Advanced school – French-Swedish Academy for Scattering Experiments & Modeling
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Neutron spectroscopy studies of perovskites for energy applications

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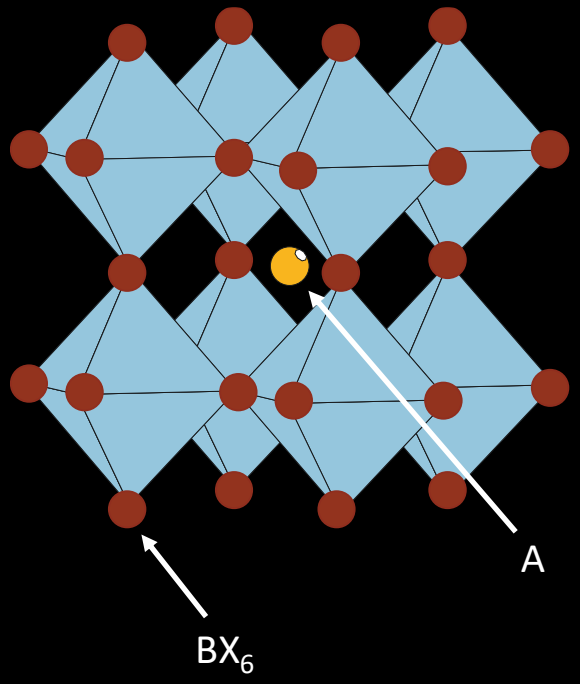
Perovskites for energy applications

Crystal structure: ABX_3

- A = a large positively charged ion (Ba, Cs, small organic ones)
- B = a smaller metal ion (e.g. Zr, Pb, Ti)
- X = an anion (often O, or a halide ion)

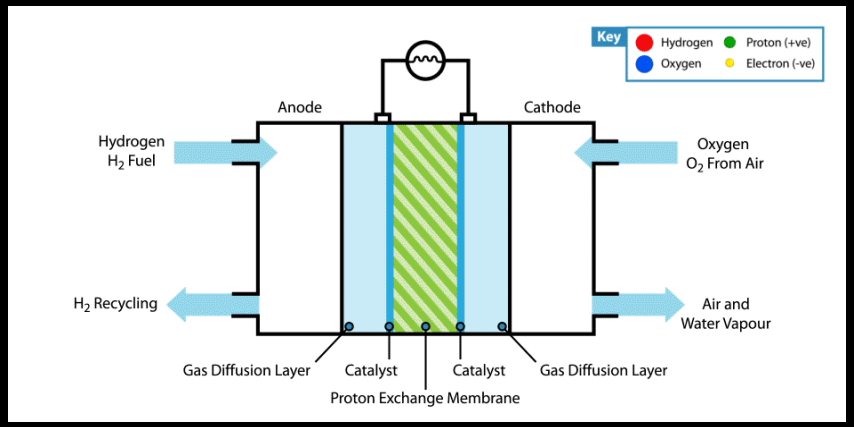
The ability to host a variety of different ions, make the materials highly tuneable in terms of their ”functional” properties:

- Optical properties, luminescence
- Magnetic properties
- Electronic and/or ionic conductivity, superconductivity



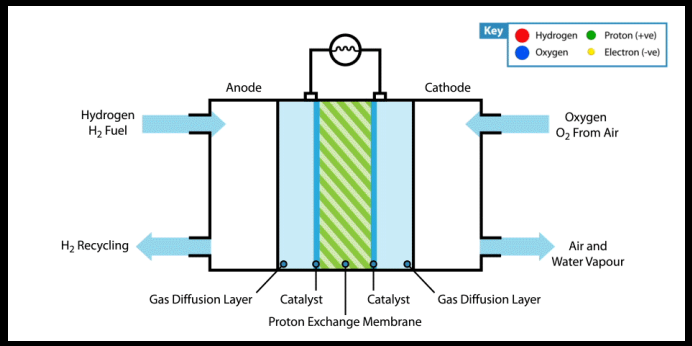
Proton conducting perovskites as fuel-cell electrolytes

Hydrogen fuel cells require a proton conductor



Proton conductors: state of the art

Hydrogen fuel cell



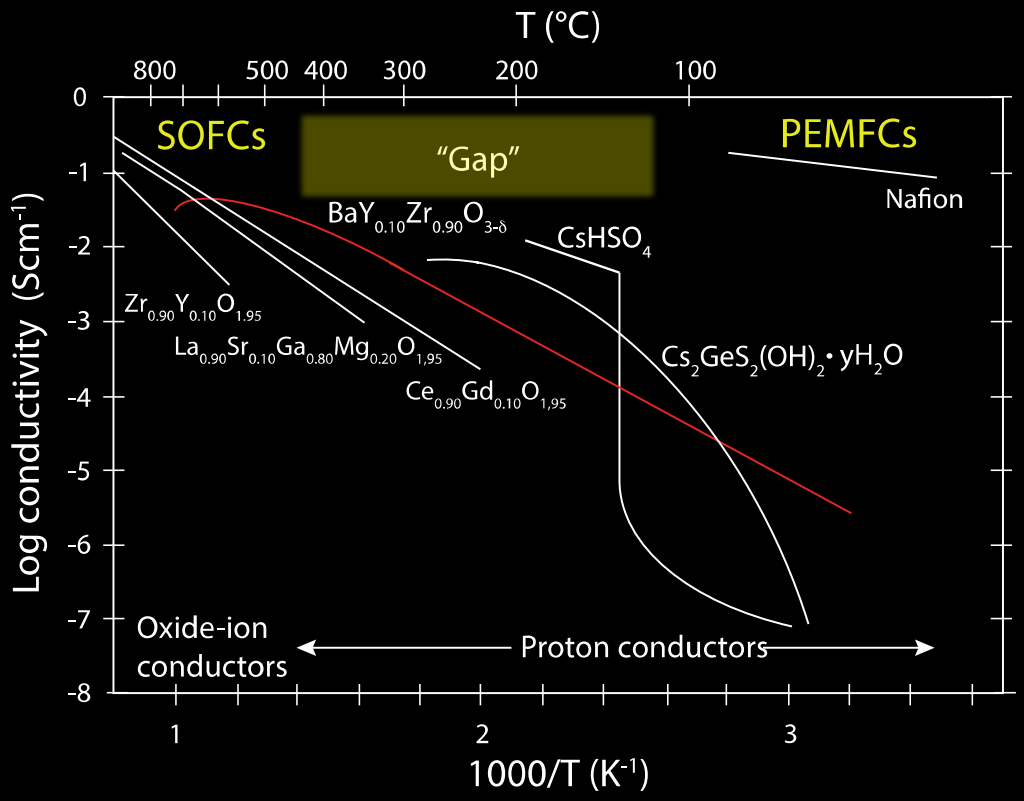
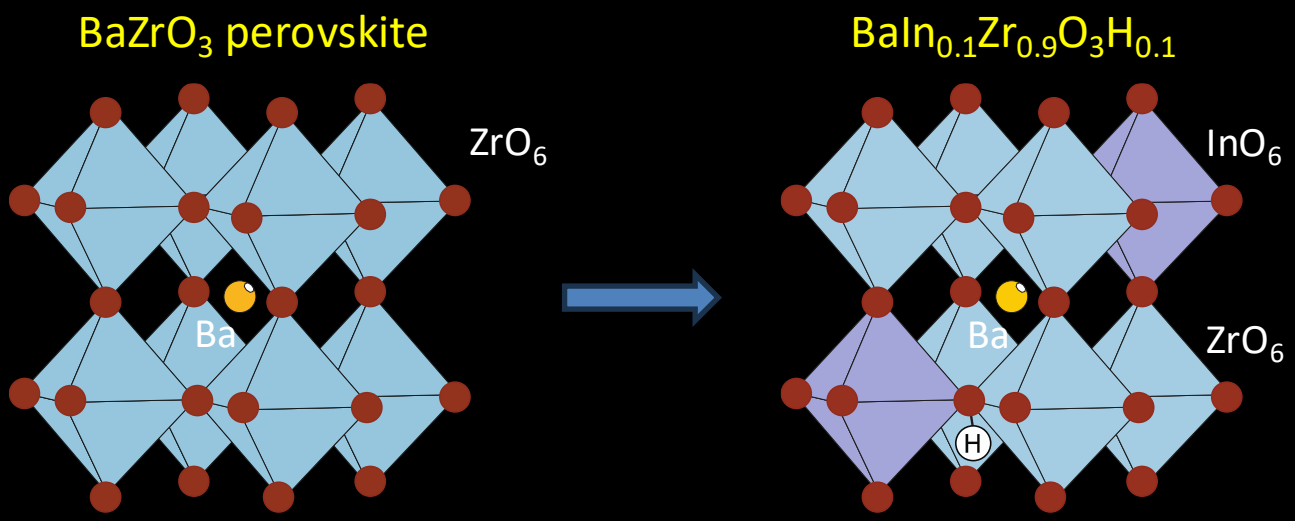


Figure taken from: M. Karlsson, *Dalton Trans. (2013)*

Proton conducting perovskite oxides

Perovskites ABO_3 (e.g. $BaZrO_3$, $BaCeO_3$)

- Cation substitution (In^{3+} to Zr^{4+}) -> $BaZr_{1-x}In_xO_{3-x/2}$
- Hydration -> $BaZr_{1-x}In_xO_3H_x$



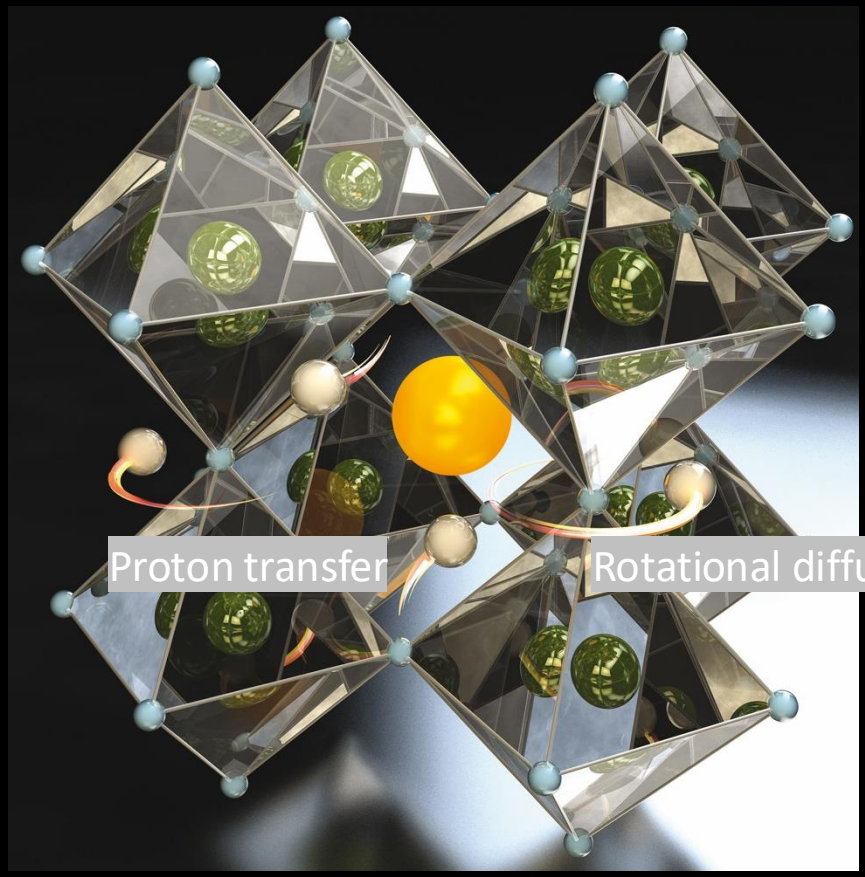
Proton conduction mechanism?

Proton dynamics

- Localized proton motions
  - O-H rotational diffusion
  - O-H···O proton transfer
- Long-range motion

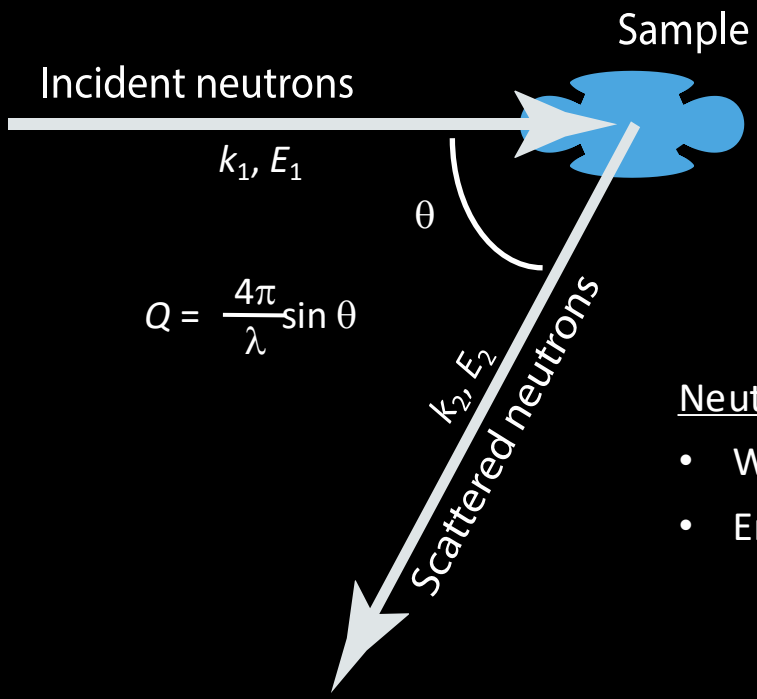
Local chemistry and structure complicates the description…. Some open questions:

- Rate-limiting process?
- Effect of dopant atoms?



Quasielastic neutron scattering (M. Koza lecture)

- Most instruments (QENS techniques) probe dynamics manifested by a typical timescale of $\tau \approx 1—1000$ ps.
- Very sensitive to hydrogen (very large incoherent scattering cross section)



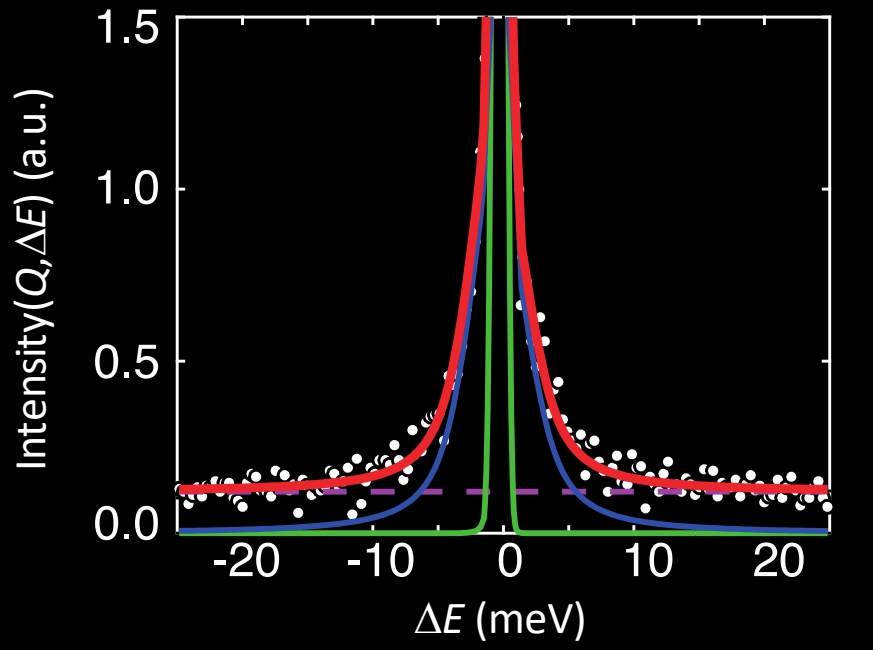
Neutrons for scattering experiments:

- Wavelength: 1—10 Å (-> interference -> structure)
- Energy: 10—100 meV (-> energy exchange -> dynamics)

M. Karlsson, *Phys. Chem. Chem. Phys.* (2015)

Quasielastic neutron scattering (QENS)

QENS spectrum of $BaIn_{0.50}Zr_{0.50}O_{2.75}H_{0.50}$
(D. Noferini *et al.*)

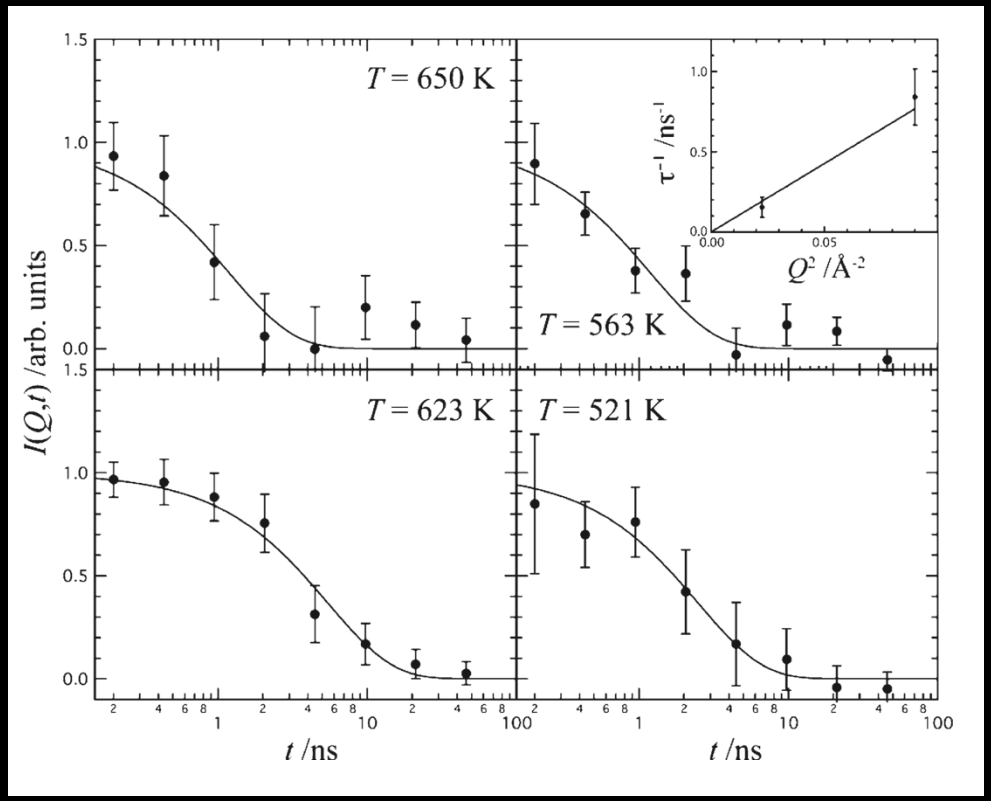


Dynamics manifested by the slight "quasielastic" broadening (blue line)
– Analysis gives information about timescale, activation energy, and spatial geometry

Neutron spin-echo (NSE)

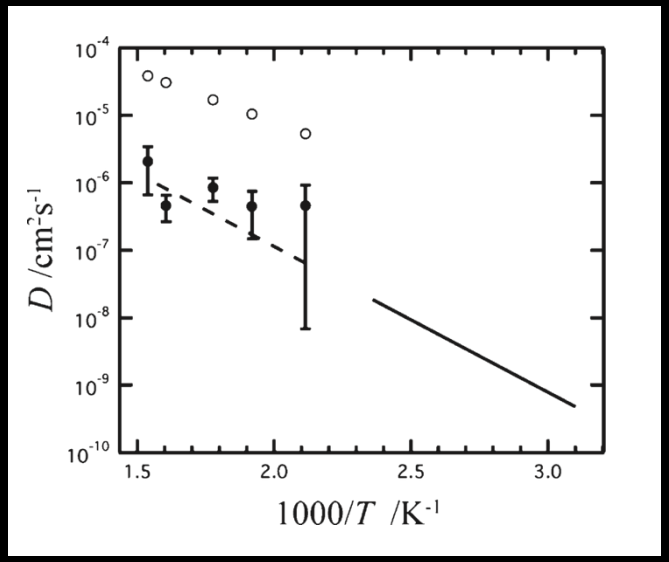
- Probes longer timescales. Intermediate scattering function, *I(Q,t)*, rather that the dynamical structure factor, *S(Q,ω)*, is probed.

NSE data of Y-doped $BaZrO_3$ at $Q = 0.2$ Å^{-1} (IN15@ILL)



M. Karlsson et al., Chem. Mater (2010)

Diffusion constant from NSE (bullets) and conductivity measurements (lines),



The effect of the dopant atoms has ”averaged out” on the length-scale ≈ 20 Å

Some very recent results on proton conductivity in heavily Sc-doped barium stannate ($BaSn_{1-x}Sc_xO_3$, x = 0.7)

nature materials

Article

https://doi.org/10.1038/s41563-025-02311-w

Mitigating proton trapping in cubic perovskite oxides via ScO_6 octahedral networks

Received: 21 November 2023

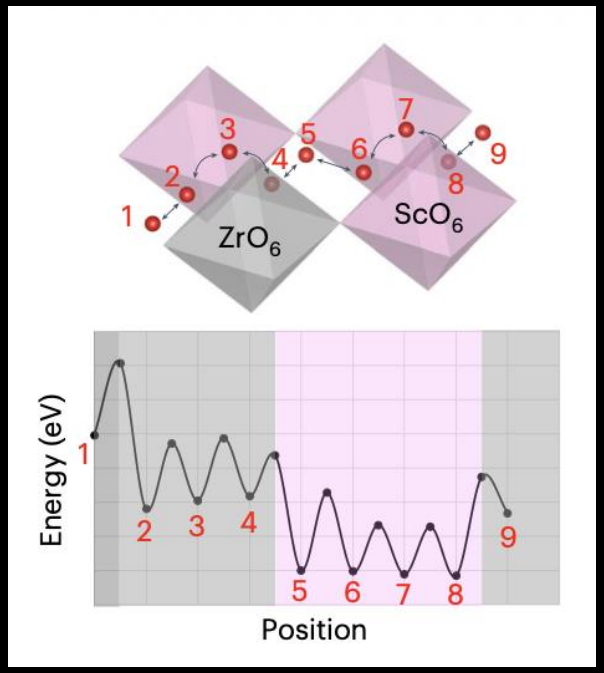
Accepted: 3 July 2025

Published online: 08 August 2025

Check for updates

Kota Tsujikawa[1,2,3], Junji Hyodo[1,2,4], Susumu Fujii[1,3,5,6], Kazuki Takahashi[7], Yuto Tomita[8], Nai Shi[1], Yasukazu Murakami[8], Shusuke Kasamatsu[9] & Yoshihiro Yamazaki[1,2,3]

Advances in electrochemical devices have been primarily driven by the discovery and development of electrolyte materials. Yet the development



- The ScO_6 octahedra form a percolating pathway (Sc atoms are connected) for the protons, so that the protons do not have to ”detrap”.
- Experimental data on the microscopic proton dynamics is lacking.

Some very recent results on proton conductivity in heavily Sc-doped barium stannate ($BaSn_{1-x}Sc_xO_3$, x = 0.7)

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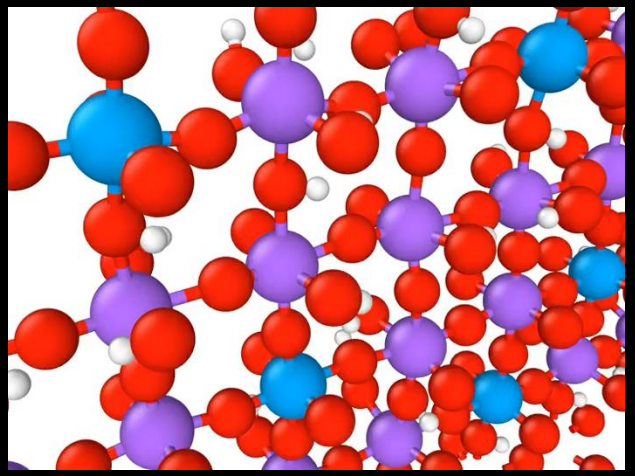
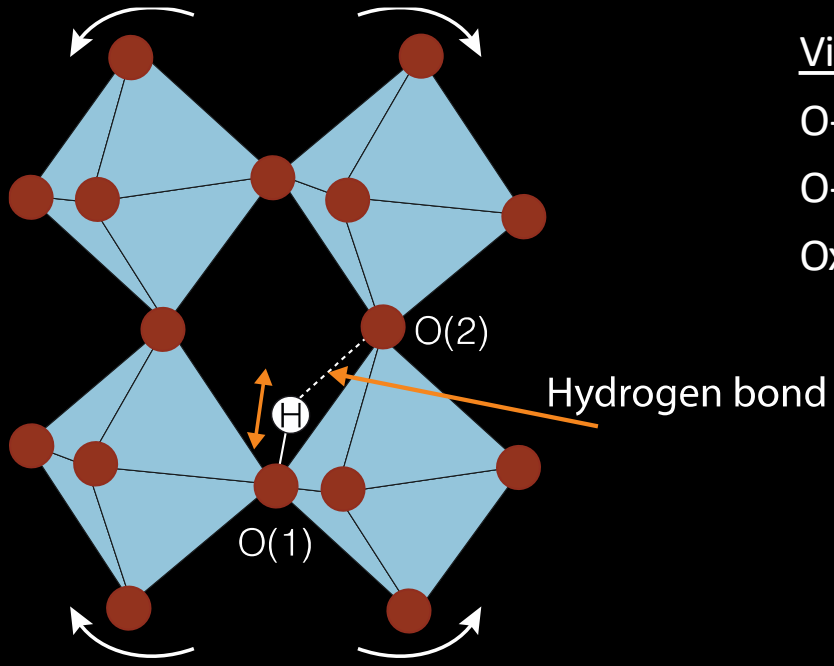
MD simulation of $BaSn_{0.3}Sc_{0.7}O_{3-\delta}$



- The ScO_6 octahedra form a percolating pathway (Sc atoms are connected) for the protons, so that the protons do not have to ”detrap”.
- Experimental data on the microscopic proton dynamics is lacking.
- Pronounced vibrational dynamics.

Vibrational dynamics



Vibrational modes:

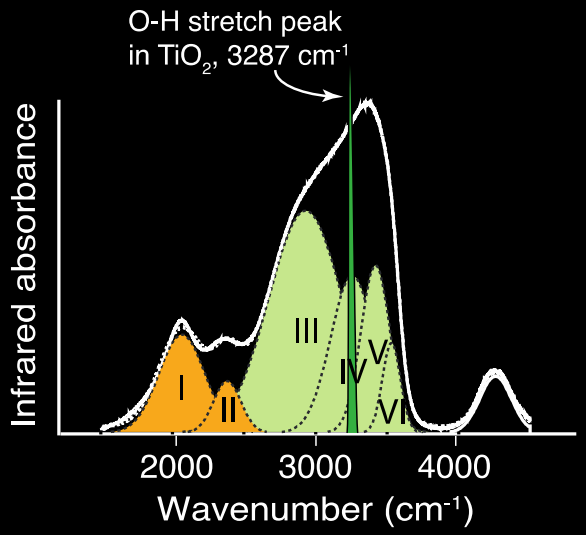
O-H stretch vibrations, ν(O-H)

O-H bend vibrations, δ(O-H)

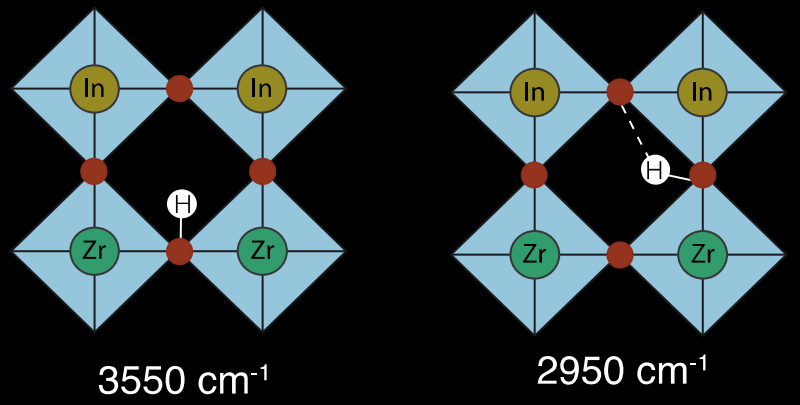
Oxygen (perovskite host lattice) vibrations

Infrared (IR) spectroscopy reveals several different local coordination environments of the protons

IR spectrum over the O-H stretch region of a hydrated sample of 50% In-doped $BaZrO_3$

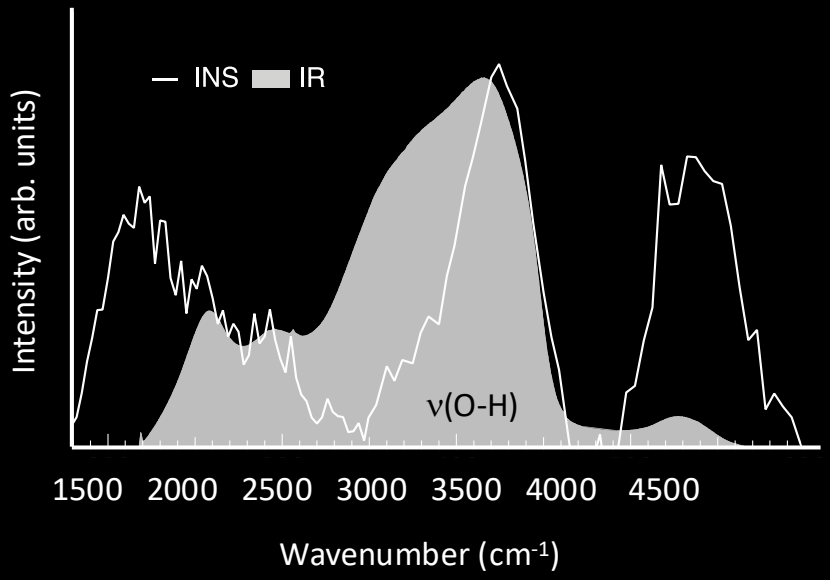


O-H stretch frequencies from *ab-initio* simulations, for various local proton structures (Mazzei *et al., J. Mater. Chem. A*, 2019)



Which configuration is most likely?

IR – INS comparison



- IR selection rule: the vibration must cause a change in dipole moment
- No selection rule in INS
- Therefore, the large IR intensity at ≈ 3000 cm^{-1} does not manifest many protons, but that the IR activity is higher in this range compared to at higher energy

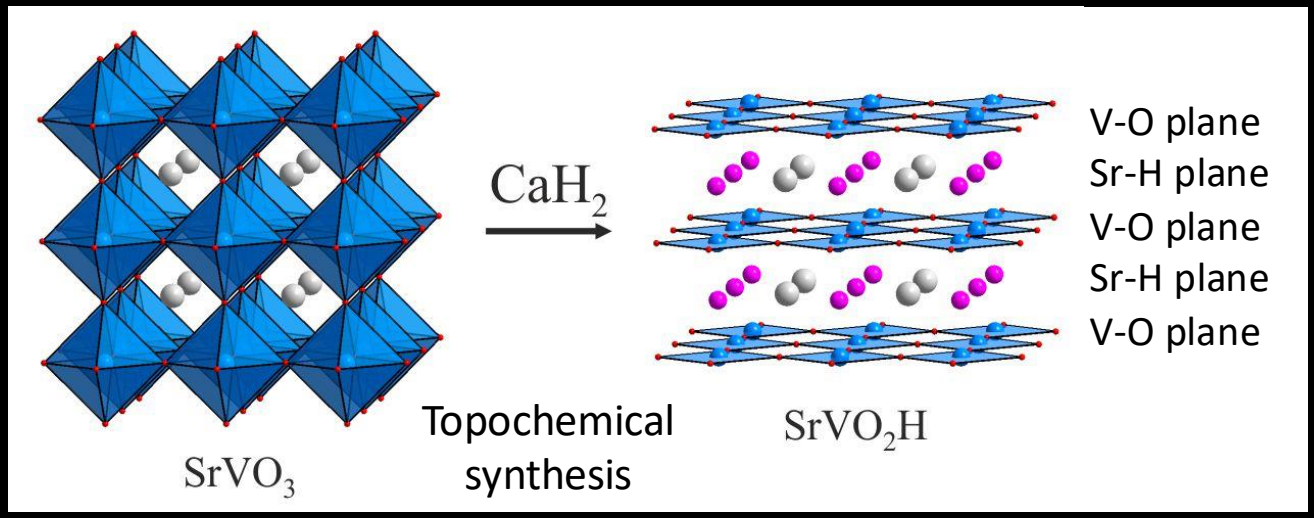
Oxyhydrides

- Contain both oxide-ions and hydride-ions in the same anion substructure
- Rare
- Exciting properties; magnetic, catalytic, electron and/or ionic conductivity
- Potential application in energy storage- and conversion devices

Strontium vanadium oxyhydride, $SrVO_2H$

(Hayward *et al., Ang. Chemie* **53** (2014) 7556)

A layered and fully ordered hydride-ion sublattice



Quasielastic neutron scattering experiments of hydride-ion dynamics in $SrVO_2H$

Instruments

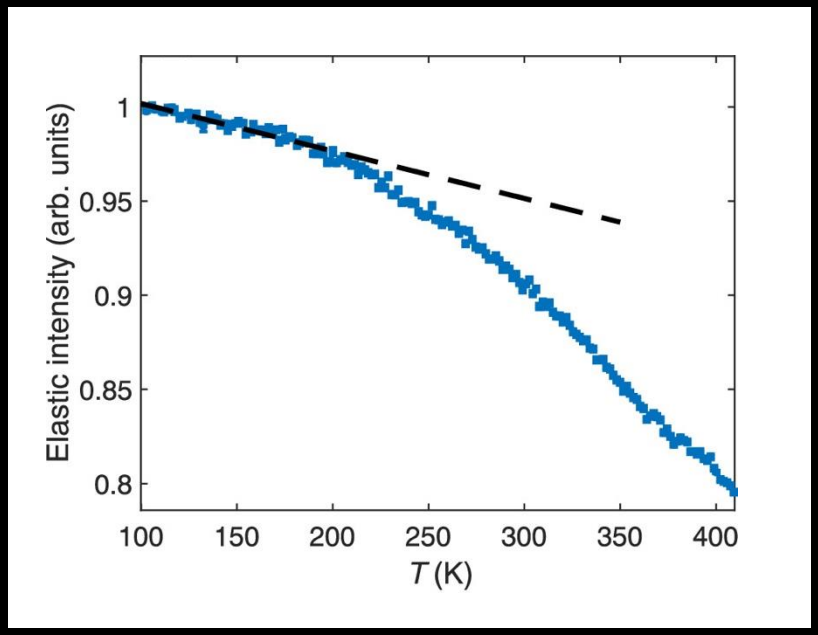
- High-flux backscattering spectrometer (HFBS) at NIST
- Disc chopper spectrometer (DCS) at NIST
- Time-of-flight near-backscattering spectrometer (OSIRIS) at ISIS

Complementary in terms of measurable length and timescales, allow to probe both long-range (slow) and short-range (localized, fast) dynamics

Long-range dynamics in $SrVO_2H$

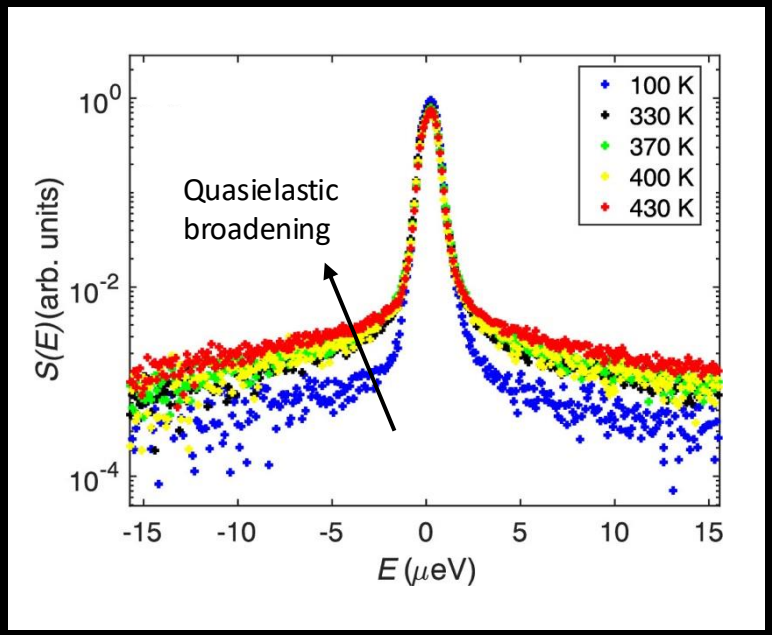
- HFBS@NIST, measurable time-range $\tau \approx 100$ ps – 3 ns

Elastic intensity from 100 to 415 K



- Harmonic vibrations below T ≈ 200 K
- Relaxational dynamics for T > 200 K

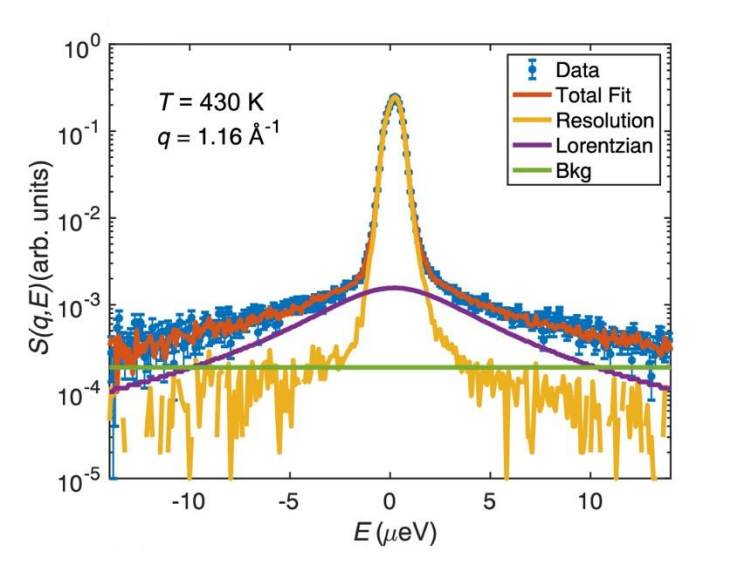
QENS spectra summed over the q-range of 0.6 – 1.6 $Å^{-1}$



- Quasielastic broadening, due to relaxational dynamics, for T > 330 K

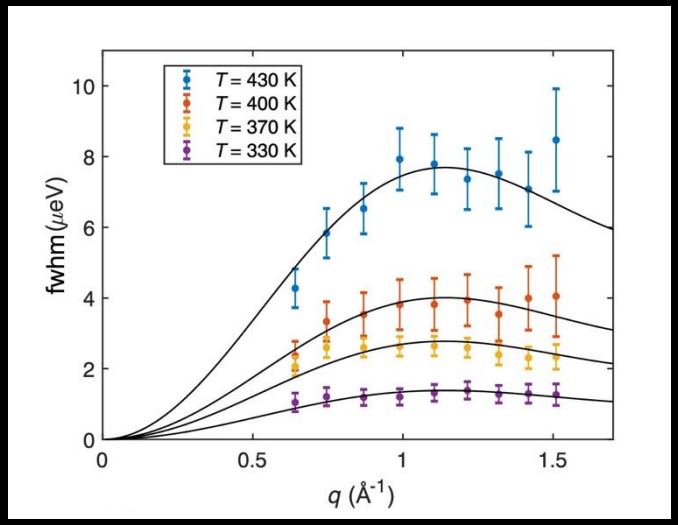
Long-range dynamics in $SrVO_2H$

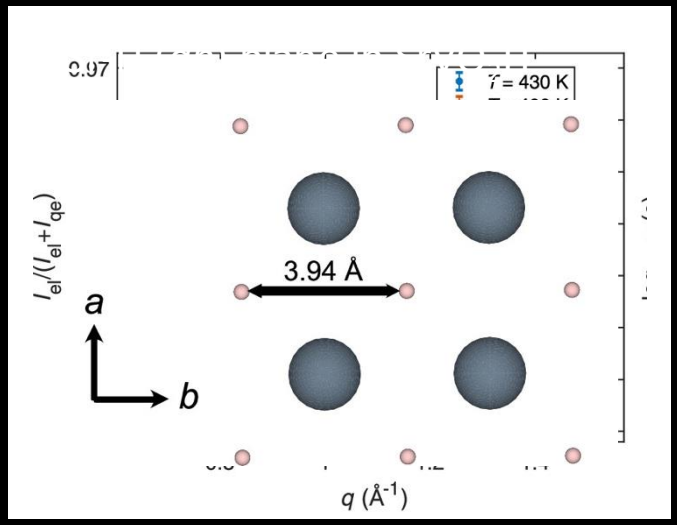
Lorentzian fitting to QENS spectrum at T = 430 K and q = 1.16 $Å^{-1}$



Long-range dynamics in $SrVO_2H$

Quasielastic width (left) and elastic intensity (right) reveals long-range jump diffusion





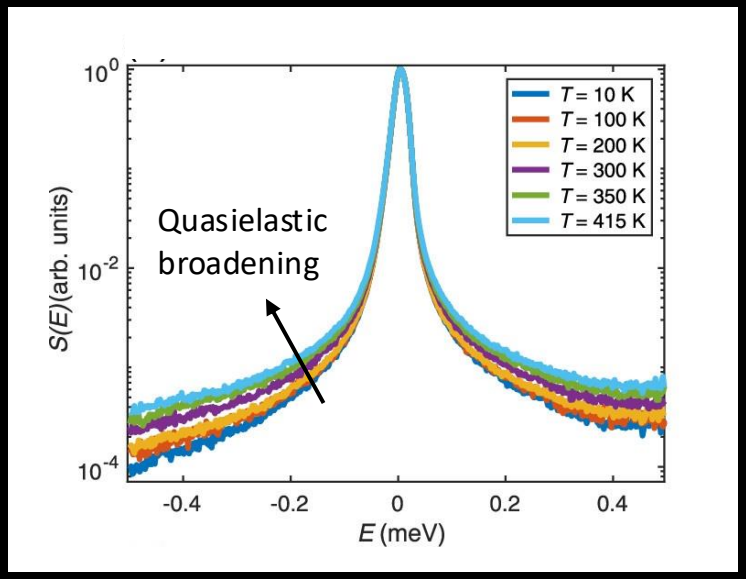
- Chudley-Elliott model of jump diffusion: $\text{fwhm} = \frac{2\hbar}{\tau}[1 - j_0(qd)]$

- Jump distance (d) = 3.94 Å (fixed), corresponding to the nearest H-H distance in $SrVO_2H$.
- Mean residence time τ = 1.2 ns (T = 330 K) and 0.2 ns (T = 430 K).

Localized dynamics in $SrVO_2H$

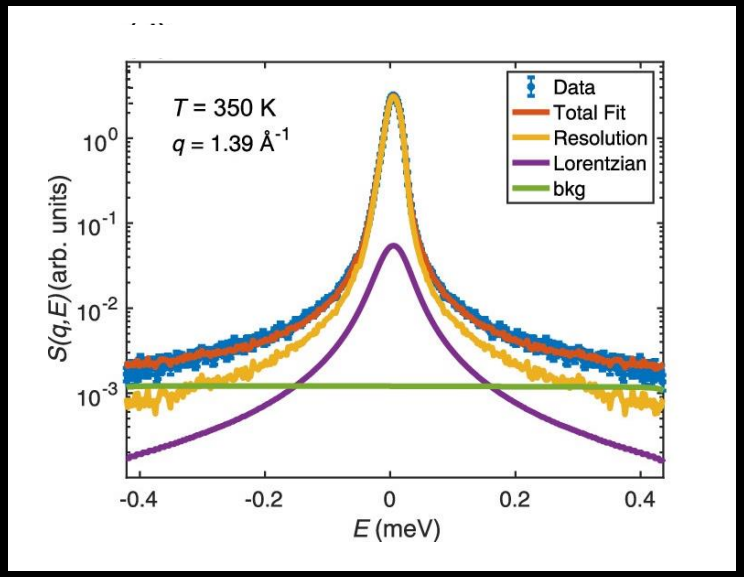
- OSIRIS@ISIS, measurable time-range $\tau \approx 1$ - 65 ps

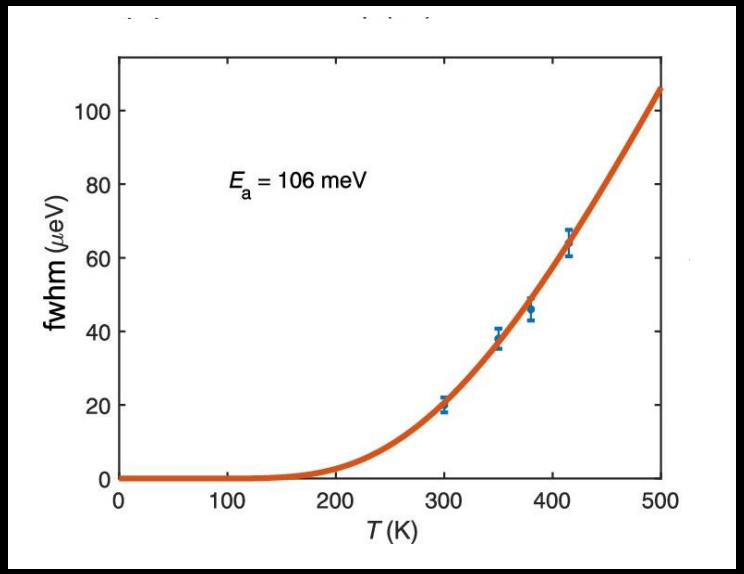
Quasielastic spectra summed over all q-values



- Quasielastic broadening/relaxational dynamics for T > 300 K
- Like the HFBS data, the quasielastic component can be described by one Lorentzian

Localized dynamics in $SrVO_2H$ (two-site jump diffusion model)



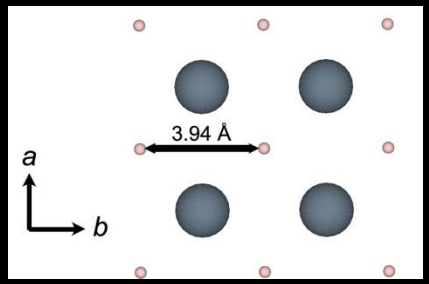


<u>Fitting function (assumption of jump dynamics between two sites)</u>

$$S(q,E) = Ae^{-\langle u^2\rangle q^2/3}[A_0(q)\delta(E) + (1 - A_0(q))L(E;\gamma)] \otimes R(q,E) + bkg(q,E)$$

EISF fixed to the expression for the two-site model with jump distance = 3.94 Å (H-H distance)

Sr-H (*ab*) plane in $SrVO_2H$

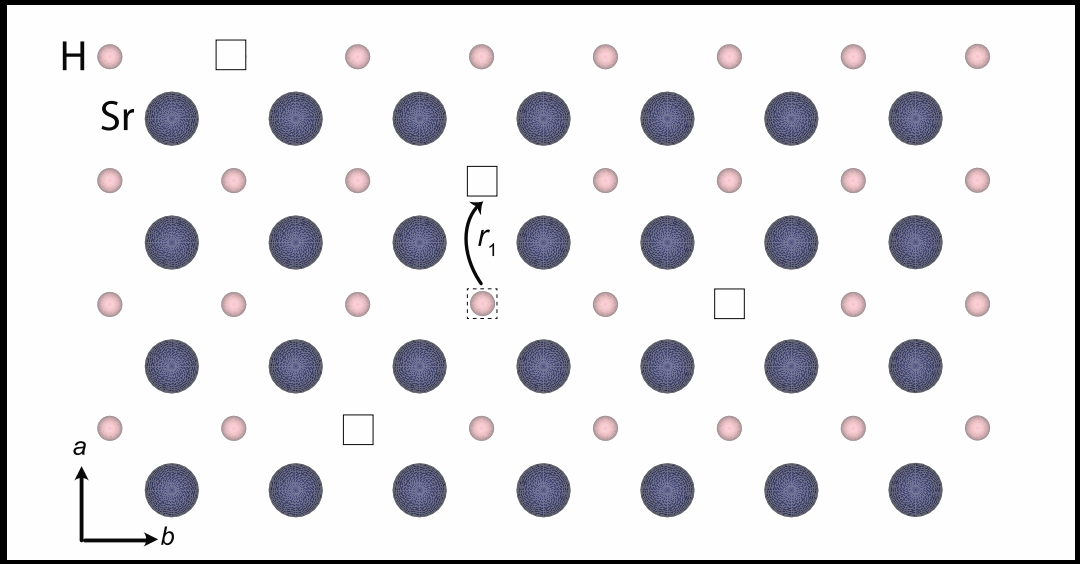


Sum up so far…

- Slow long-range diffusion of hydride ions in the Sr-H (*ab)*-plane of $SrVO_2H$
- Faster localized diffusion between two neighboring hydride-ion sites

Correlated diffusion mechanism

- The concentration of hydride-ion vacancies in $SrVO_2H$ is low.
- The probability for a backward jump should be higher than to jump in any other direction.
- The residence time for a backward jump would be relatively short and would be observable as a fast localized motion in the experiment. In agreement with the experimental results.



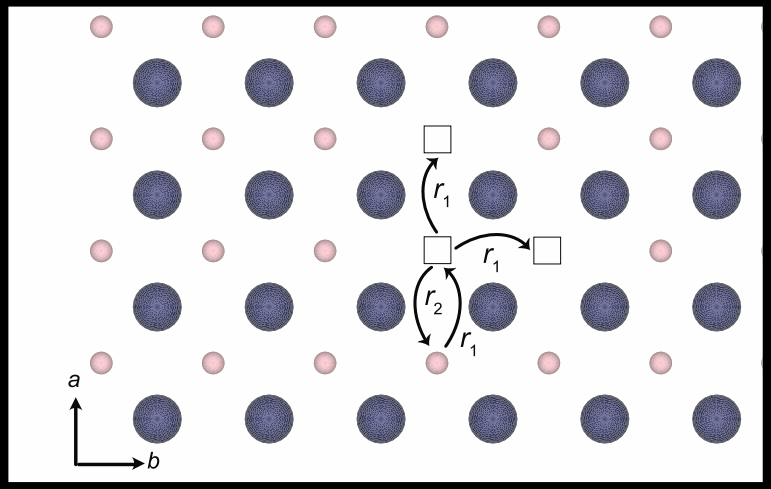
Comparison of the QENS data to the backward jump model on a 2D square lattice

References to the model

Haus and Kehr. *J. Phys. Chem. Solids* **40** (1979) 1019-1035

Haus and Kehr. *Phys. Rep.* **150** (1987) 263-406

- r_1 = rate for forward and sideways jumps
- r_2 = rate for backward jumps (> r_1)



S(q,E) can, for a 2D square lattice, be described by a sum of two Lorentzians; one diffusive and one localized

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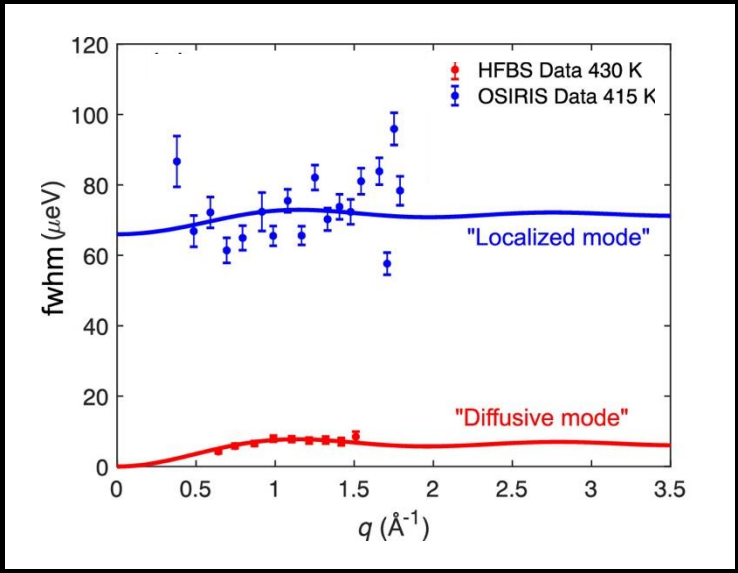
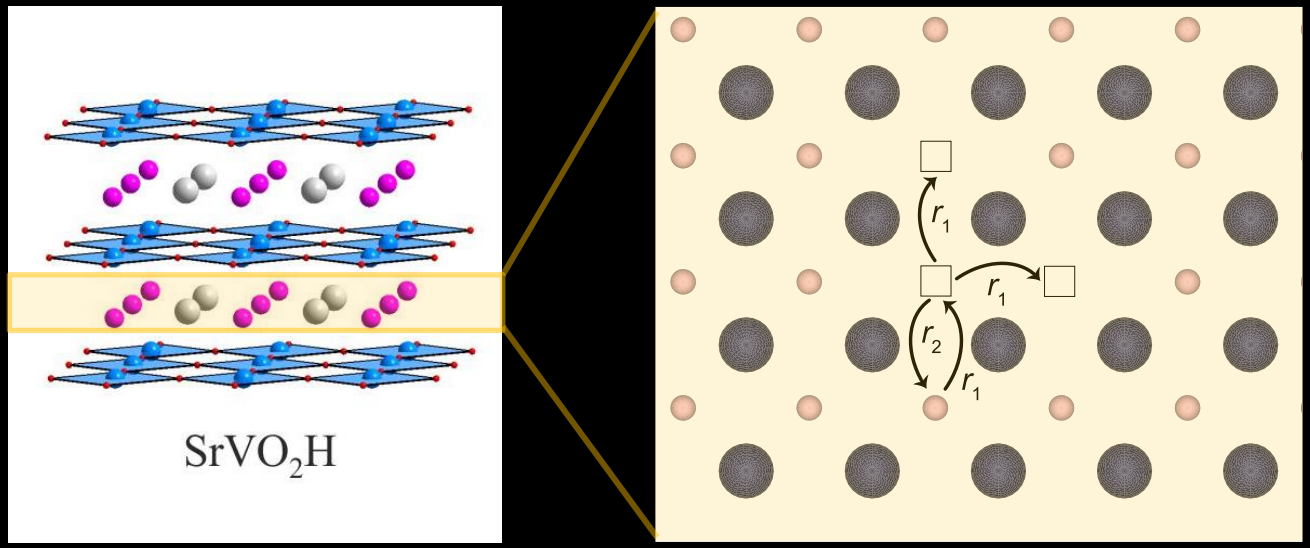


Excellent agreement between the experimentally determined quasielastic widths with the theoretically predicted ones from the backward jump diffusion model, with the jump rates $r_2 = 10 \cdot r_1$

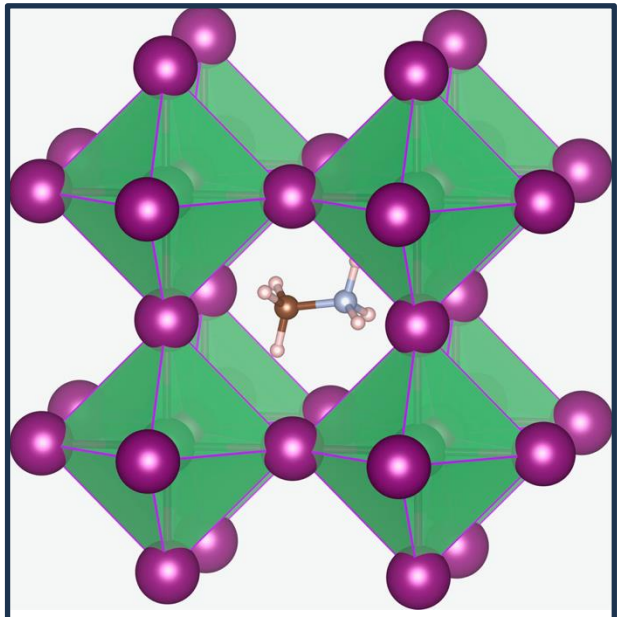
QENS reveals 2D correlated H^- diffusion mechanism

(R. Lavén *et al., Chem. Mater.* (2021))



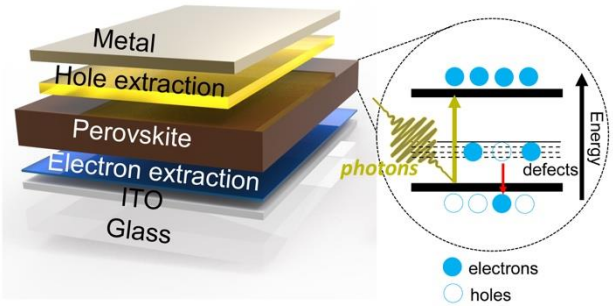
- Enhanced rate for backward jumps, compared a forward or sideway jump ($r_2 \approx 10r_1$)
- Vacancies are needed for diffusion. Is there any optimum vacancy concentration?

Halide perovskites



Crystal structure

- Perovskite structure ABX_3
- A = Organic cation, or Cs^+
- B = Metal ion (e.g. Pb^+, Sn^+)
- X = Halide ions (e.g. I^-, Br^-)



Underlying property & applications

- Photo-generation of electron-hole pairs (excitons).
- Absorber in solar cell, and phosphor in LEDs.

<u>Dynamics of the organic cations affect:</u>

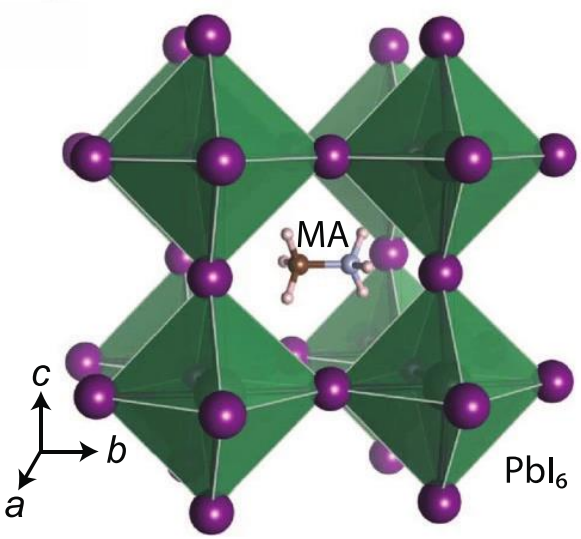
- Ferroelectric domains & surface ferroelectricity (Leguy *et al., Nat. Commun* ***6*** (2015))
- Exciton binding energy (*Chen et al., PCCP* **17** (2015))
- Hot carrier cooling (Guo *et al., Science* **356** (2017))
- Charge carrier recombination rates (Zhu *et al., JPCL* **6** (2015), *Ma et al., Nano Lett.* **15** (2015))

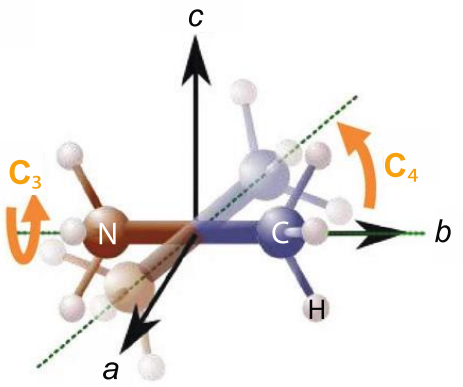
Organic cation (rotational) dynamics

Examples of results from QENS experiments

MA cation dynamics in $MAPbI_3$ (from QENS, probes dynamics on the 1-100 ps timescale)

- High-temperature (T > 330 K) cubic phase -> Fully isotropic MA cation rotations.
- Room-temperature tetragonal phase -> preferred C_4 rot. around the crystallographic *c*-axis.
- Low-temperature (T < 170 K) orthorhombic phase ->, C_3 rot. of CH_3/NH_3 around C-N axis.



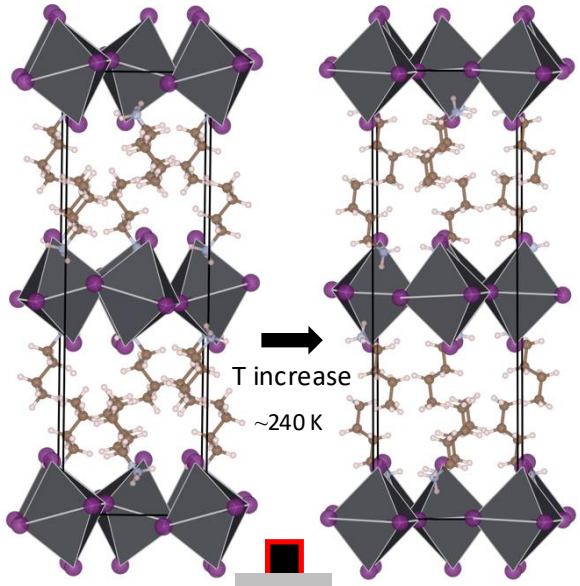


Leguy *et al., Nat. Commun.* **6** (2015)

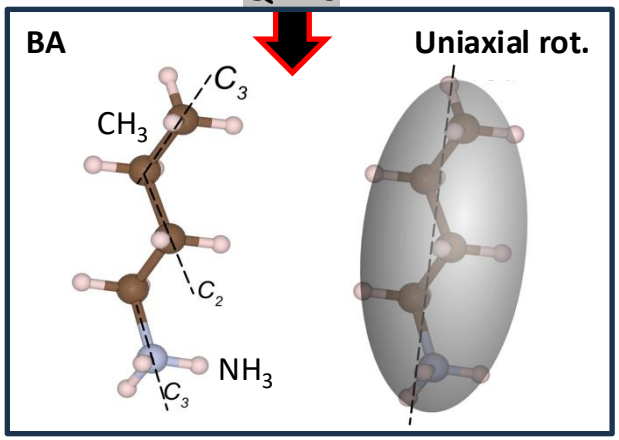
Organic cation dynamics in layered structures

(R. Lavén, M. Karlsson *et al., J. Phys. Chem. Lett* (2025)

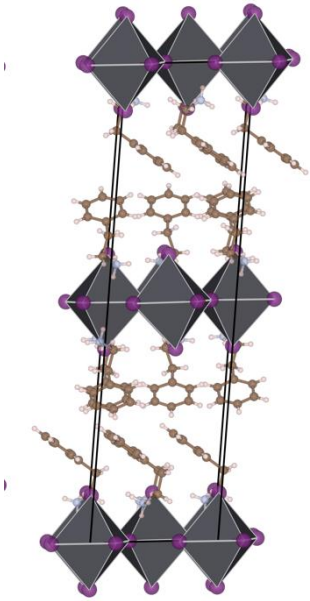
BA_2PbI_4 (BA = $CH_3(CH_2)_3NH_3$)

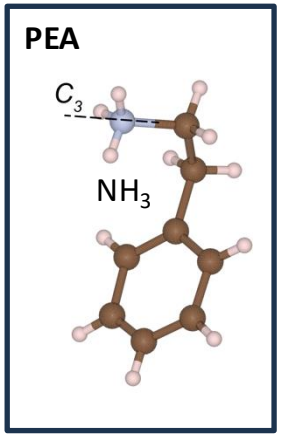


QENS



PEA_2PbI_4 (PEA = $C_6H_5(CH_2)_2NH_3$)





<u>Correlation to optical properties</u>:

The longer carrier lifetimes, and faster diffusion and longer exciton diffusion lengths in PEA_2PbI_4 may relate to its more restricted dynamics. (Seitz *et al., Nat. Comm.* (2020))

More restricted dynamics for PEA_2PbI_4

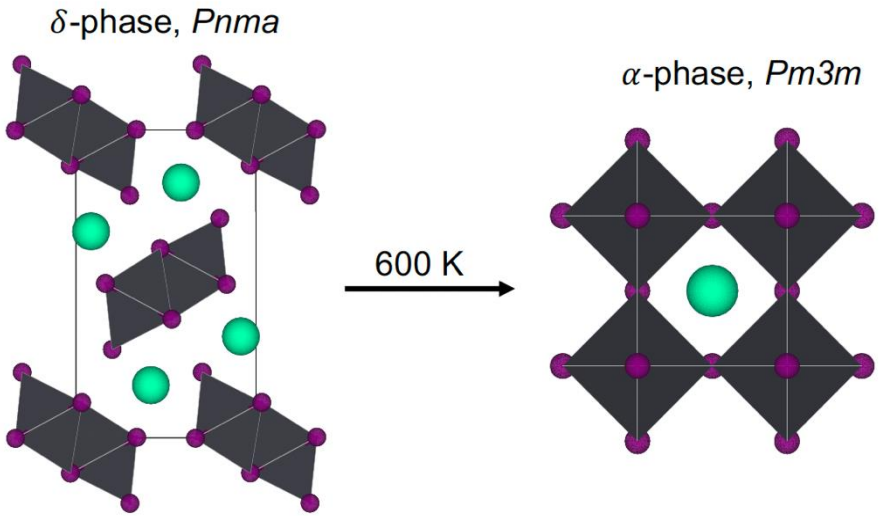
Vibrational dynamics in halide perovskites

- Overdamped* phonons related to octahedral tilting modes have been correlated with the unique optical properties of these materials (T. Lanigan-Atkins *et al. Nature Mater.* (2021))
- Also plays a central role in displacive phase transitions

**The lifetime of the vibration is shorter than the time for one oscillation*

Vibrational dynamics and all-inorganic $CsPbI_3$

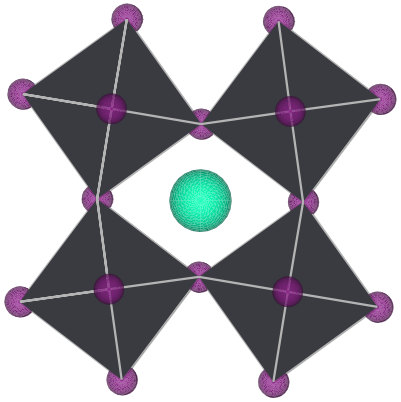
All-inorganic $CsPbI_3$ (INS study on FOCUS@PSI)



Irreversibility

The α-phase may transform to tetragonal (β-phase, T ≈ 550 K) and orthorhombic (γ-phase, T ≈ 450 K). (M. Liao *et al., J. Phys. Chem. Lett* (2019)).

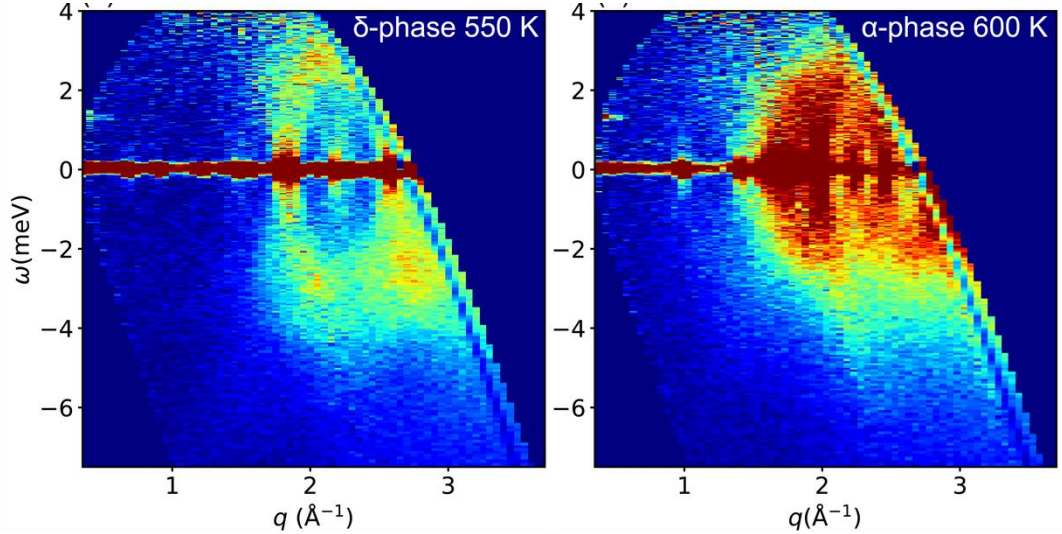
The nature of octahedral tilting motions and their correlation with structural and optical properties are unclear



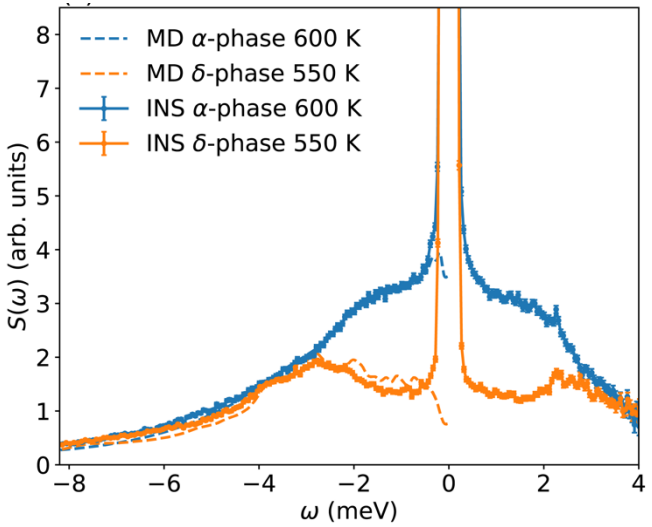
Dynamical structure factor for $CsPbI_3$

(R. Lavén, M. Karlsson *et al., J. Phys. Chem. Lett* (2025))

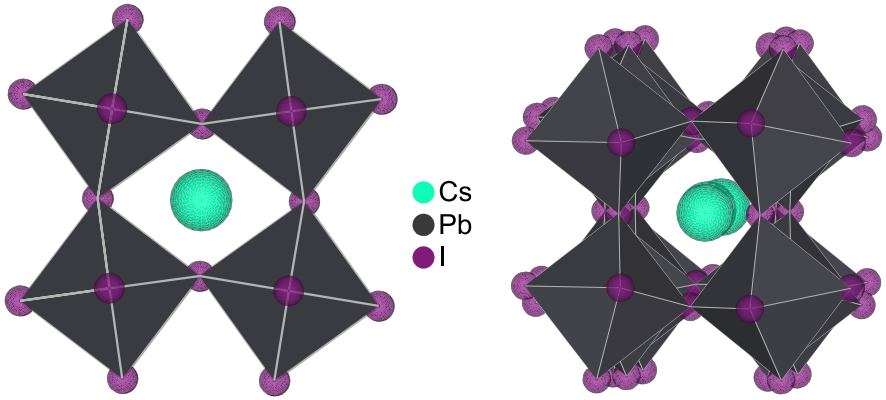
Experimental $S(q, \omega)$ – data from the FOCUS spectrometer at the Paul-Scherrer Institute



q-integrated $S(q, \omega)$ – Experiment *vs.* calculations

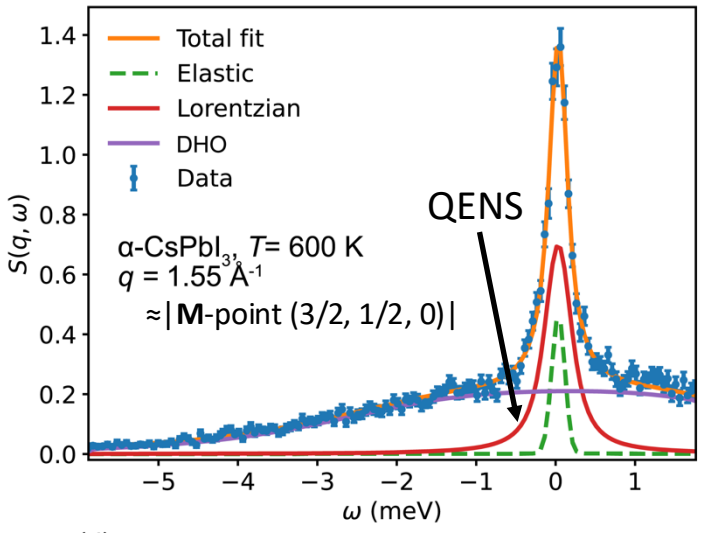


Overdamped octahedral tilting modes



M-point mode (in phase) **R-point mode (out of phase)**

Dynamical structure factor



Results and conclusions

- The overdamped octahedral tilting motions relate to the cubic-tetragonal ($\alpha-\beta$) and tetragonal-orthorhombic ($\beta-\gamma$) phase transition at 550 K and 450 K.
- Timescale of the dynamics ≈ 2-4 ps, suggesting structural fluctuations to these lower symmetry structures on this timescale.
- May explain the discrepancy in the literature between the average cubic structure (diffraction) and local, non-cubic structure (total scattering and x-ray absorption spectroscopy)

Concluding remarks

- Neutron spectroscopy is a powerful technique for studies of dynamics, and has played an important role in the study of many energy-related perovskite materials
- Information about diffusional dynamics of ions (localized and long-range), molecular reorientations, vibrational dynamics can be obtained.
- Very complementary to several other techniques, such as NMR, IR/Raman, computer simulations etc.

Main drawbacks

- Need for large samples and long measuring times.
- QENS data analysis can be challenging, and even very small amounts of impurities may severely affect the measured data.

Not all single-crystal samples are this big….

References

<u>Some useful references related to the presented work:</u>

Neutron spectroscopy on proton and hydride-ion conducting perovskite oxides:

M. Karlsson, PCCP (2015)
D. Noferini, J. Mater. Chem. A (2018)
R. Lavén, Chem. Mater. (2021)

Neutron spectroscopy on halide perovskites:

R. Lavén et al., *J. Phys. Chem. Lett.* **14** (2023) 2784-2791.
R. Lavén et al., *J. Phys. Chem. Lett.* **16** (2025) 10282-10290.
R. Lavén et al., *J. Phys. Chem. Lett.* **16** (2025) 4812-4818.

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Thanks!