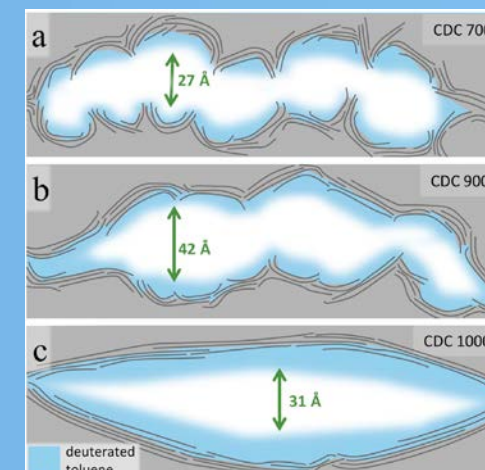
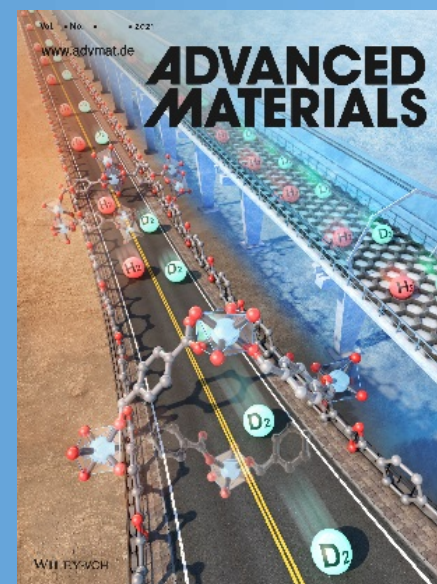
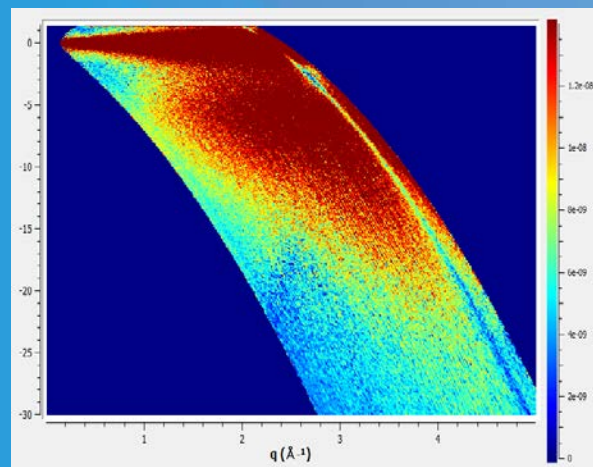
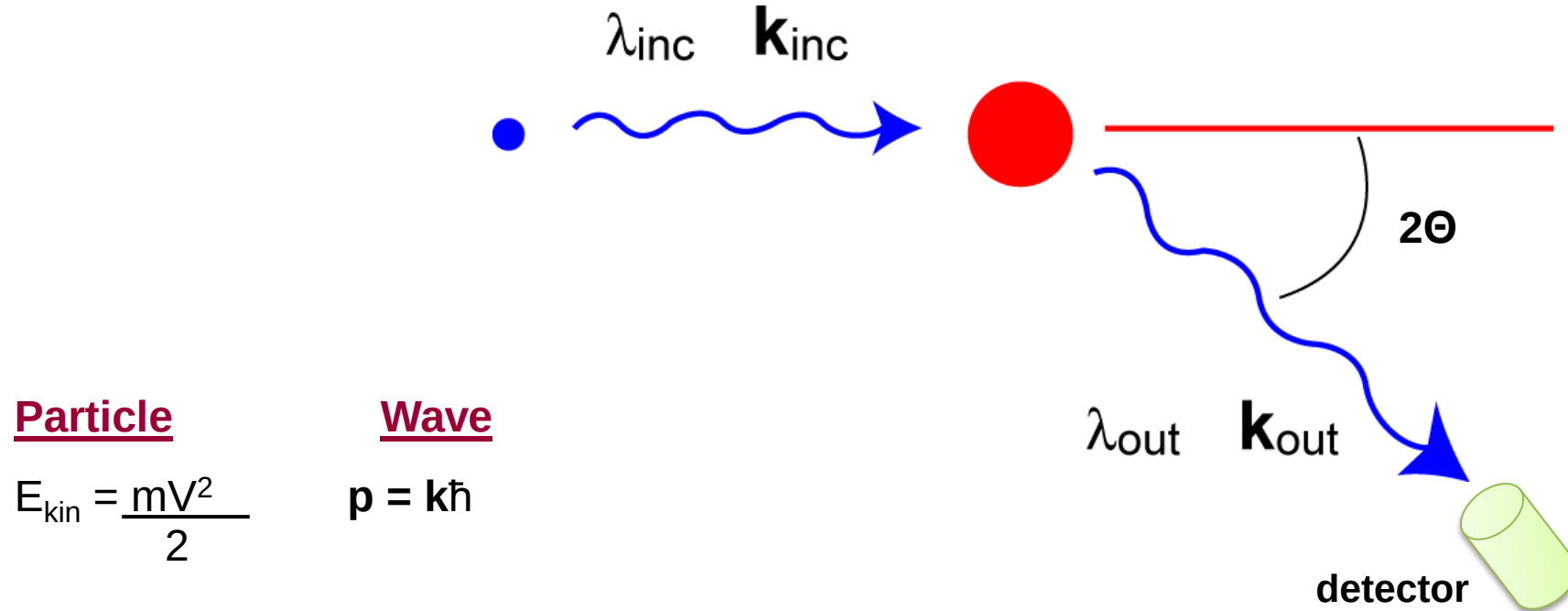


Exploring Dynamics with Neutrons: An Introduction to Time-of-Flight Spectroscopy

Margarita Russina

Helmholtz Zentrum Berlin für Materialien und Energie Germany





Scattering proces

$$\hbar\omega = E_{\text{out}} - E_{\text{inc}} = \frac{m}{2}(V_{\text{out}}^2 - V_{\text{inc}}^2)$$



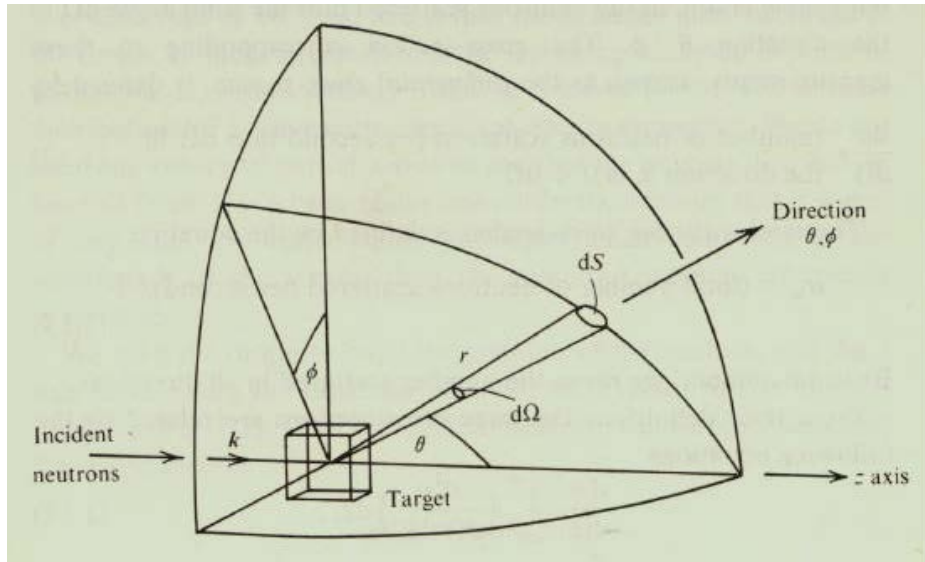
Information about the atomic motion or energy of quantum states

$$\mathbf{Q} = \mathbf{k}_{\text{out}} - \mathbf{k}_{\text{inc}}$$



Information about structure

WHAT DO WE MEASURE

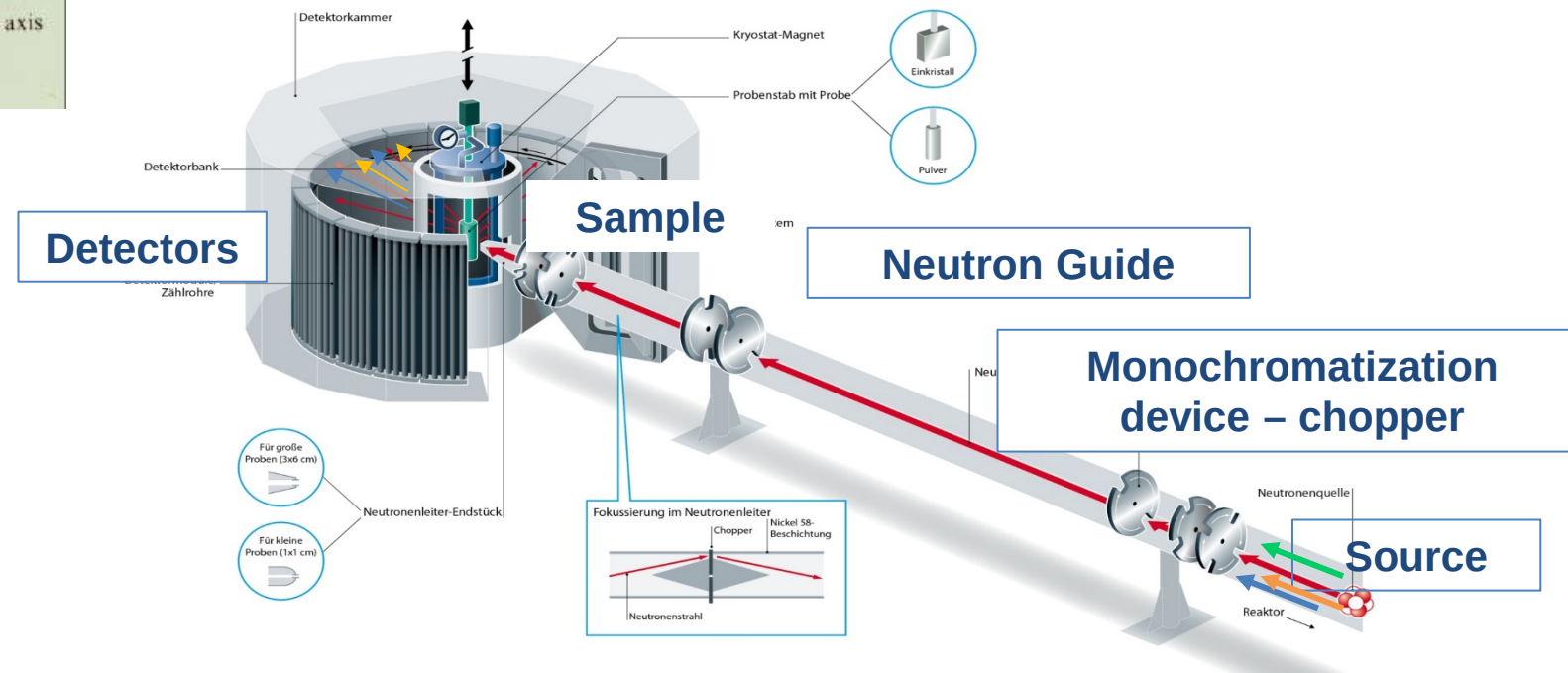


Differential cross-section

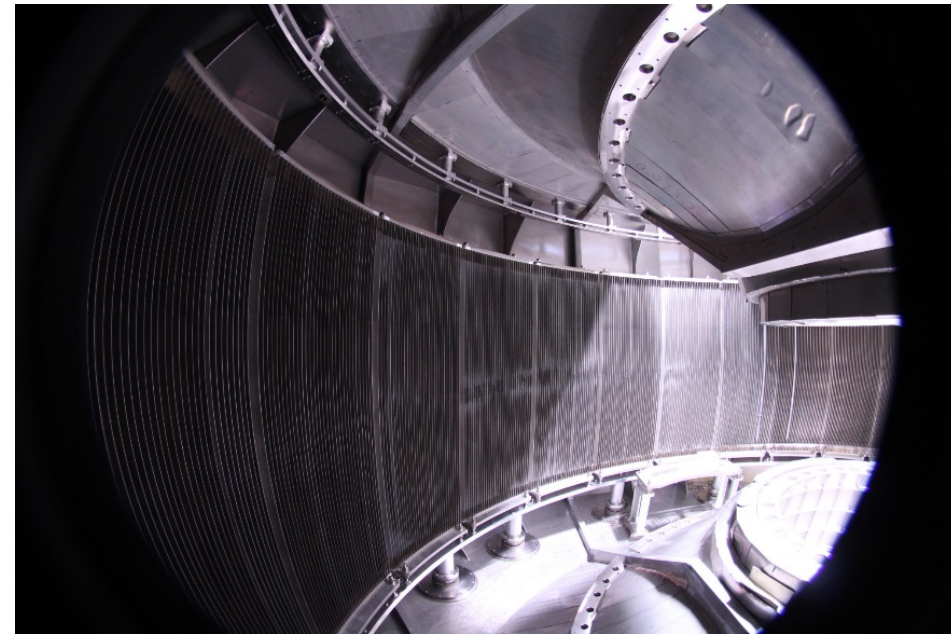
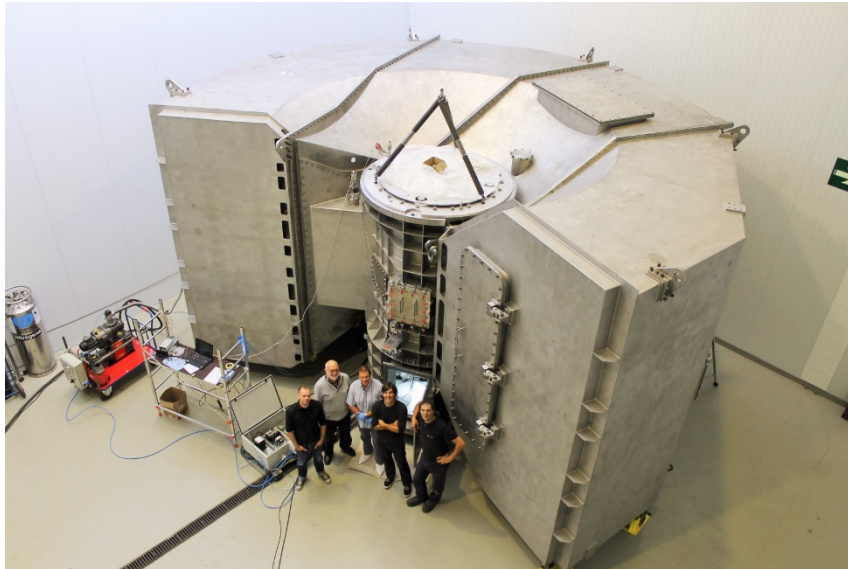
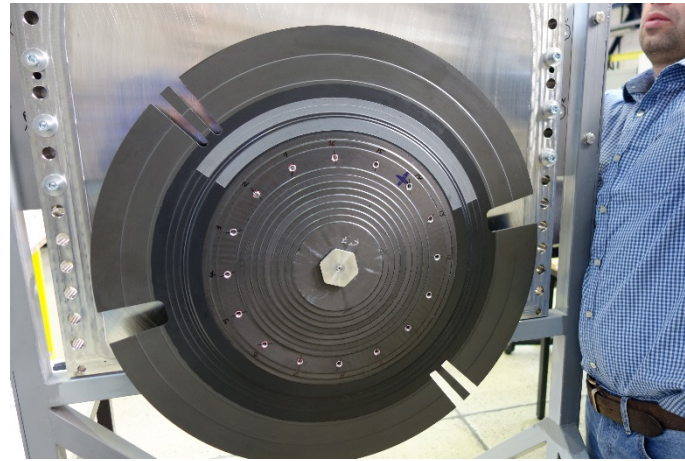
=

number of neutrons scattered per second into solid angle $d\Omega$ and dE

Flugzeitspektrometer NEAT II



INSTRUMENT COMPONENTS



- A neutron beam incident on a single atom. The incident neutron can be described as a complex plane wave.

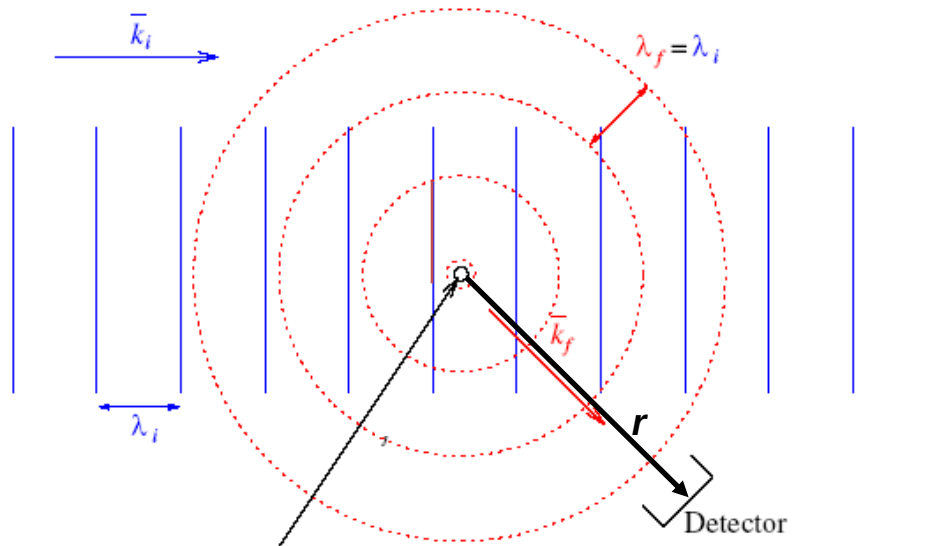
$$\psi_{\text{incident}} = \frac{1}{\sqrt{Y}} \exp(i\mathbf{k}_i \cdot \mathbf{r}) \quad \Phi_0 = |\psi_i|^2 v_i = \psi_{\text{incident}} \psi_{\text{incident}}^* v_i = \frac{1}{Y} \frac{\hbar k_i}{m_n}$$

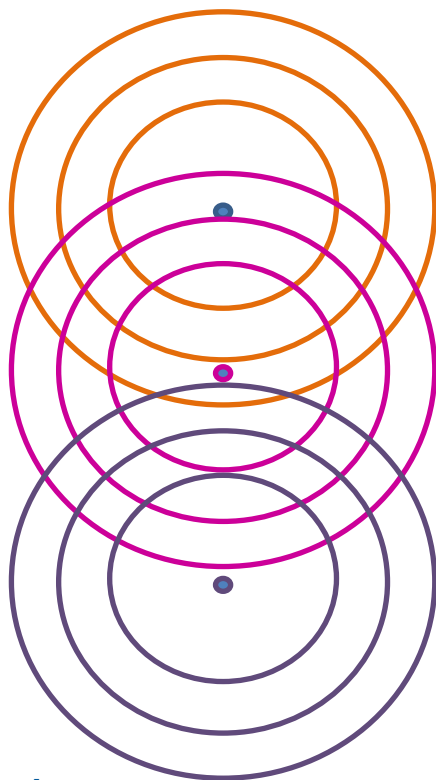
Where Y is the normalisation constant.

- Assuming just nuclear forces, which are very short range, the neutron sees the scattering centre as a point and as a result the scattering will be isotropic. The scattered wavefunction is

$$\psi_f(\mathbf{r}) = \psi_i(\mathbf{r}_j) \left(\frac{-b_j}{r} \right) \exp(i\mathbf{k}_f \cdot \mathbf{r})$$

The quantity b_j is known as the scattering length





- What we see in the detector is the sum of all spherical waves, which in its turn reflect the position of scattering centers R_i
- These positions can be time dependent – we see the dynamics $R_i(t)$

$$S(Q, \omega) = \frac{1}{h} \frac{k_f}{k_i} \sum_{i,j} b_i b_j \int_{-\infty}^{\infty} \langle \exp\{-\mathbf{Q} \mathbf{R}_i(0)\} \exp\{-\mathbf{Q} (\mathbf{R}_j(t))\} \exp\{-i\omega t\} \rangle dt$$

Where $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$

Van Hove correlation function

$$G(\vec{r}, t) = \frac{1}{N} \sum_{i,j} \delta(\vec{r} - [\vec{R}_i(0) - \vec{R}_j(t)])$$

Following one molecule :

$$S_{inc}(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \int G_{self}(\vec{r}, t) e^{-i\omega t} d\vec{r} dt$$

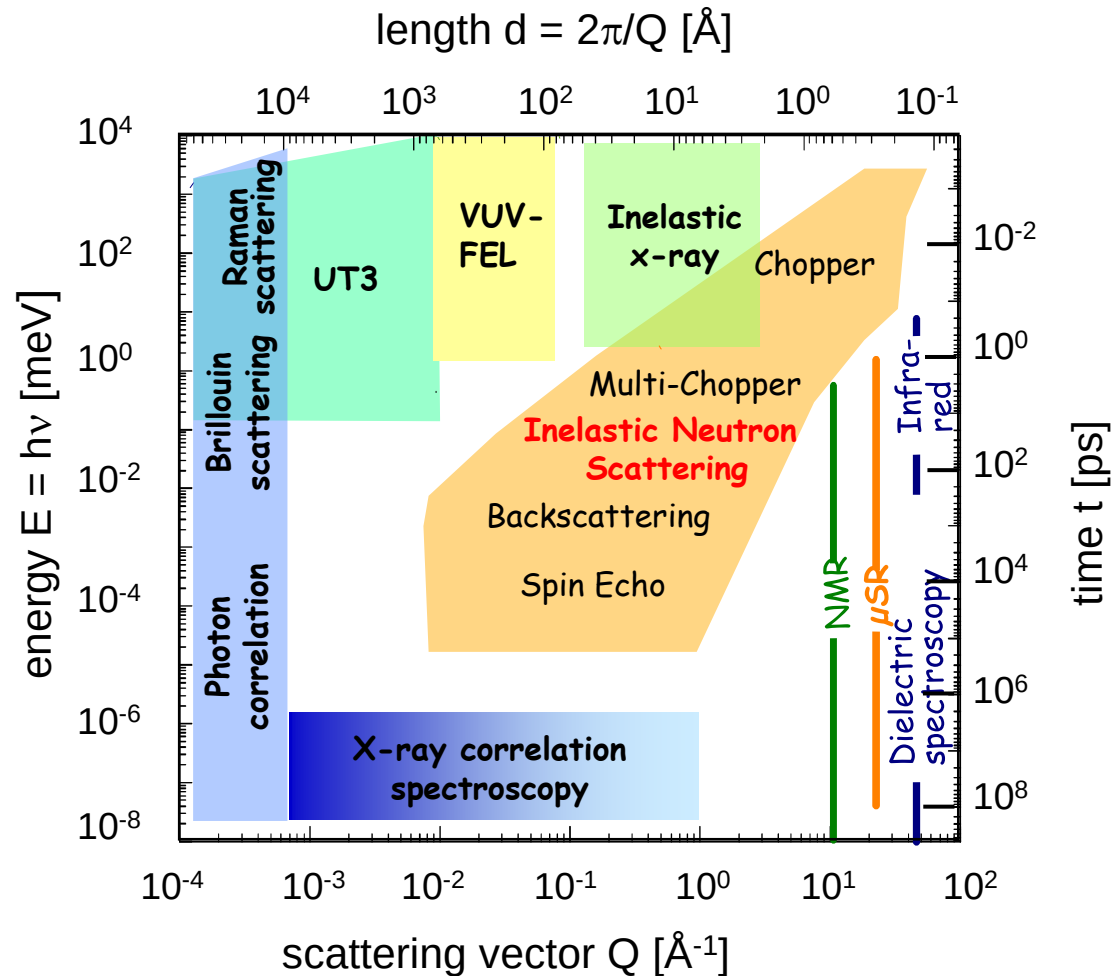
Cooperative interactions

$$S_{coh}(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \int G_{pair}(\vec{r}, t) e^{i\vec{Q} \cdot (\vec{r} - \omega t)} d\vec{r} dt$$

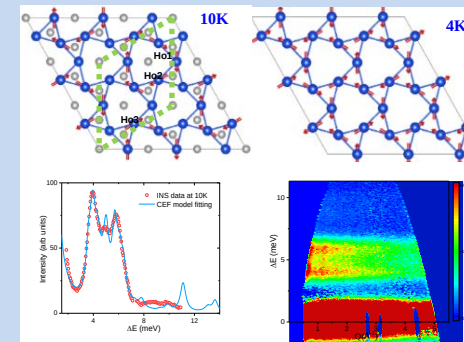
$$\frac{d^2\sigma}{d\Omega dE} = \frac{N}{4\pi} \frac{k_{sc}}{k_{inc}} [\sigma_{coh} S_{coh}(\vec{Q}, \omega) + \sigma_{inc} S_{inc}(\vec{Q}, \omega)]$$

$$1 \text{ meV} \cong 8 \text{ cm}^{-1} \cong 240 \text{ GHz} \cong 12 \text{ K} \cong 0.1 \text{ kJ/mol} \sim \text{ps}$$

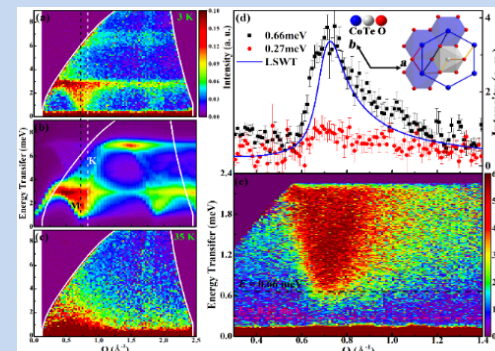
Novel materials for AI and quantum computing



Kagome spin ice state in non-artificial compounds Science 2020

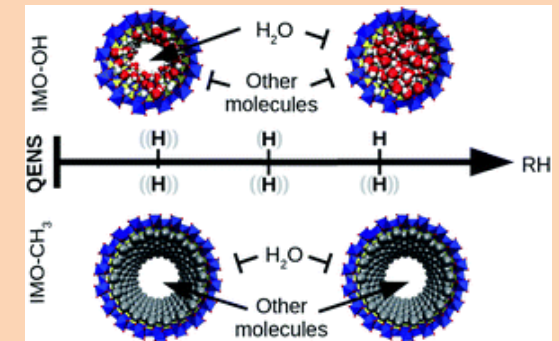


Exotic excitations in quantum spin liquid in Kitaev systems Nat Communication 2021

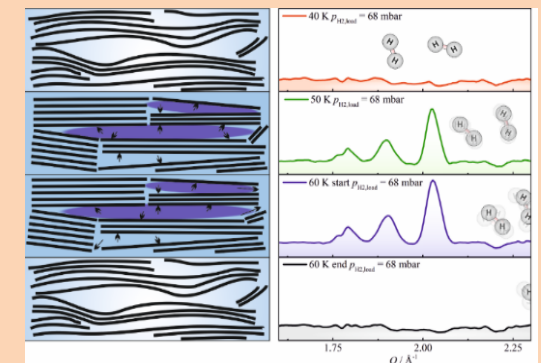


Energy materials

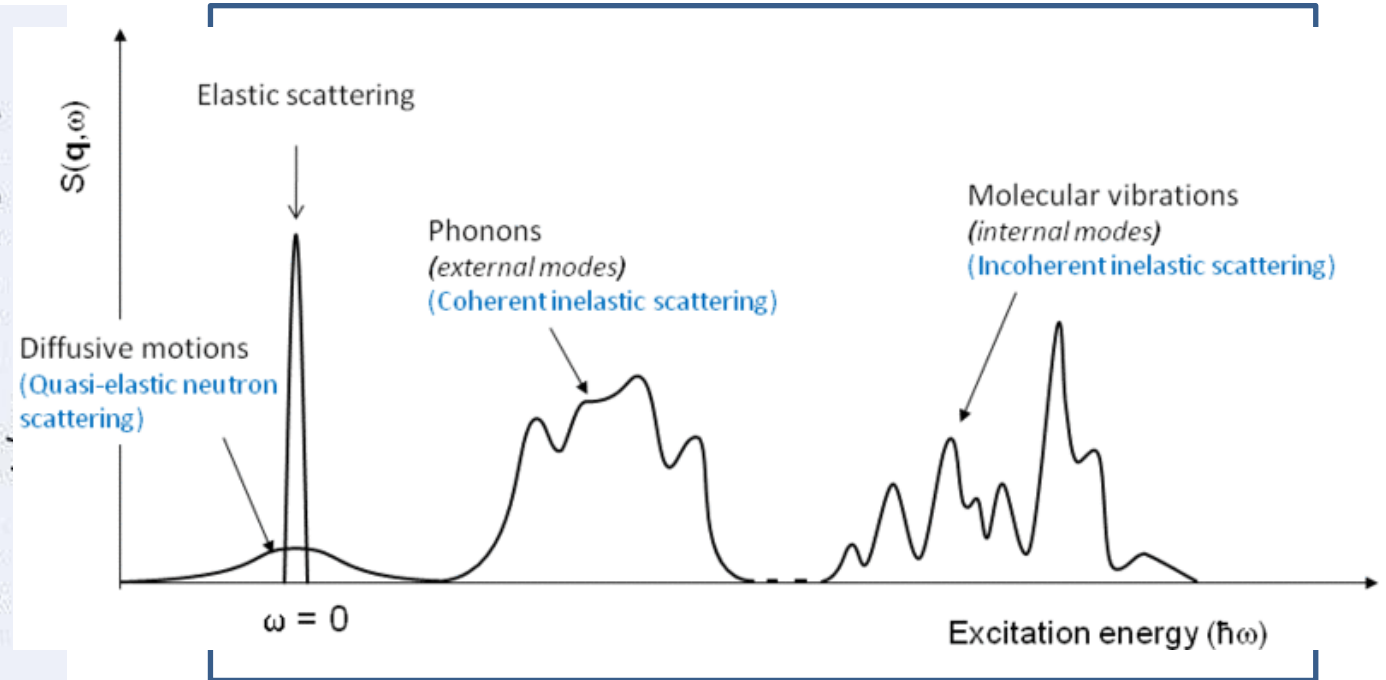
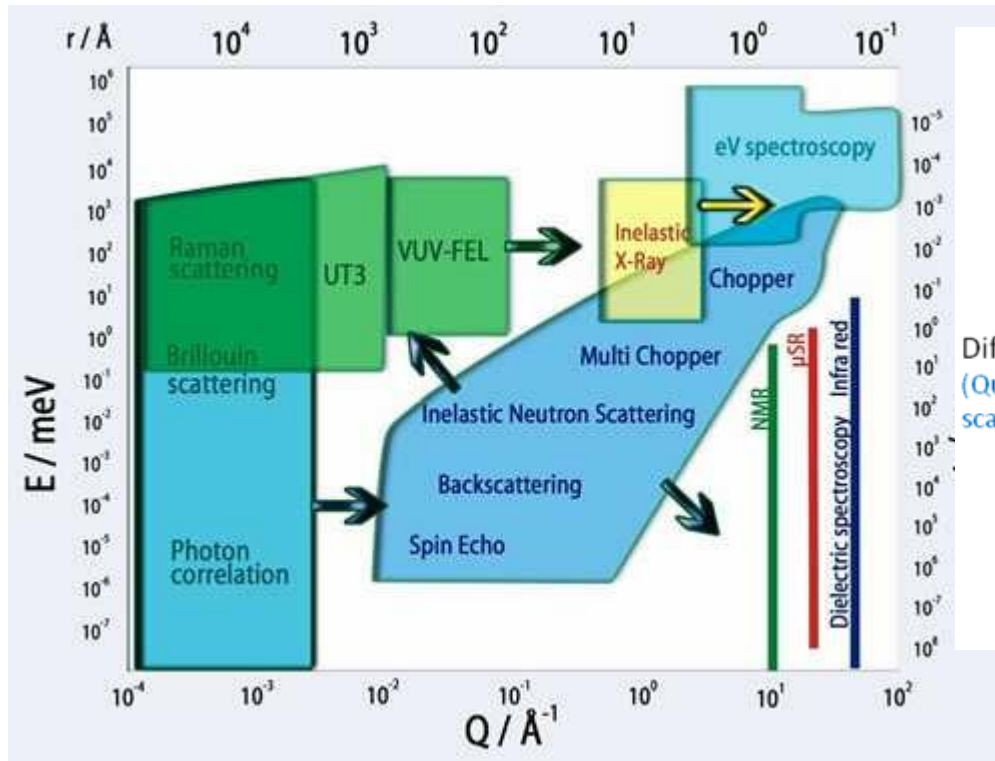
Self-diffusion in hydrated NT Nanoscale advances 2020



Reversible adsorption induced graphitization of porous carbon CARBON 2021



- Neutron spectroscopy is in nanoscope that allows to follow ionic diffusion in space



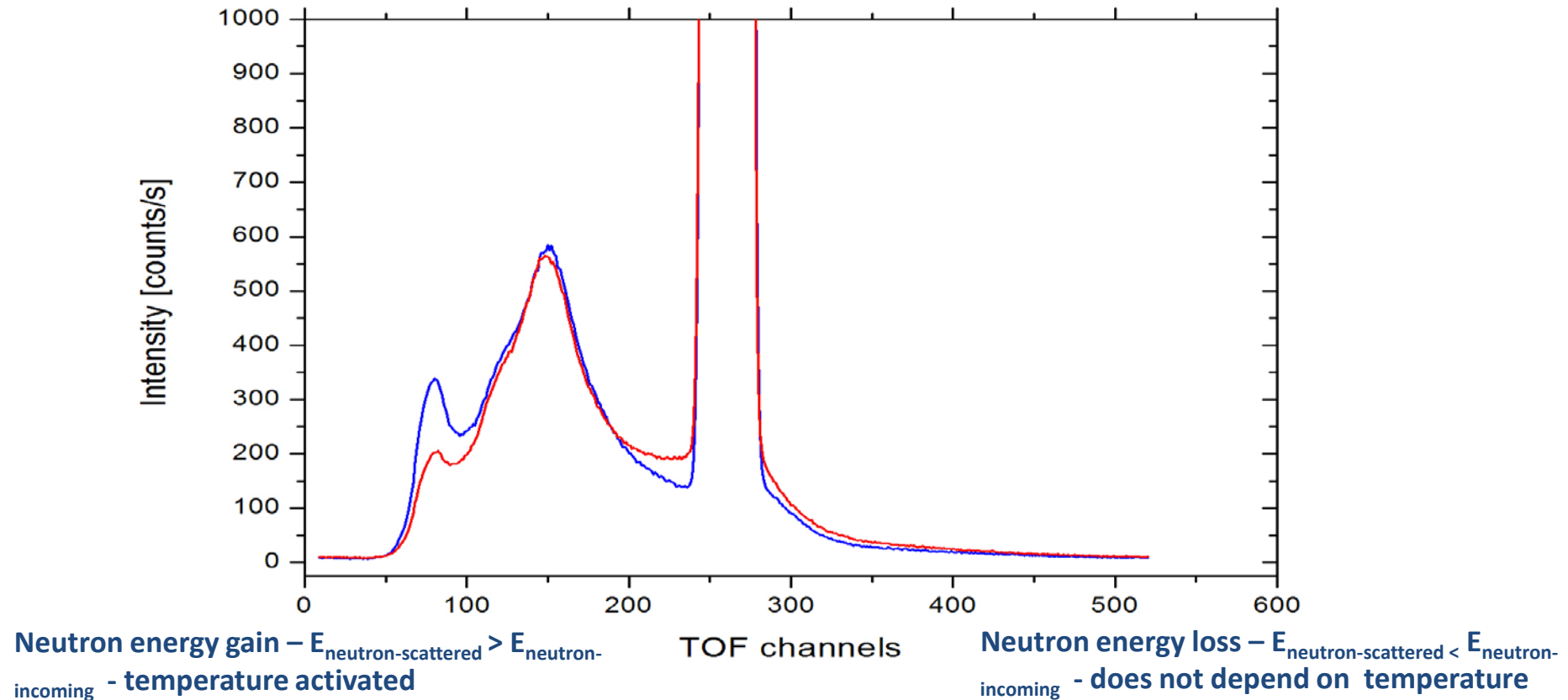
Nagy, Gergely. (2011). Structure and Dynamics of Photosynthetic Membranes as Revealed by Neutron Scattering.

Time scale : from picoseconds to 500 nanoseconds

Q and length scale domain : $0.02\text{-}6 \text{ \AA}^{-1} \sim 30 - 0.05 \text{ nm}$

Sensitive to hydrogen, different cross sections for H and D

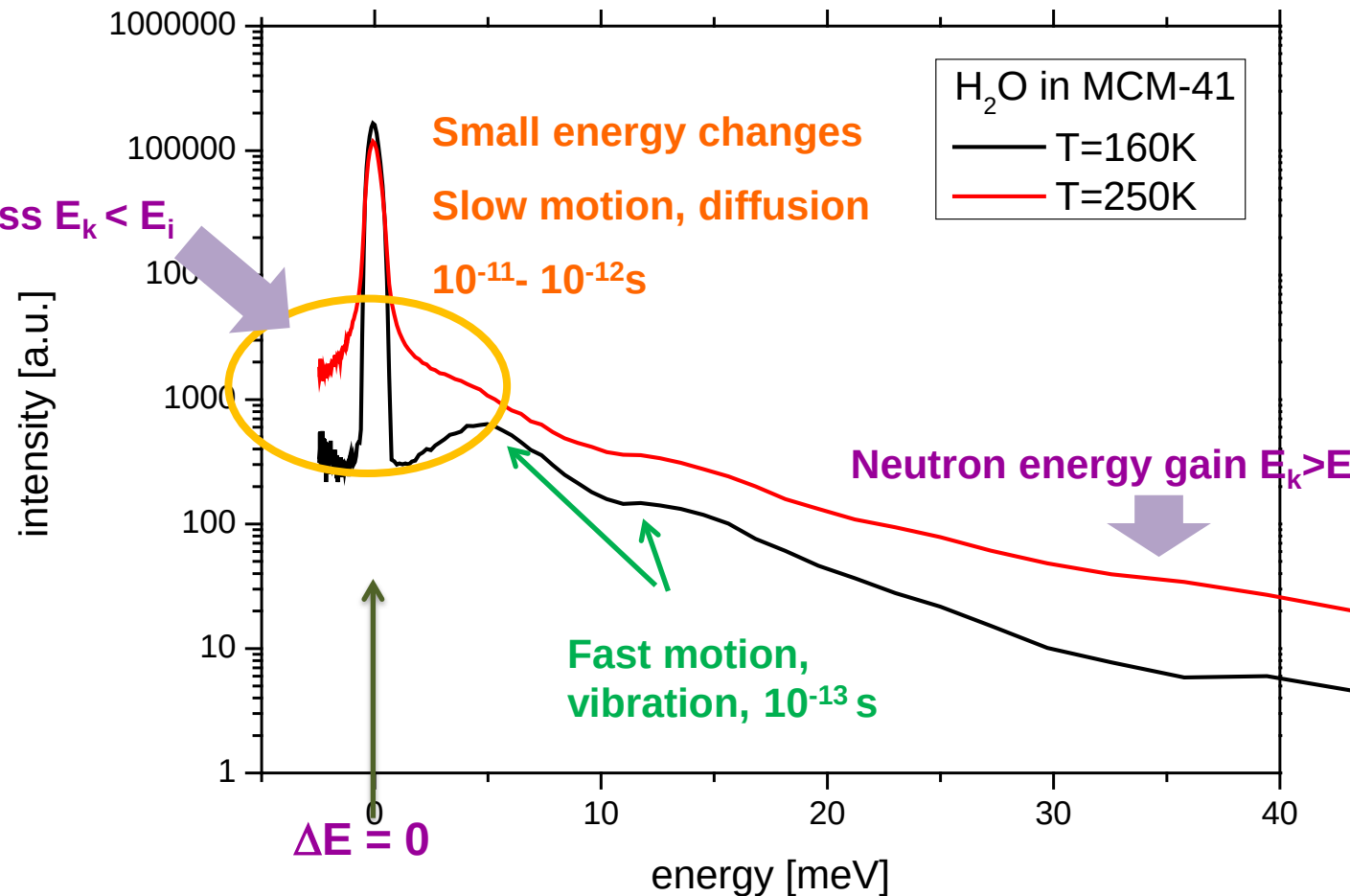
Sample: confined H₂O



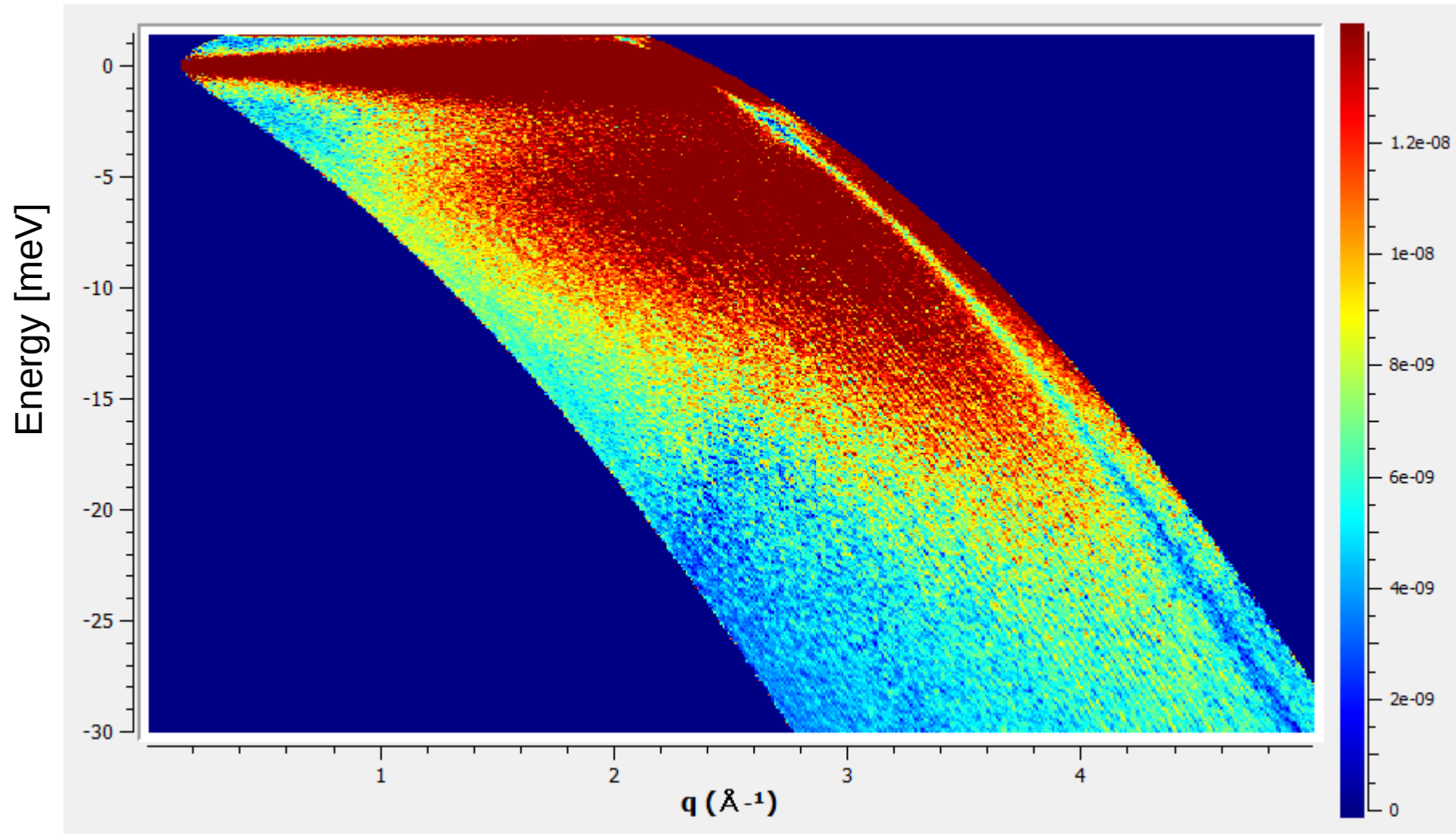
In time

Sample: H₂O in MCM-41

In energy



Elastic resolution of instrument defines us the slowest motion what we can observe in the experiment



Diffusion – motion of particles when
time average position within certain
time window is not constant

Types of diffusion:

- ☐ Long range translation diffusion - related to mass transfer
- ☐ Diffusion in confinement – no mass transfer
- ☐ Rotational diffusion – reorientation of molecules

$$S(Q, \omega) \sim e^{-Q/3\langle u^2 \rangle} A_0^0(Qr_0) \delta(Q, \omega) + \sum_l^{n-1} A_l(Qr_n) L(\omega, \Gamma(Q))$$

Stationary part

Mobile part



- Particles immobile within time window defined by instrumental resolution
- Preferential positions of motion if they stay the same over long period of time

Long range translational diffusion :

Fickian diffusion:

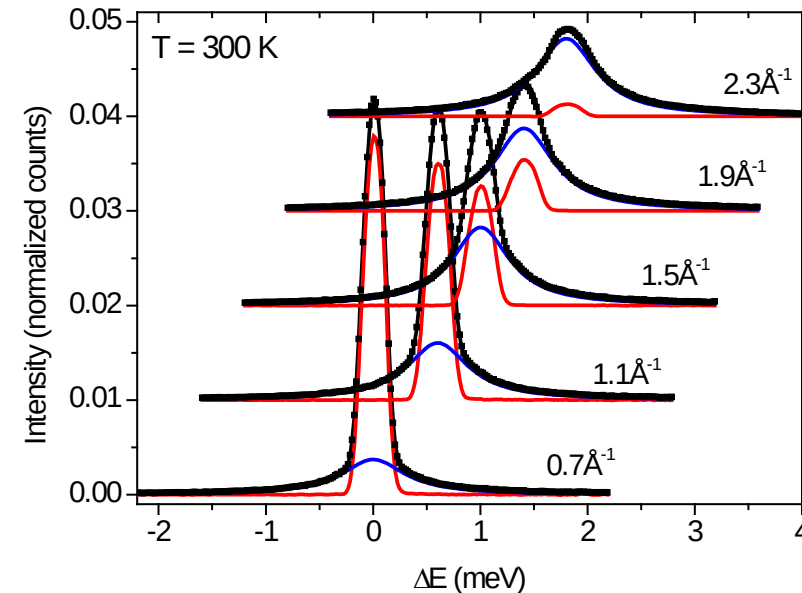
$$G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}$$



$$S(Q, \omega) \sim \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

$$\Gamma(Q) \sim DQ^2 \quad D = \frac{1}{6t} \langle r^2 \rangle$$

- **Continuous flow usually due gradient of concentration**
- **$A_0 = 0$ since all particles are moving**
- **No interaction between the particles**



Long range translational diffusion :

$$S(Q, \omega) \sim \frac{1}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}$$

Random jump diffusion :

$$\Gamma(Q) = \frac{DQ^2}{1 + DQ^2/E_0} \quad \tau = \frac{\hbar}{E_0} \quad \text{and } l = \sqrt{6D\tau}$$

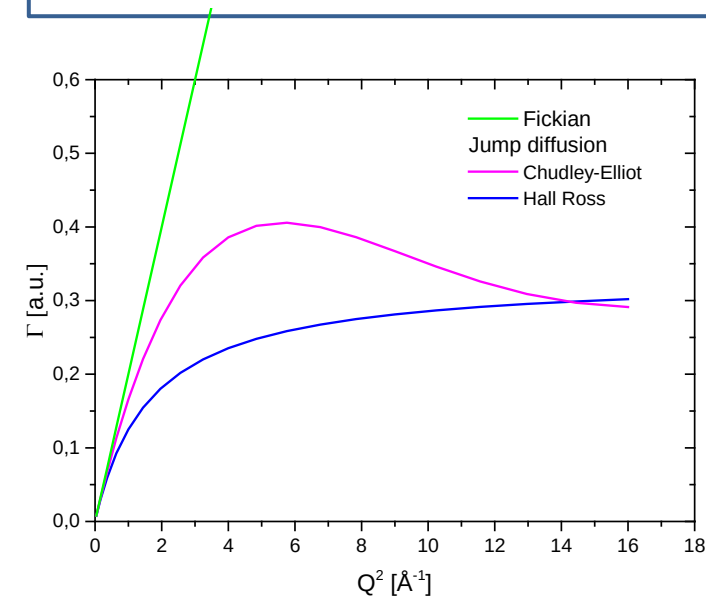
Chudley Elliott – jump diffusion in crystals

$$\Gamma = \frac{\hbar}{\tau} \left(1 - \frac{\sin(Ql)}{Ql}\right)$$

Gaussian distribution

$$\Gamma = \frac{\hbar}{\tau} \left(1 - \exp\left(-\frac{Q^2 l^2}{6}\right)\right)$$

- Stronger interactions between the particles
- Particles are caged in between the neighbors
- Particles resides time τ and undergo jumps with the length l



Solid-state NMR primarily detects:

- ns-ms
- residence times
- jump rates (indirectly)
- chemical environments
- slower dynamics

However:

- ! no information about space propagation of diffusion motion
- ! no direct jump geometry
- ! limited sensitivity to very fast processes

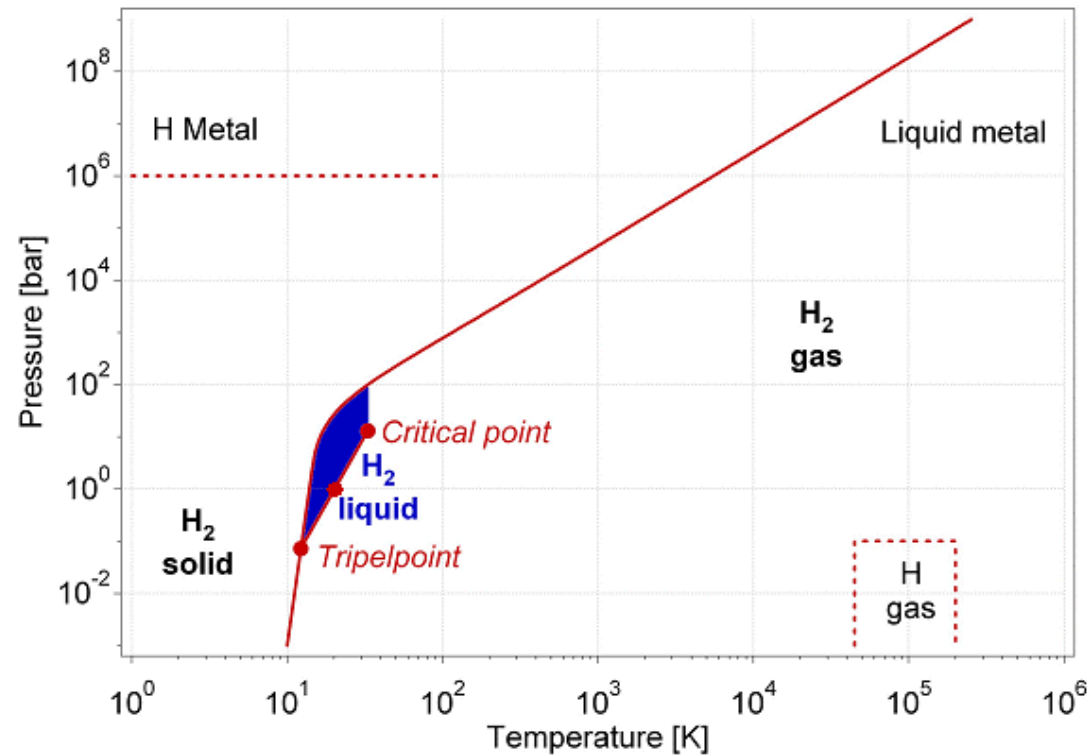
QENS:

- ps-ns
 - jump length
 - residence times
 - diffusion geometry
 - confined vs long-range motion
 - correlation effects
 - dimensionality of diffusion
- 👉 This information is **not accessible with NMR**.

Application of TOF spectroscopy to investigation of molecular diffusion

- Hydrogen isotope transport effects
- Ion diffusion in solid electrolytes

Properties of bulk hydrogen



Melting point

14.01K at ambient pressure

Boiling point

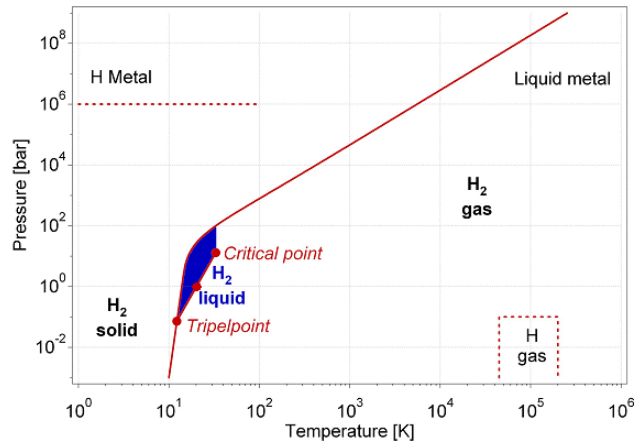
20.28K at ambient pressure

Critical point

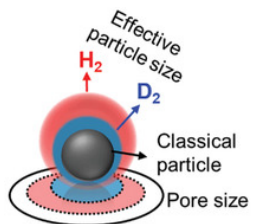
32.9K

Triple point

13.8033 at 7.042kPa



Ordinary bulk diffusion:
 $v(\text{H}_2) \approx \sqrt{2}v(\text{D}_2)$



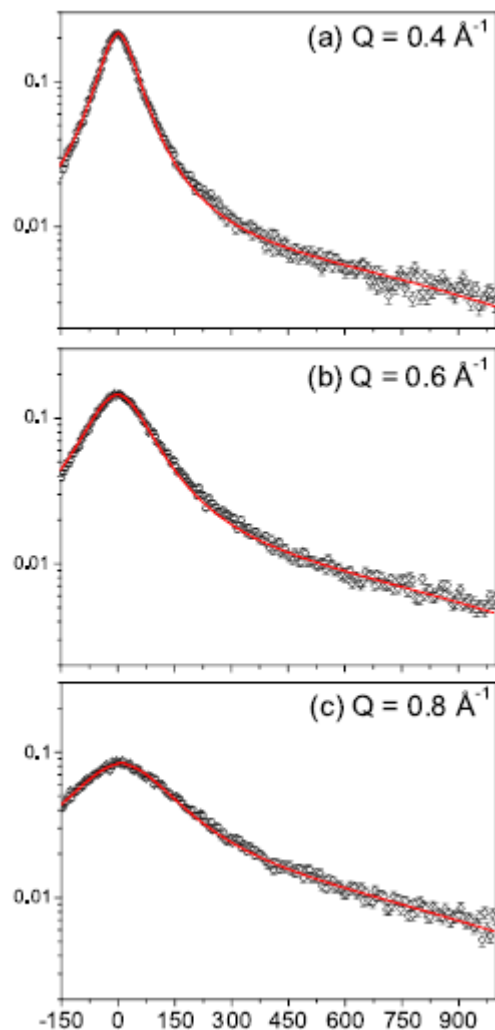
Concept of kinetic quantum sieving (KQS)^[13]

Hydrogen isotopes are geometrically identical but quantum mechanically very different.

Classical quantum sieving exploits these differences, whereas lattice-driven gating can even reverse the expected isotope mobility

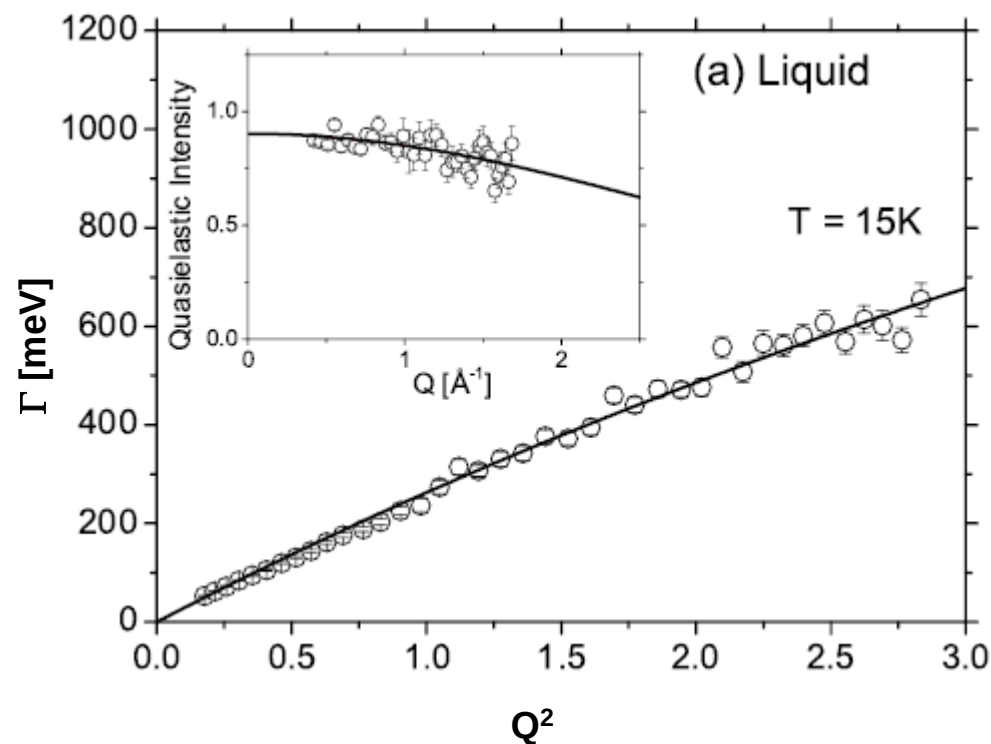
Property	H ₂	D ₂	T ₂
Molecular mass (u)	2.016	4.028	6.032
H–H bond length (Å)	0.741	0.741	0.741
Van der Waals diameter (Å)	~2.9	~2.9	~2.9
Melting point (K)	13.99	18.73	20.6
Boiling point (K)	20.27	23.67	25.0
$\lambda_{\text{de Broglie}}$ at boiling point (Å)	~3.4	~2.4	~2.0
$\lambda_{\text{de Broglie}}$ at 77 K (Å)	~1.74	~1.23	~1.01

Bulk Hydrogen at T=15K



No stationary part – not confined

Long range translational diffusion :

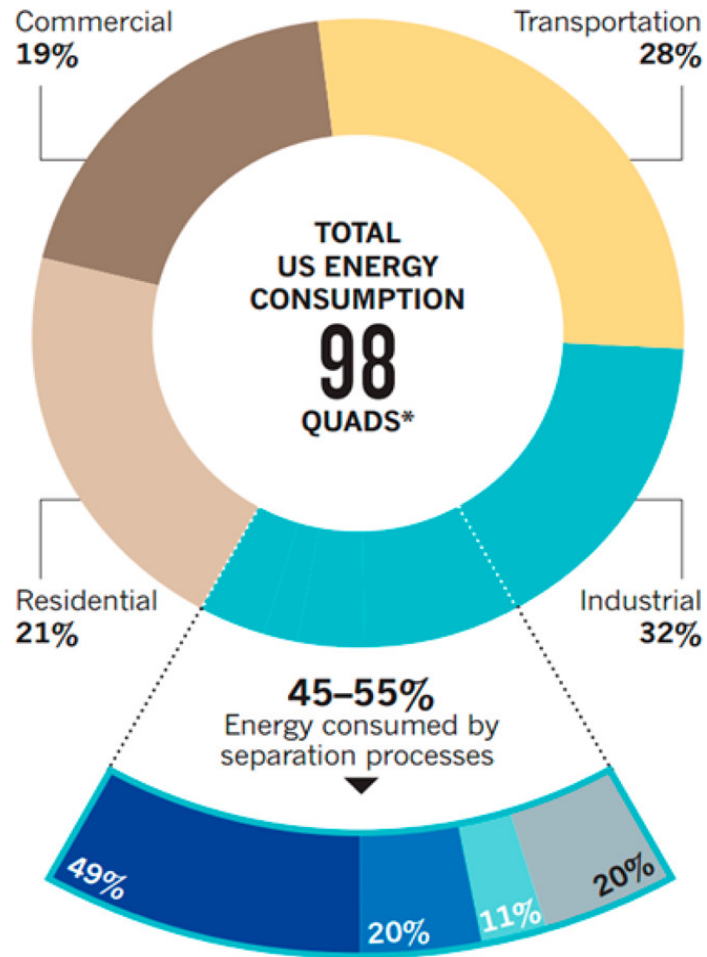


Linewidth is a function of Q^2

$D \sim Q^2$ and is $0.43 \pm 0.01 \text{ \AA}^2 / \text{ps}$ at 15K
 $E_0 = 3.38 \pm 0.27 \text{ meV}$

Chemical separations account for about half of U.S. industrial energy use and 10–15% of the nation's total energy consumption. Developing alternatives that reduce energy input can make most of these separations more energy efficient.

Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* 2016, 532, 435–437.



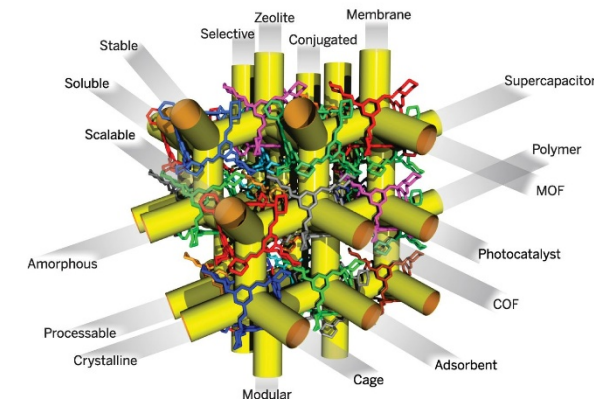
Thermal separations

- Distillation
- Drying
- Evaporation

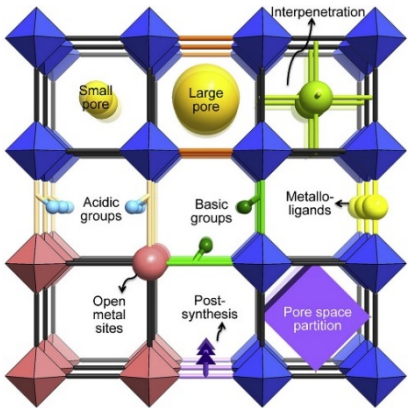
■ Non-thermal separations

Porous materials for gas storage / separation

- High surface areas
- Low density
- Tunable / hierarchical structures



Equilibrium separation



Equilibrium separation

- Separation is based on thermodynamic affinity of gasses to adsorbents
- All guest molecules can access pores
- Extra energy required for degassing

Nonequilibrium separation

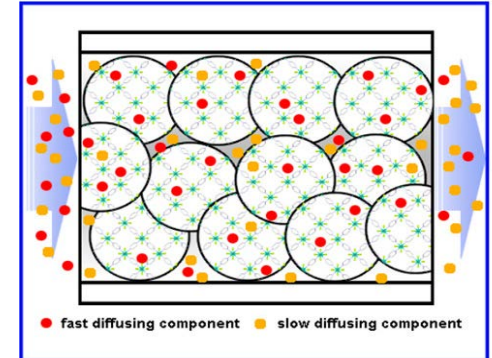
Kinetic separation

- Separation is governed by difference in the diffusivity of each gas component
- Mostly efficient in microporous materials

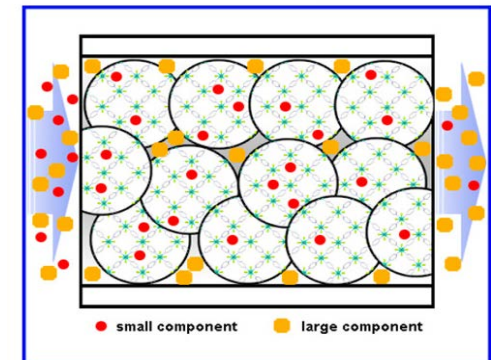
Molecular sieving

- Separation is based on inaccessibility of the pores to certain gas molecules
- Efficient only in microporous materials

Kinetic Separation



Molecular Sieving

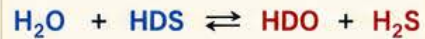


GIRDLER SULFIDE SEPARATION PROCESS

PRINCIPLE

The Girdler process separates hydrogen isotopes by the temperature-dependent equilibrium of the exchange reaction between water and hydrogen sulfide.

GIRDLER EXCHANGE REACTION



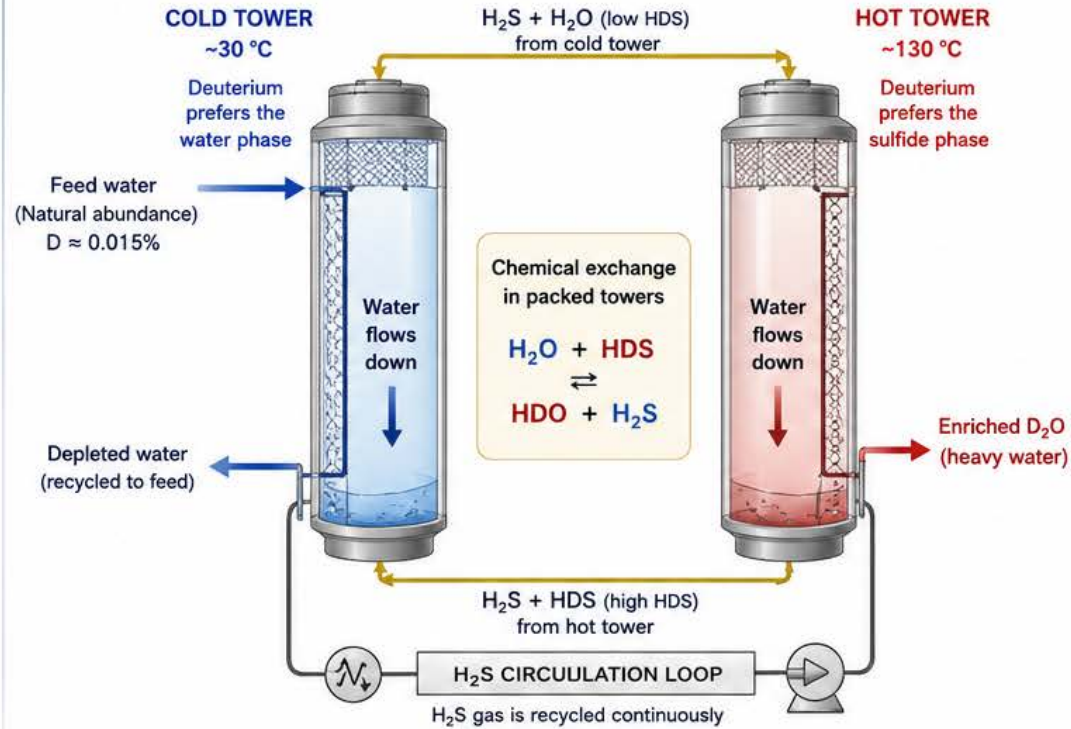
At low temperature:
Deuterium prefers the water phase (HDO)

At high temperature:
Deuterium prefers the H_2S phase (HDS)

ISOTOPE SPECIES

	H_2O	light water
	HDO	semi-heavy water
	D_2O	heavy water
	H_2S	hydrogen sulfide
	HDS	semi-heavy sulfide
	D_2S	heavy sulfide
(D = deuterium)		

GIRDLER PROCESS FLOW DIAGRAM (COUNTER-CURRENT EXCHANGE)



DRIVING FORCE: TEMPERATURE-DEPENDENT EQUILIBRIUM

Equilibrium constant $K_{\text{eq}} = (\text{a}_{\text{HDO}} \cdot \text{a}_{\text{H}_2\text{S}}) / (\text{a}_{\text{H}_2\text{O}} \cdot \text{a}_{\text{HDS}})$ increases with temperature.

Low T → D in water

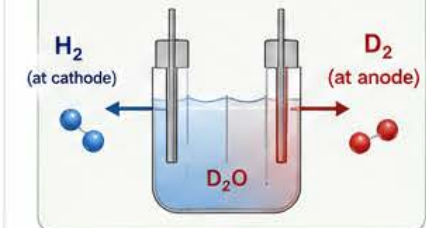
High T → D in H_2S

FROM HEAVY WATER TO D_2 GAS

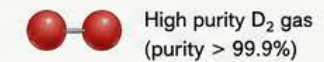
1 Heavy water product



2 Electrolysis of heavy water



3 D_2 gas product



H_2 gas (by-product)
can be recovered from the cathode stream.

KEY FEATURES OF THE GIRDLER PROCESS

- ✓ Uses well-known chemical reaction and proven industrial technology.
- ✓ Counter-current contacting in two towers (cold and hot).
- ✓ Continuous process with H_2S recycle.
- ✓ Produces high-purity heavy water (D_2O).
- ✓ Basis of industrial heavy water production for nuclear, research and special applications.

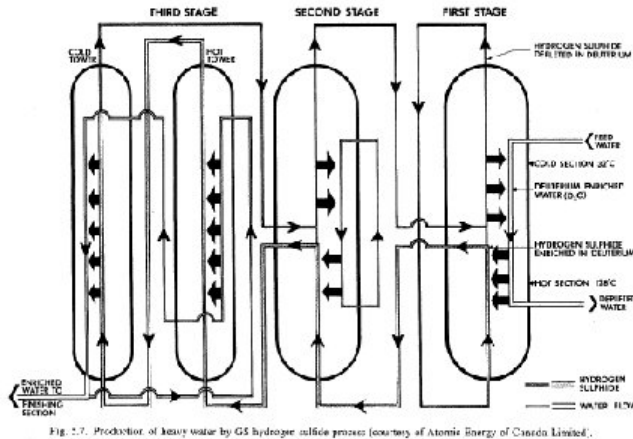
OVERALL ROUTE TO D_2 GAS



NOTES

- H_2S is toxic and corrosive – containment and materials are critical.
- Energy required for heating (hot tower) is the main utility demand.
- Modern alternatives (e.g., membrane and adsorption processes) are under development.

Girdler sulfide separation process



Quantum sieving effect

De Broglie wavelength of hydrogen isotopes

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{3mk_B T}}$$

h – Planck constant (6.626×10^{-34} J s)

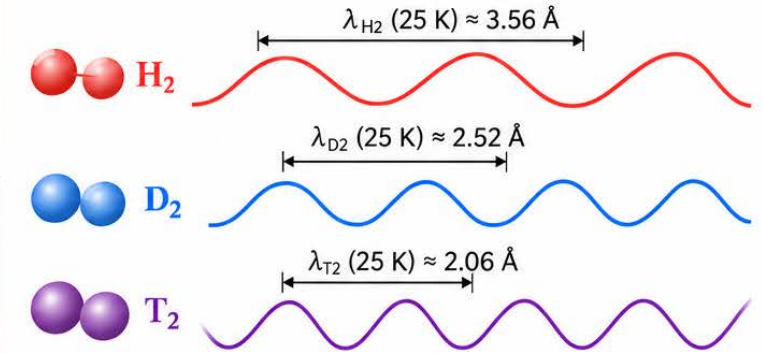
m – particle mass

k_B – Boltzmann constant (1.381×10^{-23} J/K)

T – temperature

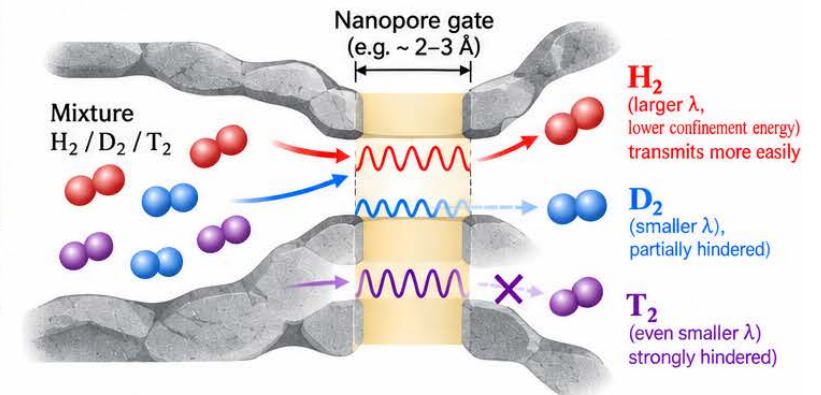
Isotope	Mass m (u)	Mass (kg)	λ at 300 K (Å)	λ at 100 K (Å)	λ at 50 K (Å)	λ at 25 K (Å)
H₂	2.016	3.347×10^{-27}	1.03	1.78	2.52	3.56
D₂	4.028	6.694×10^{-27}	0.73	1.26	1.78	2.52
T₂	6.032	1.002×10^{-26}	0.59	1.03	1.45	2.06

Matter waves of hydrogen isotopes at 25 K (same thermal energy, different de Broglie wavelengths)

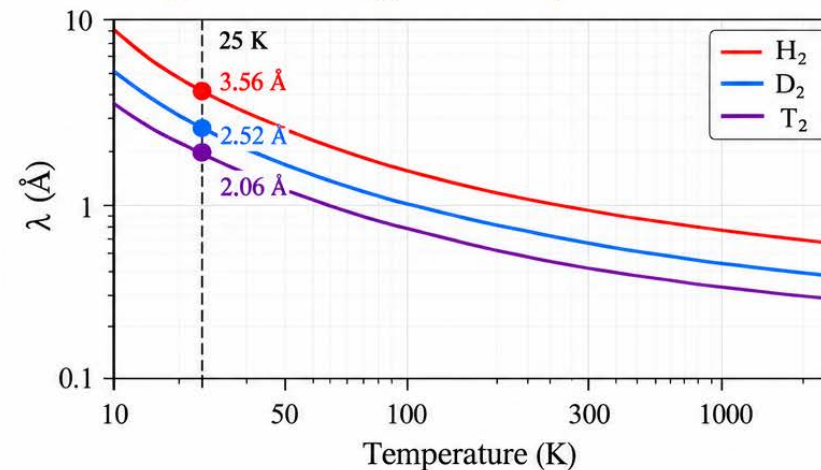


Quantum-sieving separation based on de Broglie wavelength

In nanoporous materials, the motion of light molecules such as H₂ can be strongly influenced by quantum effects. The de Broglie wavelength determines how well the matter wave fits into confined spaces and interacts with the pore walls and potential barriers, leading to isotope-dependent adsorption and diffusion.



De Broglie wavelength vs temperature



- Uses several steps to achieve enriched heavy water
- Isotope produced through electrolysis of H₂O and D₂O
- Costly (D₂O ~ \$ 300-500/ l) and not very efficient
- Selectivity $S=1.5@ 293$ K

Girdler sulfide separation process

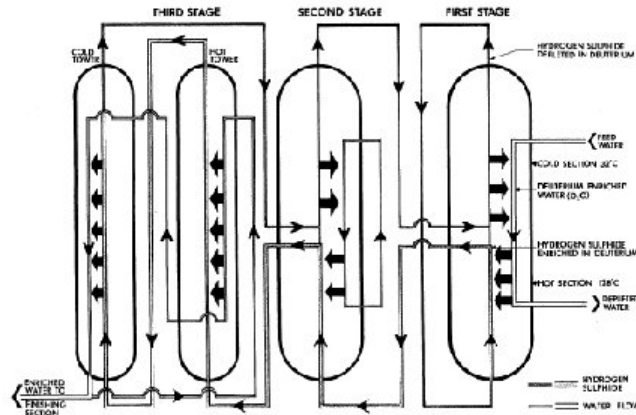
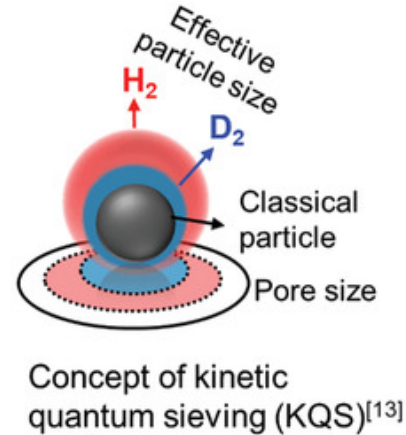


Fig. 2.7. Production of heavy water by GS hydrogen sulfide process (courtesy of Atomic Energy of Canada Limited).

Quantum sieving effect



- Based on the difference of the de Broglie wavelengths
- D_2 is smaller as H_2 , diffusion of D_2 is faster as of H_2
- Most pronounced around 23 K
- Better separation, High cost
- Selectivity $S=13$ @ 24K

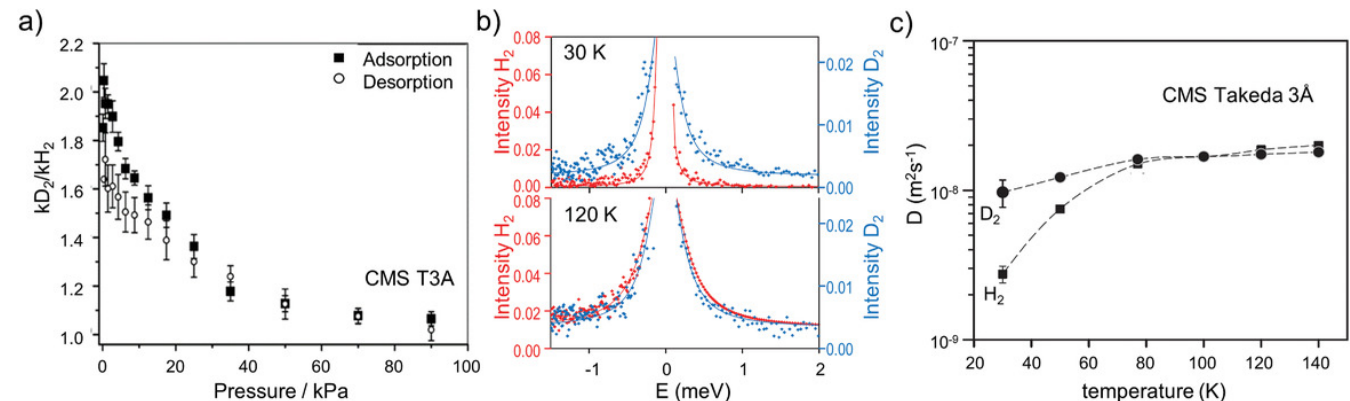
J. Am. Chem. Soc. 2017, 139, 15135-15141

de Broglie wavelength

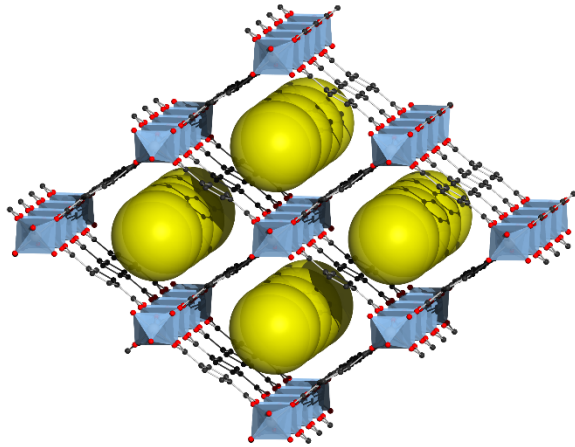
$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2\pi mk_B T}}$$

Example: microporous carbon with pores of 3-5 Å

- Uses several steps to achieve enriched heavy water
- Isotope produced through electrolysis of H_2O and D_2O
- Costly ($D_2O \sim \$ 300-500/ l$) and not very efficient
- Selectivity $S=1.5$ @ 293 K



Flexible metal organic framework MIL-53 (Al)



- Forms one-dimensional diamond-shaped channels running along the crystallographic c-axis. Depending on (P, T) and isotope

$$- np \sim 2.6 \times 13.6 \text{ \AA}^2$$

$$- lp \sim 8.5 \times 8.5 \text{ \AA}^2$$

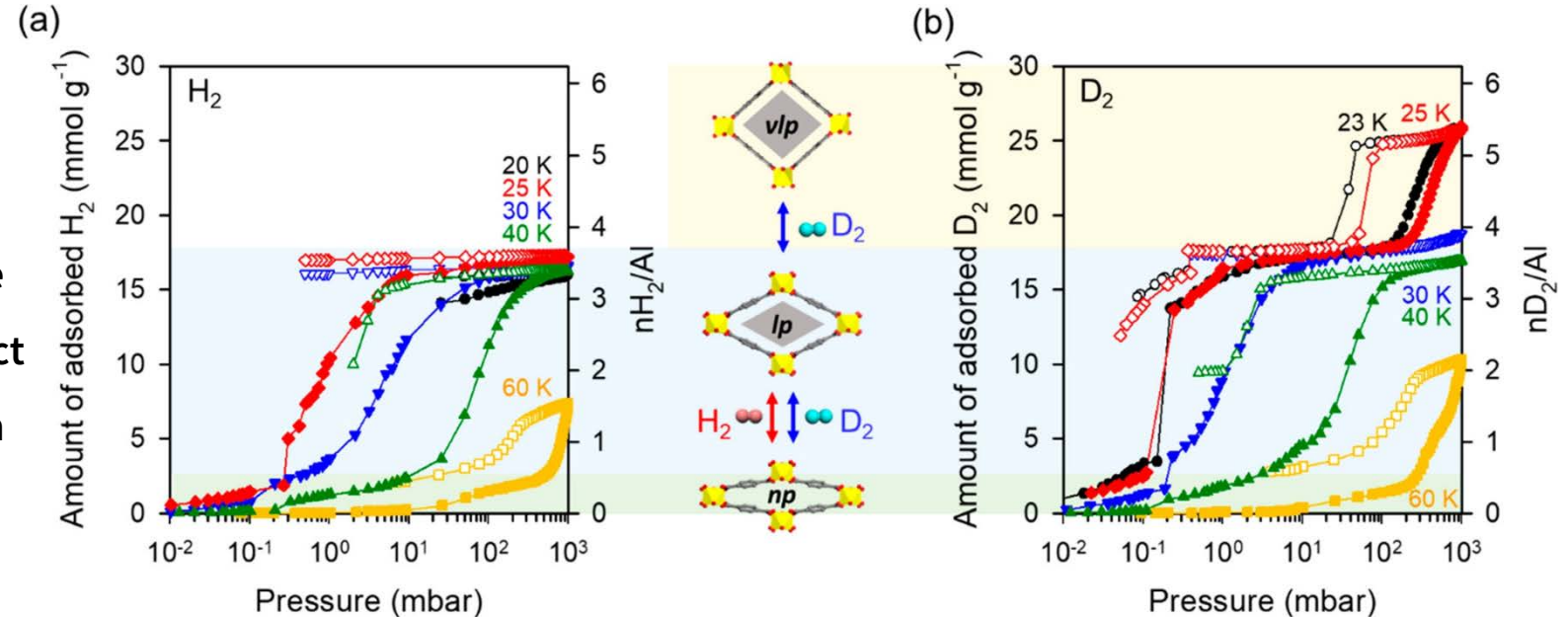
$$- vlp: d_{\text{pore}} \sim 8.5 \sim 12 \text{ \AA}$$

- Infinite chains of corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra

- Connected by terephthalate (BDC) linkers

- Flexible structure which responds to the external stimuli (P, T) => breathing effect

- Two breathing transitions depending on isotope



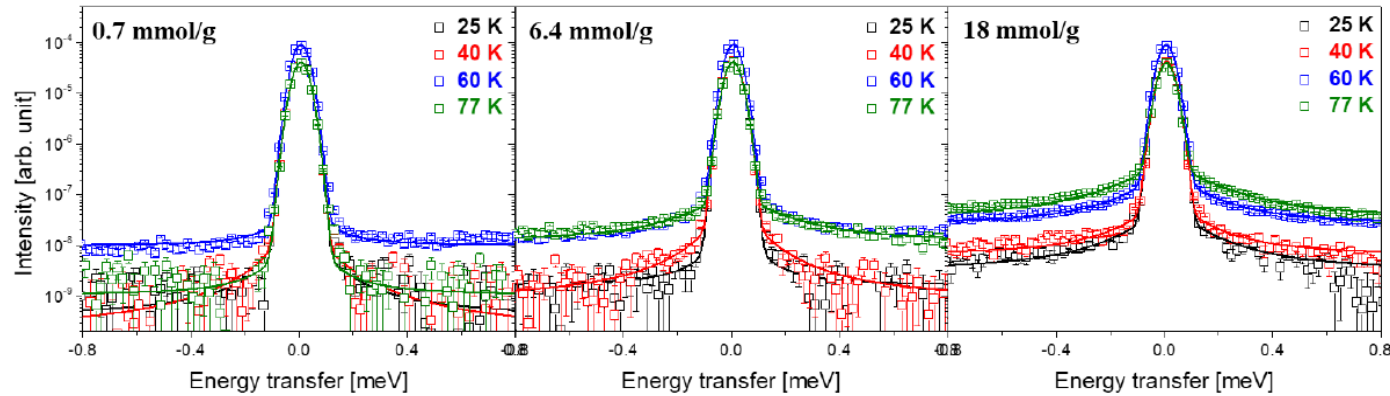
JACS, 2020, 142, 13278–13282

Advanced Materials 33 (20), 2007412

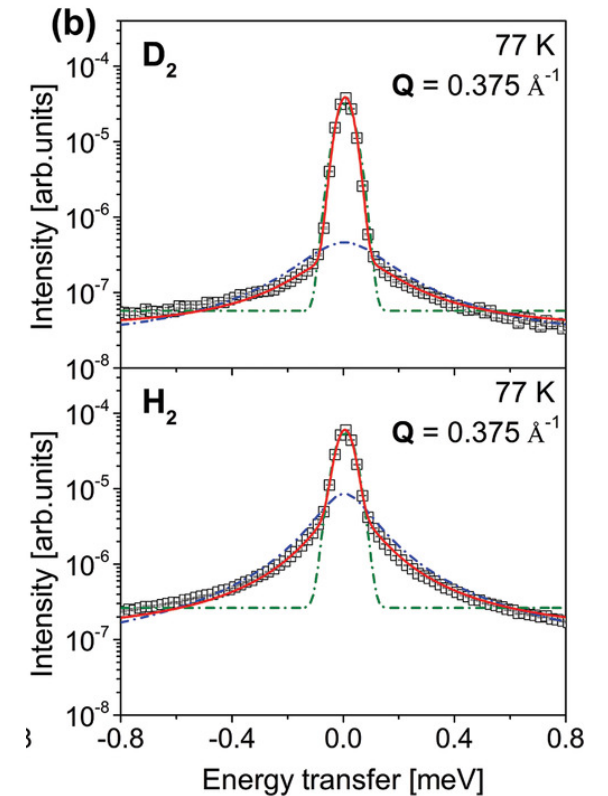
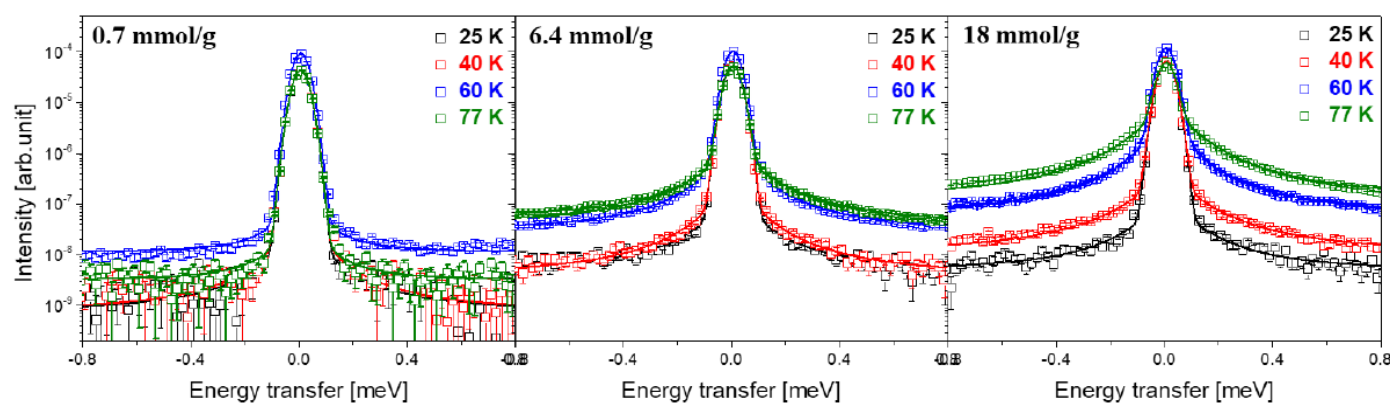
NEW MECHANISM IS INVOLVED!!!

pressure loading of
18 mmol/g

(a) Deuterium



(b) Hydrogen



QENS broadening: $\Gamma(Q) = \frac{h}{\tau_0} \left(1 - \frac{1}{1 + Q^2 l_0^2}\right)$

l – jump length and τ – residence time

$\rho(l) = l * \exp\left(-\frac{l}{l_0}\right)$ Self-diffusion coefficient $D_s = \frac{l_0^2}{\tau_0}$

Two temperature regimes:

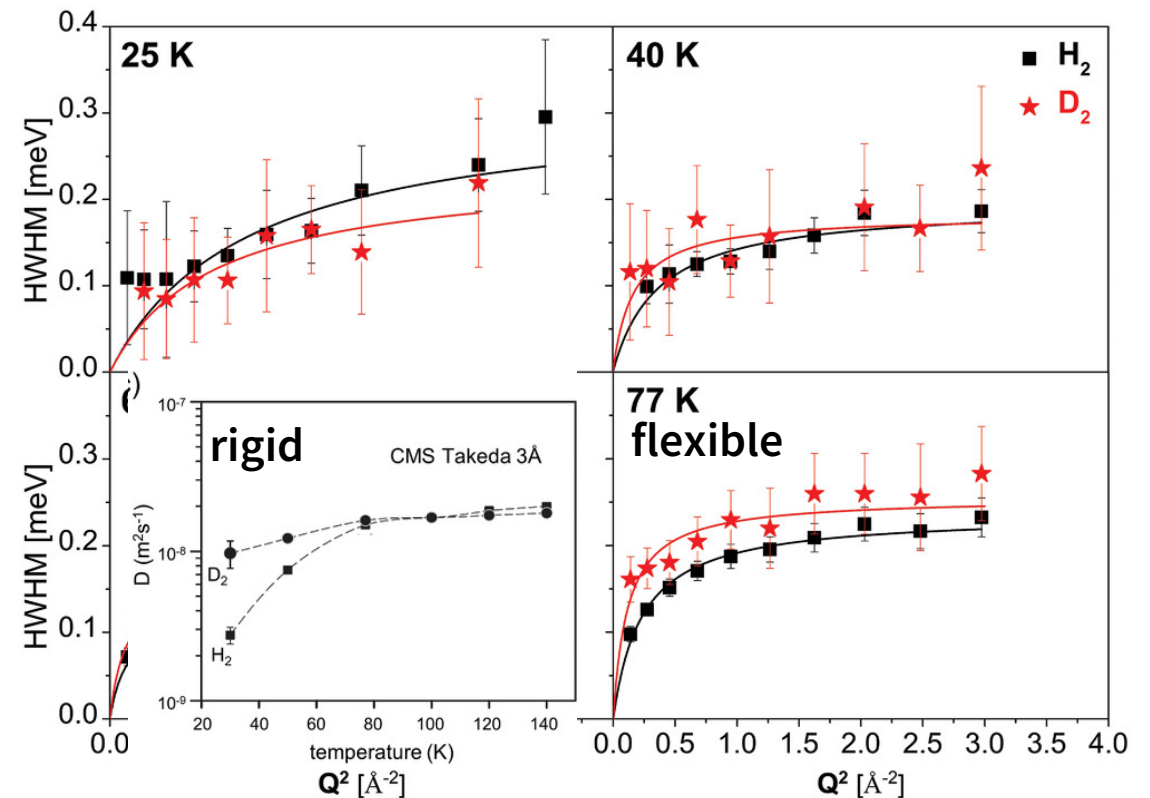
Low and medium T (< 40 K) – equal isotope diffusion, pores are accessible for D₂ or open for both isotopes

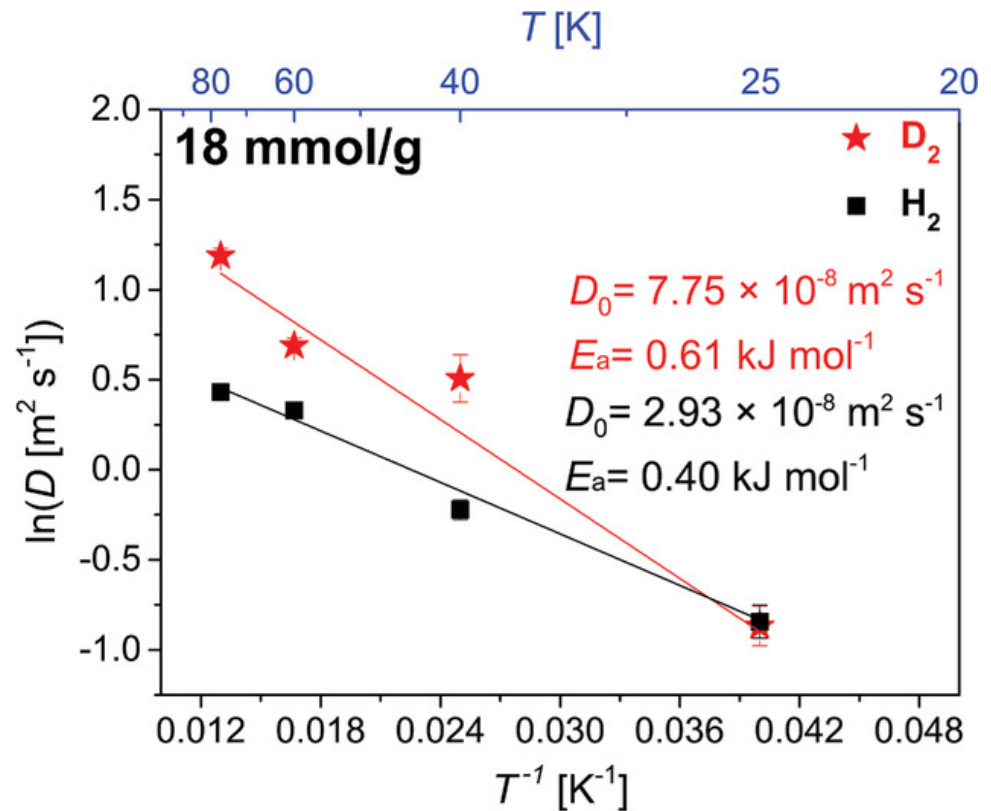
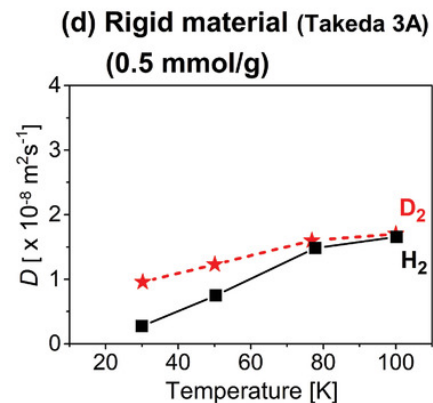
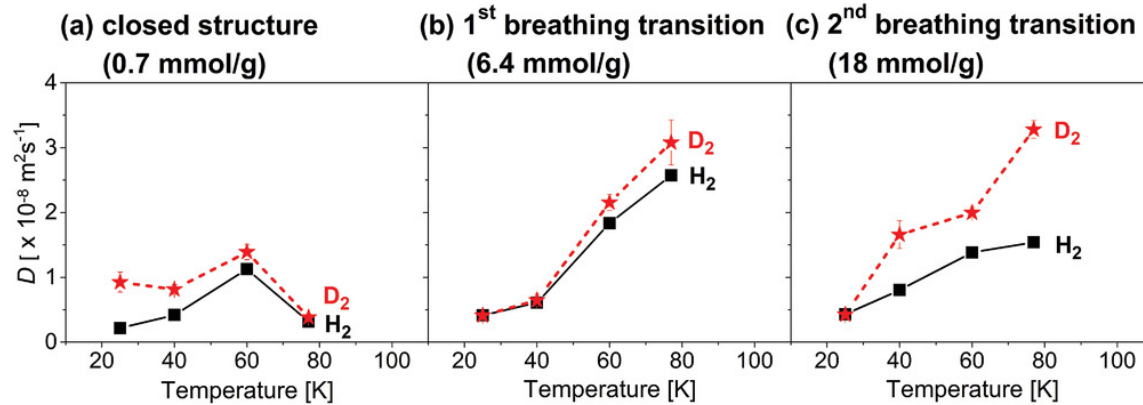
High T ≥ 60 K – D₂ diffuses faster



New mechanism

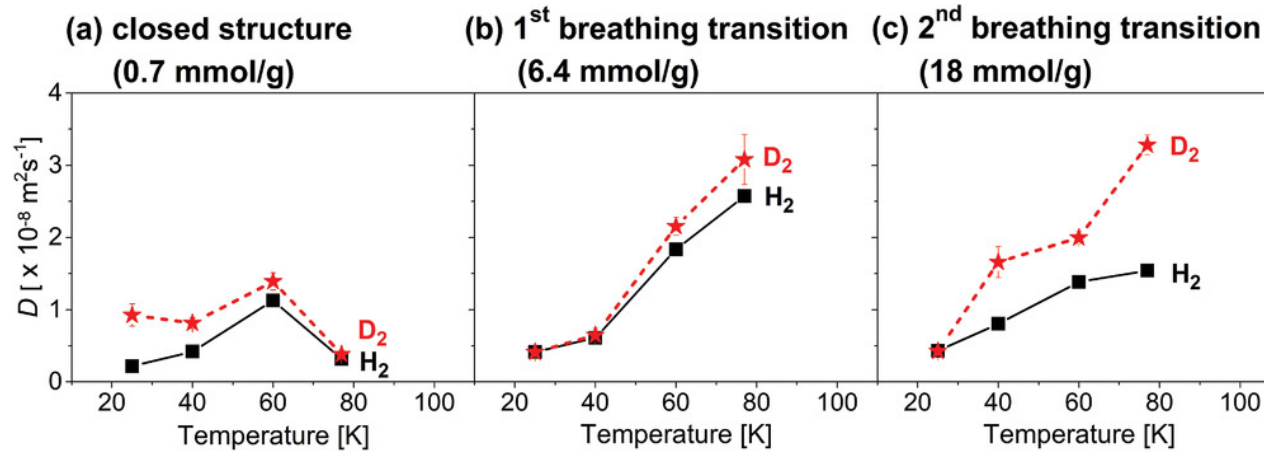
pressure loading of 18 mmol/g





The kinetic quantum sieving effect the separation is more efficient at elevated temperatures ! Why?

Why D_2 diffuse faster?



Quantum transport (~ 25K)

Transport limited by quantum confinement and pore access.

at very low loadings when $D_{D_2} > D_{H_2}$

Intermediate temperature (~40 K)

Lattice expands, pores are open and accessible for H_2 and D_2 ,

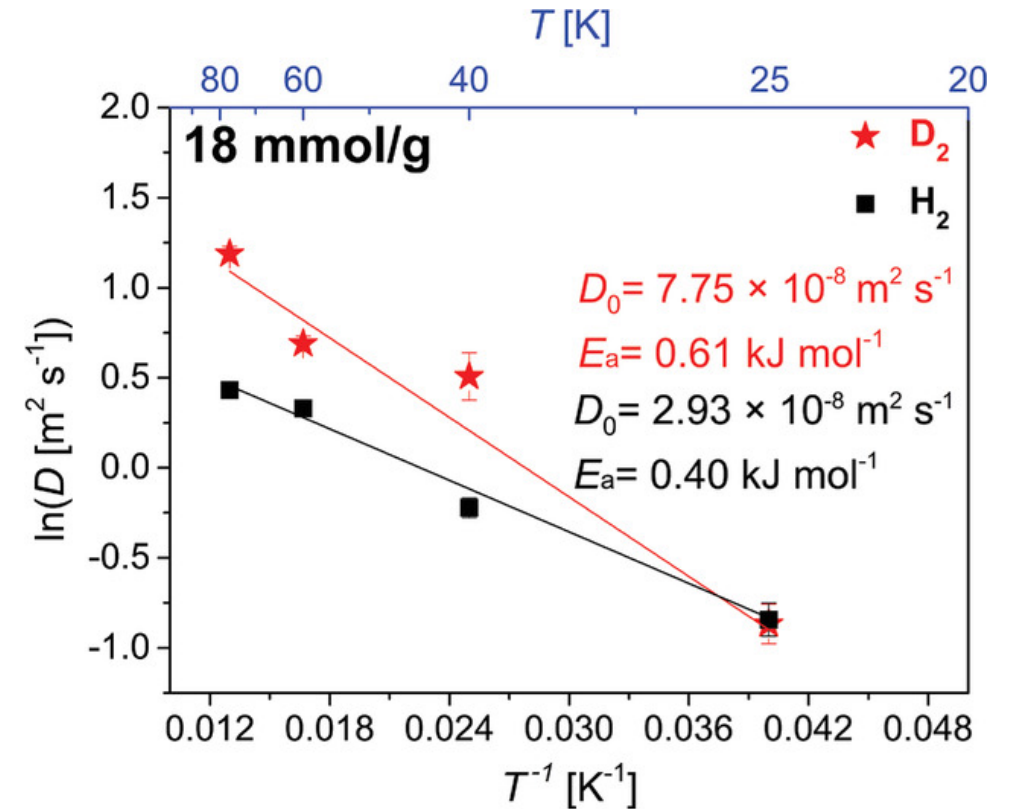
$$D_{D_2} \sim D_{H_2}$$

Framework-assisted transport (~60 K- 80 K) - Thermal Gating Kinetic Quantum Sieving

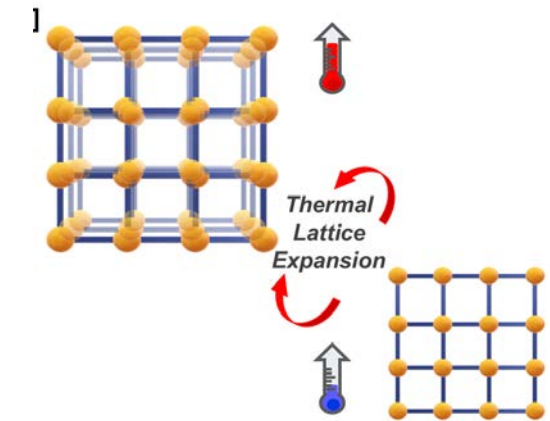
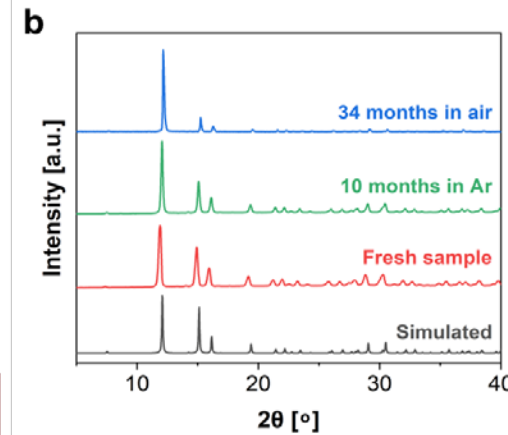
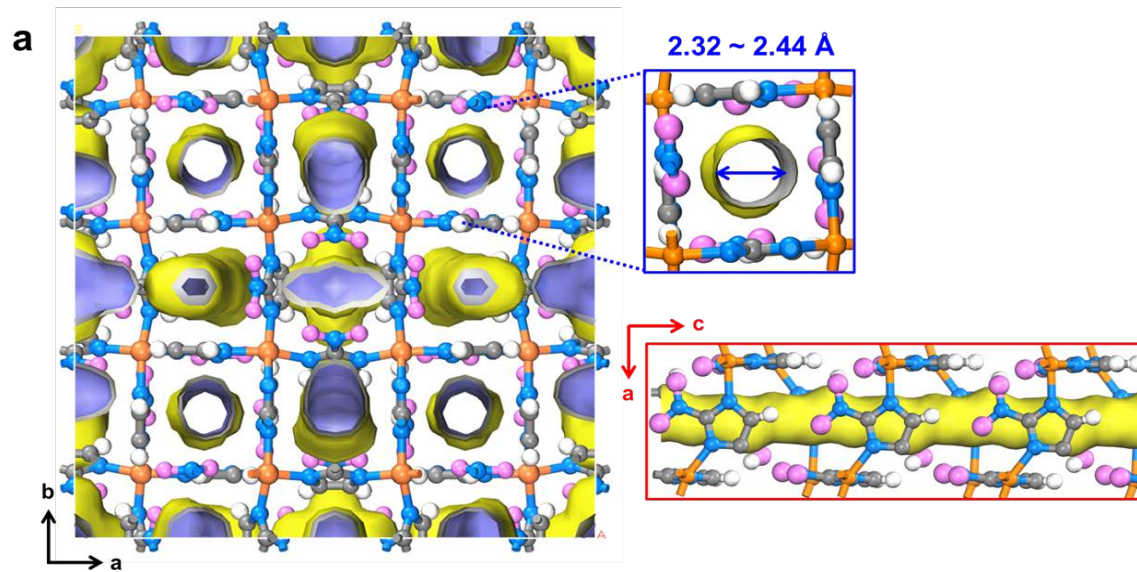
Large amplitude framework vibrations are activated and assist hopping.

D_2 couples more effectively to the fluctuating adsorption potential

$$D_{D_2} > D_{H_2}$$



How can we further improve the selection and increase the temperature range?

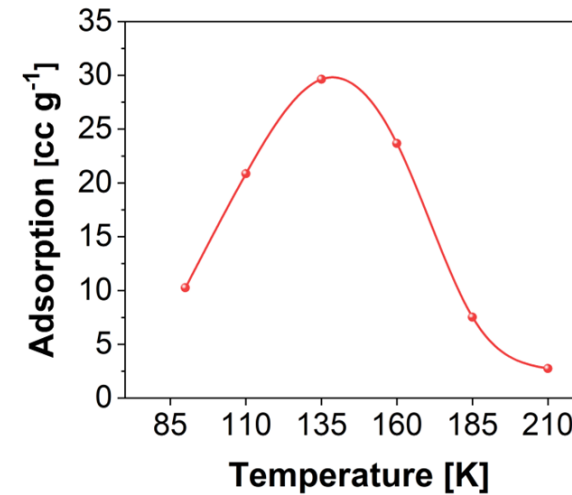
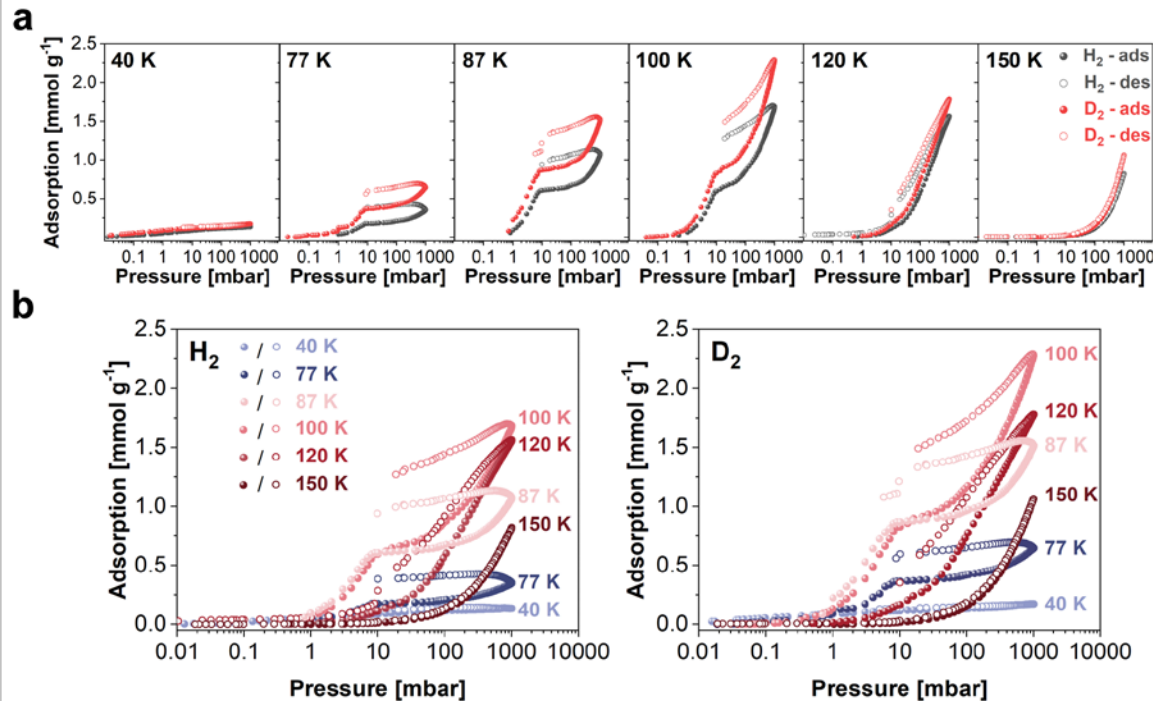


Temperature	a	b	c	V
[K]	[Å]	[Å]	[Å]	[Å ³]
100	23.392	23.392	7.693	4209.499
223	23.426	23.426	7.701	4226.136
298	23.439	23.439	7.704	4232.475

Cu-ZIF-gis Structure

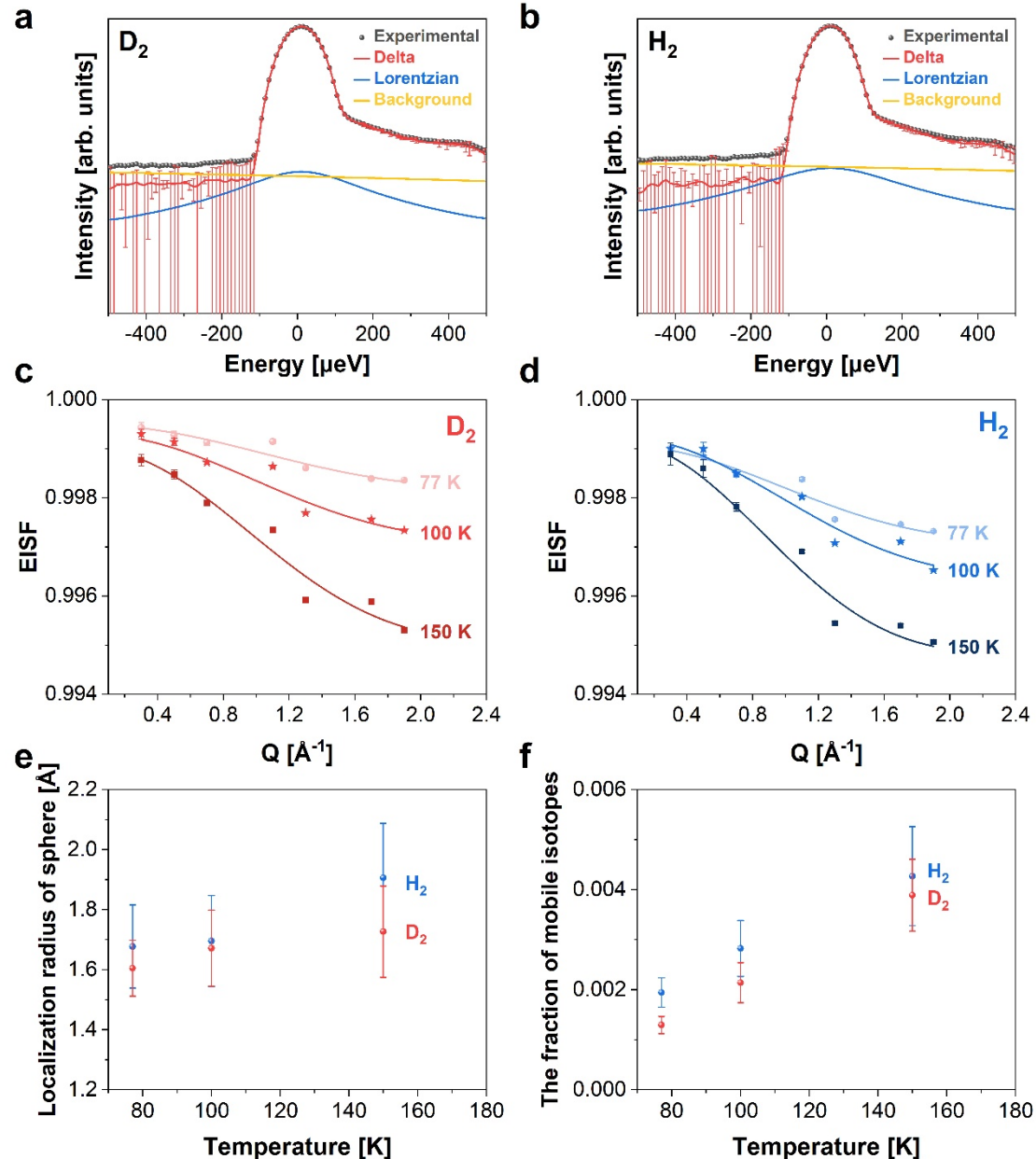
- No open sites
- Cu-based ZIF framework with GIS topology (gismondine-like)
- 3D network of cylindrical cavities with internal diameter d_p of about 2.33-2.44 Å
- Linkers are more rigid
- Expansion of lattice with temperature

Jung, M., Park, J., Muhammad, R. *et al.* Lattice-driven gating in a Cu-based zeolitic imidazolate framework for efficient high-temperature hydrogen isotope separation. *Nat Commun* 16, 2032 (2025). <https://doi.org/10.1038/s41467-025-56649-5>



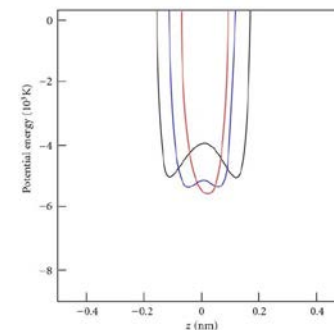
Jung, M., Park, J., Muhammad, R. *et al.* *Nat Commun* 16, 2032 (2025).
<https://doi.org/10.1038/s41467-025-56649-5>

- The adsorption isotherms exhibit a pronounced hysteresis, indicating structural deformations during the adsorption-desorption cycle.
- The maximum adsorption uptake is observed at 130–135 K, with the exact temperature depending on the hydrogen isotope.
- The isotope-dependent maximum uptake at 130–135 K coincides with the temperature range where framework dynamics become increasingly important for isotope transport.



$$EISF(Q) = \frac{I_{elastic}(Q)}{I_{elastic}(Q) + I_{quasielastic}(Q)} = A + (1 - A) \left(\frac{3j_1(Qr)}{Qr} \right)^2$$

- The subtle quasielastic broadening observed by QENS reveals that H_2 and D_2 remain largely localized at adsorption sites throughout the entire temperature range studied, indicating strong host-guest interactions and pronounced coupling to the MOF framework dynamics.
- The degree of localization differs for H_2 and D_2 , reflecting their distinct quantum states and adsorption energies, and providing direct evidence for the potential of isotope-selective separation



N.Kojima, T.Ohba, Y.Urabe,
H. Kanoh, K. Kaneko, Pore-Width-
Dependent , *Journal of Nanomaterials*,
2011,
853989, <https://doi.org/10.1155/2011/853989>

Hydrogen isotope separation in porous materials is governed not only by pore size, but by the interplay of quantum effects, host–guest interactions, and framework dynamics. Advanced porous materials enable efficient H₂/D₂ separation beyond the limits of classical quantum sieving and extend isotope selectivity to unprecedented temperature regimes

MIL-53(Al)

Flexible breathing framework

Strong D₂ localization in adsorption sites

Enhanced D₂ coupling to framework vibrations

Separation up to 80-100 K

Cu-ZIF-gis

Rigid-looking framework with dynamic gate

Temperature-dependent pore aperture

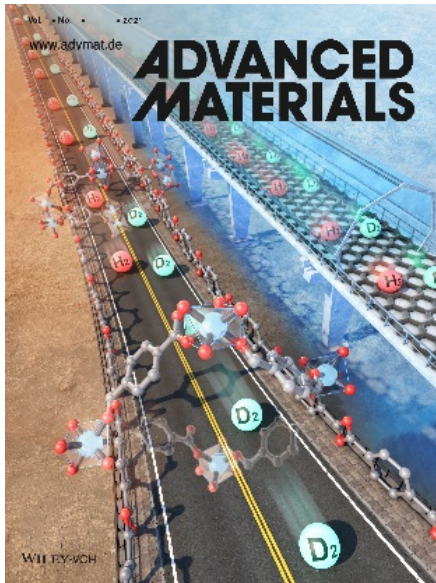
Lattice-driven gating

Separation up to ~120-150 K

Neutron spectroscopy provides a unique link between molecular-scale dynamics and macroscopic separation performance, revealing:

- adsorption-site localization,
- diffusion pathways,
- host–guest coupling

COLLABORATORS AND WORK PUBLISHED



Advanced Materials 33, 2021, 2170152

Advanced Materials 33, 2021, 2007412



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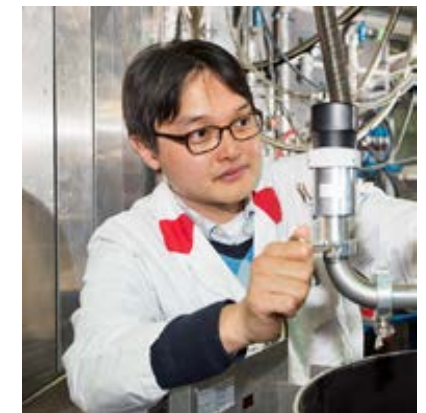
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[Nature Communications](#) **16**, Article number: 2032 (2025) | [Cite this article](#)

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