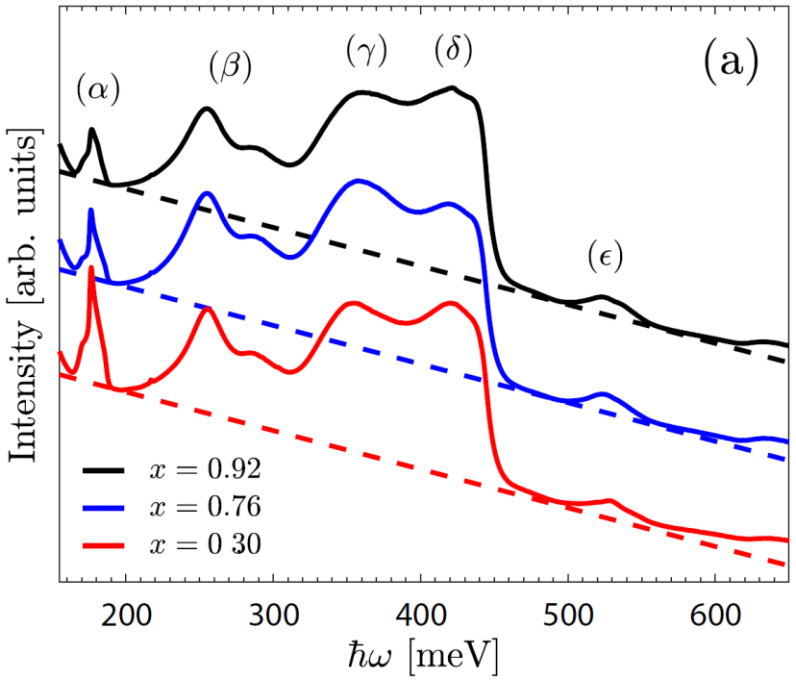


Neutron vibrational spectroscopy

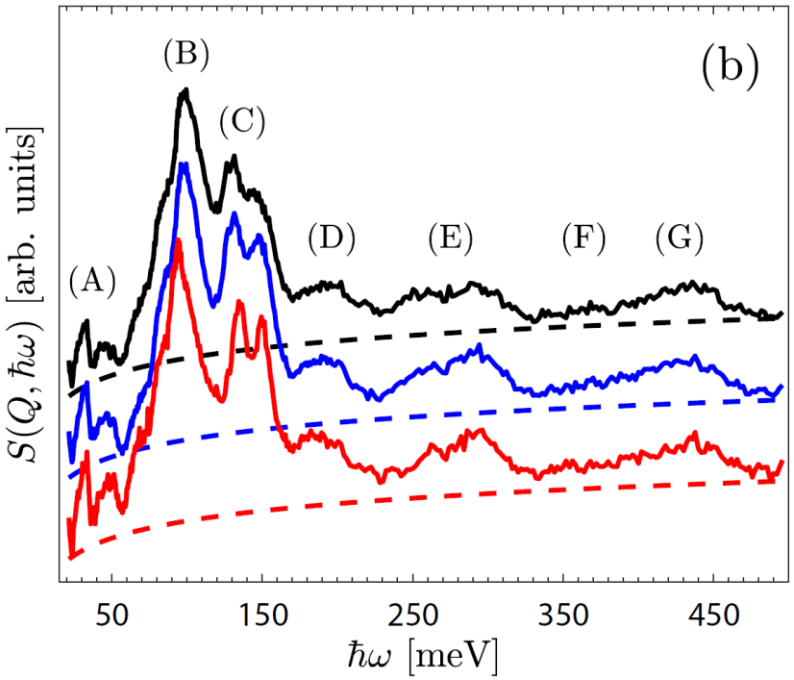
Proton vibrational dynamics with NVS and IR

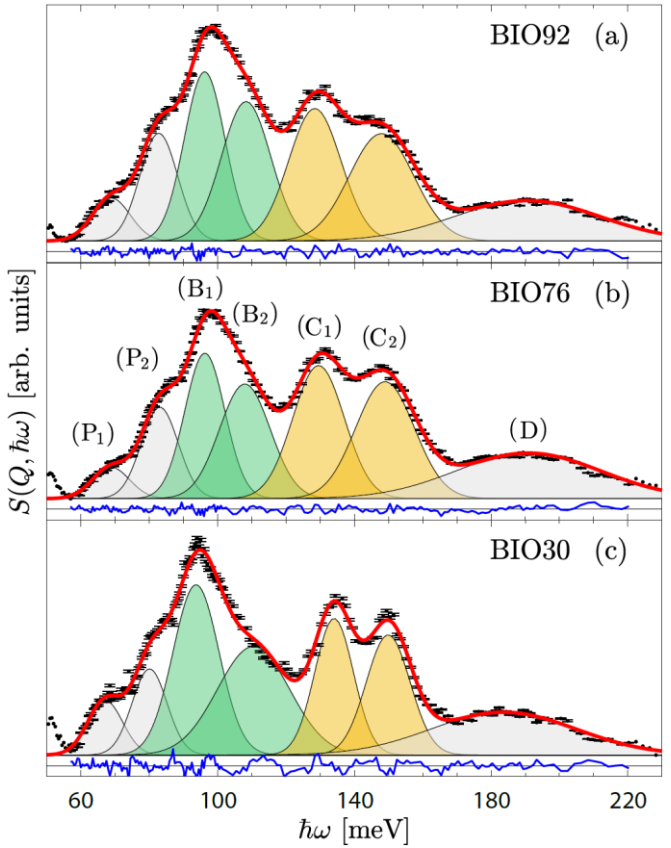
Spectra are mostly independent from the hydration level, *x*
Proton configurations are mostly identical, but different proportions H(1)/H(2)

IR



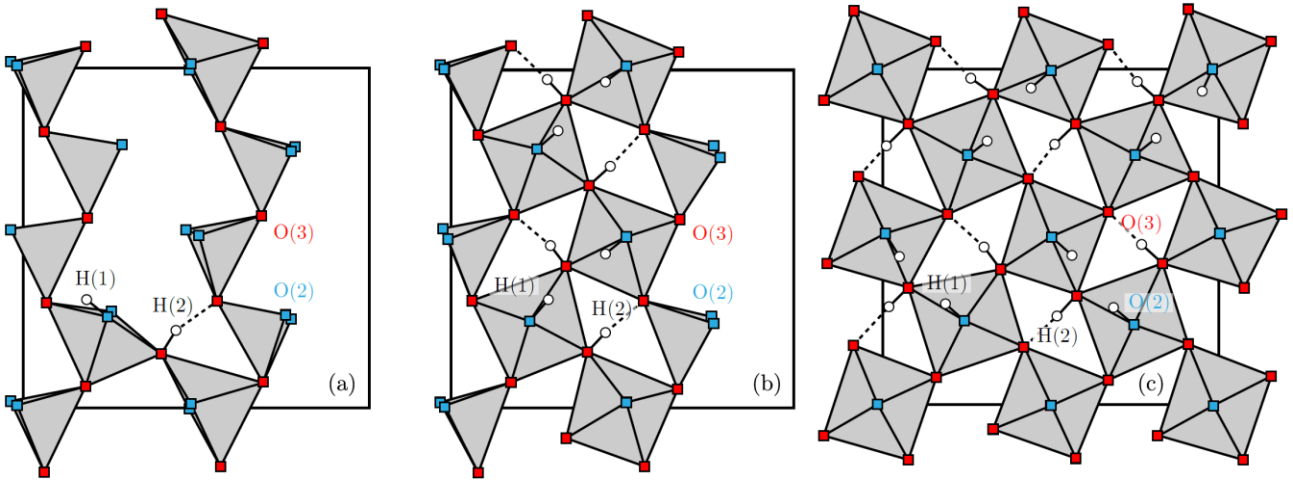
NVS (LAGRANGE @ILL)

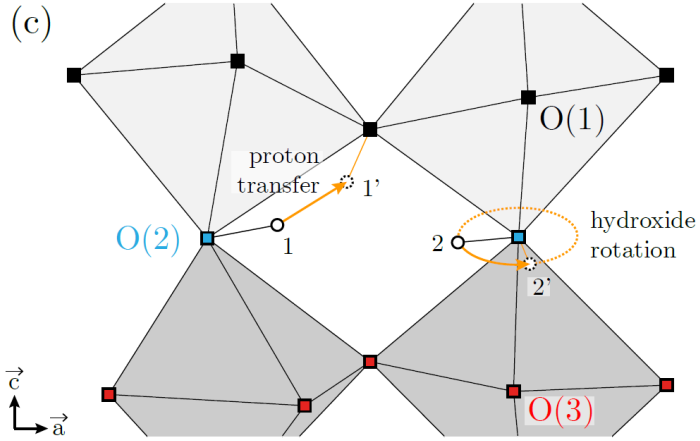


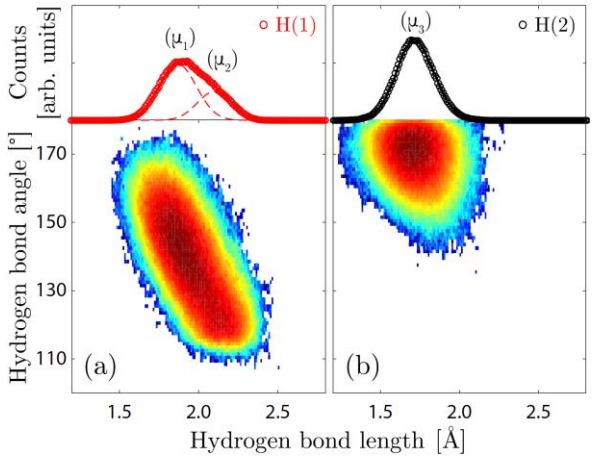


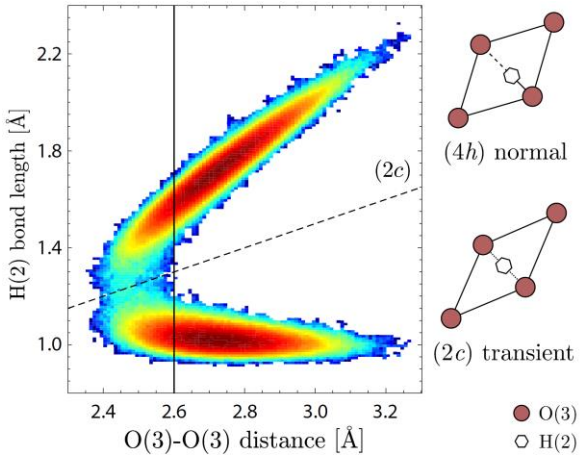
Neutron vibrational spectroscopy

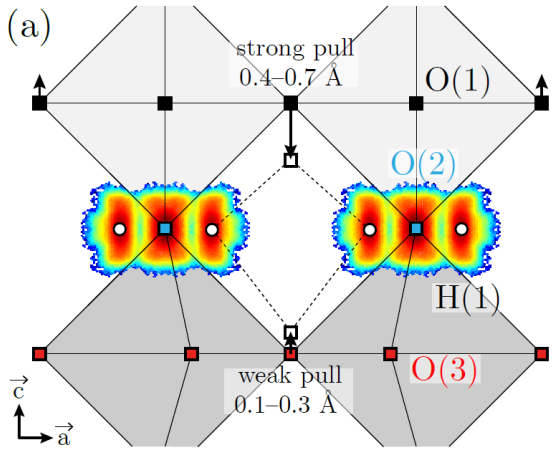
Ab initio molecular dynamics (AIMD) simulations: local structures and diffusion pathways

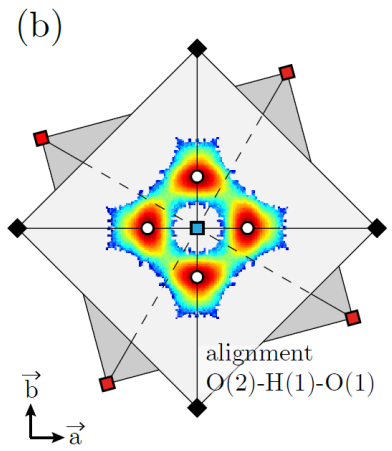






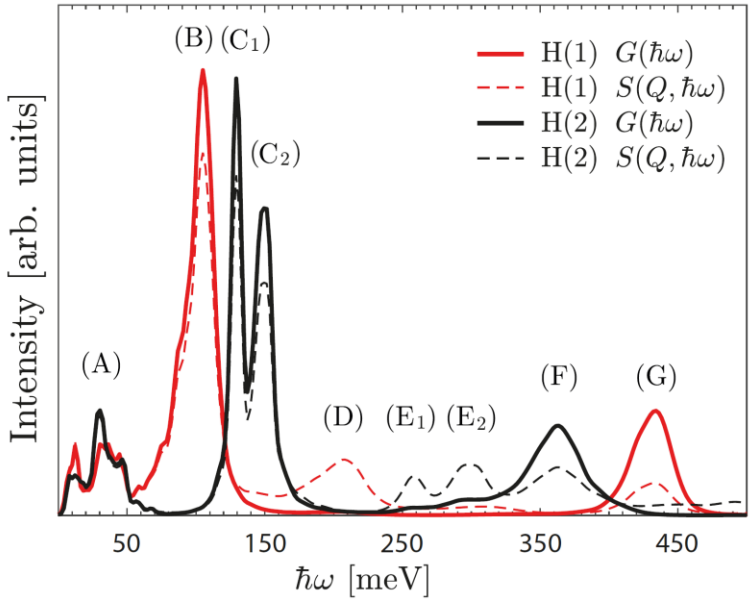


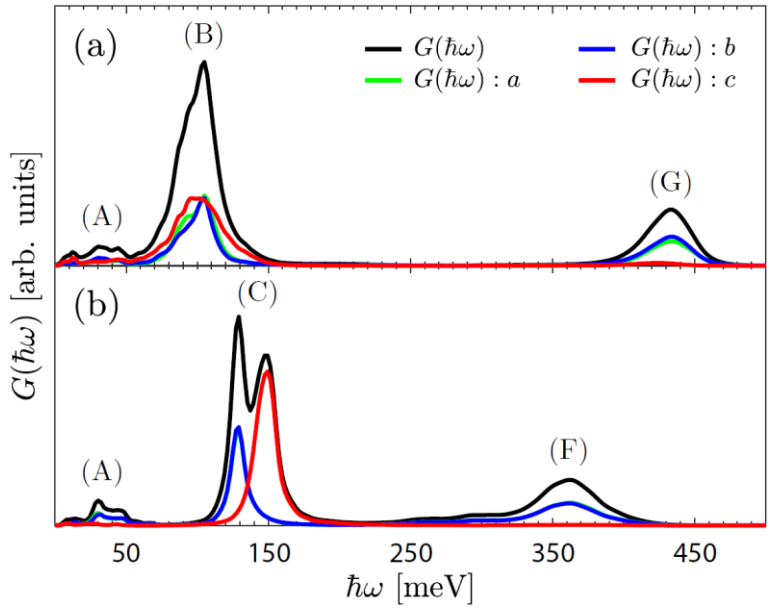


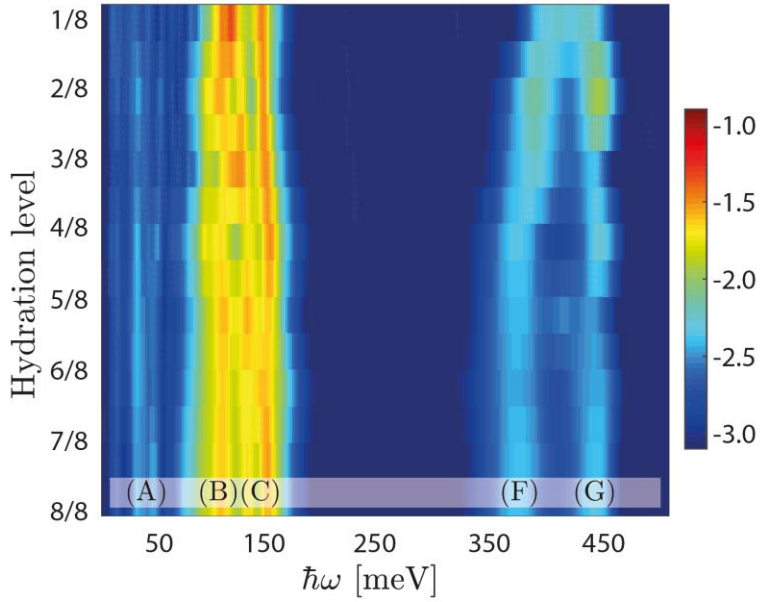


Neutron vibrational spectroscopy

AIMD simulations: spectral analysis







Density of states
Scattering function
Multi-phonon terms
Debye-Waller (if Q known)

Partials density of states:
per atom, per direction, over
sections of the trajectories
(short-lived configurations)

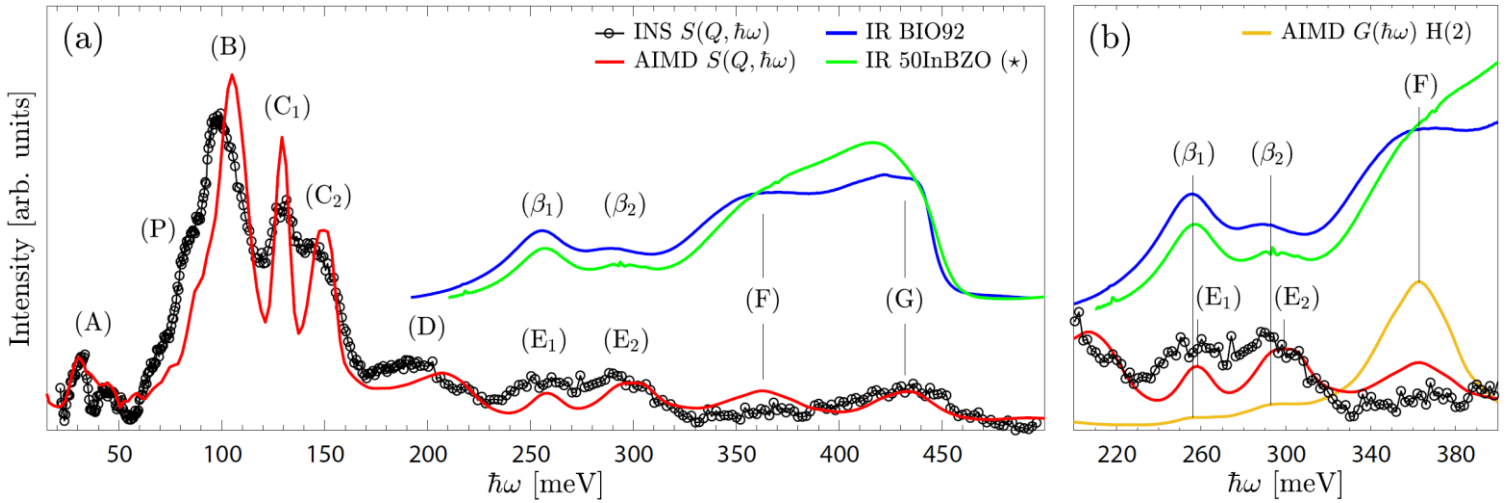
Band assignment

As a function of
hydration level

BIO always in
high-*x* regime

Neutron vibrational spectroscopy

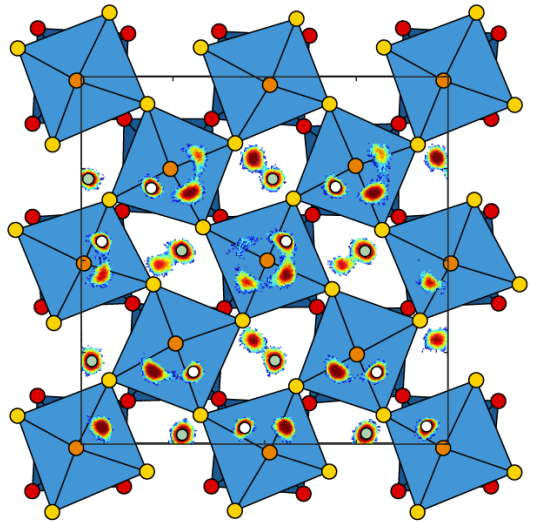
Proton vibrational dynamics in high-*x* phase?



Label	$\hbar\omega$ [meV]	Assignment
A	10–55	Riding modes, lattice dynamics
P	67–83	Phonon-related excitations
B	93–110	(p=1) δ(O-H(1))
C_1	126–131	(p=1) "in-plane" δ(O-H(2))
C_2	142–150	(p=1) "out-of-plane" δ(O-H(2))
D	183–204	(p=2) δ(O-H(1))
E_1	240–266	(p=2) "in-plane" δ(O-H(2))
E_2	278–308	(p=2) "out-of-plane" δ(O-H(2))
F	356–374	(p=1) ν(O-H(2))
G	418–444	(p=1) ν(O-H(1))
$\beta 1$	249–260	(p=1) ν(O-H(2))
$\beta 2$	285–297	(p=1) ν(O-H(2))

Effect of hydration level?
Limited from experiment, marked from AIMD, pointing towards the segregation of protons in oxygen-rich hydrogen-rich domains with the pseudo-cubic structure

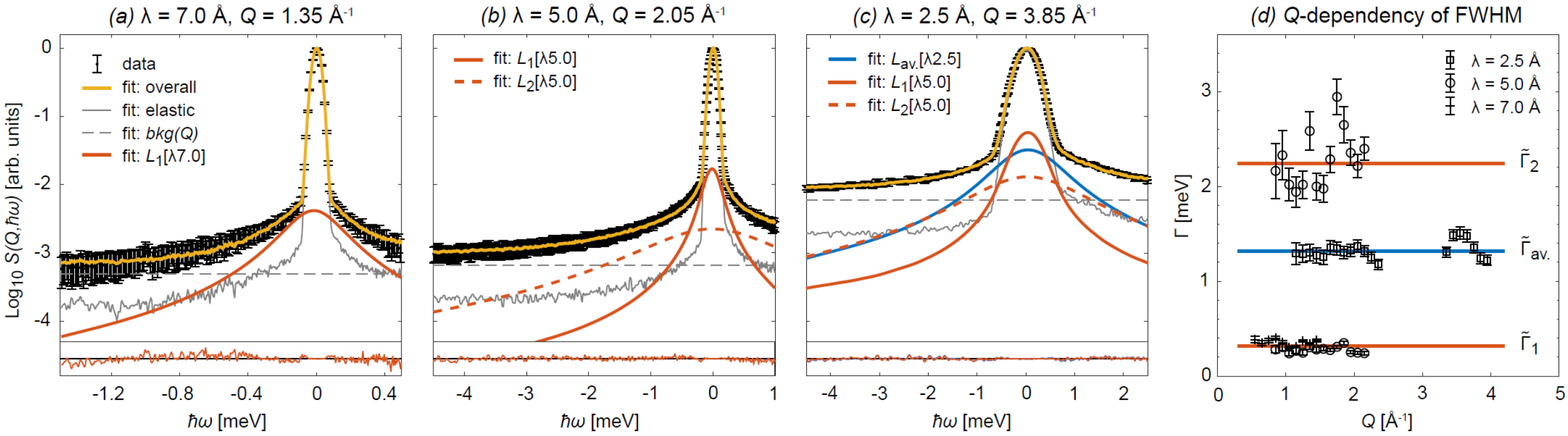
Diffusion processes?
AIMD shows preferential
- O-H(1) rotation
- H(2) proton transfer



Quasielastic neutron scattering

Localised diffusion with TOFTOF (@ MLZ), multiple λ at *T* = 485 K

Clear evidence of two processes, with Γ = 0.32(7) meV and 2.2(3) meV



Fitting model: $S_{meas.}(Q,\hbar\omega) \propto bkg(Q) + \left[a_D(Q)\delta(\hbar\omega) + \sum_j a_{L,j}(Q)\, L(\hbar\omega)\right] * R(Q,\hbar\omega)$

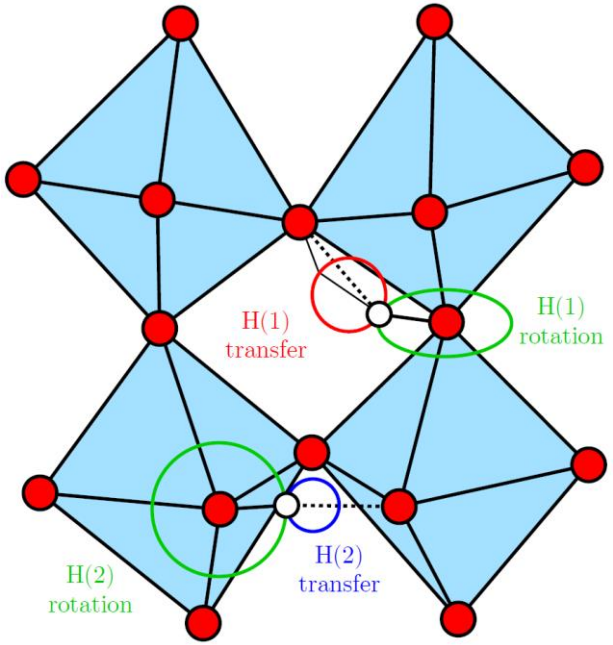
Quasielastic neutron scattering

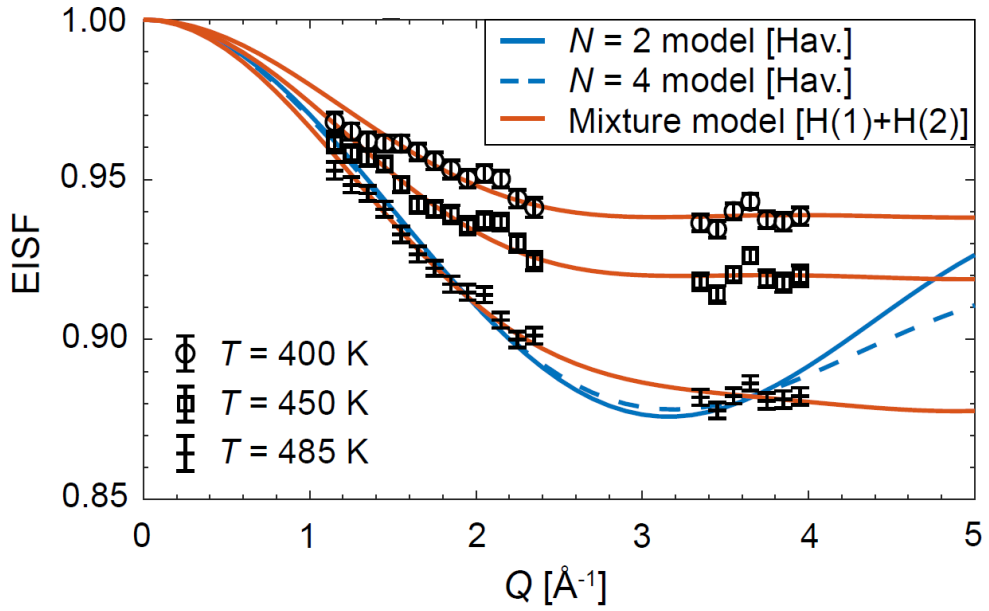
Localised diffusion with TOFTOF, elastic incoherent structure factor (EISF) at λ = 2.5 Å

$$EISF(Q) = \frac{a_D(Q)}{a_D(Q) + a_L(Q)}$$

Elementary motion of a proton in an oxide:

- Proton transfer (jump diffusion with N=2)
- O-H rotation (jump diffusion with N=4)





Limited agreement if only one process

Best agreement with **two processes**

- 60% of H(2) transfer (r=0.35 Å, $\Gamma_2 \approx 2.2$ meV)
- 40% of O-H(1) rotation (r=0.99 Å, $\Gamma_1 \approx 0.3$ meV)

Quasielastic neutron scattering

Localised diffusion with IN6 (@ILL), temperature dependence

Fit based on TOFTOF's EISF

- Mixture model with 60% of H(2) and 40% of H(1)
- Three Lorentzian with fixed relative intensities

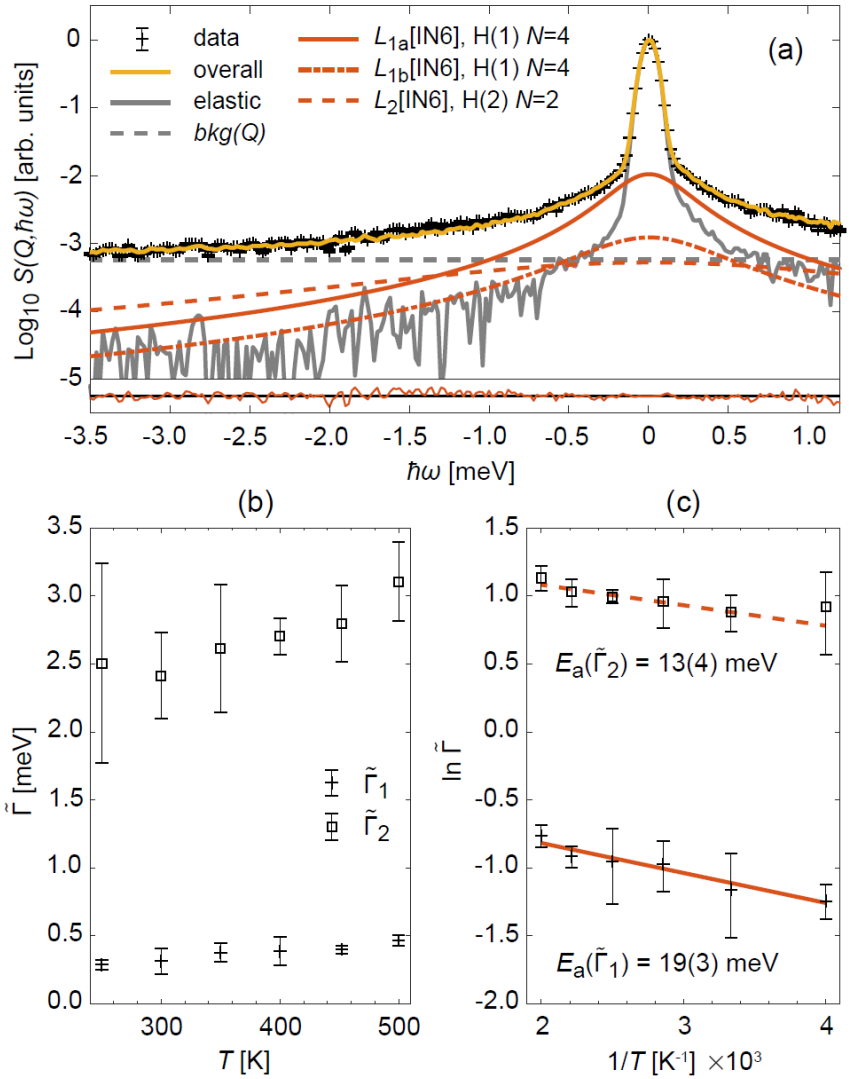
Activation energy from $\Gamma(T) = \Gamma_0 \exp\left(\frac{-E_a}{k_B T}\right)$

For O-H(1) rotation

- Γ = 0.29(4)—0.47(4) meV for *T* = 250—500 K
- Activation energy of **19(3) meV**

For H(2) proton transfer

- Γ = 2.4(4)—3.1(3) meV for *T* = 250—500 K
- Activation energy of **13(4) meV**

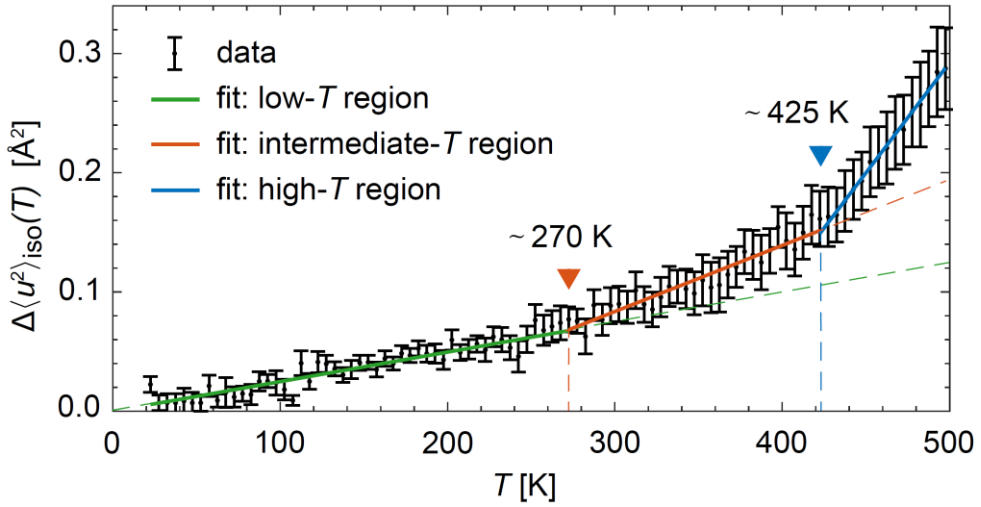


Quasielastic neutron scattering

Processes in the nanosecond timescale with IN16b (@ ILL)

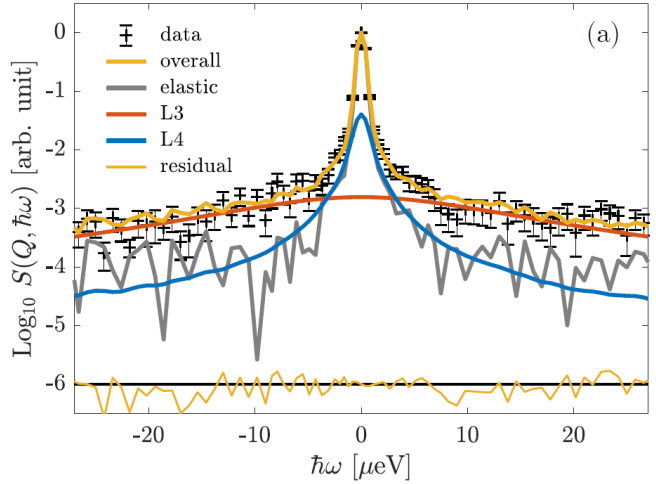
Elastic fixed window scan

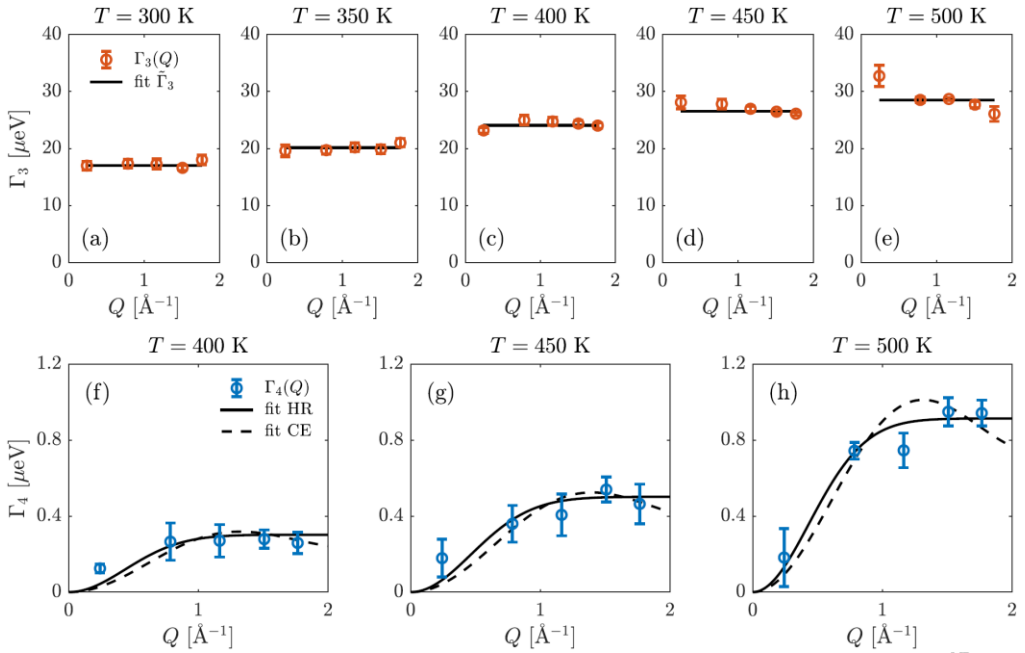
- Onset of thermally-activated dynamic processes
- Two distinct relaxation processes



QENS spectra

- Intermediate-*T*: localised motion
- High-*T*: translational diffusion

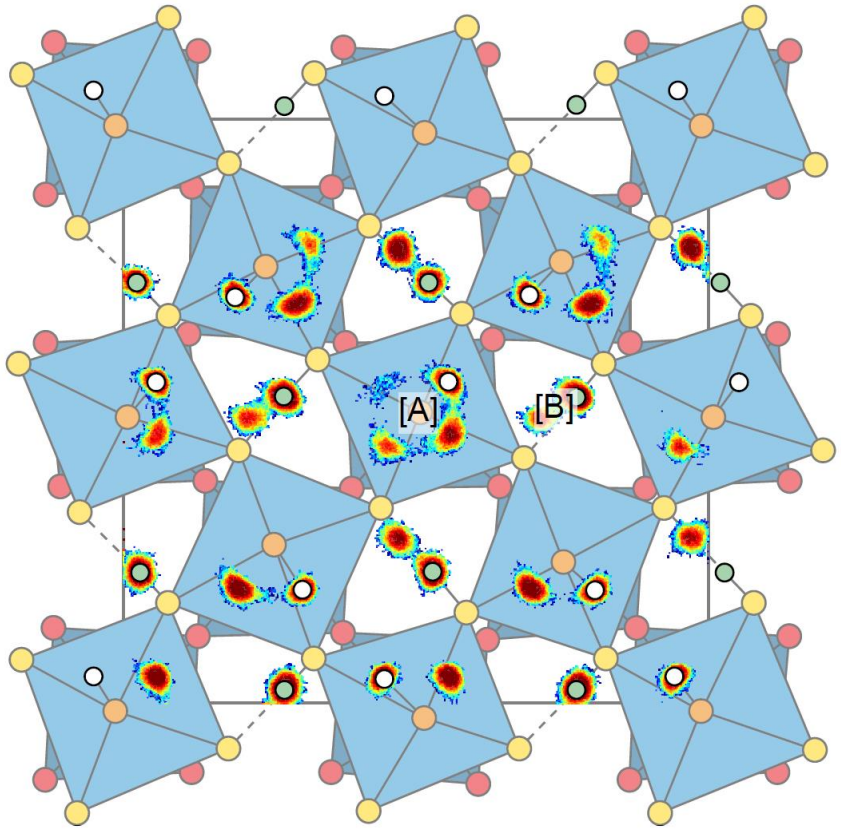




Quasielastic neutron scattering

Diffusion mechanisms hinted in the AIMD

300 K

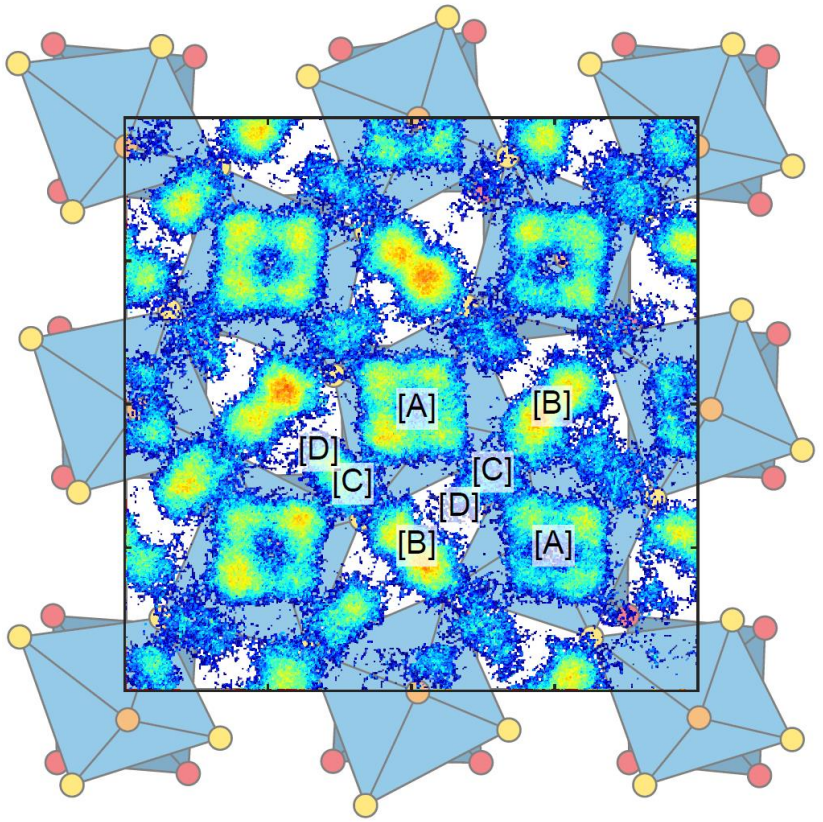


O(1) O(2) O(3) H(1) H(2)

[A] N = 4, O-H(1) rotation

[B] N = 2, H(2) proton transfer

1200 K



O(1) O(2) O(3)

[A] H(1) proton sites

[B] H(2) proton sites

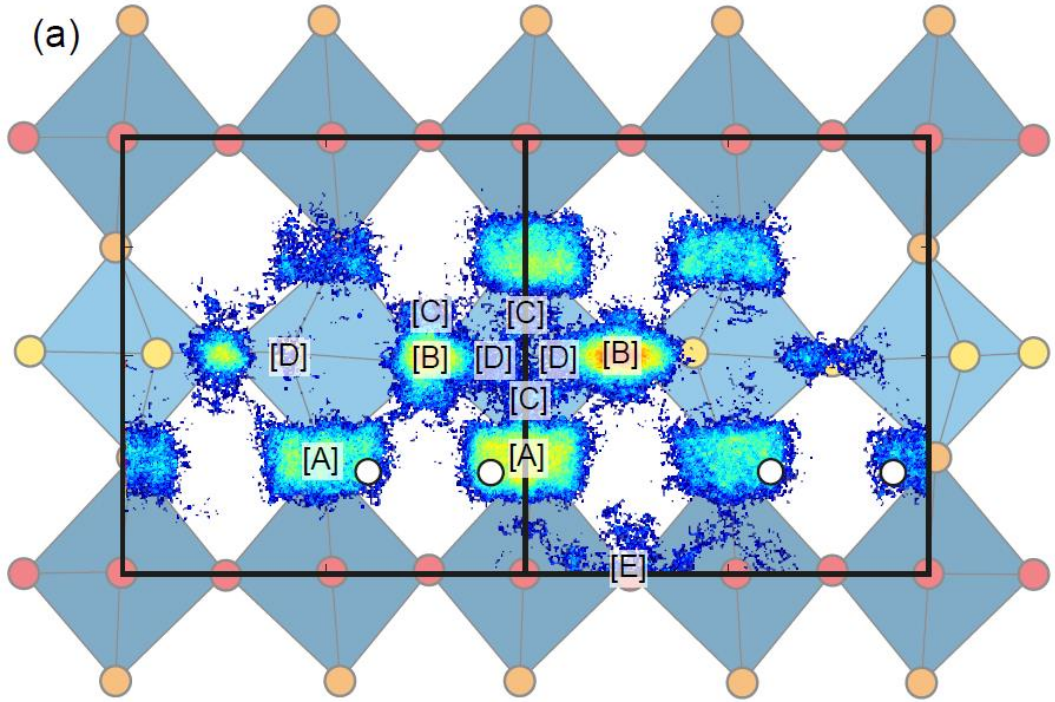
[C] H(3) proton sites

[D] H(4) proton sites

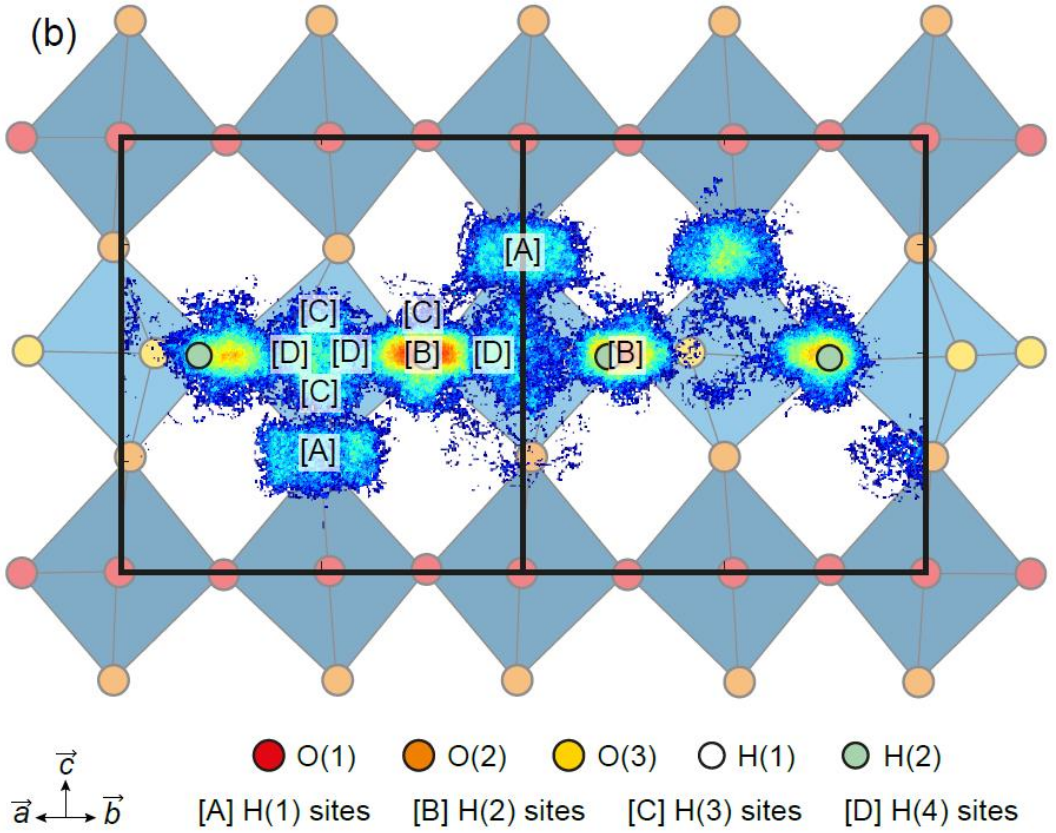
Quasielastic neutron scattering

Diffusion mechanisms hinted in the AIMD

1200 K, former H(1)



1200 K, former H(2)



- Interchangeable H(1) and H(2) regardless of the origin site (4 localised motions)
- Long-range diffusion is mainly confined in the pseudo-cubic layer

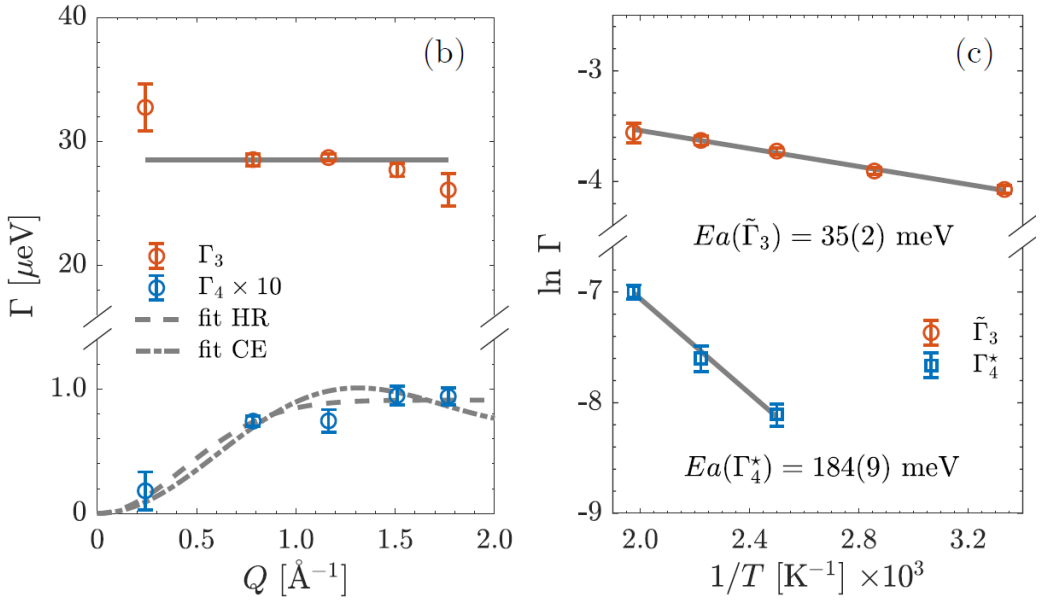
Quasielastic neutron scattering

Fitting the IN16b QENS spectra

L3 fit
- Localised diffusion
- $\tilde{\Gamma}_3 = 17(2) - 29(3)$ μeV
- Activation energy of **35(2) meV**
- Elementary motions that populates H(3)/H(4)

L4 fit
- Long-range diffusion
- Hall-Ross model with jump distance of 4(1) Å
- $\Gamma_4^\star$ = 0.2(2) – 1.1 (3) μeV
- Activation energy of **0.20(5) eV**
- Diffusion coefficients:

T [K]	D_{CE} [Å^2/ns]	D_{HR} [Å^2/ns]
400	0.45(7)	0.7(2)
450	0.7(2)	1.2(3)
500	1.6(3)	2.4(4)

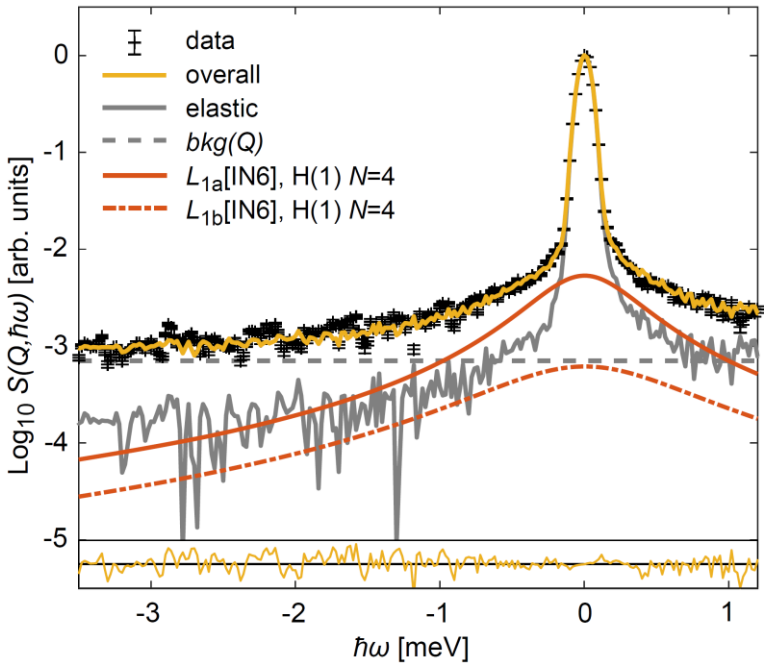


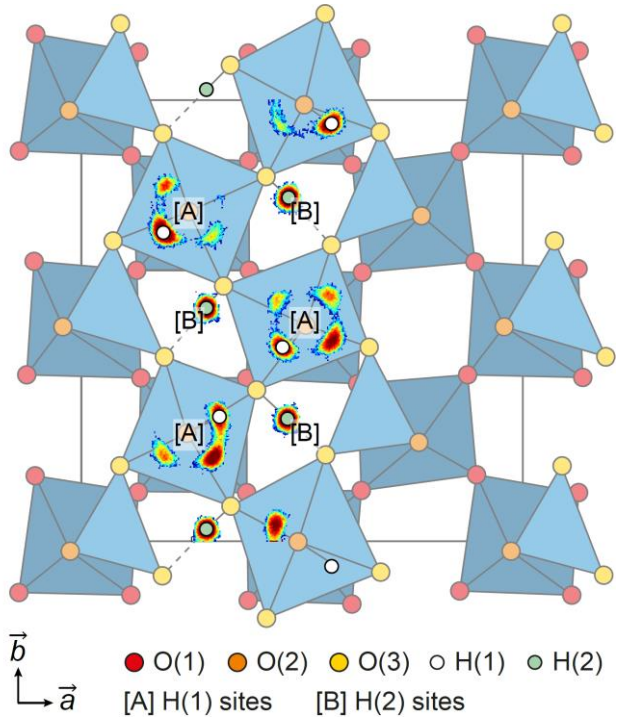
- Similar activation energies and diffusion coefficients that in related-perovskite oxides
- High proton concentration, but low concentration of empty sites, which reduces the probability of diffusion

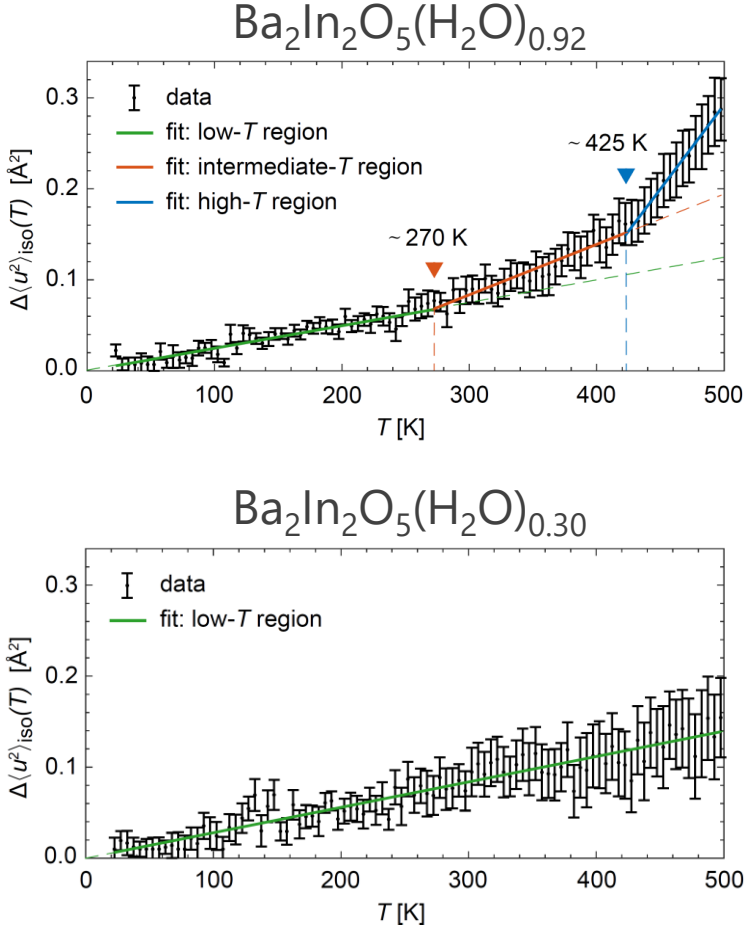
NVS and QENS in partially-hydrated BIO

In $Ba_2In_2O_5(H_2O)_{0.30}$

- Fast dynamics: only O-H(1) rotation is detected with QENS
- H(2) transfer is hindered close to oxygen vacancy in the AIMD
- Slow dynamics: no QENS signal



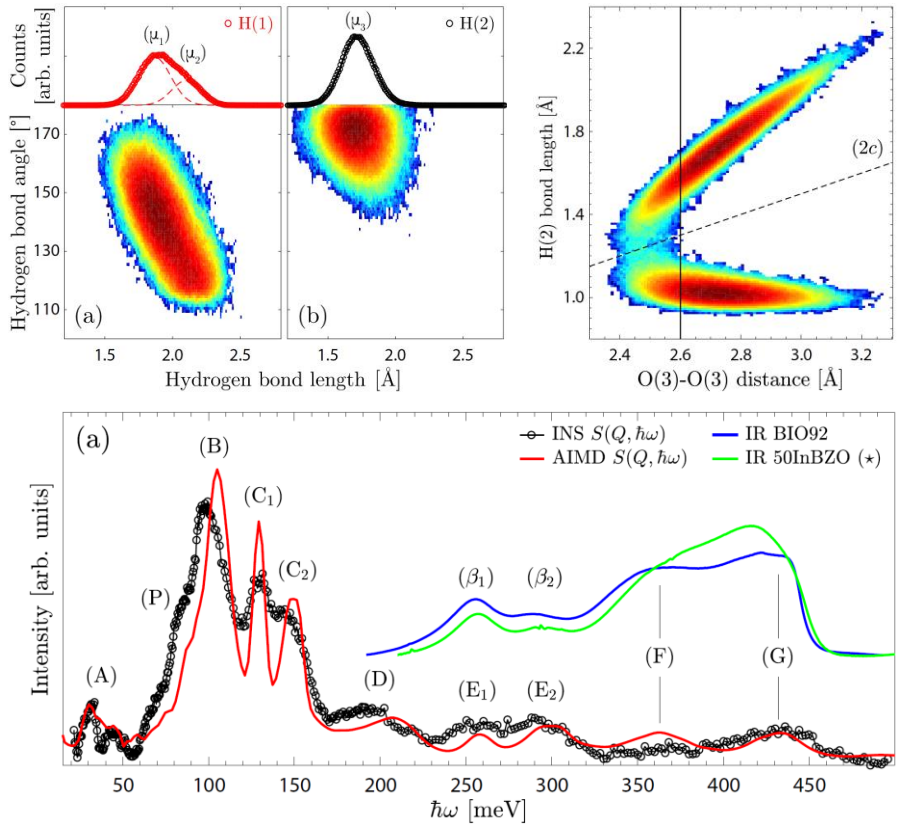




Summary

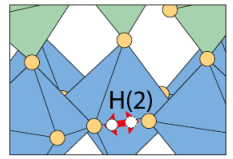
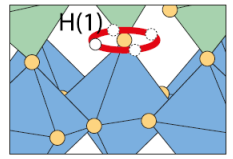
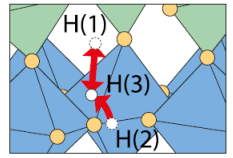
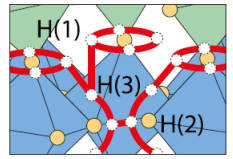
NVS in barium indate (+IR +AIMD)

- Characterisation of proton sites
- Number and geometry of proton environments



QENS in barium indate (+AIMD)

- Characterisation of diffusion mechanism
- Pathways, timescales, activation energies of rotational/translational diffusion processes

Processes	Onset T	Timescales	E_a [meV]	Scheme
H(2) proton transfer, $N = 2$ jump diffusion model with a 0.70 Å jump distance	< 250 K	0.4–0.5 ps	13(4)	
O–H(1) rotation, $N = 4$ jump diffusion model with a 1.40 Å jump distance	< 250 K	2.8–4.6 ps	19(3)	
Higher energy localized motions of H(1) and H(2) that populate H(3) and H(4)	~270 K	45–77 ps	35(2)	
Long-range diffusion, Hall-Ross model with ~4 Å jump distances and $D = 0.7$–2.4 Å^2/ns	~425 K	1.2–6.6 ns	200(50)	

Acknowledgments

Chalmers University of Technology,
Dpt. Chemistry & Chem. Eng., Sweden

Maths Karlsson
Laura Mazzei
Seikh M. Habibur Rahman

Institut Laue Langevin, France

Mónica Jiménez-Ruiz (LAGRANGE)
Michael Marek Koza (IN6)
Bernhard Frick (IN16b)
Peter Fouquet (IN11c)

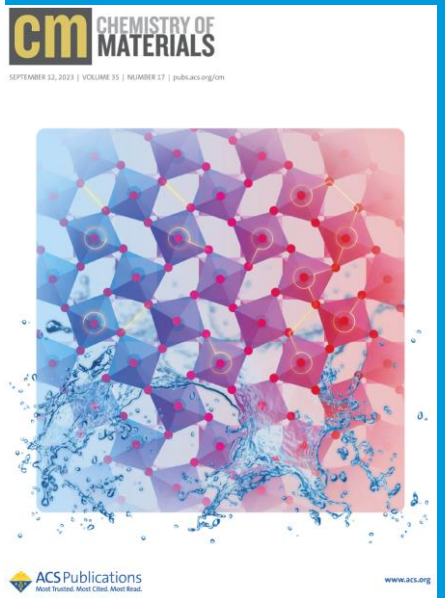
Heinz Maier-Leibnitz Zentrum, Germany

Zach Evenson (TOFTOF)

ISIS Neutron and Muon Source, U.K.

Franz Demmel (OSIRIS)

Thank you for your attention!



For more information:

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- A. Perrichon, M. Jiménez-Ruiz, L. Mazzei, S. M. H. Rahman, M. Karlsson, *J. Mater. Chem. A*, **7**, 17626 (2019)