

**Advanced school – French-Swedish Academy for
Scattering Experiments & Modeling
@ Institut Laue-Langevin, March 19, 2026**

Neutron spectroscopy studies of perovskites for energy applications

MATHS KARLSSON
DEPT. OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden

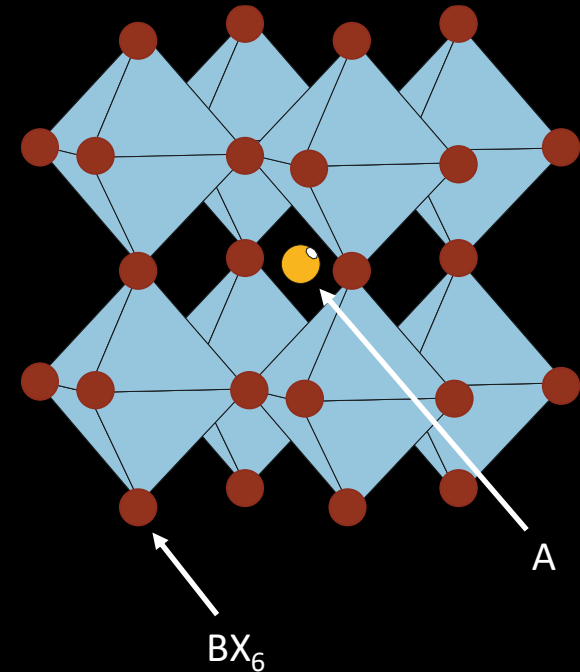
Perovskites for energy applications

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)

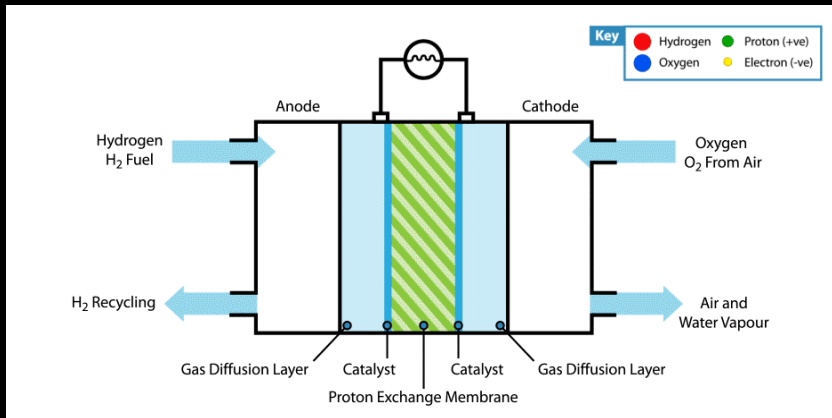
The ability to host a variety of different ions, make the materials highly tuneable in terms of their "functional" properties:

- 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

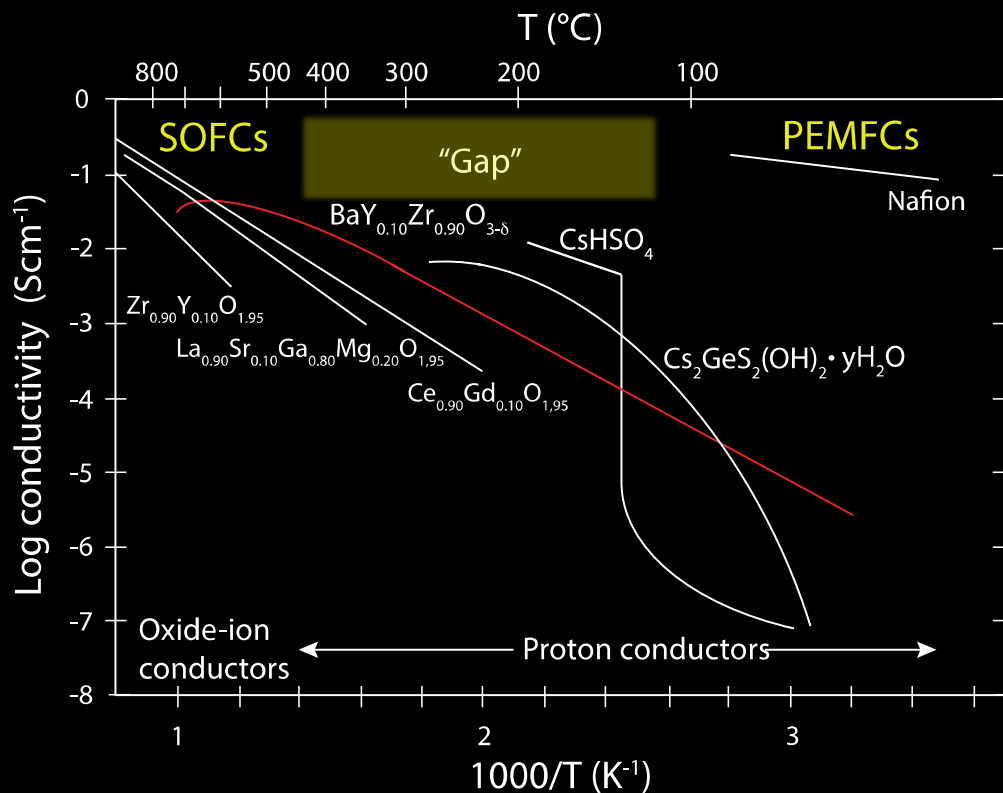
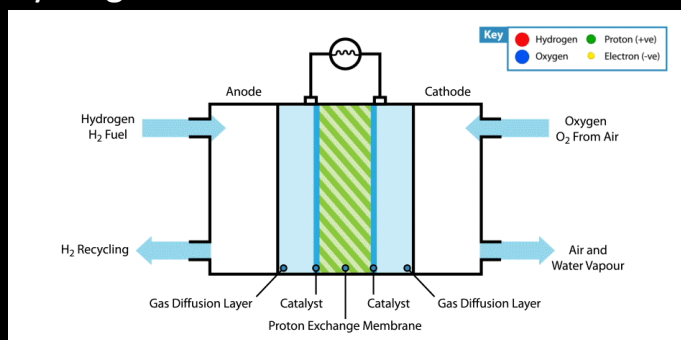
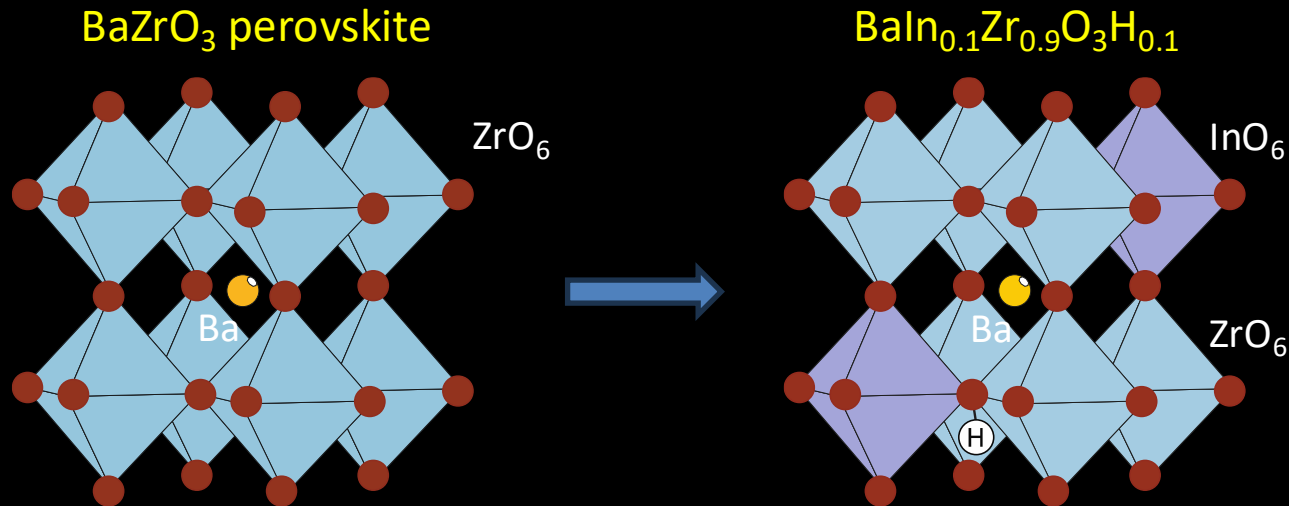


Figure taken from: M. Karlsson, *Dalton Trans.* (2013)

Proton conducting perovskite oxides

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

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



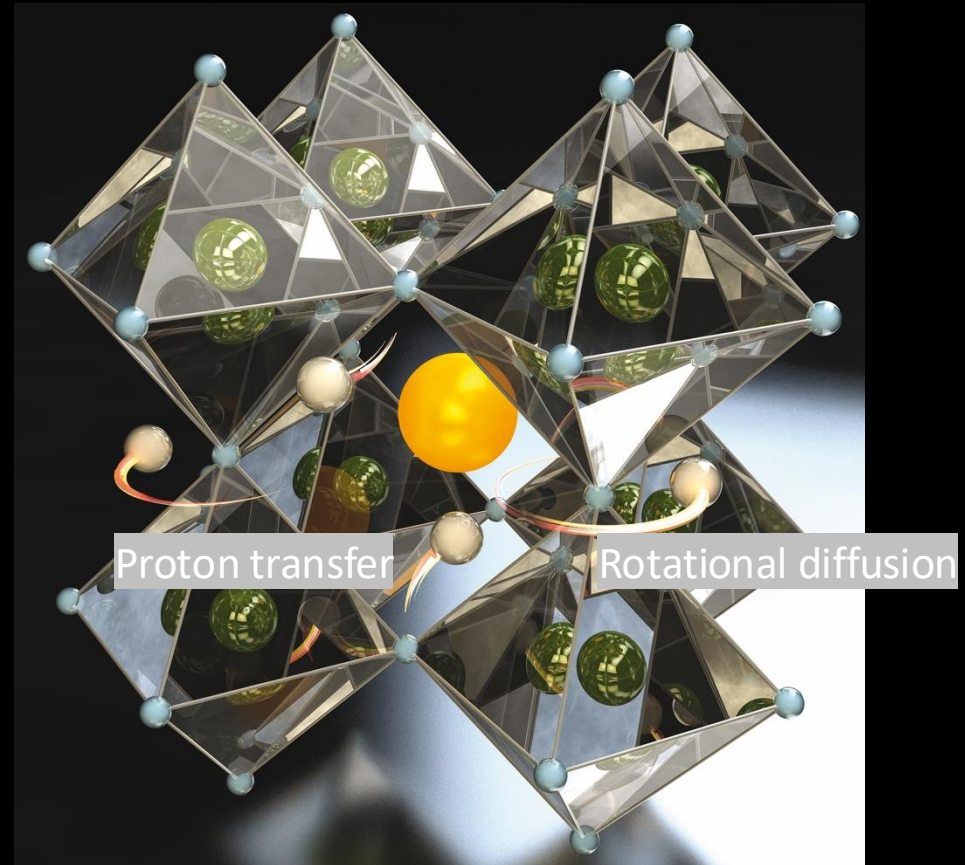
Proton conduction mechanism?

Proton dynamics

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

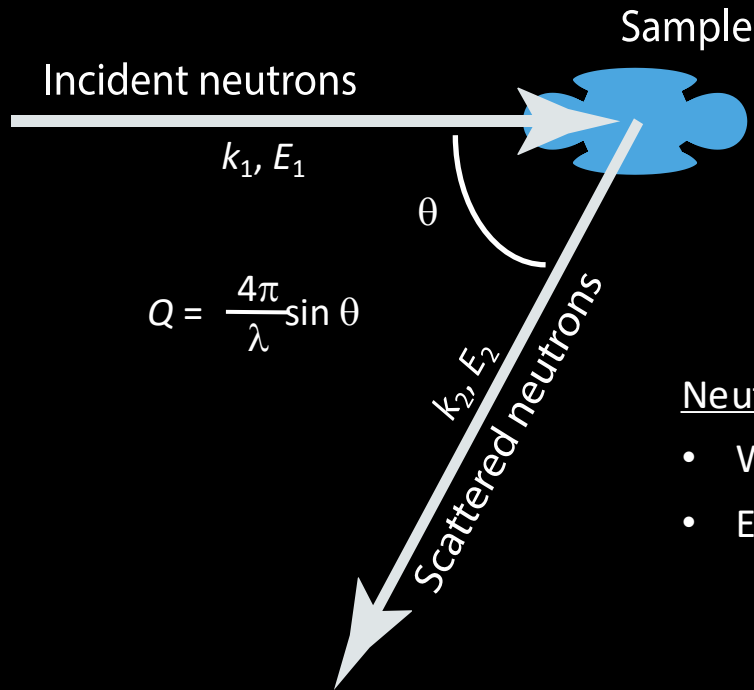
Local chemistry and structure complicates the description.... Some open questions:

- 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 $\tau \approx 1\text{--}1000$ ps.
- Very sensitive to hydrogen (very large incoherent scattering cross section)

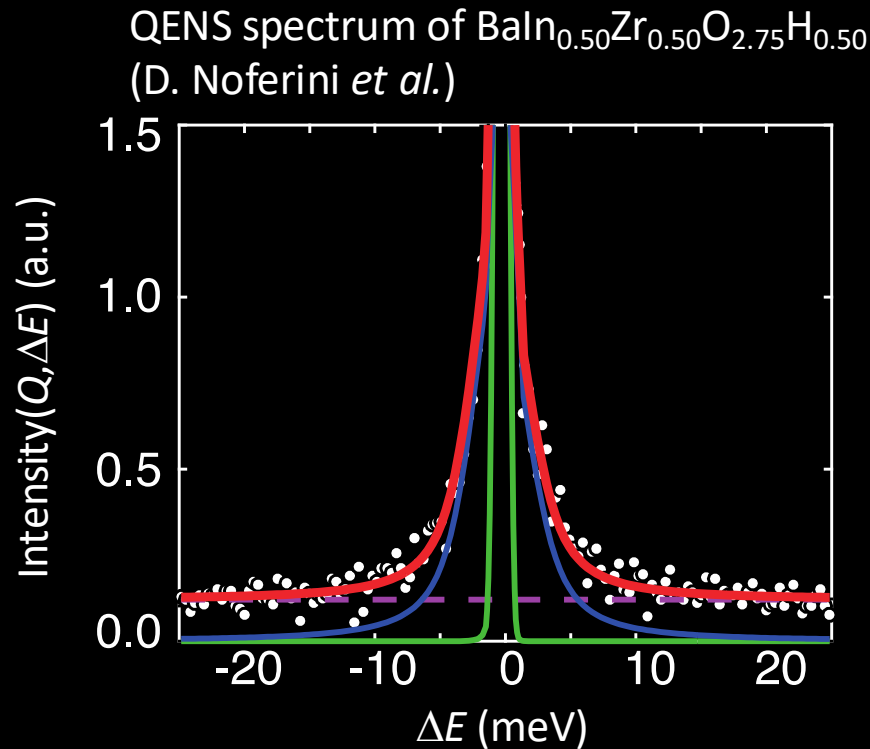


Neutrons for scattering experiments:

- Wavelength: $1\text{--}10$ Å (-> interference -> structure)
- Energy: $10\text{--}100$ meV (-> energy exchange -> dynamics)

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

Quasielastic neutron scattering (QENS)



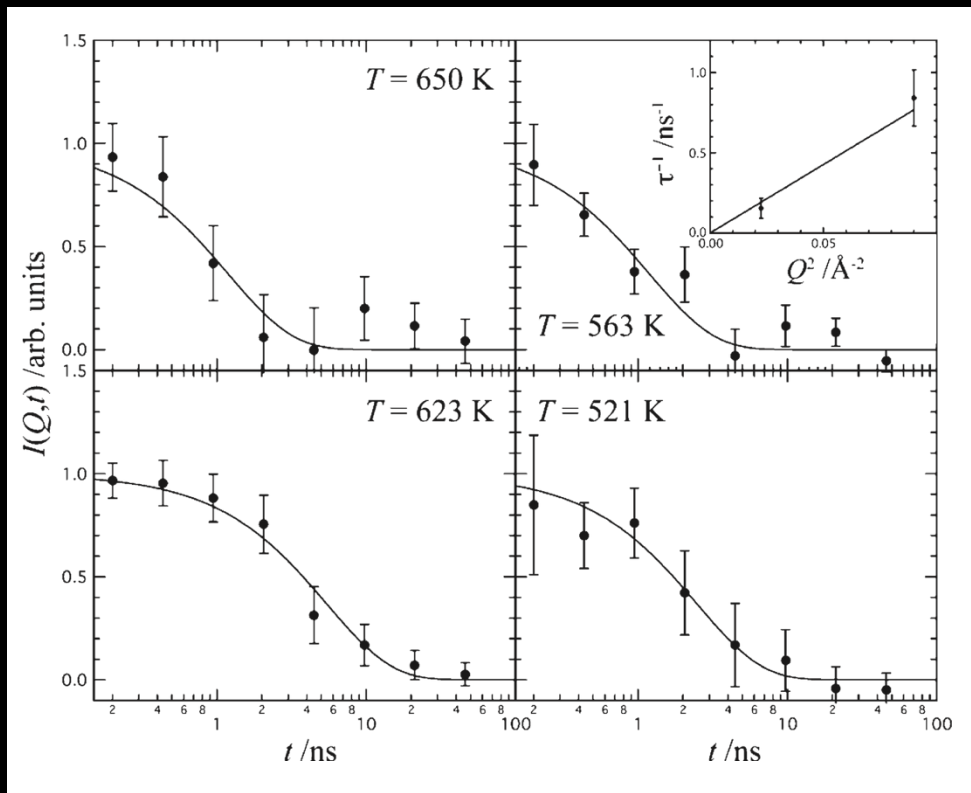
Dynamics manifested by the slight “quasielastic” broadening (blue line)

– Analysis gives information about timescale, activation energy, and spatial geometry

Neutron spin-echo (NSE)

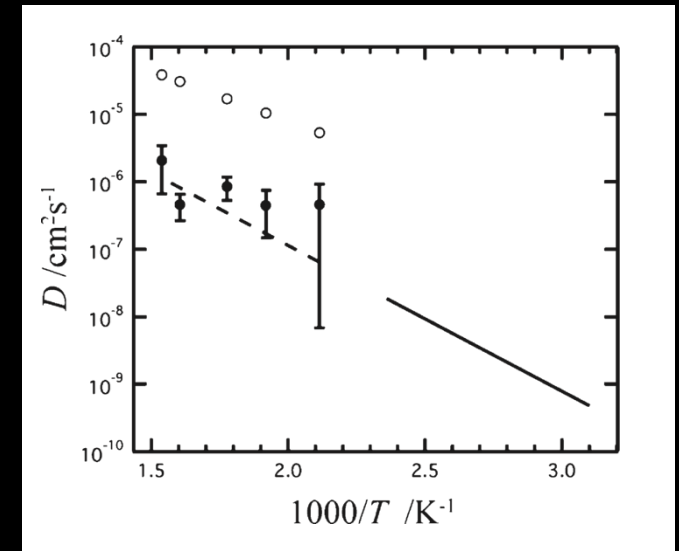
- Probes longer timescales. Intermediate scattering function, $I(Q,t)$, rather than the dynamical structure factor, $S(Q,\omega)$, is probed.

NSE data of Y-doped BaZrO₃ at $Q = 0.2 \text{ \AA}^{-1}$ (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 $\approx 20 \text{ \AA}$


Some very recent results on proton conductivity in heavily Sc-doped barium stannate ($\text{BaSn}_{1-x}\text{Sc}_x\text{O}_3$, $x = 0.7$)

nature materials 

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

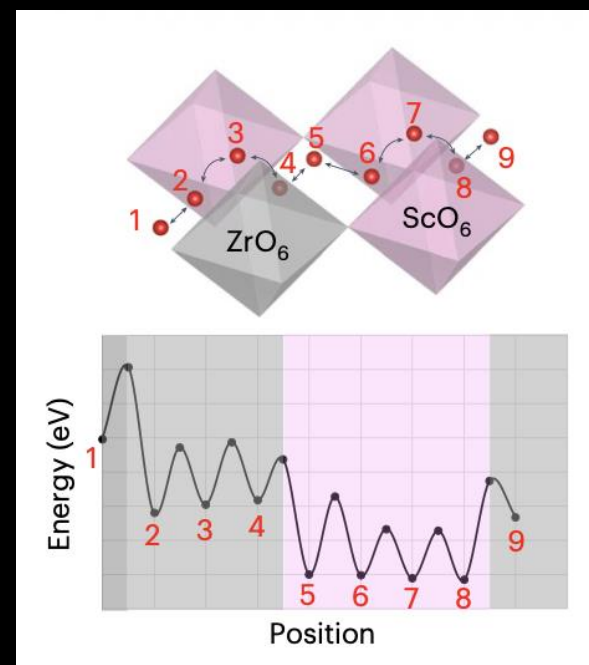
Mitigating proton trapping in cubic perovskite oxides via ScO_6 octahedral networks

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 Takahashi⁷, Yuto Tomita⁸, Nai Shi¹, Yasukazu Murakami⁸, Shusuke Kasamatsu⁹ & 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 ($\text{BaSn}_{1-x}\text{Sc}_x\text{O}_3$, $x = 0.7$)

nature materials 

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

Mitigating proton trapping in cubic perovskite oxides via ScO_6 octahedral networks

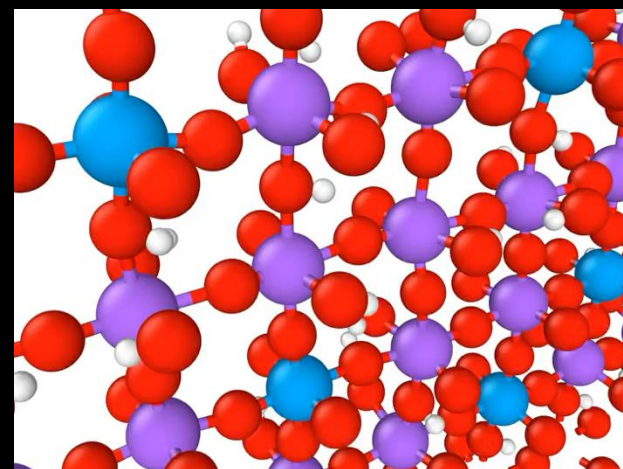
Received: 21 November 2023
Accepted: 3 July 2025
Published online: 08 August 2025

 Check for updates

Kota Tsujikawa^{1,2,3}, Junji Hyodo^{1,2,4}, Susumu Fujii^{1,3,5,6}, Kazuki Takahashi⁷, Yuto Tomita⁸, Nai Shi¹, Yasukazu Murakami⁹, Shusuke Kasamatsu⁹ & Yoshihiro Yamazaki^{1,2,3} ✉

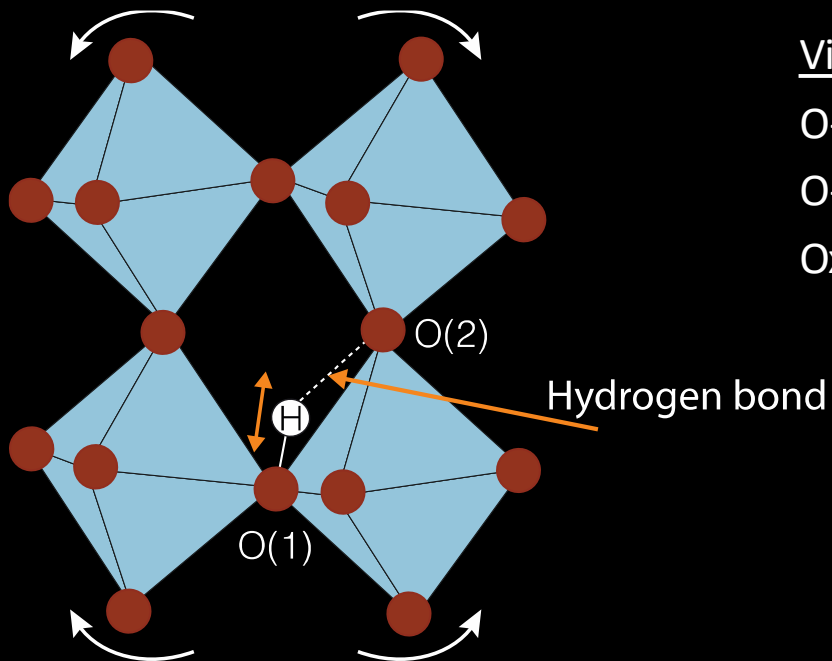
Advances in electrochemical devices have been primarily driven by the discovery and development of electrolyte materials. Yet the development

MD simulation of $\text{BaSn}_{0.3}\text{Sc}_{0.7}\text{O}_{3-\delta}$



- 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:

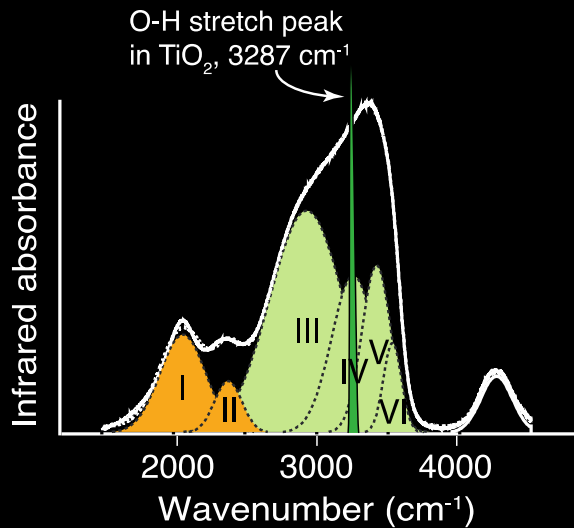
O-H stretch vibrations, $\nu(\text{O-H})$

O-H bend vibrations, $\delta(\text{O-H})$

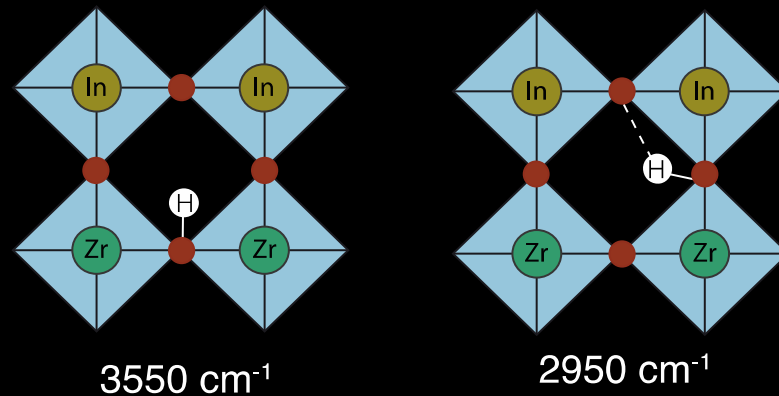
Oxygen (perovskite host lattice) vibrations

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 BaZrO₃

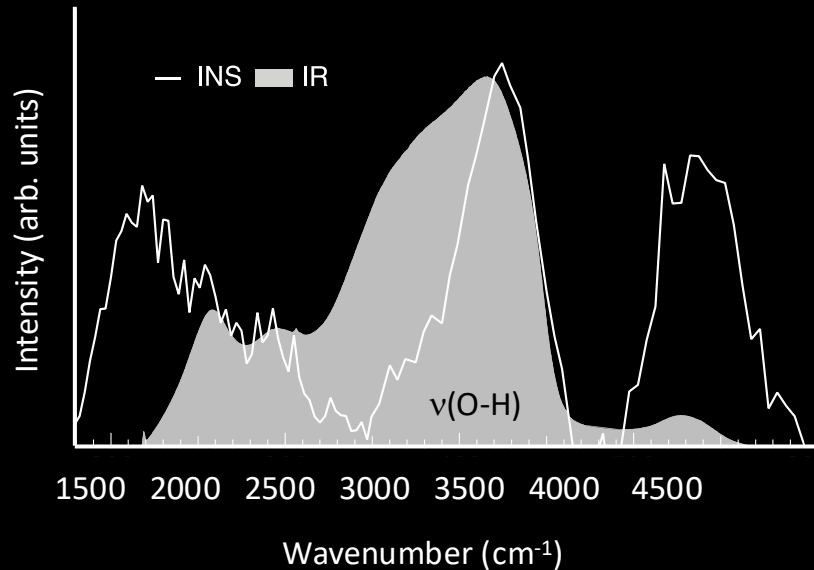


O-H stretch frequencies from *ab-initio* simulations, for various local proton structures (Mazzei *et al.*, *J. Mater. Chem. A*, 2019)



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 $\approx 3000 \text{ cm}^{-1}$ 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

nature materials LETTERS
PUBLISHED ONLINE: 15 APRIL 2012 | DOI: 10.1038/NMAT3302

An oxyhydride of BaTiO₃ exhibiting hydride exchange and electronic conductivity

Yoji Kobayashi¹, Olivier J. Hernandez², Tatsunori Sakaguchi¹, Takeshi Yajima¹, Thierry Roisnel², Yoshihiro Tsujimoto¹, Masaki Morita³, Yasuto Noda³, Yuuki Mogami³, Atsushi Kitada⁴, Masatoshi Ohkura¹, Saburo Hosokawa¹, Zhaofei Li⁴, Katsuro Havashi⁵, Yoshihiro Kusano⁶

SCIENCE AND TECHNOLOGY OF ADVANCED MATERIALS, 2017
VOL. 18, NO. 1, 905–918
<https://doi.org/10.1080/14686996.2017.1394776>

Taylor & Francis
Taylor & Francis Group

FOCUS ISSUE REVIEW

New chemistry of transition metal oxyhydrides

Yoji Kobayashi¹, Olivier Hernandez², Cédric Tassel³ and Hiroshi Kageyama^{1,5}

¹Department of Energy & Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan; email: kage@sd.kyoto-u.ac.jp
²Solid State Chemistry and Materials Group, Institute of Chemical Sciences, Centre for Catalysis, Ecole Normale Supérieure de Lyon, 69622 Villeurbanne, France

OPEN ACCESS Check for updates

ABSTRACT

In this review we describe recent advances in transition metal oxyhydride synthesis via topochemical routes, such as low temperature reduction with solid-state reactions. Besides the crystal chemistry, magnetic bulk powder and epitaxial thin film samples, the remarkable properties of these materials, particularly highlighted as a new strategy to discover unexpected

RESEARCH | REPORTS

Pure H⁻ conduction in oxyhydrides

Genki Kobayashi,^{1,2*} Yoyo Hinuma,³ Shinji Matsuoka,⁴ Akihiro Watanabe,^{1,4} Muhammad Iqbal,⁵ Masaaki Hirayama,⁶ Masao Yonemura,⁷ Takashi Kamiyama,⁸ Isao Tanaka,⁹ Kyōji Kanno^{5*}

A variety of proton (H⁺)-conducting oxides are known, including those used in electrochemical devices such as fuel cells. In contrast, pure H⁻ conduction, not mixed with electron conduction, has not been demonstrated for oxide-based materials. Considering that hydride ions have an ionic size appropriate for fast transport and also a strong reducing ability suitable for high-energy storage and conversion devices, we prepared a series of K₂NiF₄-type oxyhydrides, La_{2-x}Sr_xLiH_{1-x+y}O_{3-y}, in the hope of observing such H⁻ conductors. The performance of an all-solid-state TH₂/o-La₂LiH_{0.2}O_{2.8} (x = y = 0, *o*: orthorhombic)/Ti cell provided conclusive evidence of pure H⁻ conduction.

Electronic conduction is generally classified into two categories, electronic and ionic, which (mayenite structure) (20–22). However, none of these displays pure H⁻ conductivity.

were prepared under the same conditions as outlined for o-La₂LiH_{0.2}O_{2.8}. Regarding the Sr-substituted series of La_{2-y}Sr_yLiH_{1-y}O_{3-y}, the diffraction peaks continuously shifted to lower angles with increasing *y* (Fig. 1B) and the lattice symmetry changed from *I*mmn (*y* < 1) to *I*hmmn (*y* ≥ 1) (Fig. 1C). The compositions and structures of La_{2-y}Sr_yLiH_{1-y}O_{3-y} (*y* = 0, 1, 2) were determined by x-ray and neutron Rietveld analyses. Details of the analyses are given in Figs. S2 and S3, in tables S2 and S3, and in the supplementary text. In La₂LiH_{0.2}O_{2.8}, the two apical sites of the LiX₆ octahedra are occupied only by O²⁻, as illustrated schematically in Fig. 2, whereas the four in-plane apices are occupied by O²⁻ and H⁻. These results indicate that the highly charged cations (i.e., La³⁺ and Sr²⁺) require highly charged anions around them. LaSrLiH_{0.5}O_{2.5} is composed of tetragonal (LiH₂)²⁻ and (LaSrO₂)⁴⁺ layers alternately stacked along the *c* axis. The further increase in hydride content up to Sr₂LiH₂O results in the formation

Angewandte International Edition Chemie

GDCh

Transition-Metal Hydrides

LaSr₃NiRuO₄H₄: A 4d Transition-Metal Oxide–Hydride Containing Metal Hydride Sheets

Lun Jin, Michael Lane, Dihao Zeng, Franziska K. K. Kirschner, Franz Lang, Pascal Manuel, Stephen J. Blundell, John E. McGrady, and Michael A. Hayward*

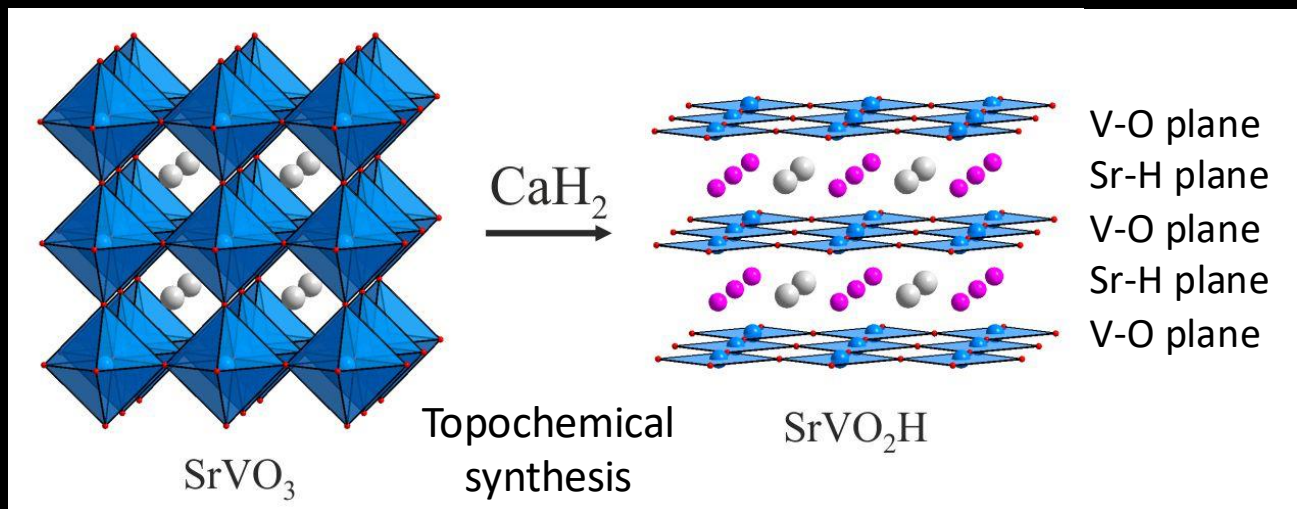
Yoji Kobayashi,^{1,2} Yoshihiro Tsujimoto,^{3,4} and Hiroshi Kageyama^{1,5}

¹Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan; email: kage@sd.kyoto-u.ac.jp

Strontium vanadium oxyhydride, SrVO₂H

(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 SrVO₂H

Instruments

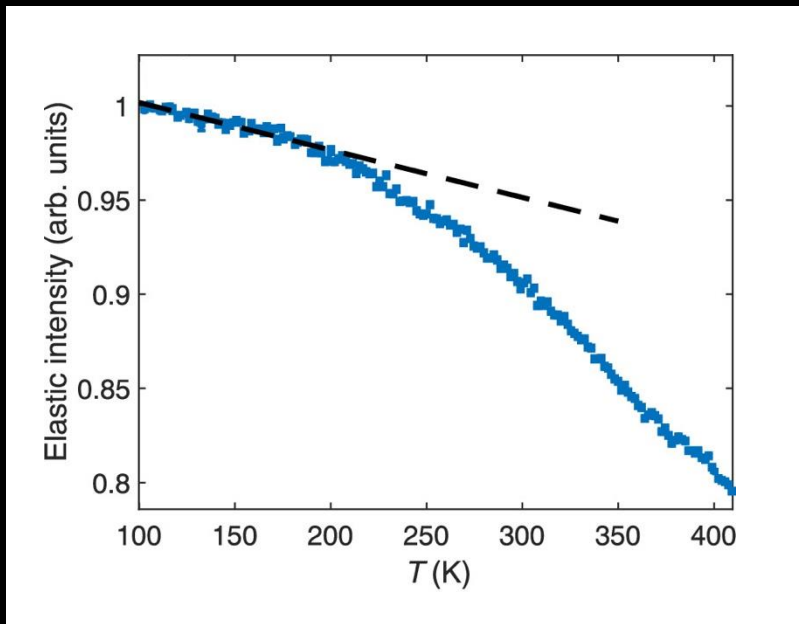
- High-flux backscattering spectrometer (HFBS) at NIST
- Disc chopper spectrometer (DCS) at NIST
- Time-of-flight near-backscattering spectrometer (OSIRIS) at ISIS

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 SrVO₂H

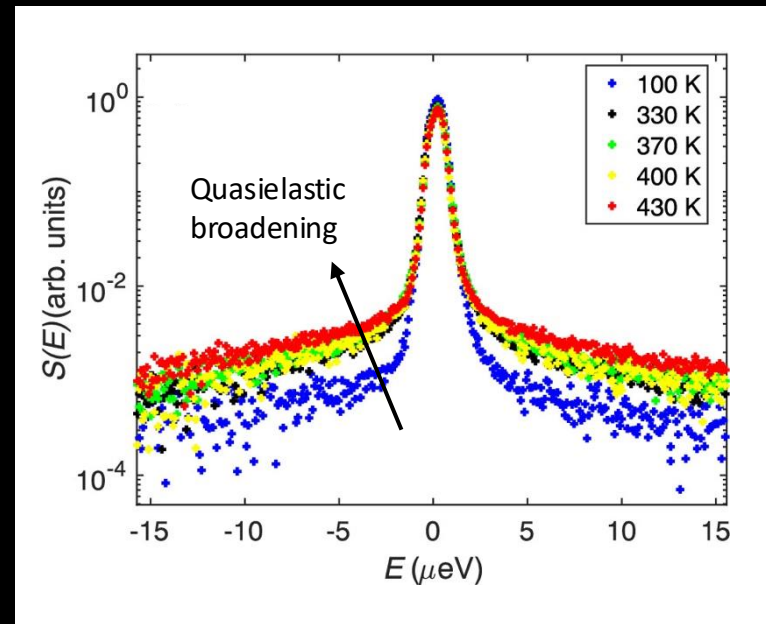
- HFBS@NIST, measurable time-range $\tau \approx 100$ ps – 3 ns

Elastic intensity from 100 to 415 K



- Harmonic vibrations below $T \approx 200$ K
- Relaxational dynamics for $T > 200$ K

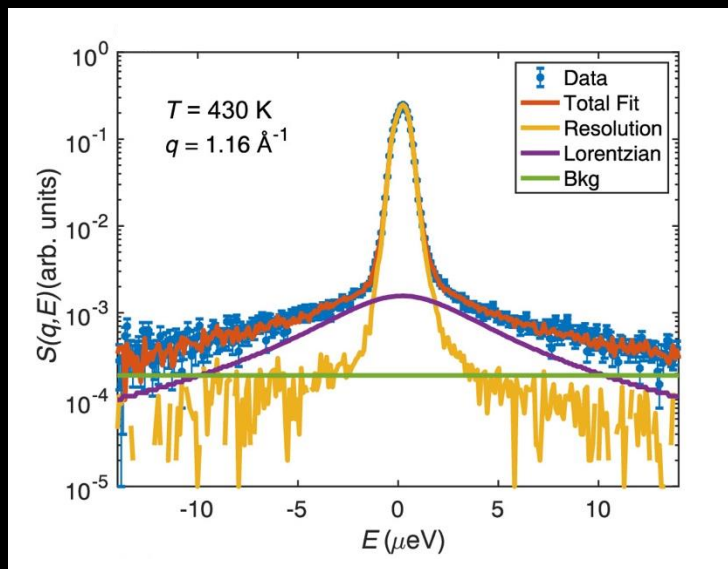
QENS spectra summed over the q-range of $0.6 - 1.6 \text{ \AA}^{-1}$



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

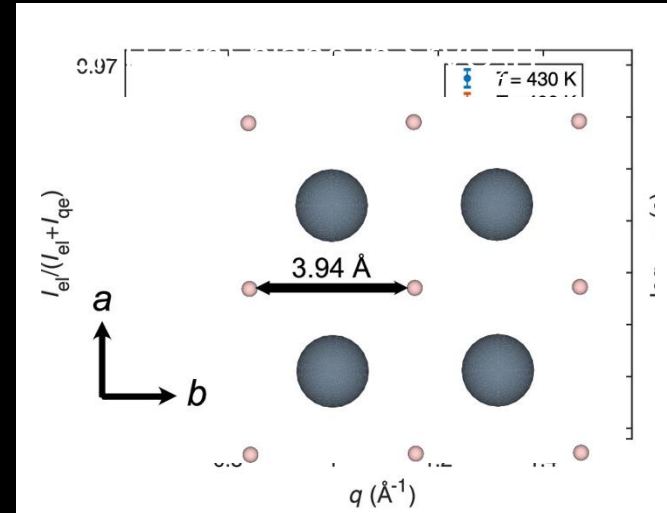
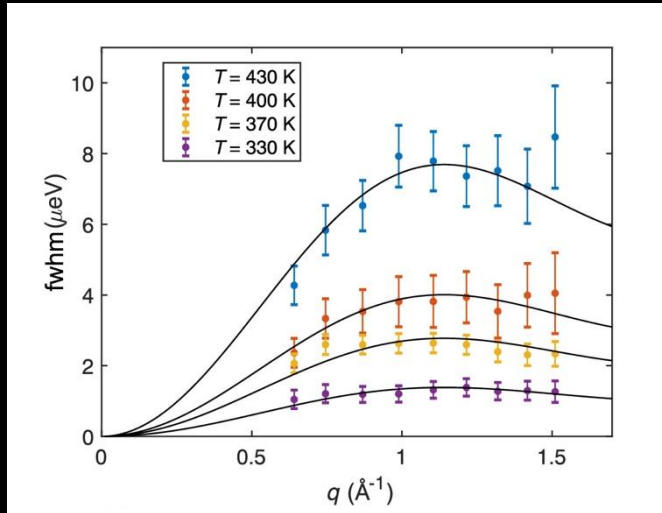
Long-range dynamics in SrVO₂H

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



Long-range dynamics in SrVO₂H

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

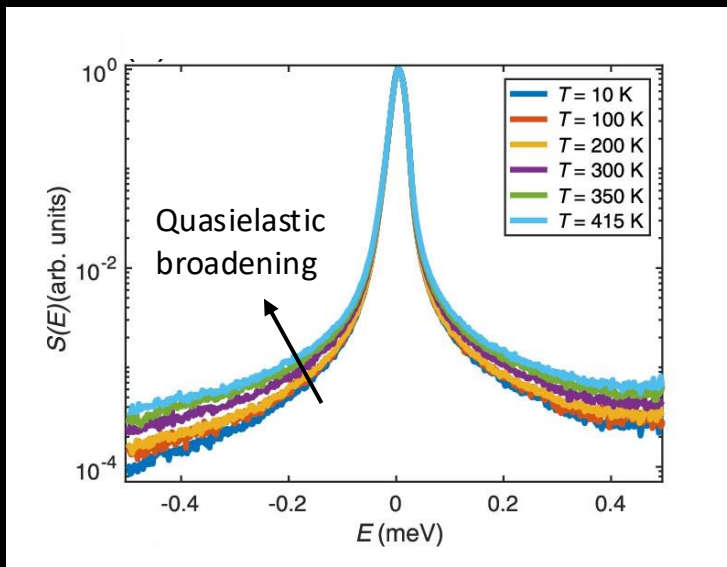


- Chudley-Elliott model of jump diffusion:
$$\text{fwhm} = \frac{2\hbar}{\tau} [1 - j_0(qd)]$$
- Jump distance (d) = 3.94 \AA (fixed), corresponding to the nearest H-H distance in SrVO₂H.
- Mean residence time $\tau = 1.2\text{ ns}$ ($T = 330\text{ K}$) and 0.2 ns ($T = 430\text{ K}$).

Localized dynamics in SrVO₂H

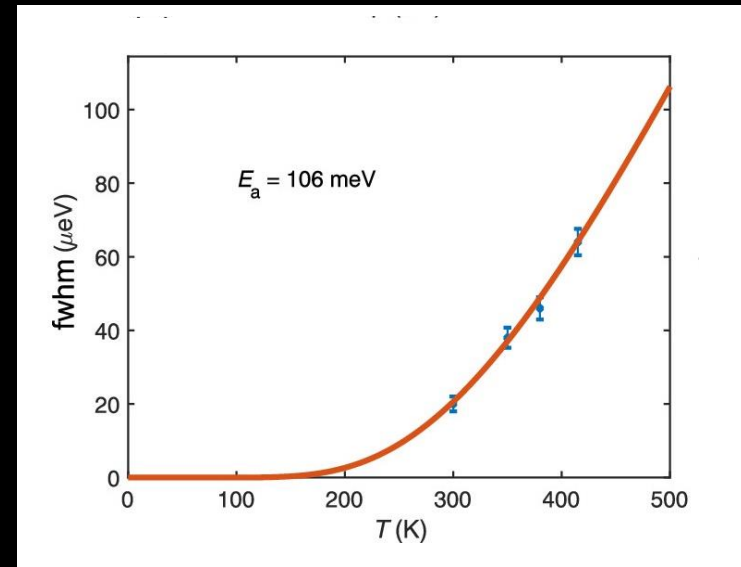
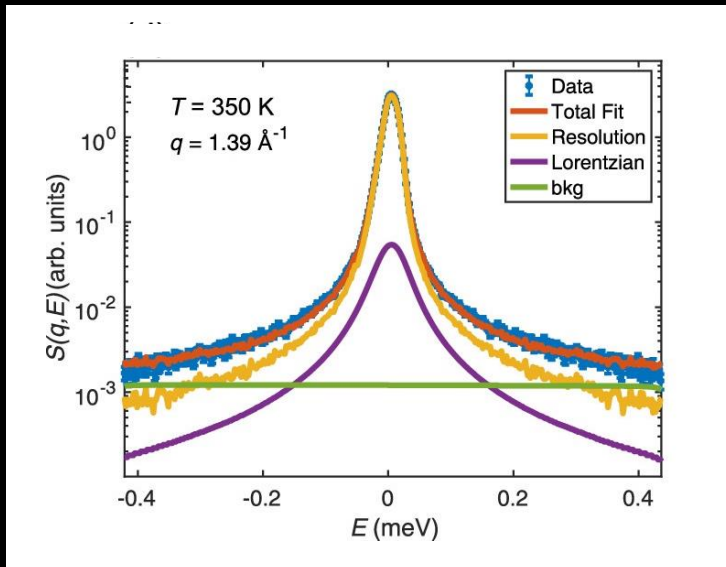
- OSIRIS@ISIS, measurable time-range $\tau \approx 1 - 65$ ps

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 SrVO₂H (two-site jump diffusion model)



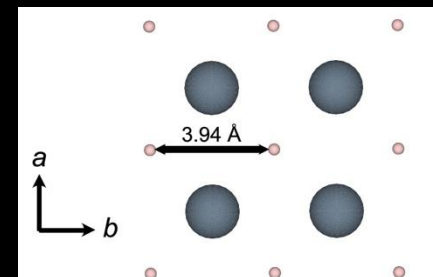
Fitting function (assumption of jump dynamics between two sites)

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



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

Sr-H (*ab*) plane in SrVO₂H

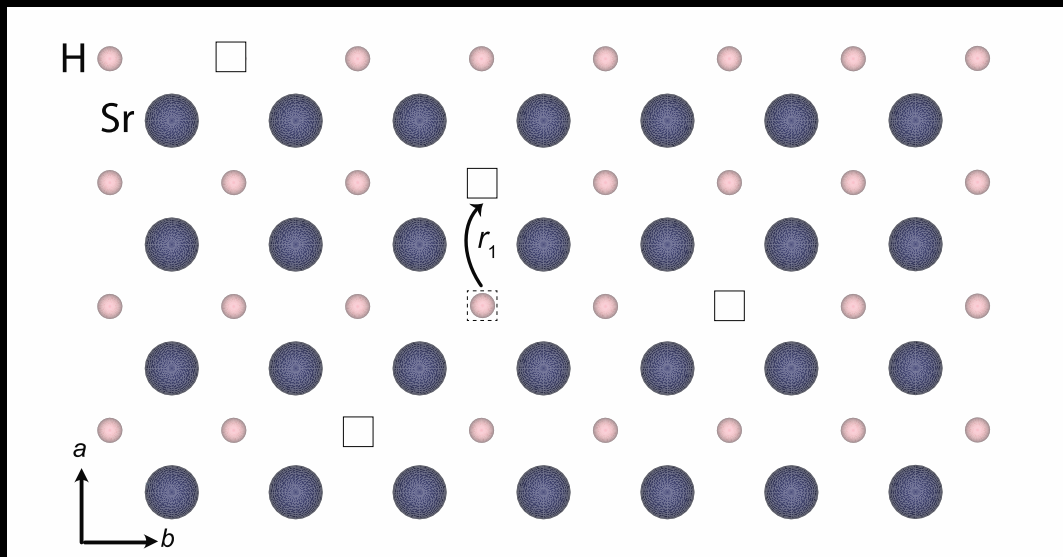


Sum up so far...

- Slow long-range diffusion of hydride ions in the Sr-H (*ab*)-plane of SrVO₂H
- Faster localized diffusion between two neighboring hydride-ion sites

Correlated diffusion mechanism

- The concentration of hydride-ion vacancies in SrVO₂H 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.



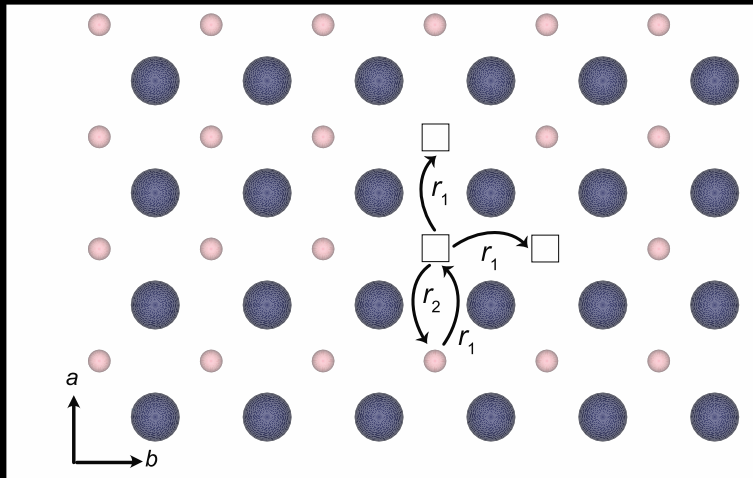
Comparison of the QENS data to the backward jump model on a 2D square lattice

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 ($> r_1$)



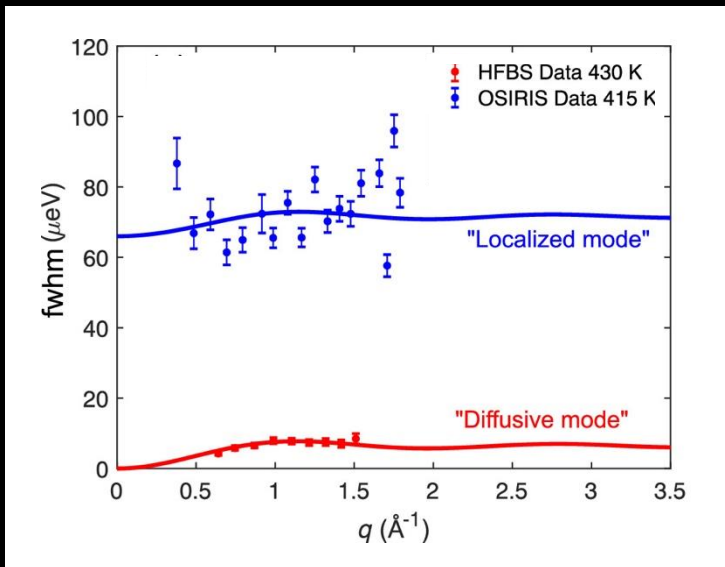
$S(q,E)$ can, for a 2D square lattice, be described by a sum of two Lorentzians; one diffusive and one localized

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

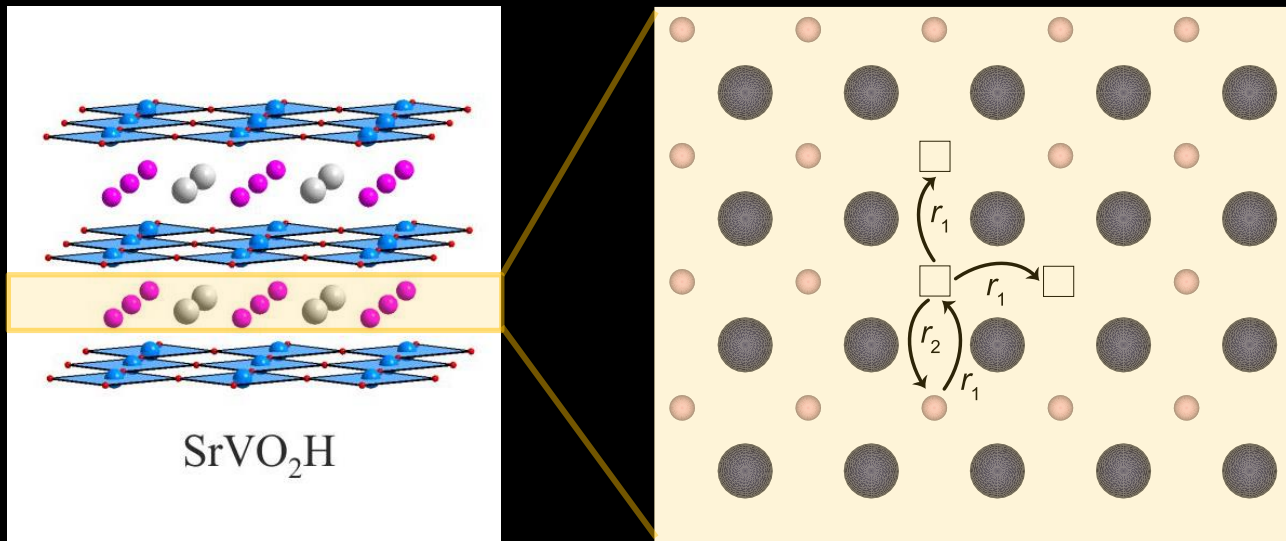
Haus and Kehr. *Phys. Rep.* **150** (1987) 263-406



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

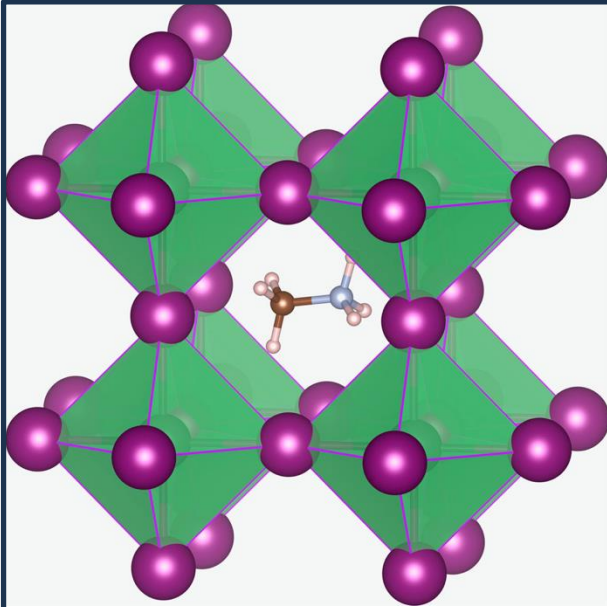
QENS reveals 2D correlated H⁻ diffusion mechanism (R. Lavén *et al.*, *Chem. Mater.* (2021))

“Correlated” (2D) diffusion in the Sr-H plane



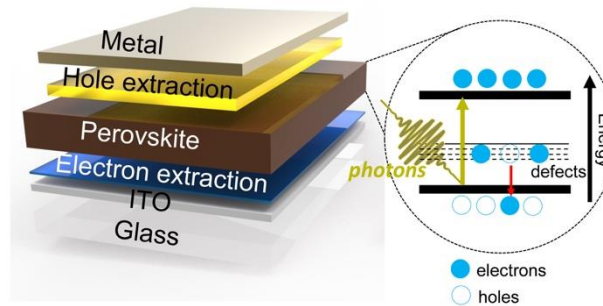
- Enhanced rate for backward jumps, compared a forward or sideway jump ($r_2 \approx 10r_1$)
- Vacancies are needed for diffusion. Is there any optimum vacancy concentration?

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.

Dynamics of the organic cations affect:

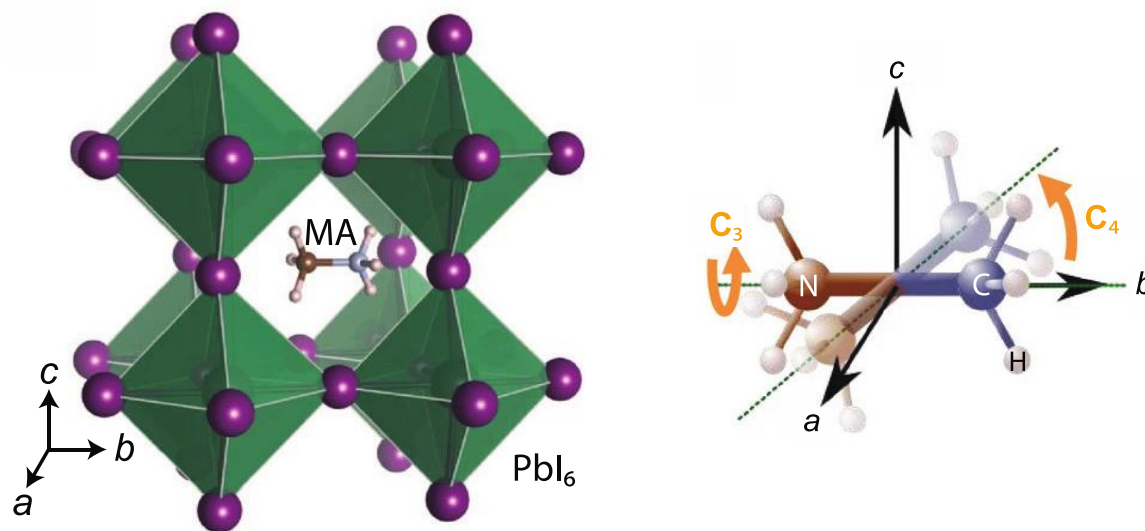
- Ferroelectric domains & surface ferroelectricity (Leguy *et al.*, *Nat. Commun* **6** (2015))
- Exciton binding energy (Chen *et al.*, *PCCP* **17** (2015))
- Hot carrier cooling (Guo *et al.*, *Science* **356** (2017))
- Charge carrier recombination rates (Zhu *et al.*, *JPLCL* **6** (2015), Ma *et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

Organic cation (rotational) dynamics

Examples of results from QENS experiments

MA cation dynamics in MAPbI₃ (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 CH₃/NH₃ around C-N axis.



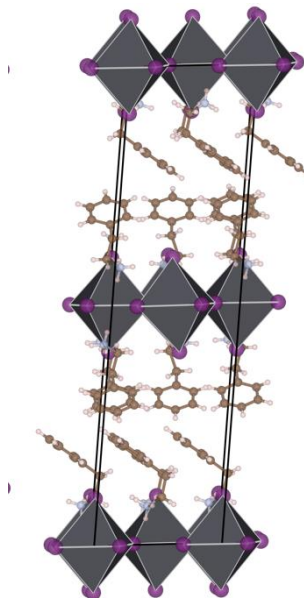
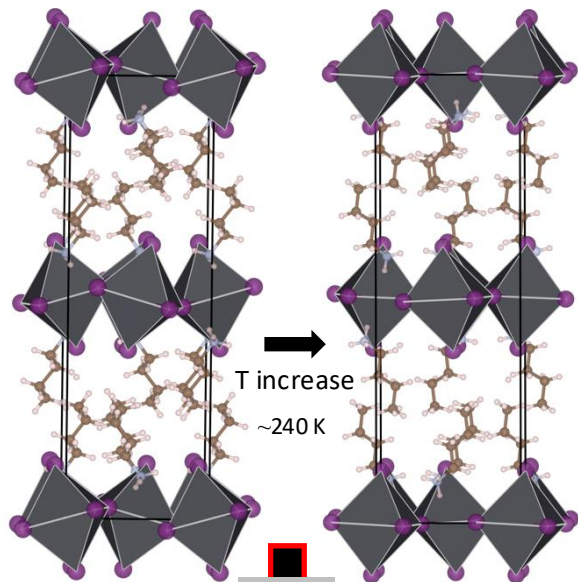
Leguy *et al.*, *Nat. Commun.* **6** (2015)

Organic cation dynamics in layered structures

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

BA_2PbI_4 (BA = $\text{CH}_3(\text{CH}_2)_3\text{NH}_3$)

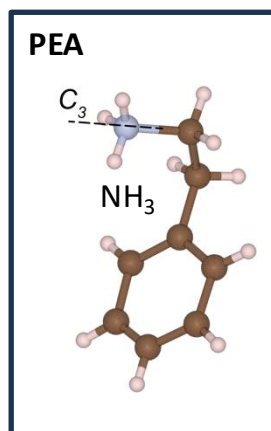
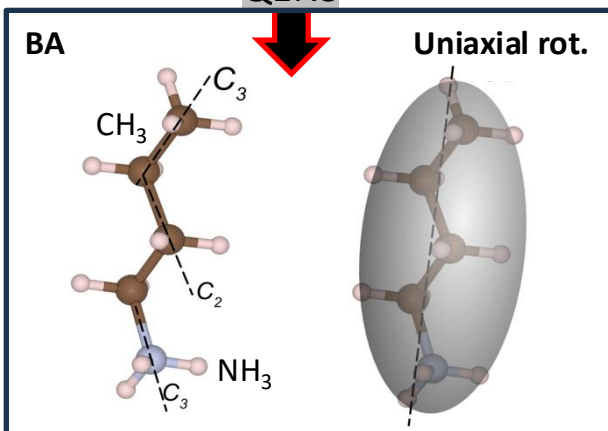
PEA_2PbI_4 (PEA = $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3$)



Correlation to optical properties:

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))

QENS



More restricted dynamics for PEA_2PbI_4

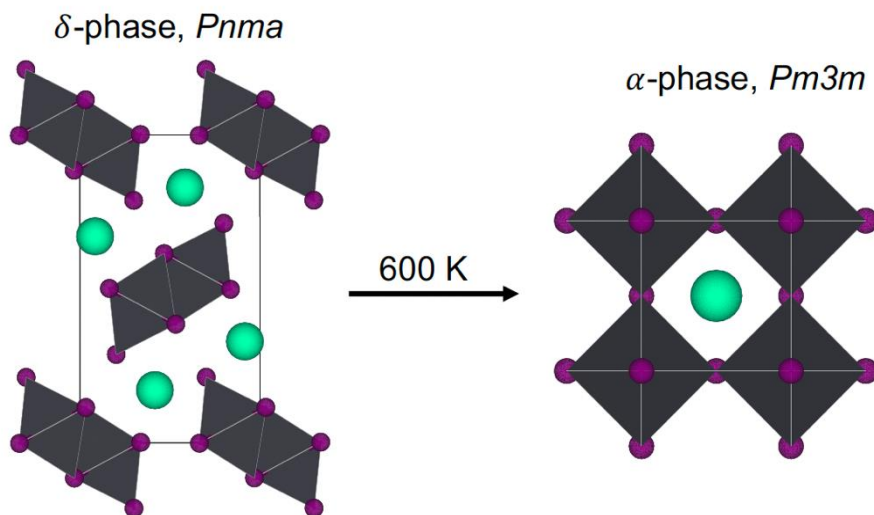
Vibrational dynamics in halide perovskites

- 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 CsPbI₃

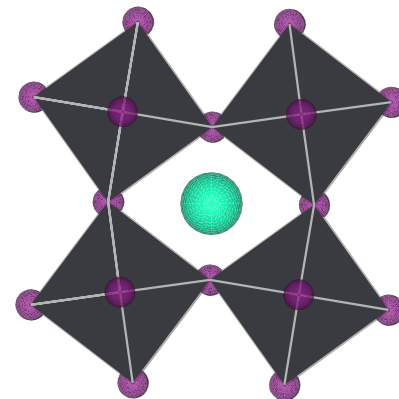
All-inorganic CsPbI₃ (INS study on FOCUS@PSI)



Irreversibility

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

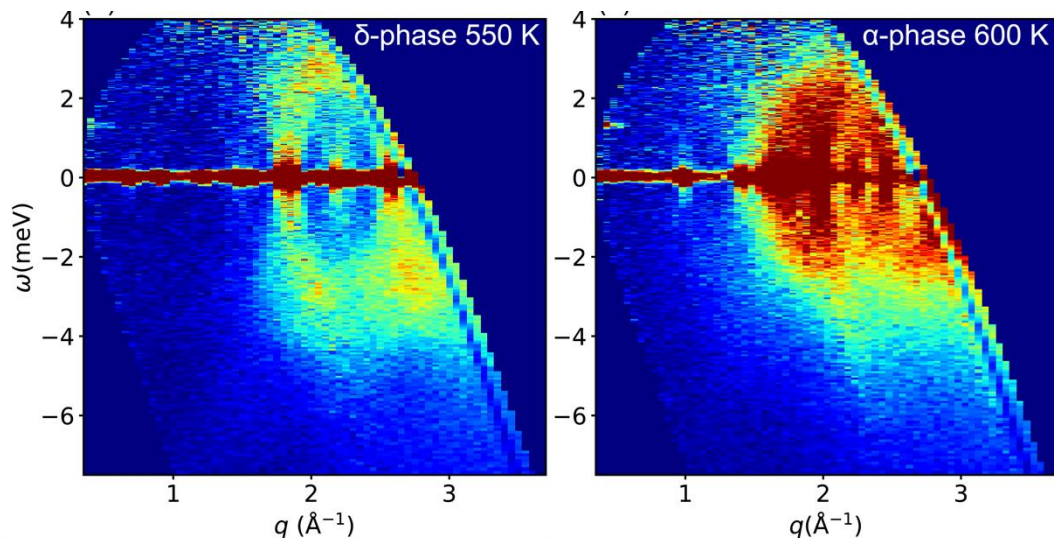
The nature of octahedral tilting motions and their correlation with structural and optical properties are unclear



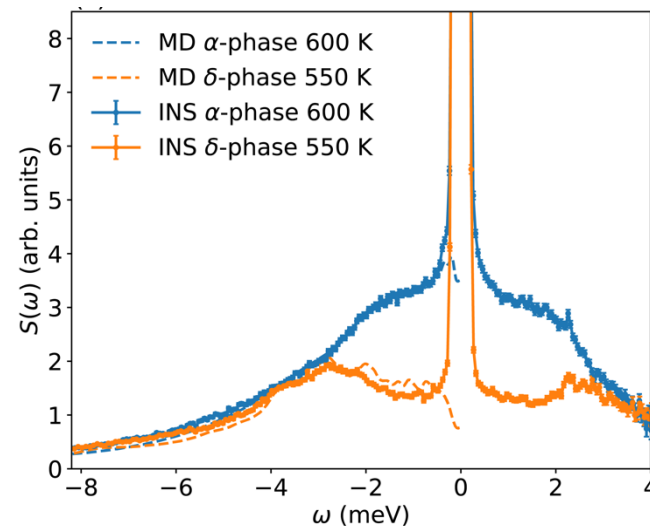
Dynamical structure factor for CsPbI₃

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

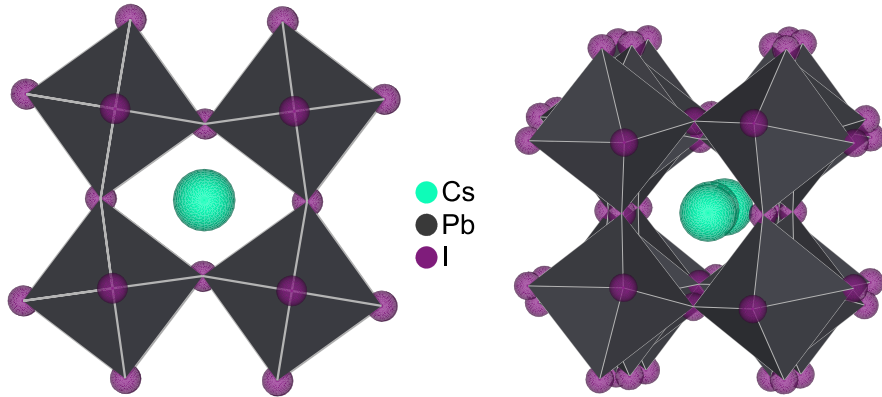
Experimental $S(q, \omega)$ – data from the FOCUS spectrometer at the Paul-Scherrer Institute



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

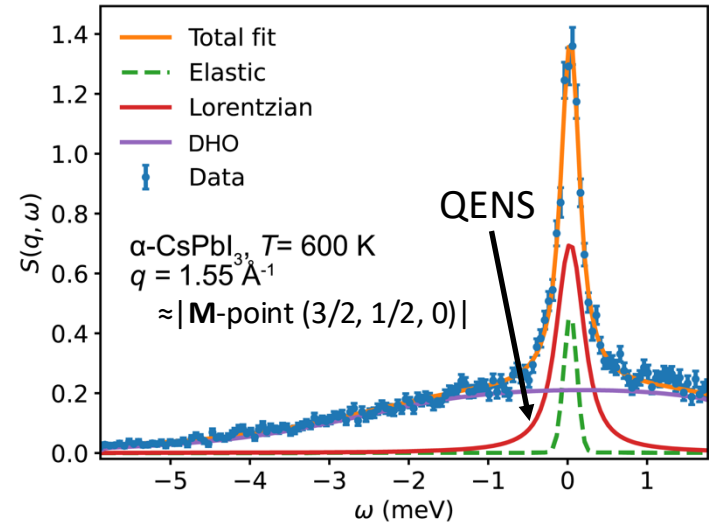


Overdamped octahedral tilting modes



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 (α - β) and tetragonal-orthorhombic (β - γ) phase transition at 550 K and 450 K.
- Timescale of the dynamics $\approx 2\text{-}4\text{ ps}$, 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

Some useful references related to the presented work:

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.

maths.karlsson@chalmers.se

Thanks!