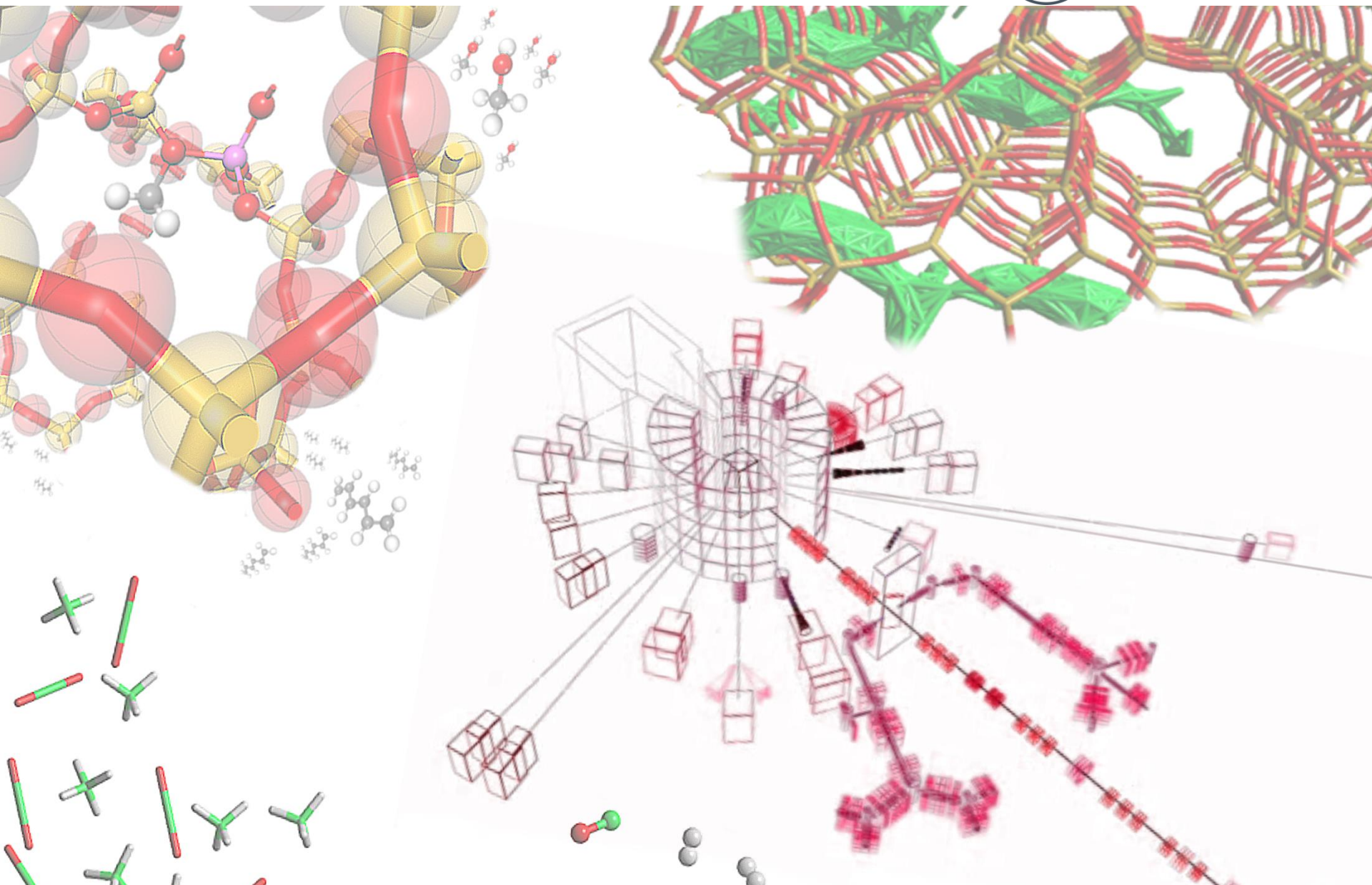
Molecular Behaviour in Zeolite Catalysts

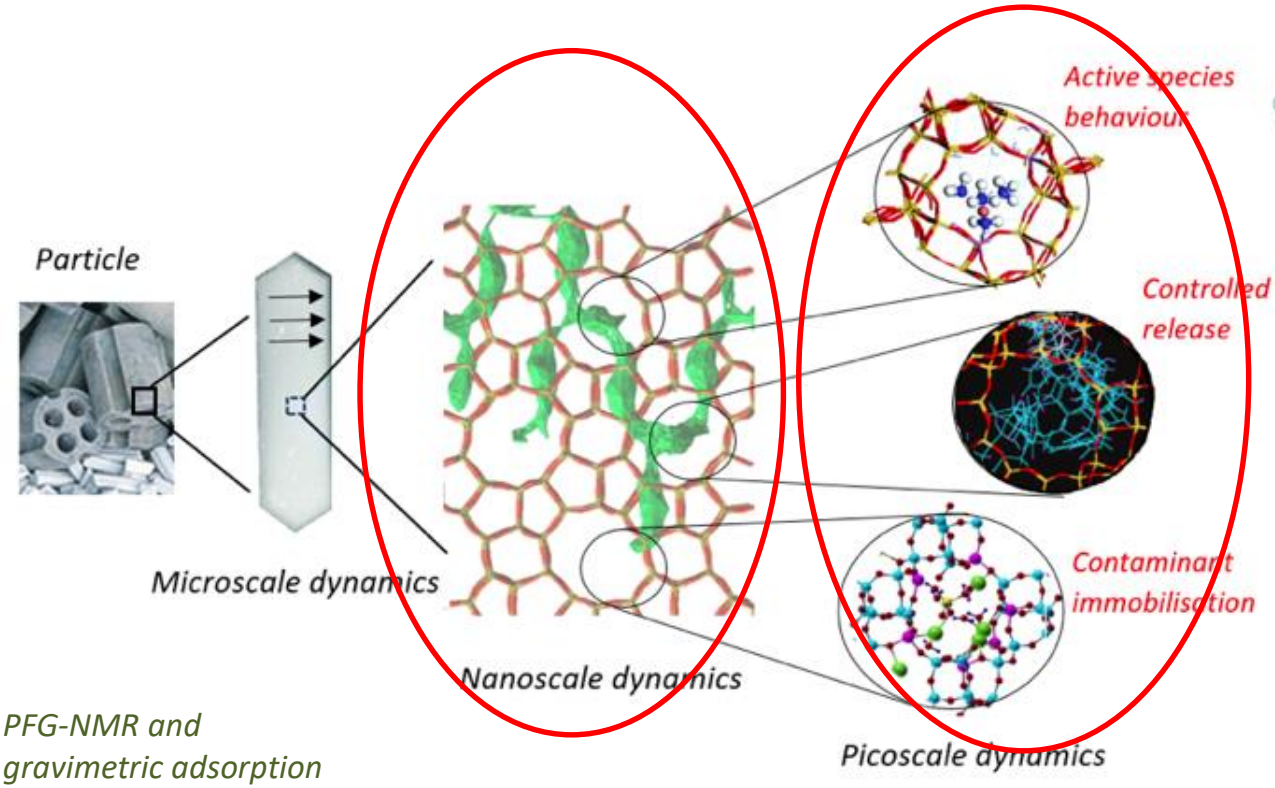
Alexander O'Malley

UNIVERSITY OF BATH



Molecular Mobility in Microporous Materials

UNIVERSITY OF BATH

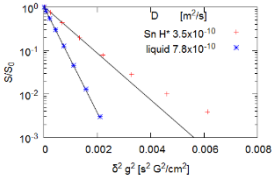


Catalysis

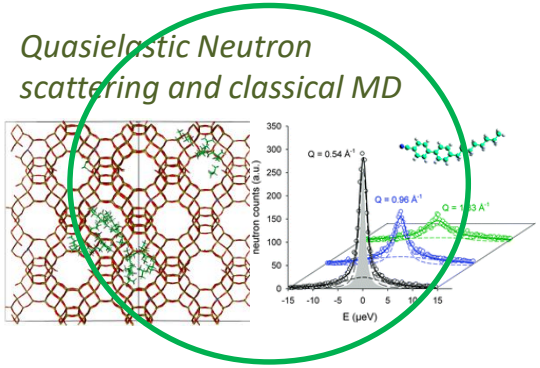
Drug delivery

Water treatment

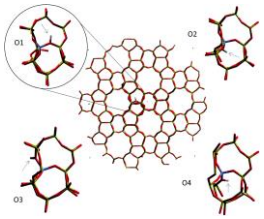
PFG-NMR and gravimetric adsorption

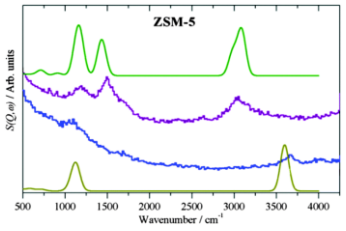


Quasielastic Neutron scattering and classical MD



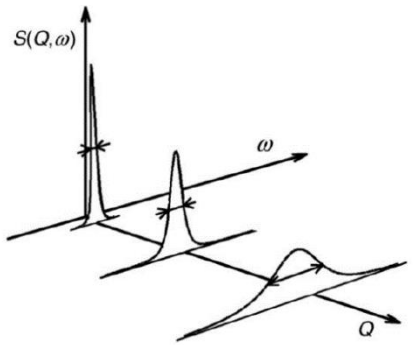
QM calculations and vibrational spectroscopy



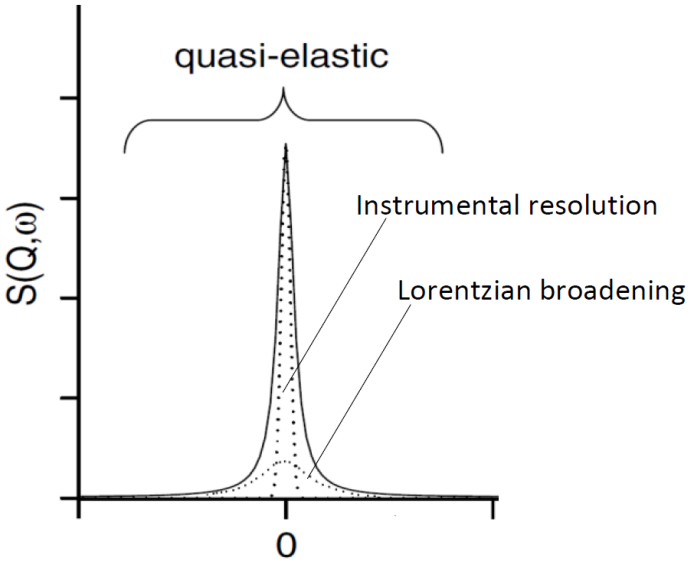


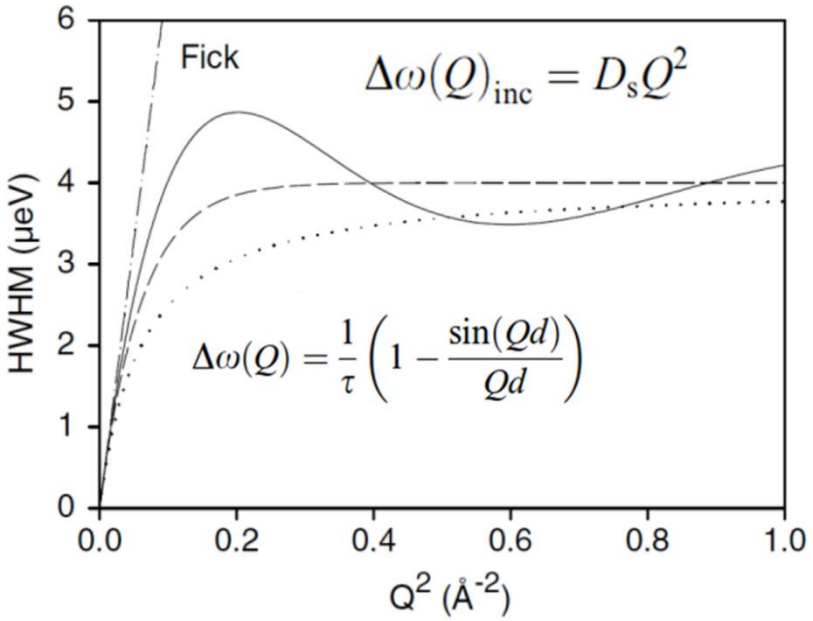
Quasielastic Neutron Scattering – Translational motion

- Very small changes in neutron energy (μeV-meV)
  - Interact with translational motion.
  - Sensitive to ^{1}H (useful for confined sorbates)



- Change in spectral profile around the elastic line.
  - Broadening of a Lorentzian component
  - Fitting HWHM to models of jump/fickian diffusion
  - **Matches scales of an MD simulation**



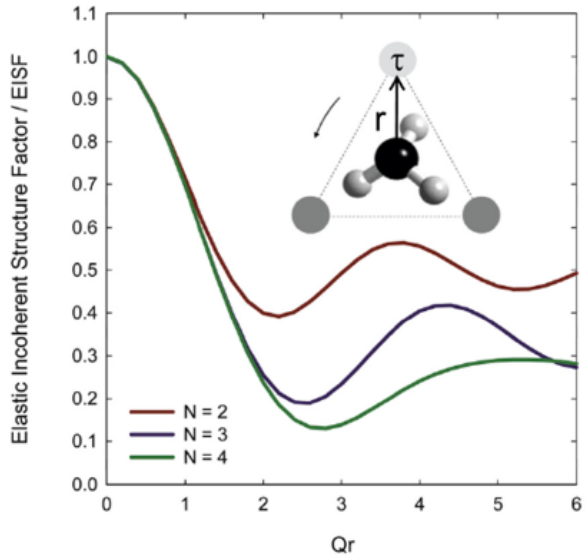


Quasielastic Neutron Scattering – localised motion

$$EISF = \frac{S_{inc}^{el}(\boldsymbol{Q})}{S_{inc}^{el}(\boldsymbol{Q}) + S_{inc}^{qel}(\boldsymbol{Q})}$$

The **EISF** is the area of the elastic curve divided by the total are, ie. The fraction of elastic contribution.

Particles move in a restricted space having a specific **geometry of motion**



- Jumps between 2, 3, … *n* sites
- Rotational diffusion on a circle
- Diffusion on a sphere
- Diffusion inside a sphere, cylinder…

For a CH_3 group – site site jumps

$$EISF = \frac{1}{3}\left[1 + 2j_0\left(\sqrt{3}\,Qr\right)\right]$$

Jumps between 2 sites

$$EISF = \frac{1}{2}\left[1 + \frac{\sin(2Qd)}{2Qd}\right]$$

Free diffusion inside a sphere

$$EISF = \left(\frac{3j_1(Qr)}{Qr}\right)^2$$

Complementarity of QENS and current MD simulations in porous materials

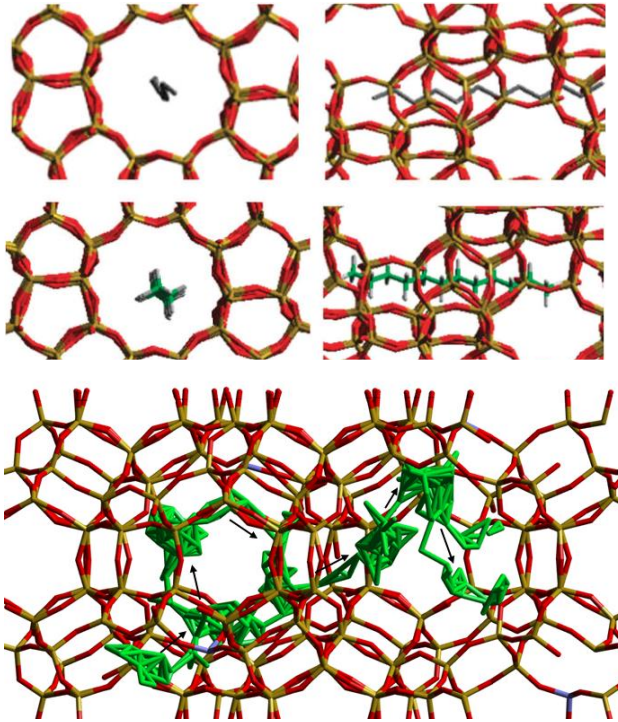
UNIVERSITY OF BATH

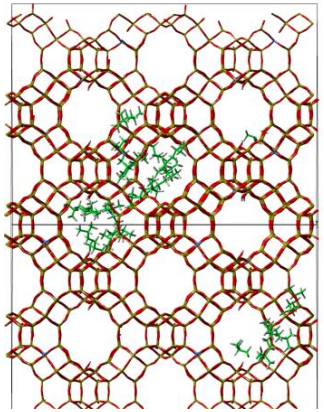
- Increases in computational power have facilitated more sophisticated and accurate classical MD simulations.

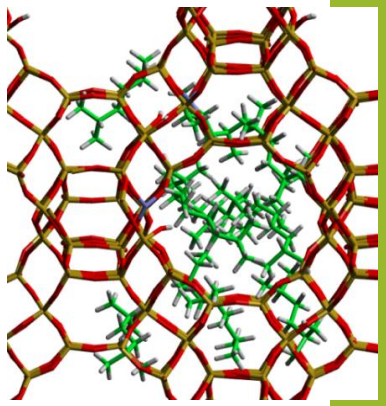
- Flexible frameworks
  - Removal of energy traps
  - Non-elastic sorbate/framework interactions
  - “Breathing” allowing access to areas

- Explicit/flexible hydrocarbons
  - Potential less smooth than united atom models
  - Degrees of freedom in molecular flexibility

- Simulation size/length
  - 10-100 ns with c. 4000 atoms
  - Allows qualitative and quantitative phenomena to be observed
  - Channel switching/clustering





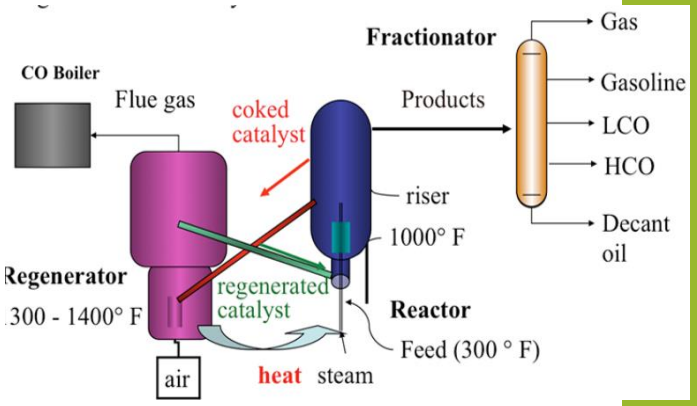


1. A. J. O’Malley, and C. R. A. Catlow. *Phys. Chem. Chem. Phys.* 15.43 (2013): 19024
2. A. J. O'Malley, and C. R. A. Catlow. *Phys. Chem. Chem. Phys.* 17.3 (2015): 1943

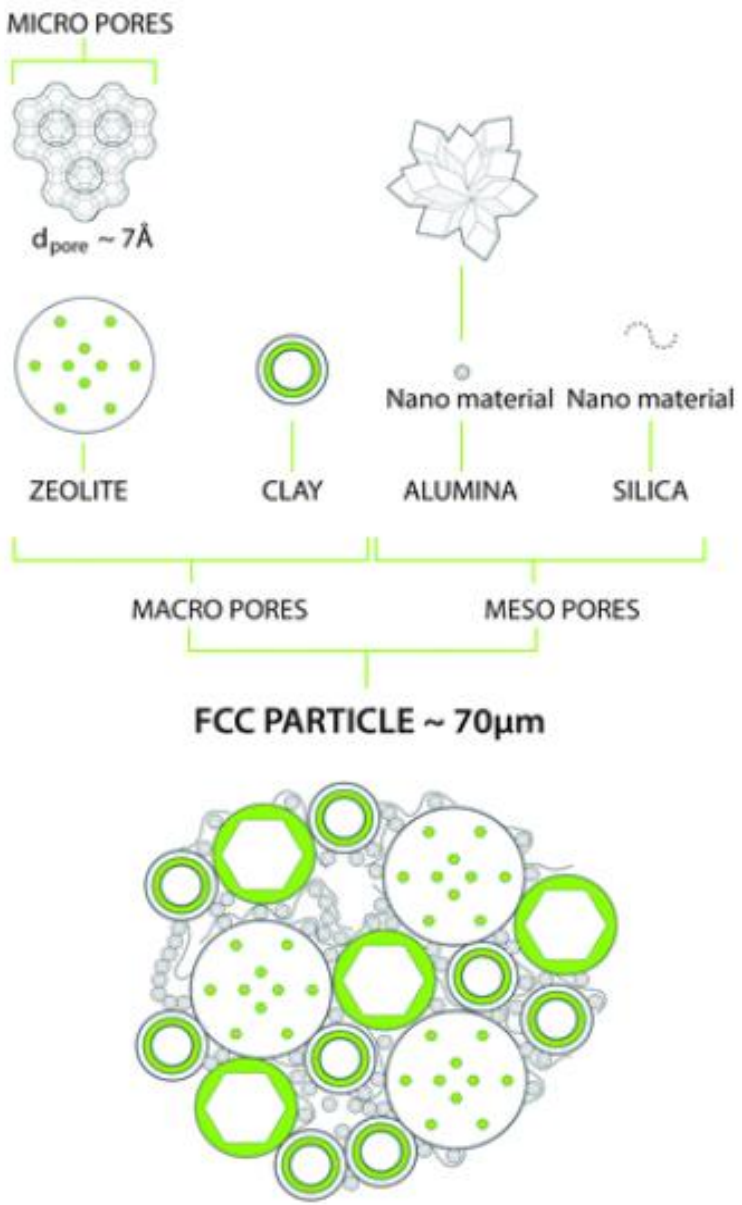
Fluid Catalytic Cracking

- FCC is one of the major conversion technologies in the petrochemical industry and produces the majority of the world's gasoline.
- Catalytically breaking down the large molecules in crude oil fractions to gasoline range hydrocarbons, and smaller hydrocarbons such as propene.
- "During 2007, the FCC units in the United States processed a total of 5,300,000 barrels (840,000 m^3) per day of feedstock and FCC units worldwide processed about twice that amount."
- "It is estimated that ~2300 metric tons of FCC catalyst are produced per day, or ~840,000 metric tons per year."

https://www.eia.gov/todayinenergy/detail.php?id=9150
Reproduced from Valero energy corporation

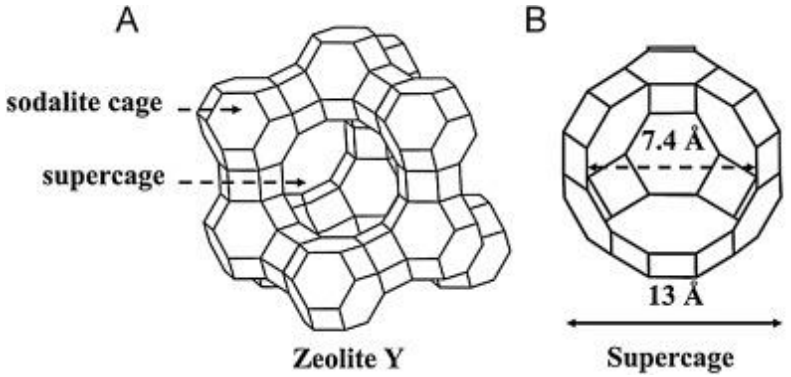


https://www.e-education.psu.edu/fsc432/content/fluid-catalytic-cracking-fcc Source: Dr. Semih Eser

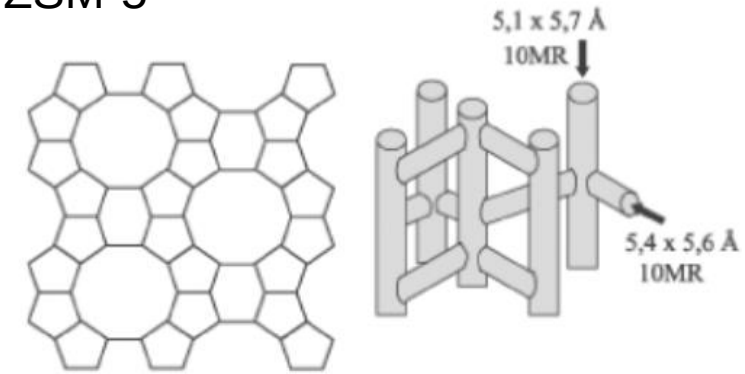


Vogt, E. T. C., and B. M. Weckhuysen. *Chemical Society Reviews* 44.20 (2015): 7342-7370.

Zeolite Y

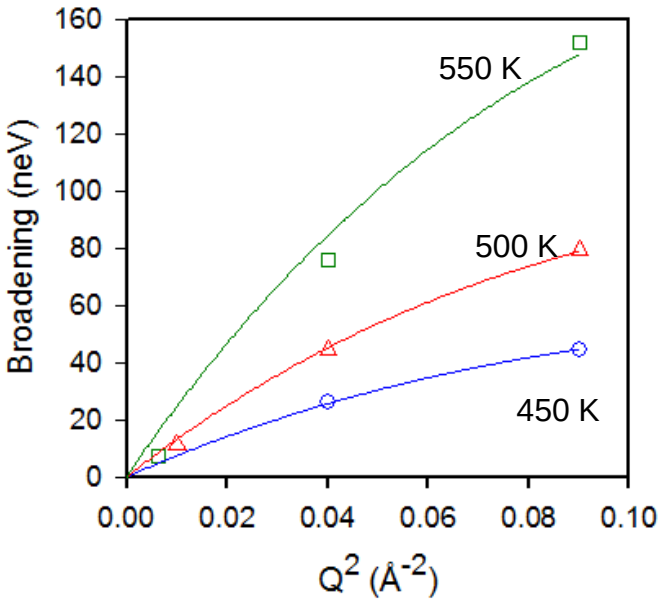


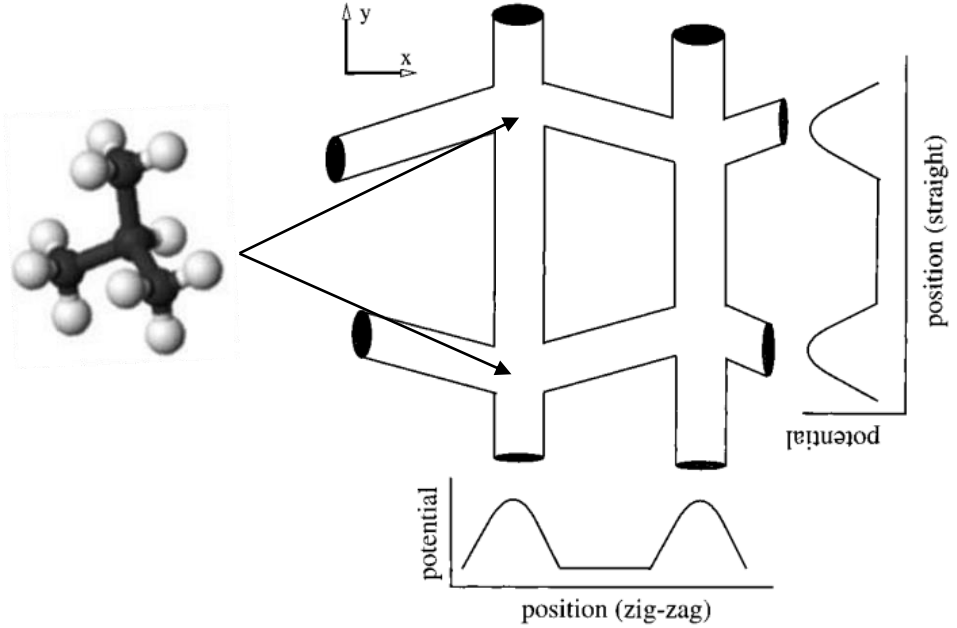
ZSM-5



Isobutane in silicalite: Combined NSE and MD study

- Collaboration with H. Jobic IRCE-Lyon using the neutron spin echo technique.
- Suited for slower moving (bulky) sorbates – very high resolution (spin relaxation)
- Jump diffusion observed through experiment – 10 Å jump distance

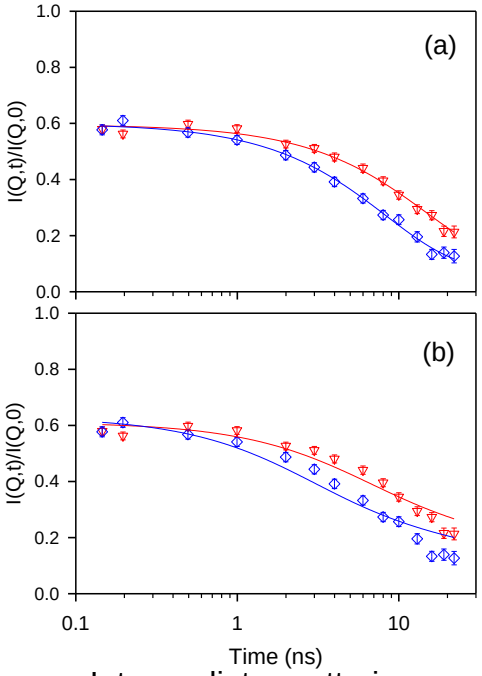




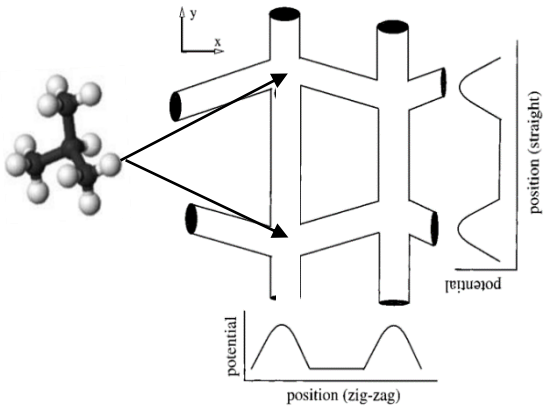
3. A. J. O'Malley., C. R. A. Catlow, M. Monkenbusch, and H. Jobic. *The Journal of Physical Chemistry C* 119, 48 **2015:** 26999-27006.

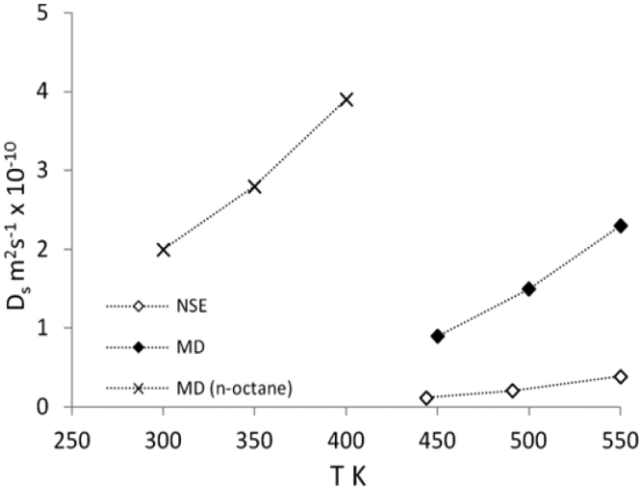
Isobutane in silicalite: Combined NSE and MD study

- 3D diffusion observed from intermediate scattering function… 1D expected?
- D_s calculated from MD giving agreement with experiment within a factor of 6.
- Differences attributed to use of a perfect crystal for simulations.



Intermediate scattering function at 450 K

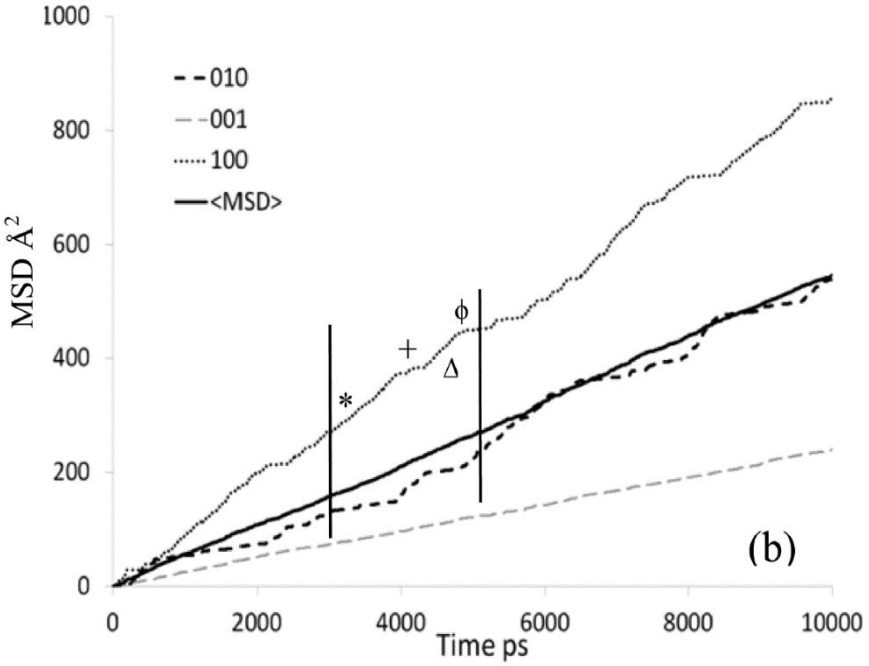


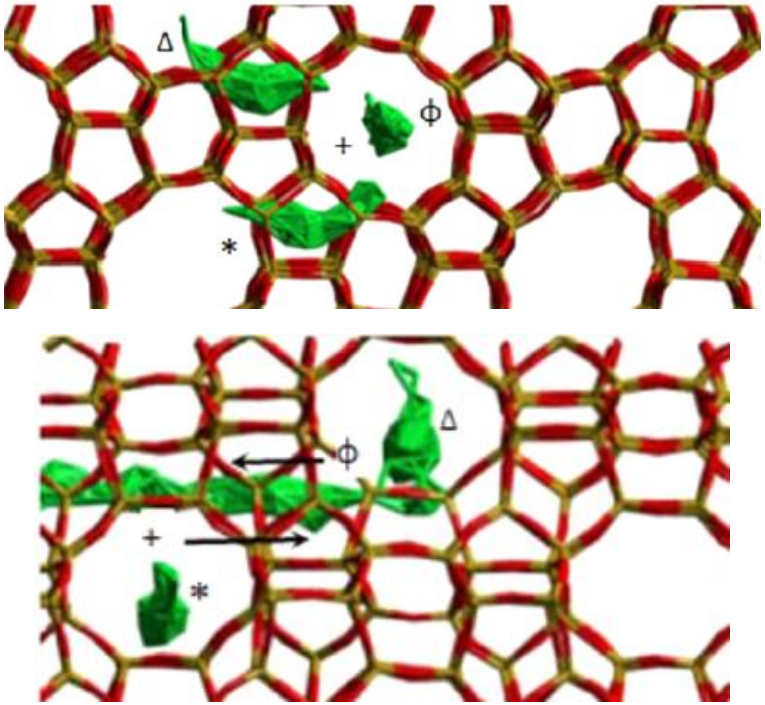


3. A. J. O'Malley., C. R. A. Catlow, M. Monkenbusch, and H. Jobic. *The Journal of Physical Chemistry C* 119, 48 **2015:** 26999-27006.

Isobutane in silicalite: Combined NSE and MD study

- MD simulations show differing behaviour to previous simulations.
- Residence time in the small section of sinusoidal channel at 450 K (still *d* =10 Å).
- Differing observation due to use of flexible zeolite framework.

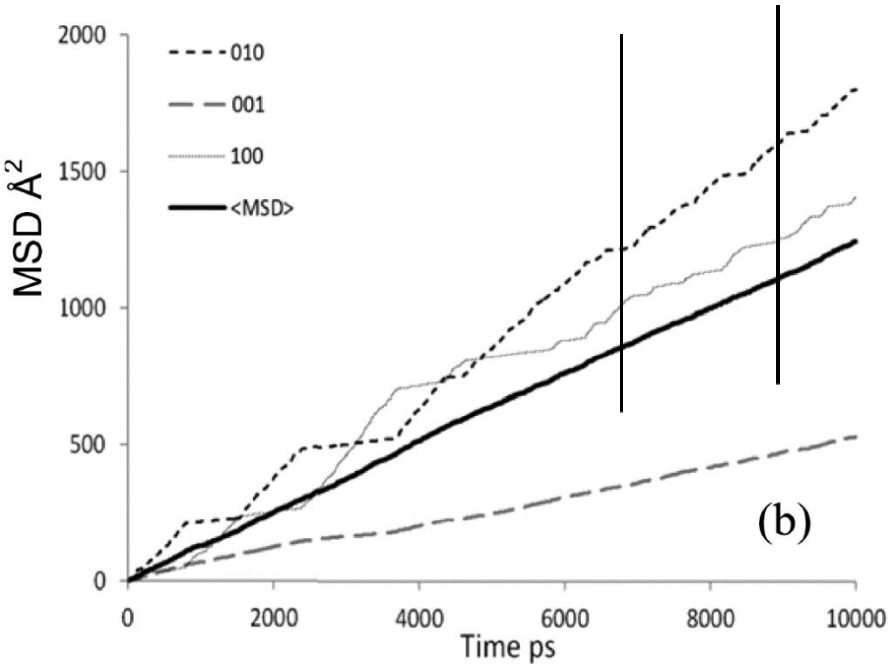


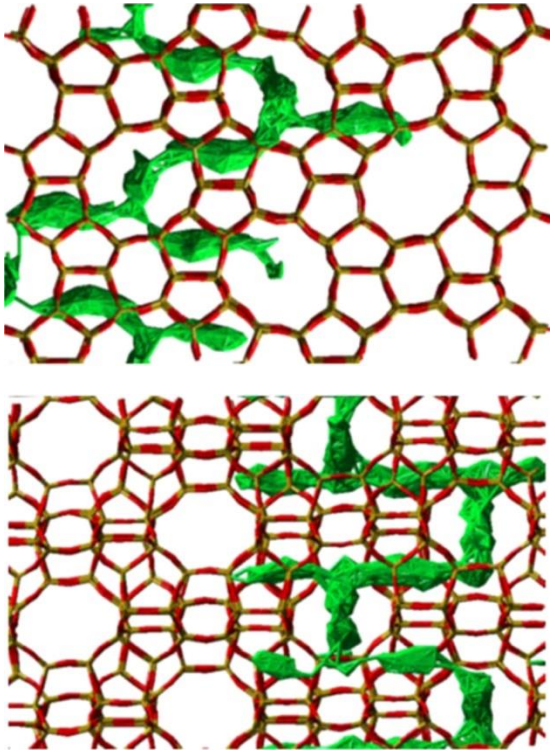


3. A. J. O'Malley., C. R. A. Catlow, M. Monkenbusch, and H. Jobic. *The Journal of Physical Chemistry C* 119, 48 **2015:** 26999-27006.

Isobutane in silicalite: Combined NSE and MD study

- At 550 K two modes of motion are observed, long term diffusion in either channel system or free diffusion with fast switching between both.
- Appears isobutane diffusion is dictated by temperature dependent trapping in small sinusoidal channel segments

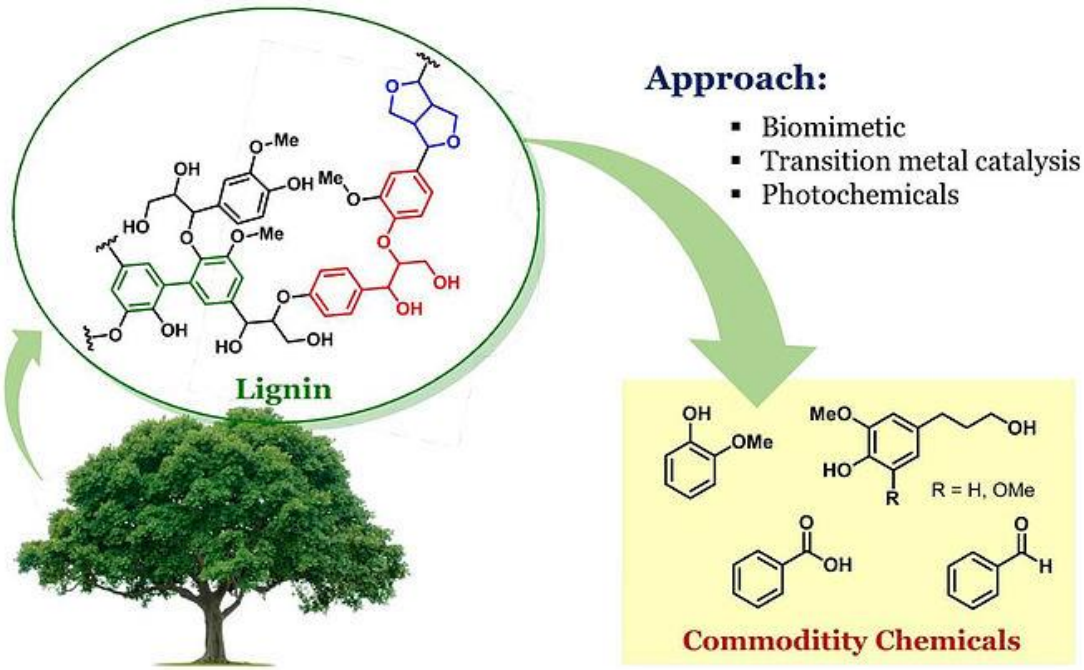




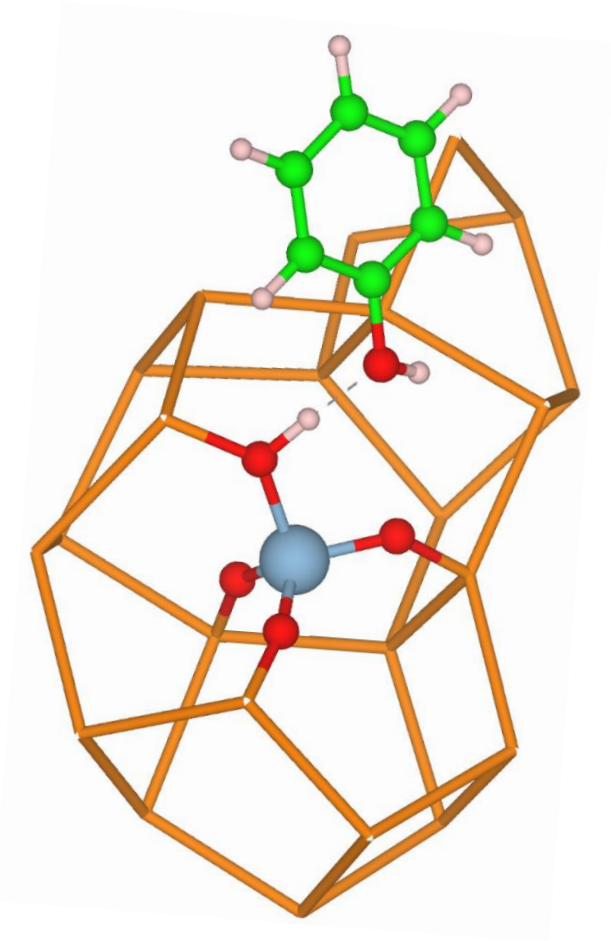
3. A. J. O'Malley., C. R. A. Catlow, M. Monkenbusch, and H. Jobic. *The Journal of Physical Chemistry C* 119, 48 **2015:** 26999-27006.

Phenol behaviour in zeolite catalysts

w/ Carlos Hernandez-Tamargo, N. H. De Leeuw (Cardiff)

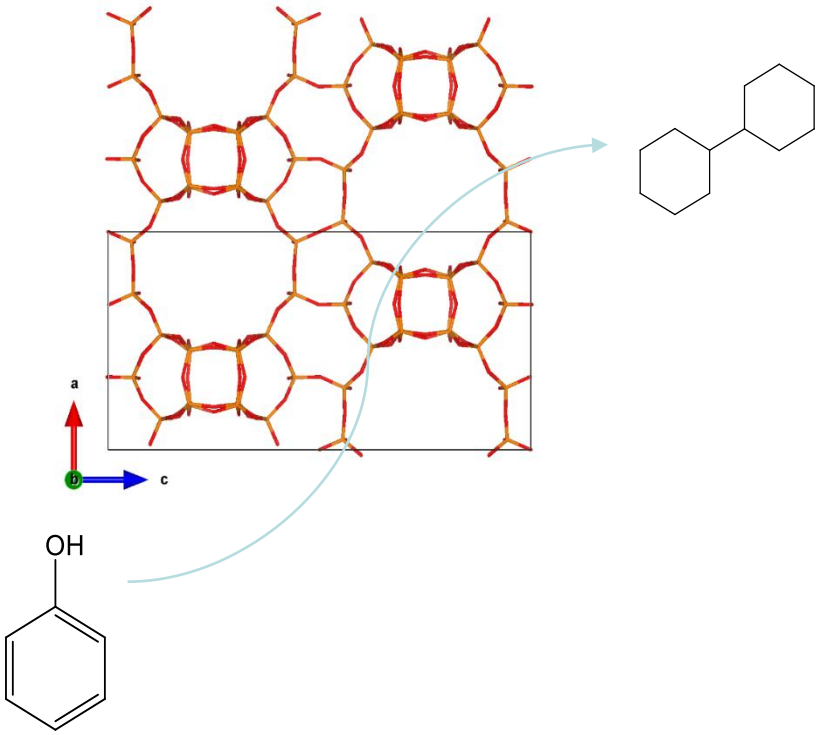


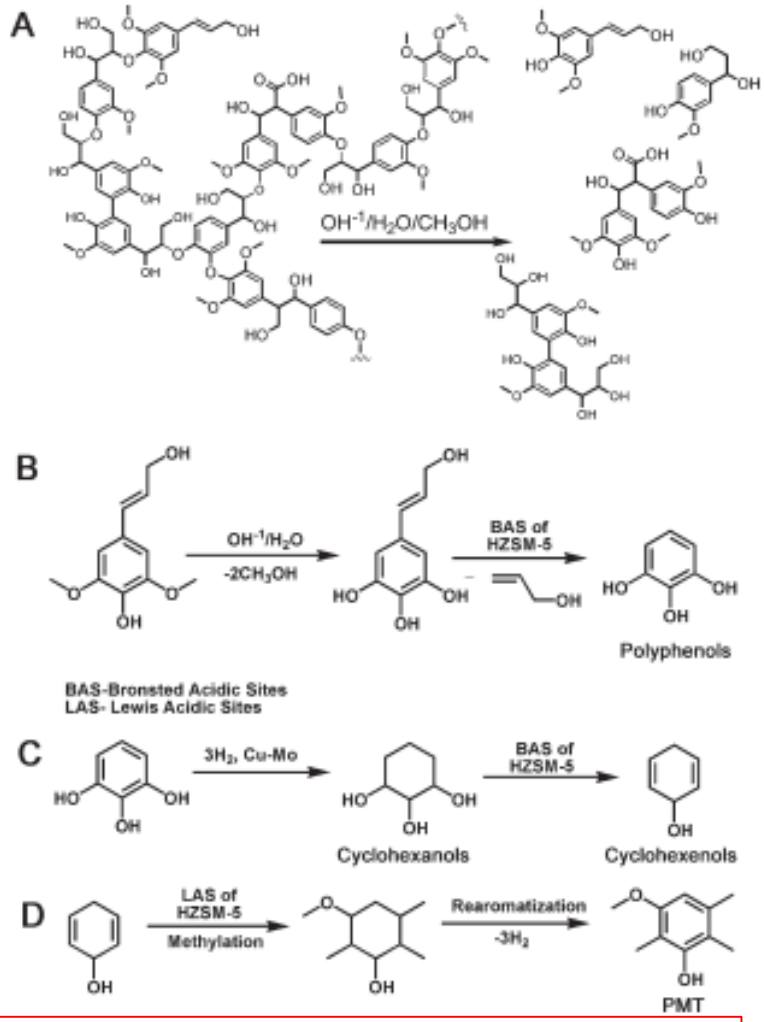
https://www.dmaiti.com/lignin-valorisation



Lignocellulosic biomass conversions

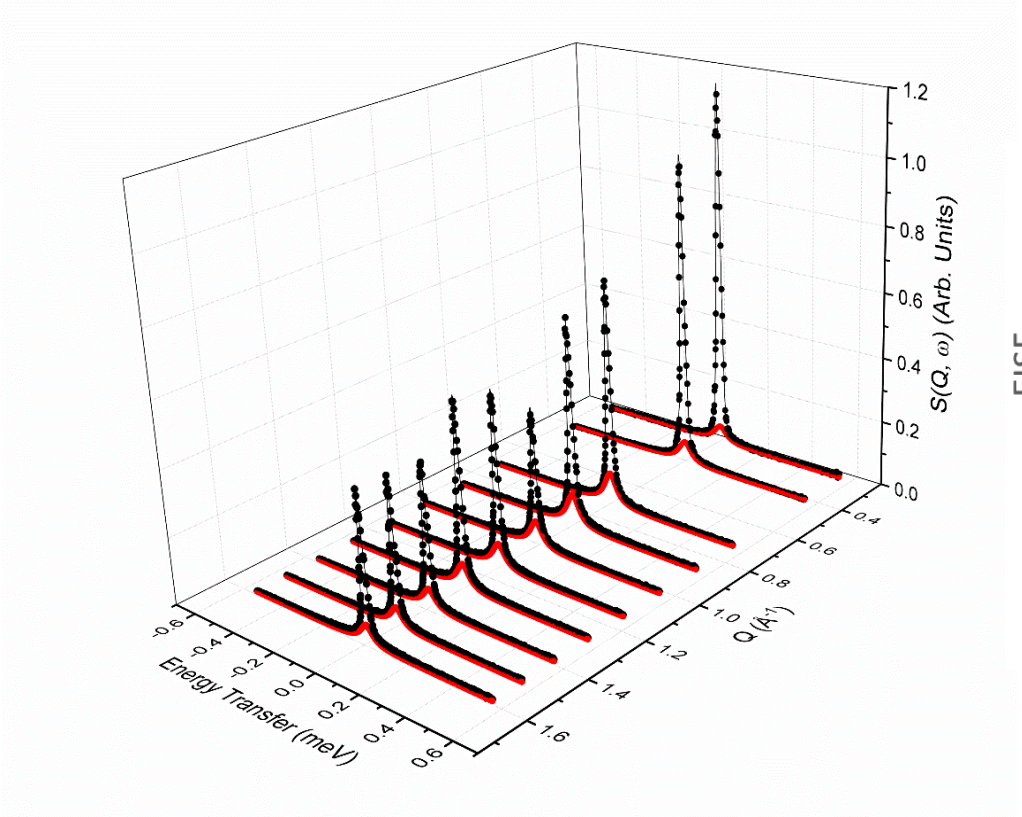
BEA (12-membered rings)

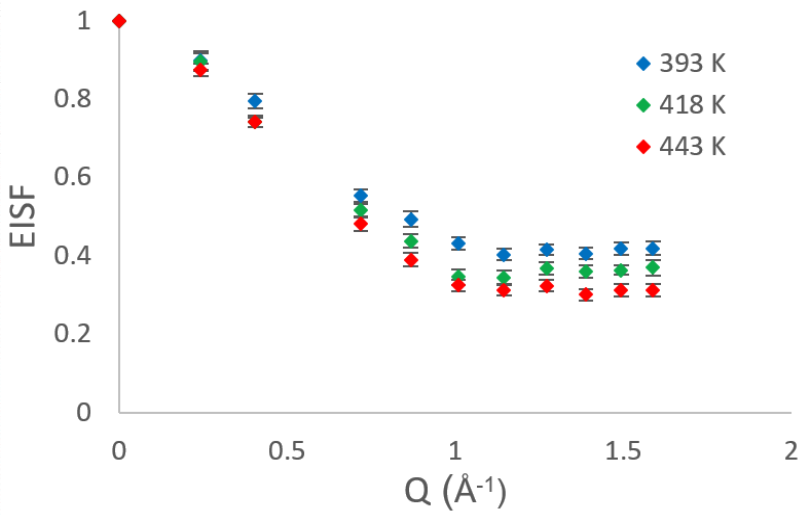




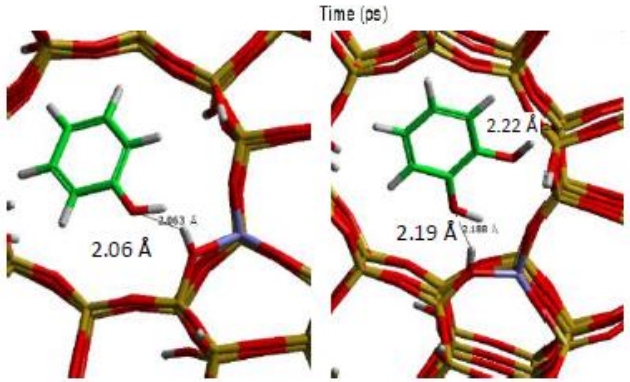
S. K. Singh *et al., Catal. Sci. Technol., (2015), 5, 2117–2124*

Phenol in zeolite beta.. Starting data





- Zeolite Beta (**Si/Al = 12.5**)
- **10 % in weight of phenol**
- Temperatures: 393, 418 and 443 K
- Pyrolitic graphite 002 analyser crystals: energy resolution of 24.5 µeV, **energy transfer window of ±0.55 meV**, ***Q*** **range of 0.2–1.6 Å^{-1}**



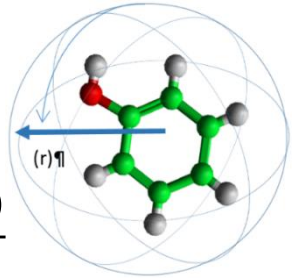
Different models fitting EISF

- Zeolite Beta (**Si/Al = 12.5**)
- **10 % in weight of phenol**
- Temperatures: 393, 418 and 443 K
- Pyrolitic graphite 002 analyser crystals: energy resolution of 24.5 μeV, **energy transfer window of ±0.55 meV**, ***Q*** **range of 0.2–1.6 Å^{-1}**

Isotropic rotation

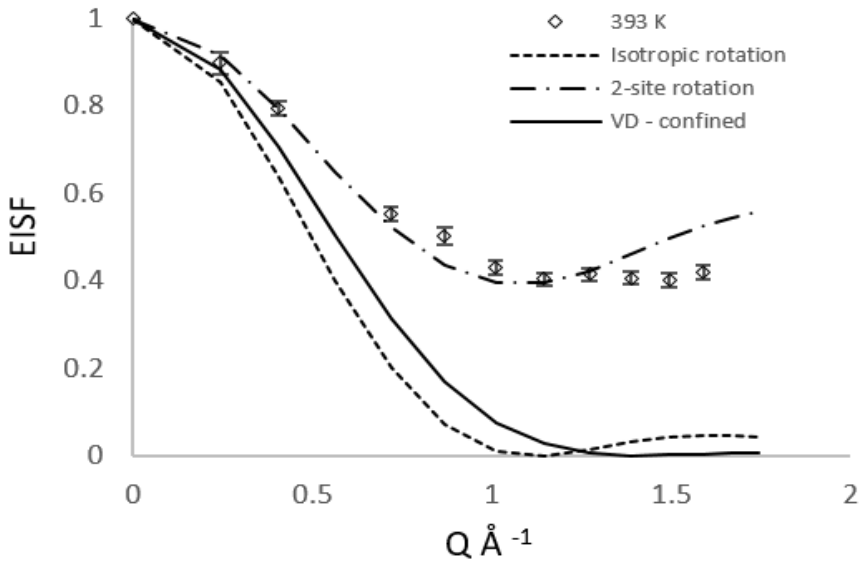
$$A_0(Q) = j_0^2(Qr)$$

$$j_0(Qr) = \frac{\sin(Qr)}{(Qr)}$$



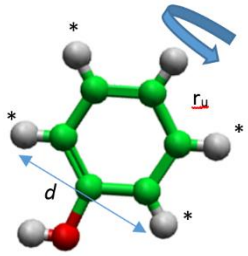
Elastic Incoherent Structure Factor (EISF)

$$A_{0\_eff}(Q) = p_x\, A_0(Q) + (1 - p_x)$$



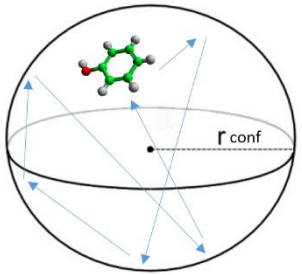
2-site rotation

$$A_0(Q) = \frac{1}{2}\,[\,1 + j_0(Qd)]$$

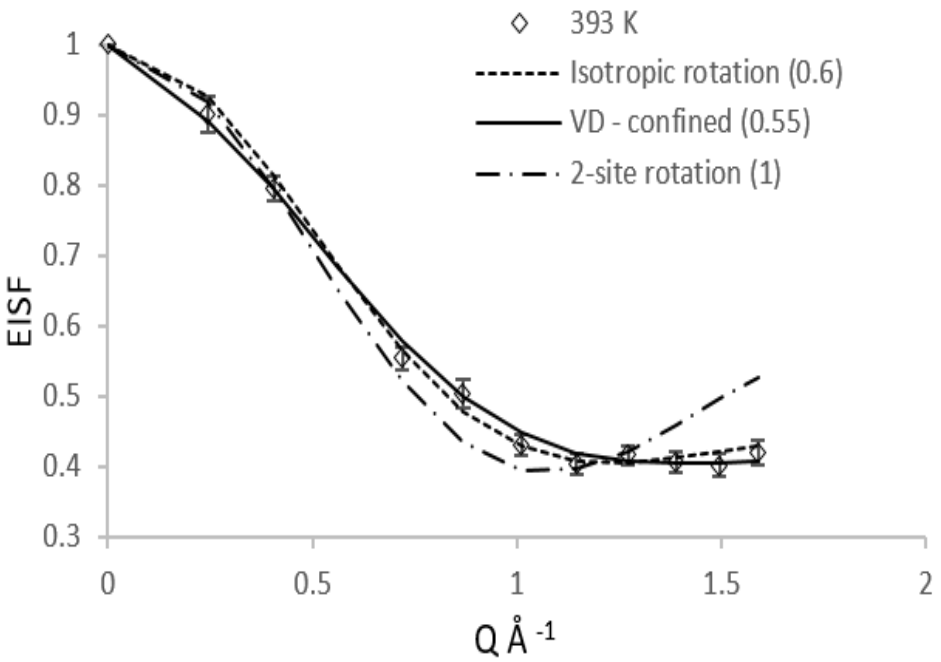


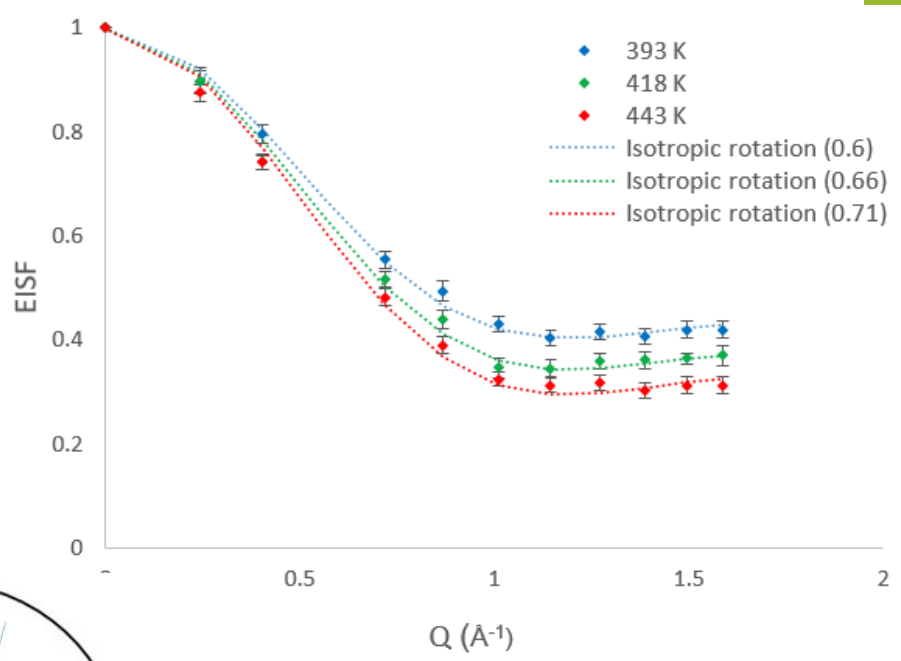
Volino and Dianoux

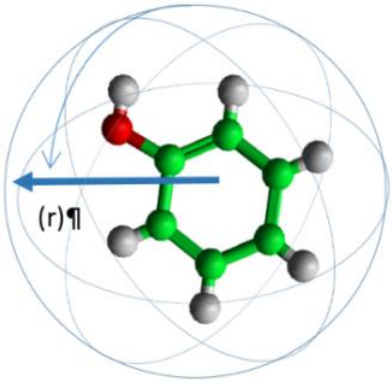
$$A_0(Q) = \left[\frac{3j_1(Qr_{conf})}{Qr_{conf}}\right]^2$$

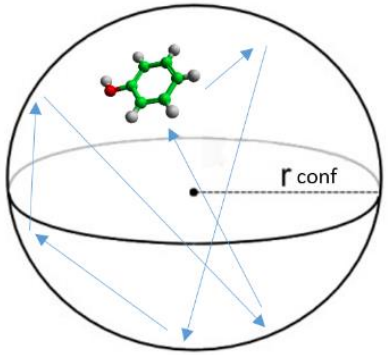


Some moving… some not





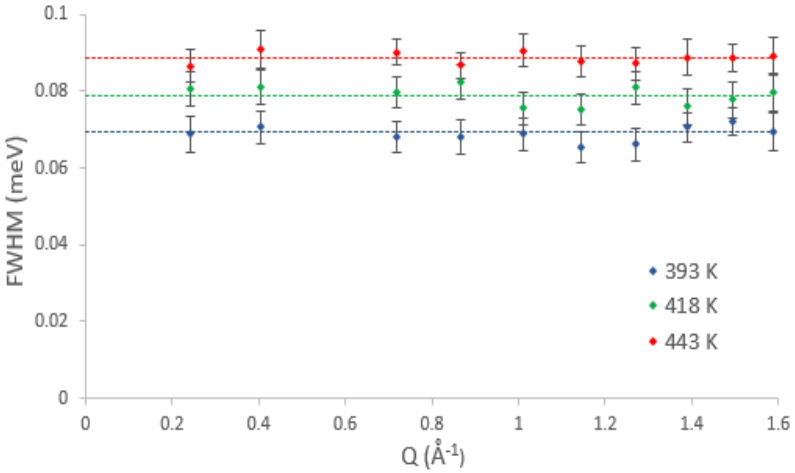




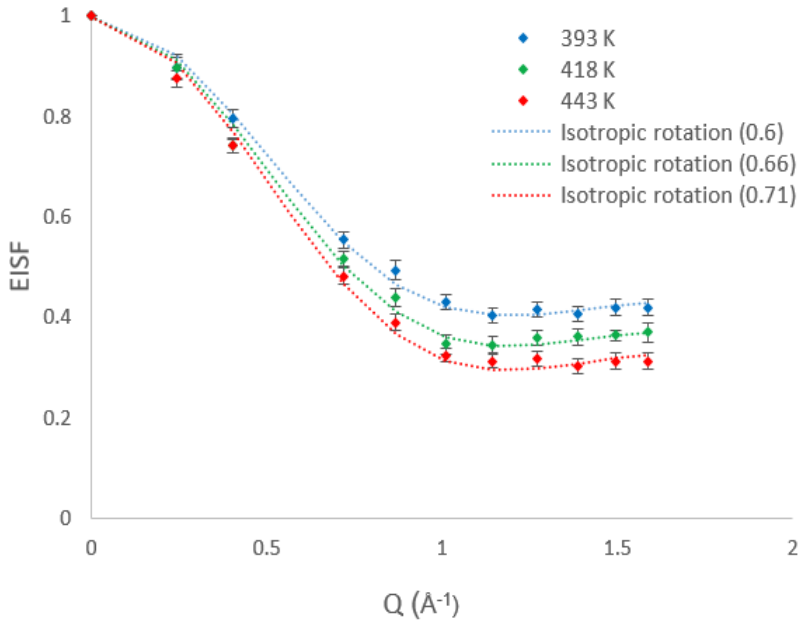
Studying the widths

- **The broadenings are independent of Q**: discounts any dynamical behaviour involving translational motion on the timescale of the instrument including diffusion confined to a spherical volume

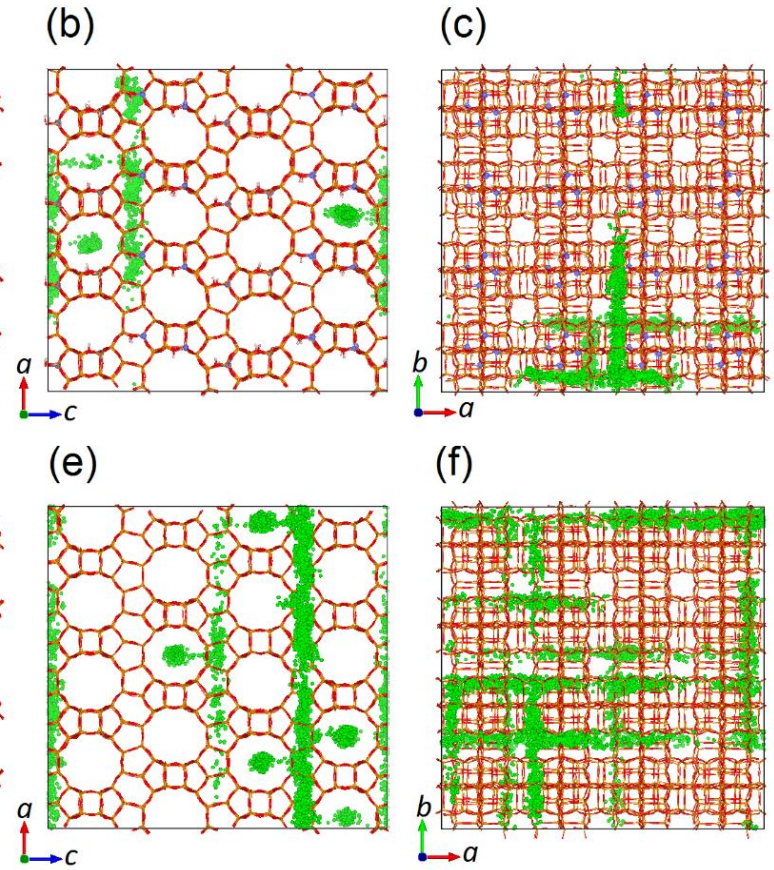
- Most likely **isotropic rotation** of phenol in the zeolite Beta channels with a **fraction of immobile molecules** (2.5 - 3.5 x 10^{10} s^{-1})



Q-dependence of the HWHM broadening of the Lorentzian components of QENS spectra of phenol in zeolite Beta at 393 K



Translational MD data..



Self-Diffusion coefficients of phenol in zeolite Beta, D_s ($\times 10^{-10}\, m^2/s$) and activation energy of diffusion, E_a (kJ/mol)

	Acidic zeolite			Pure-silica zeolite		
$\boldsymbol{T}$ $\boldsymbol{(K)}$	1 mpuc	2 mpuc	4 mpuc	1 mpuc	2 mpuc	4 mpuc
393	1.88	1.98	1.72	20.15	14.8	8.04
418	3.44	3.26	2.84	25.05	18.0	9.88
443	6.29	5.98	4.20	29.48	22.8	13.8
E_a	35	32	26	11	13	16

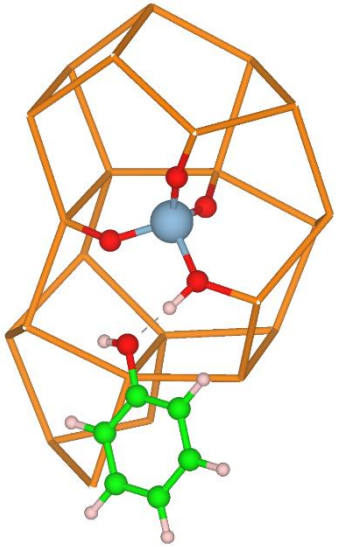
MD Rotational data

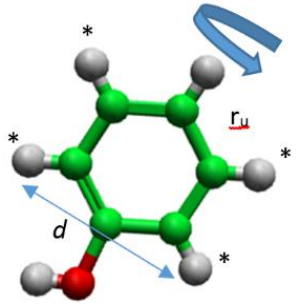
The **incoherent dynamical structure factor** $S_{inc}(\boldsymbol{Q},\omega)$ is related to the **single-particle time-correlation function** of the system, represented by the **self-part of the intermediate scattering function** $F_s\ (\boldsymbol{Q},t)$, by a **Fourier transform** in the frequency domain:

$$S_{inc}(\boldsymbol{Q},\omega) = \frac{1}{\pi}\int F_s(\boldsymbol{Q},t)\, exp(-i\omega t)dt$$

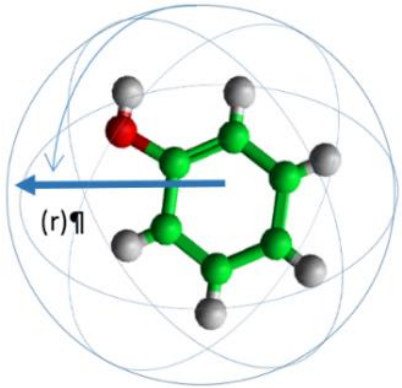
In order to extract information from the MD simulations to be compared with the experiment, it is more convenient to **retain the time-domain of the data** and work with the function $F_s\ (\boldsymbol{Q},t)$:

$$F_s^{rot}(\boldsymbol{Q},t) = \frac{1}{N}\sum_{i=1}^{N}\left\langle \frac{sin(|\boldsymbol{Q}||\boldsymbol{d}_i(t+t_0) - \boldsymbol{d}_i(t_0)|)}{|\boldsymbol{Q}||\boldsymbol{d}_i(t+t_0) - \boldsymbol{d}_i(t_0)|}\right\rangle$$

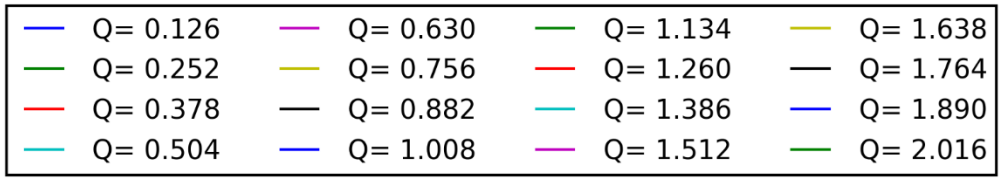


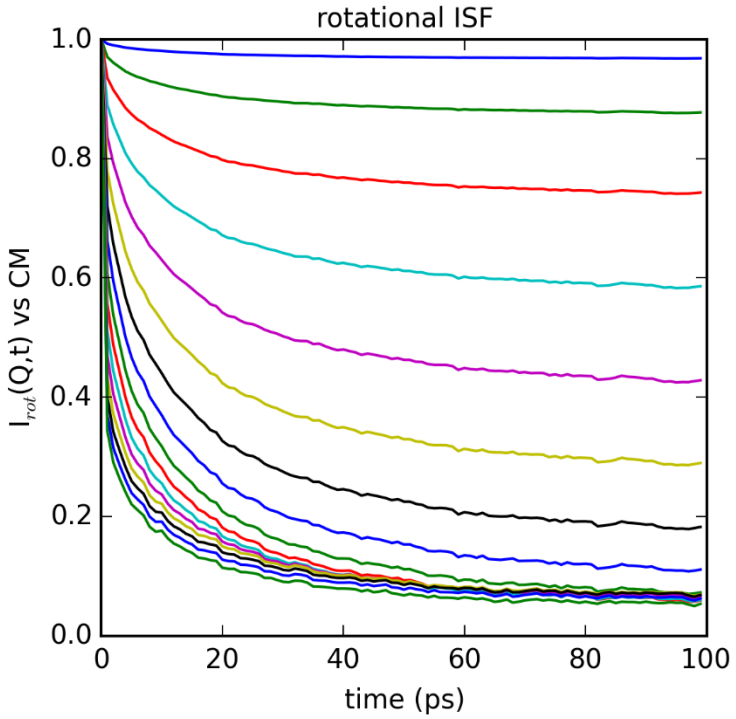


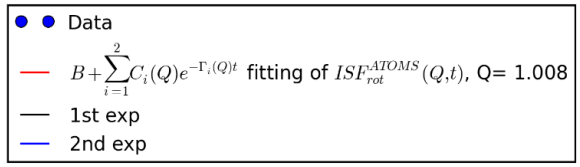
Zeolite Beta pore surface

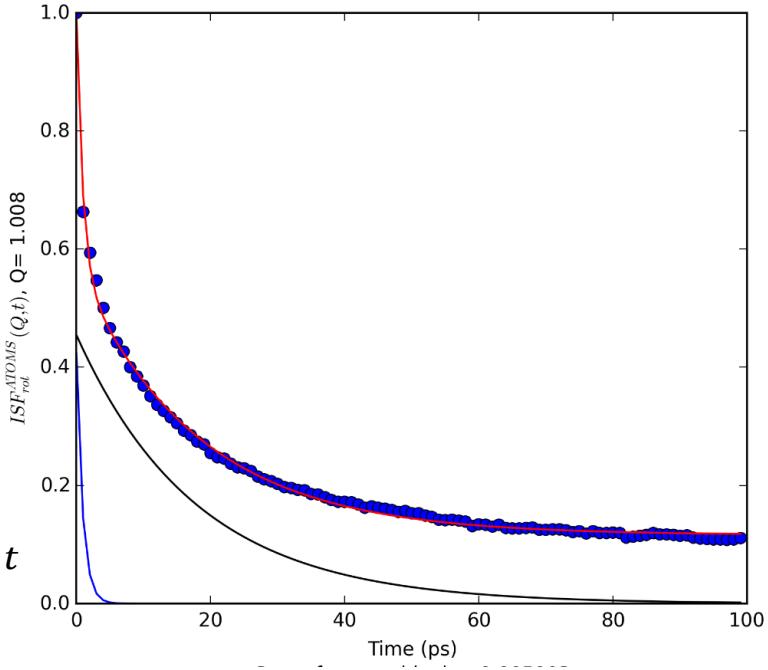


F(Q, t) onwards….







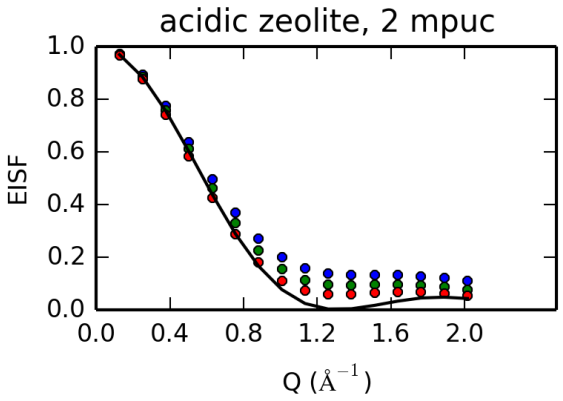


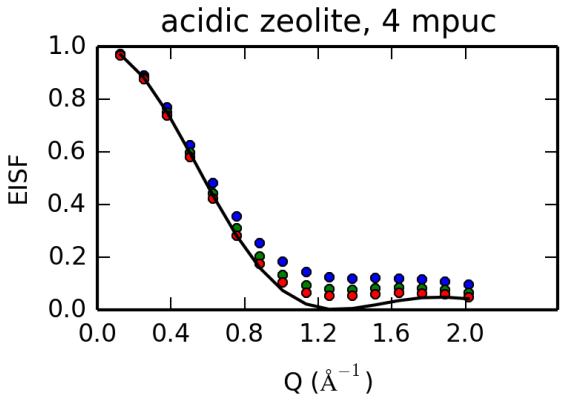
$$F_s^{rot}(\boldsymbol{Q},t) = B(\boldsymbol{Q}) + C_1(\boldsymbol{Q})e^{-\Gamma_1 t} + C_2(\boldsymbol{Q})e^{-\Gamma_2 t}$$

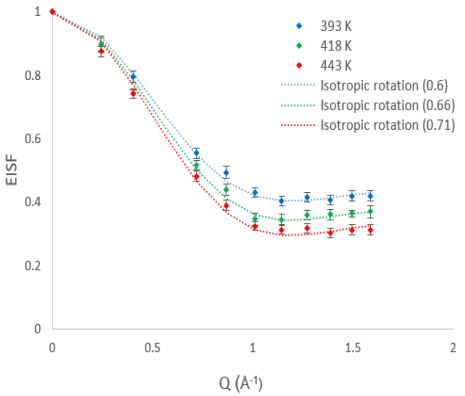
EISF Matches experiment qualitatively

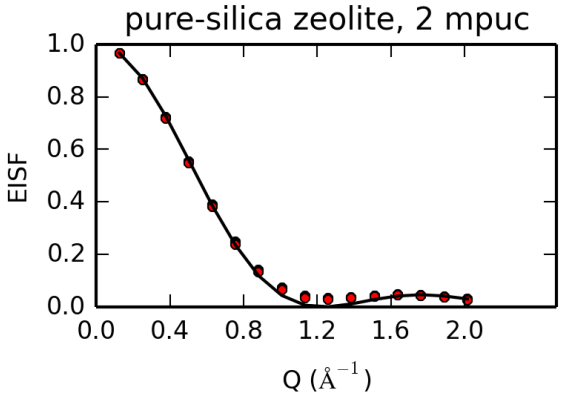
$$F_s^{rot}(\boldsymbol{Q},t) = B(\boldsymbol{Q}) + C_1(\boldsymbol{Q})e^{-\Gamma_1 t} + C_2(\boldsymbol{Q})e^{-\Gamma_2 t}$$

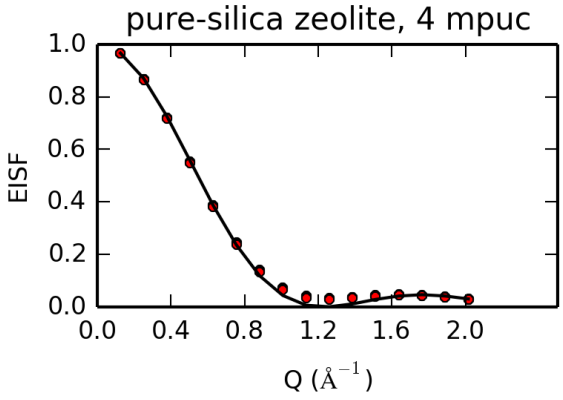
Isotropic rotation $A_0(Q) = j_0^2(Qr)$ (Prevalent motion)

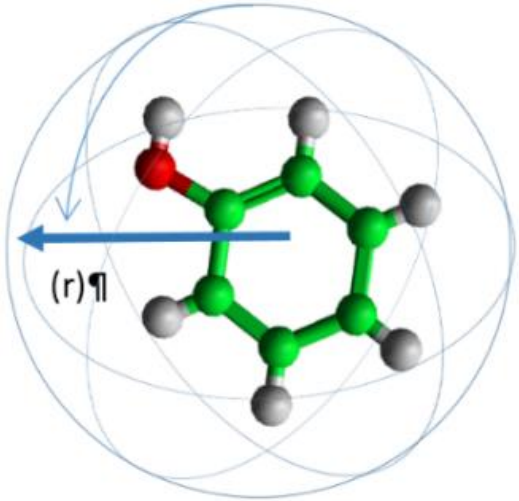


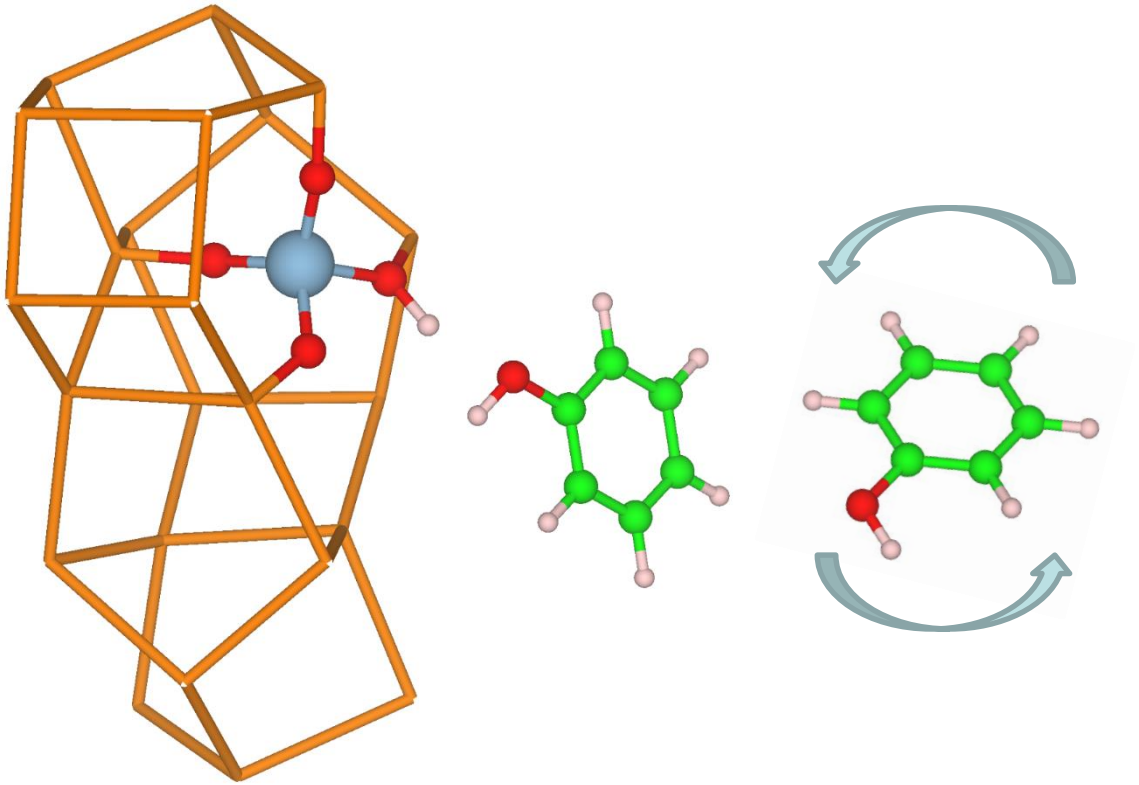






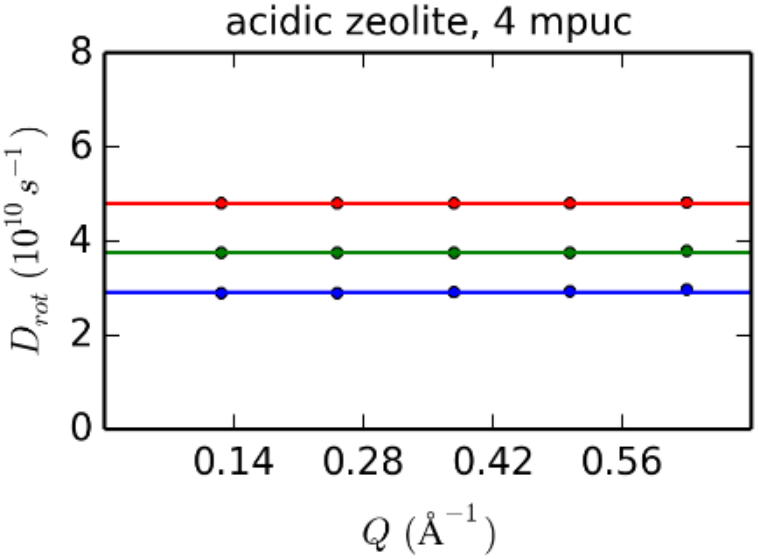


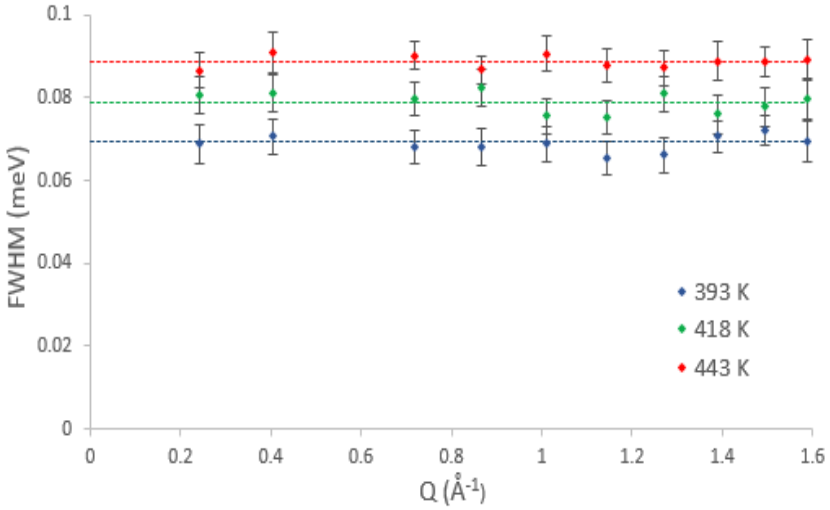




Acidic zeolite

D_{rot} almost matches quantitatively!



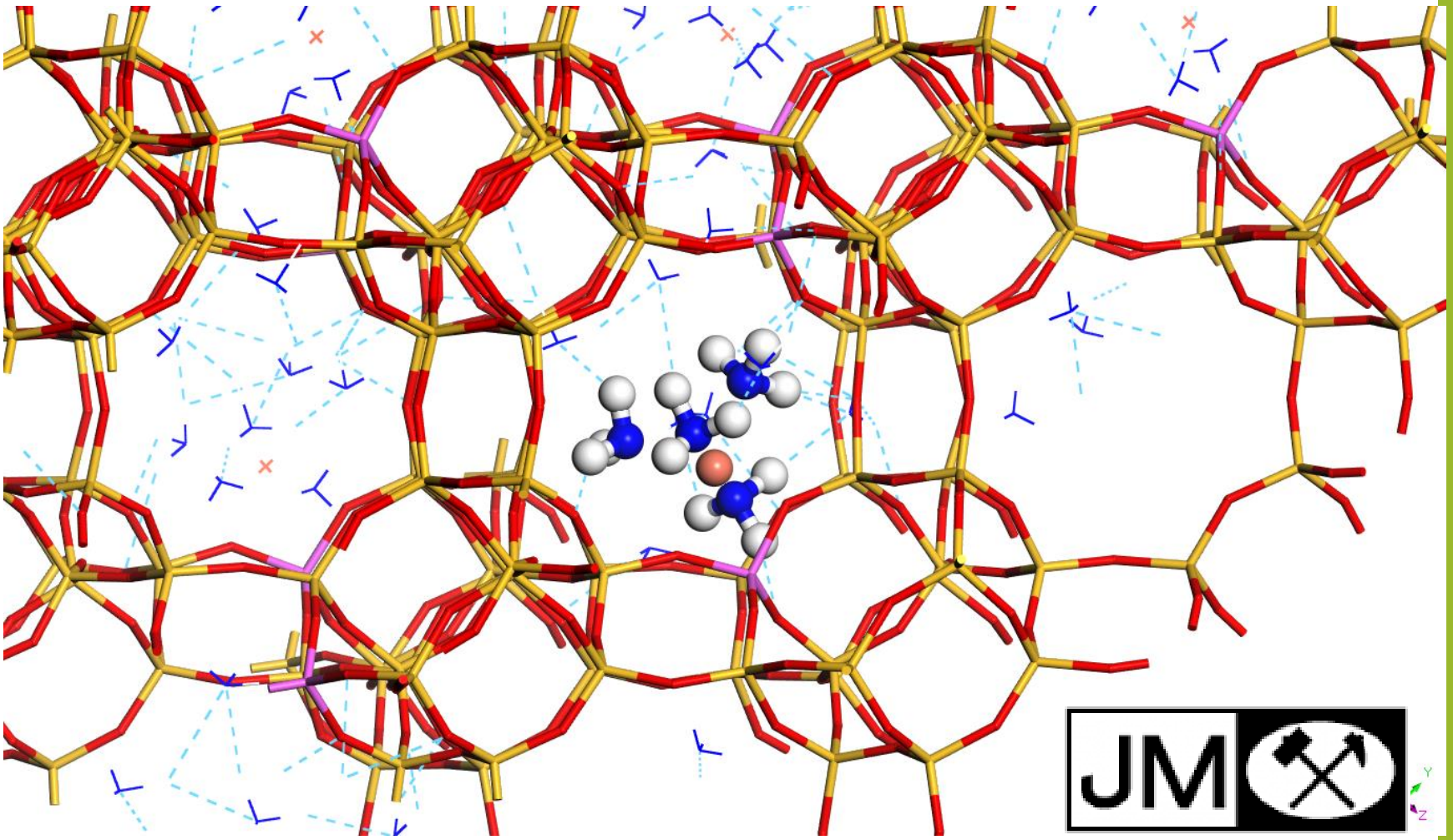


Rotational diffusion coefficients of phenol in zeolite Beta, D_r $(\times 10^{10} s^{-1})$ and activation energy of rotation, E_a (kJ/mol) derived from QENS experiments and MD simulations.

	Acidic zeolite			Pure-silica zeolite			
T (K)	1 mpuc	2 mpuc	4 mpuc	1 mpuc	2 mpuc	4 mpuc	QENS
393	2.60	2.80	2.92	7.55	6.60	5.60	2.60
418	3.44	3.56	3.76	9.80	8.88	7.30	2.97
443	4.70	4.83	4.81	11.52	10.58	9.05	3.33
E_a	17.1	15.7	14.4	12.3	13.7	14.0	7.2

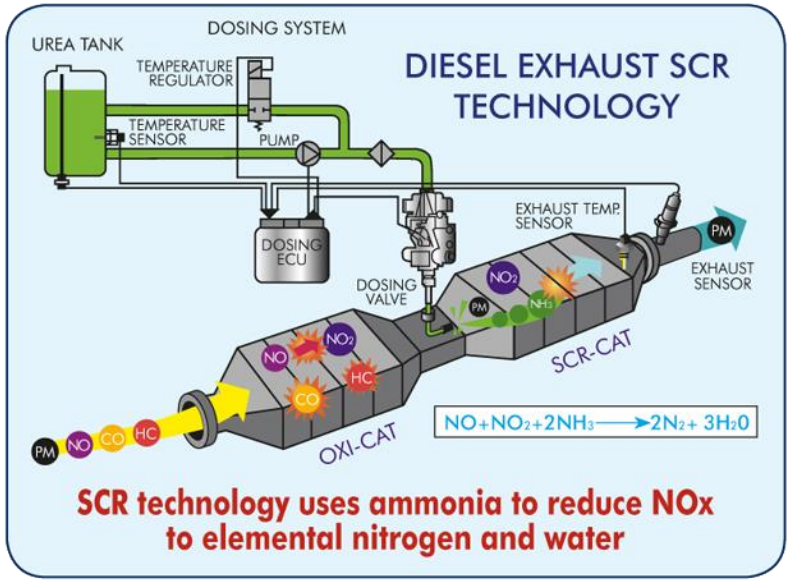
Ammonia mobility in NH_3-SCR catalysts

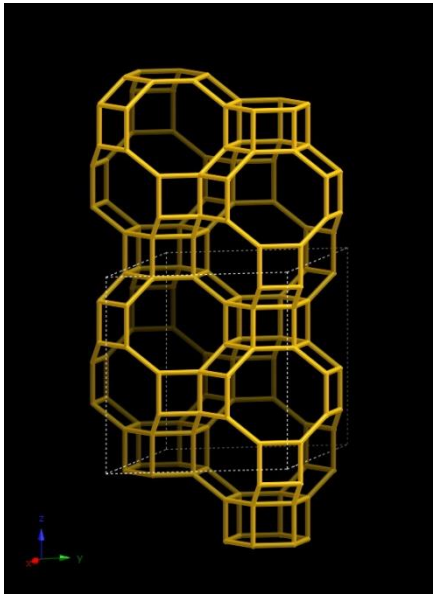
UNIVERSITY OF BATH



8. A. J. O'Malley, I. Hitchcock, M. Sarwar, I. P. Silverwood, S. Hindocha, C. R. A. Catlow, A. P. E. York and P. J. Collier, Phys. Chem. Chem. Phys., **2016**,18, 17159-17168

Cu-Chabazite: The SCR Process



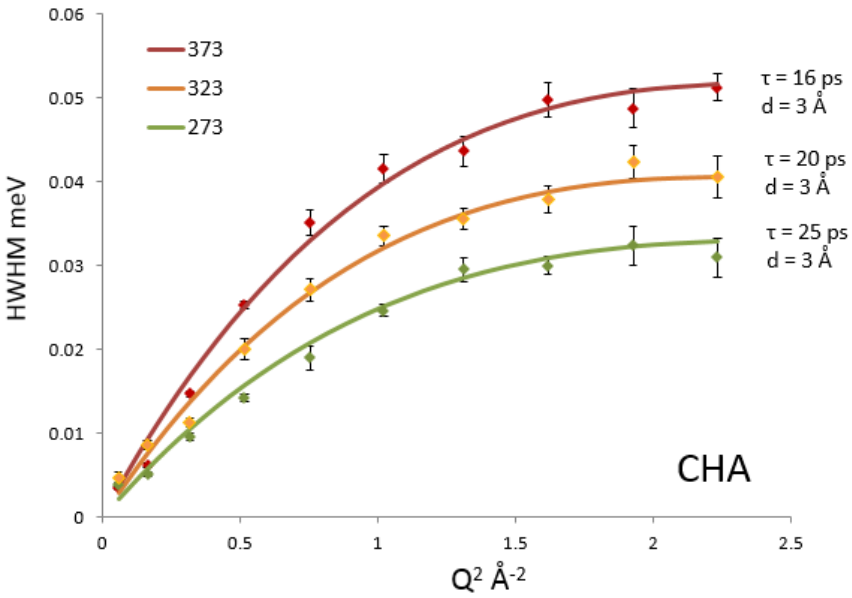


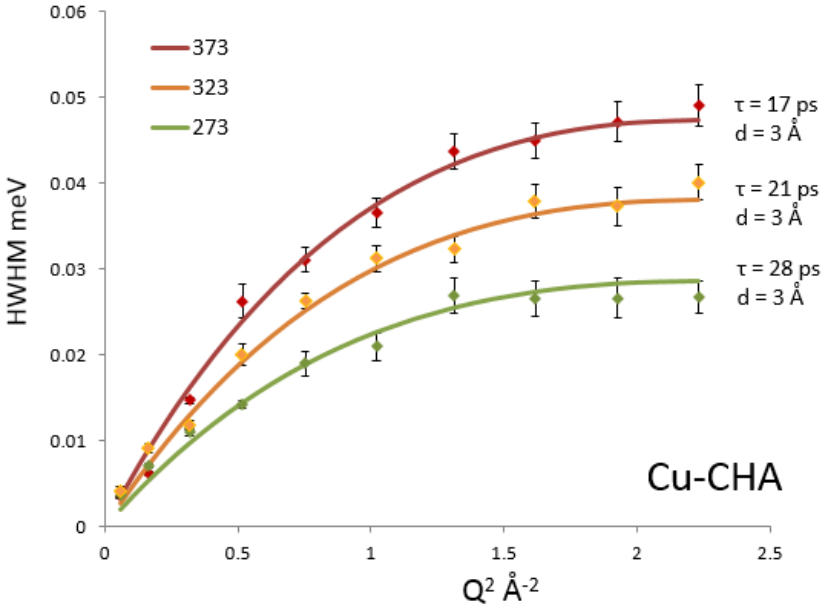
- Collaboration with Johnson Matthey using QENS to study the diffusion of ammonia in CHA and Cu-CHA, to determine the effect of counter ion presence on diffusion.

- Small pore zeolite (3.8 x 3.8 Å) – counterion location variable…

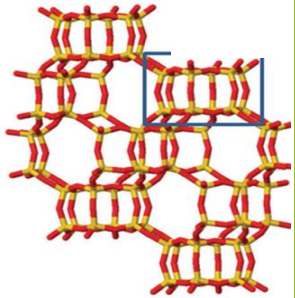
8. A. J. O'Malley, I. Hitchcock, M. Sarwar, I. P. Silverwood, S. Hindocha, C. R. A. Catlow, A. P. E. York and P. J. Collier, Phys. Chem. Chem. Phys., **2016**,18, 17159-17168

Ammonia Diffusion in Chabazite as a Function of Cu Counterion Presence





- Ammonia seems to behave basically the same in both zeolites..
- Jump distance of 3 Å, similar residence times at each T (16-28 ps)
- More likely through 8-ring than 6-ring?
- Why is the copper ion not changing anything..?

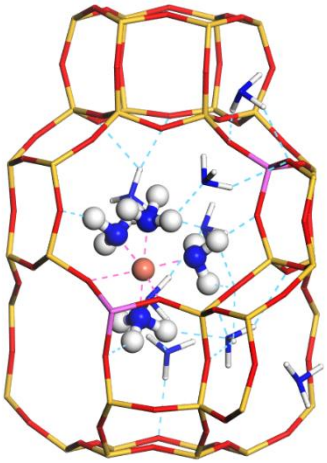


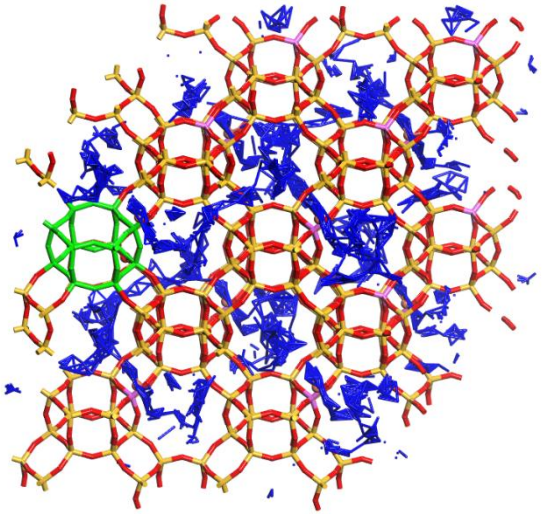
8. A. J. O'Malley, I. Hitchcock, M. Sarwar, I. P. Silverwood, S. Hindocha, C. R. A. Catlow, A. P. E. York and P. J. Collier, Phys. Chem. Chem. Phys., **2016**,18, 17159-17168

Ammonia Diffusion in Chabazite as a Function of Cu Counterion Presence

UNIVERSITY OF BATH

- MD shows clusters of NH_3 coordinated to the Cu^{2+} .
- ‘Shell’ effectively shields the remaining NH_3 from the potential sink of the Cu^{2+} .
- The coordinated NH_3 moved far too slowly to be detected by the OSIRIS instrument – so is not measured
- Trajectory plots appear to confirm that diffusion is dominant through 8-rings
- Cu^{2+} shell allows intercage diffusion through 8-ring to carry on unimpeded.





8. A. J. O’Malley, I. Hitchcock, M. Sarwar, I. P. Silverwood, S. Hindocha, C. R. A. Catlow, A. P. E. York and P. J. Collier, Phys. Chem. Chem. Phys., **2016**,18, 17159-17168

Ammonia Mobility in Levynite

PCCP

PAPER

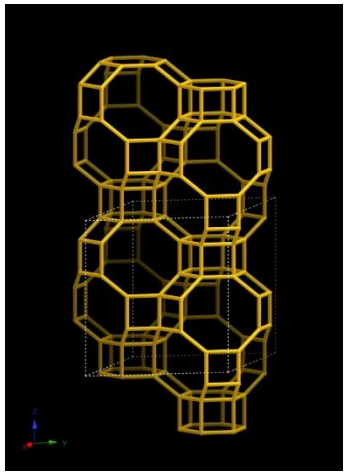
View Article Online
View Journal

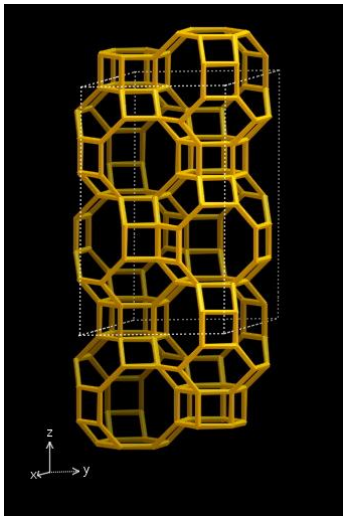
Check for updates

Cite this: DOI: 10.1039/c8cp01022f

Comparing ammonia diffusion in NH_3-SCR zeolite catalysts: a quasielastic neutron scattering and molecular dynamics simulation study

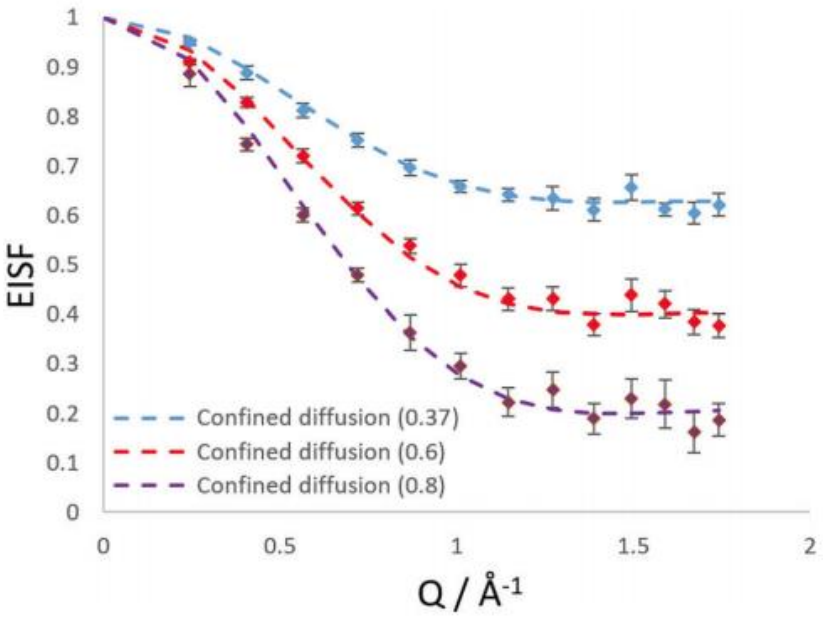
A. J. O'Malley,[ab] M. Sarwar,[c] J. Armstrong,[d] C. R. A. Catlow,[abe] I. P. Silverwood,[bd] A. P. E. York[c] and I. Hitchcock*[c]

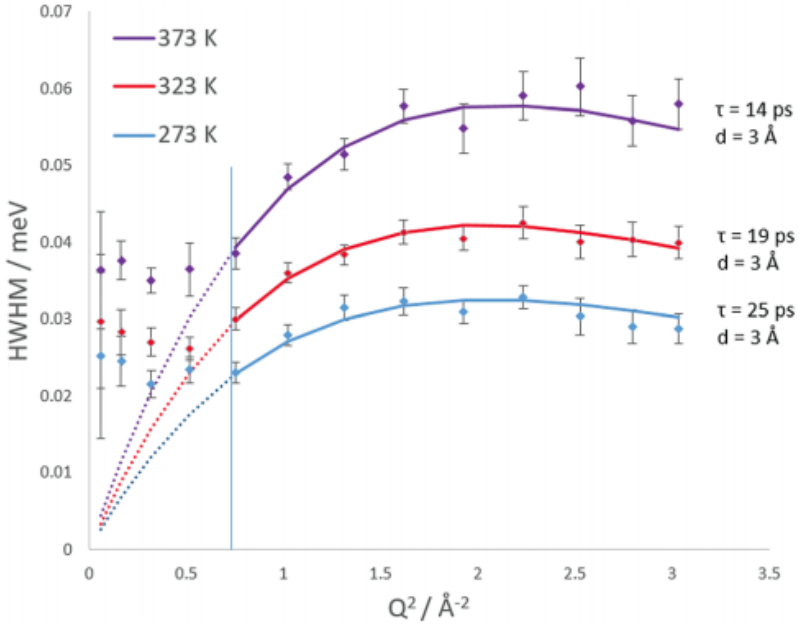




- Building on study in CHA, in the 2D framework LEV.
- Same 8-ring windows present as in CHA, however stacking leads to the channels running in 2-dimensions in LEV, (3D in CHA).
- Difference in overall diffusivity?
- QENS experiments performed on OSIRIS and complementary MD simulations performed at JMTC.

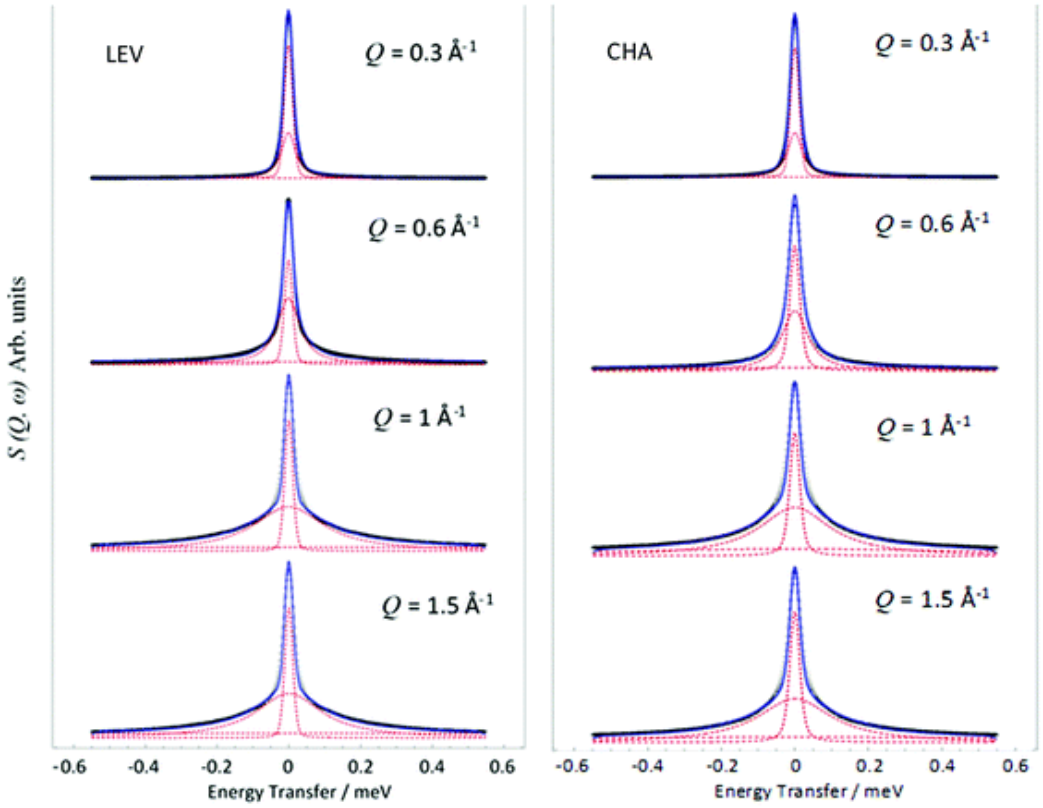
Ammonia Diffusion in Levynite

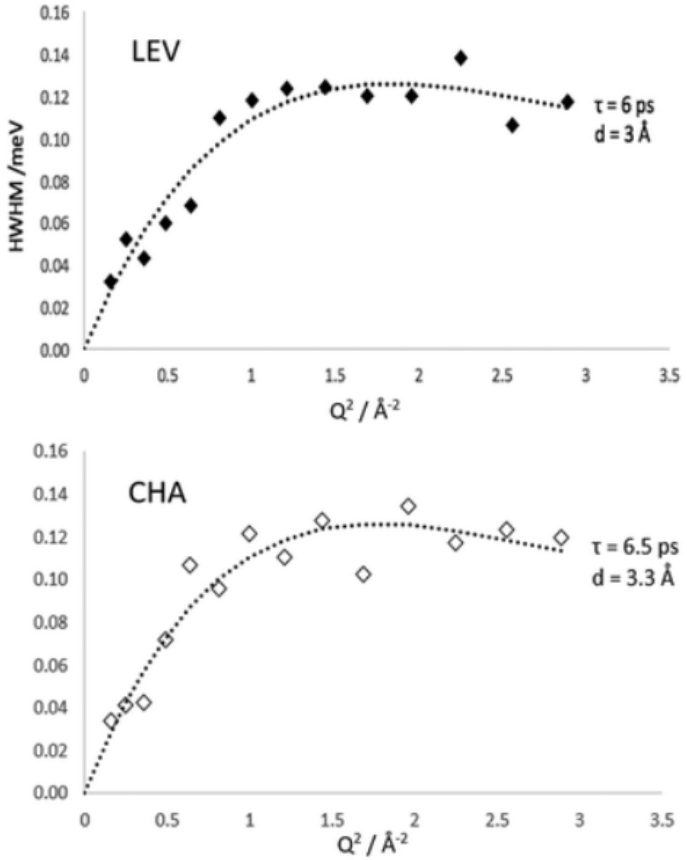


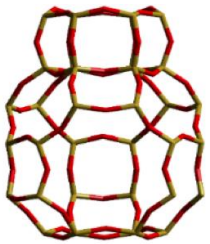


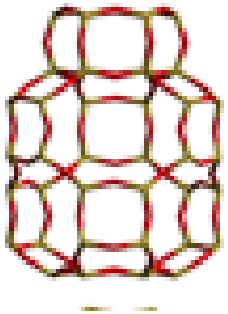
- Again, ammonia seems to behave with the same jump diffusion mechanism
- Jump distance of 3 Å, similar residence times at each T (16-25 ps)
- Same characteristics suggest inter-spherical mobility through 8-ring windows dominant motion,
- Similar D_s values obtained, same case for the MD simulations?

Directly calculating S(Q, ω) using MDANSE



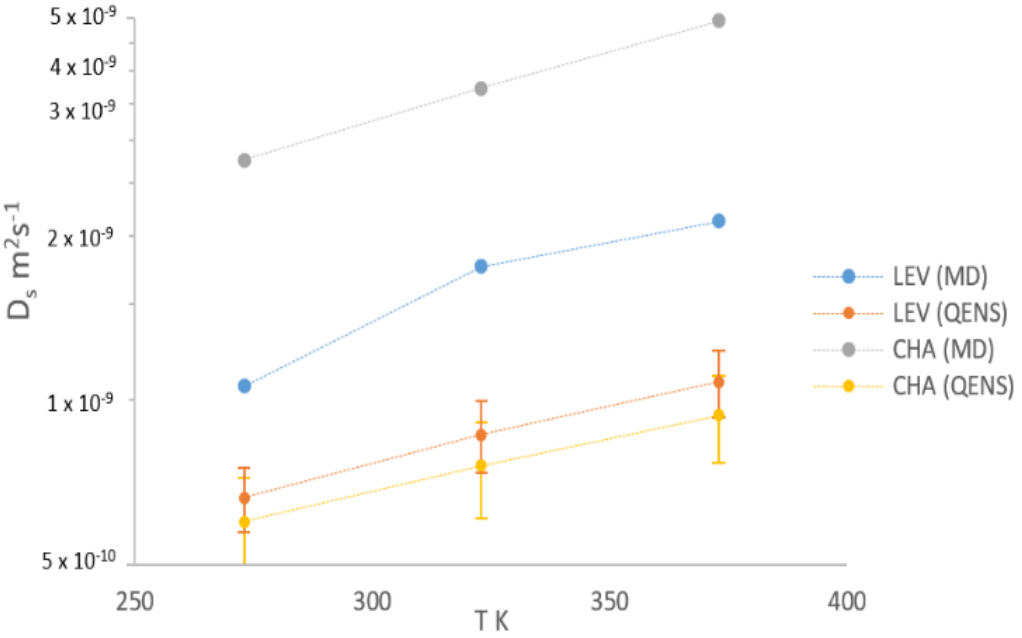


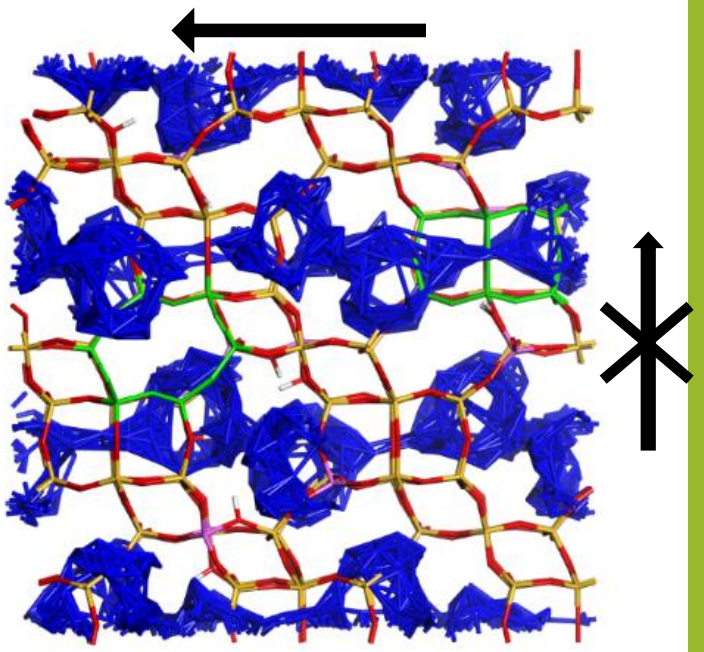




- MDANSE used to reproduce QENS spectra.
- Identical motion in both zeolites on the ***pico-scale***

Ammonia Diffusion in Levynite





- While QENS experiments show similar diffusivity, the MD simulations suggest diffusion is faster in CHA by over a factor of 2.

- 2-dimensional diffusion responsible? Trajectory plot shows anisotropy, no diffusion allowed through 6-rings linking cages.

Comparing ammonia mobility in different NH_3-SCR catalysts

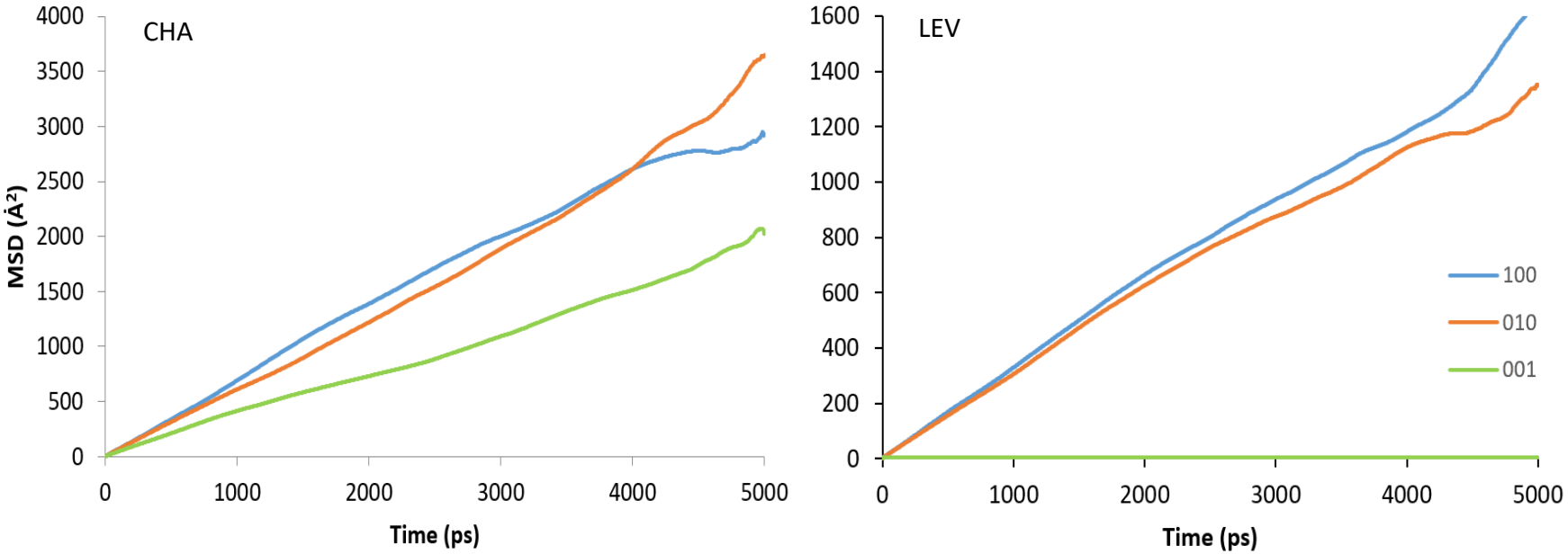
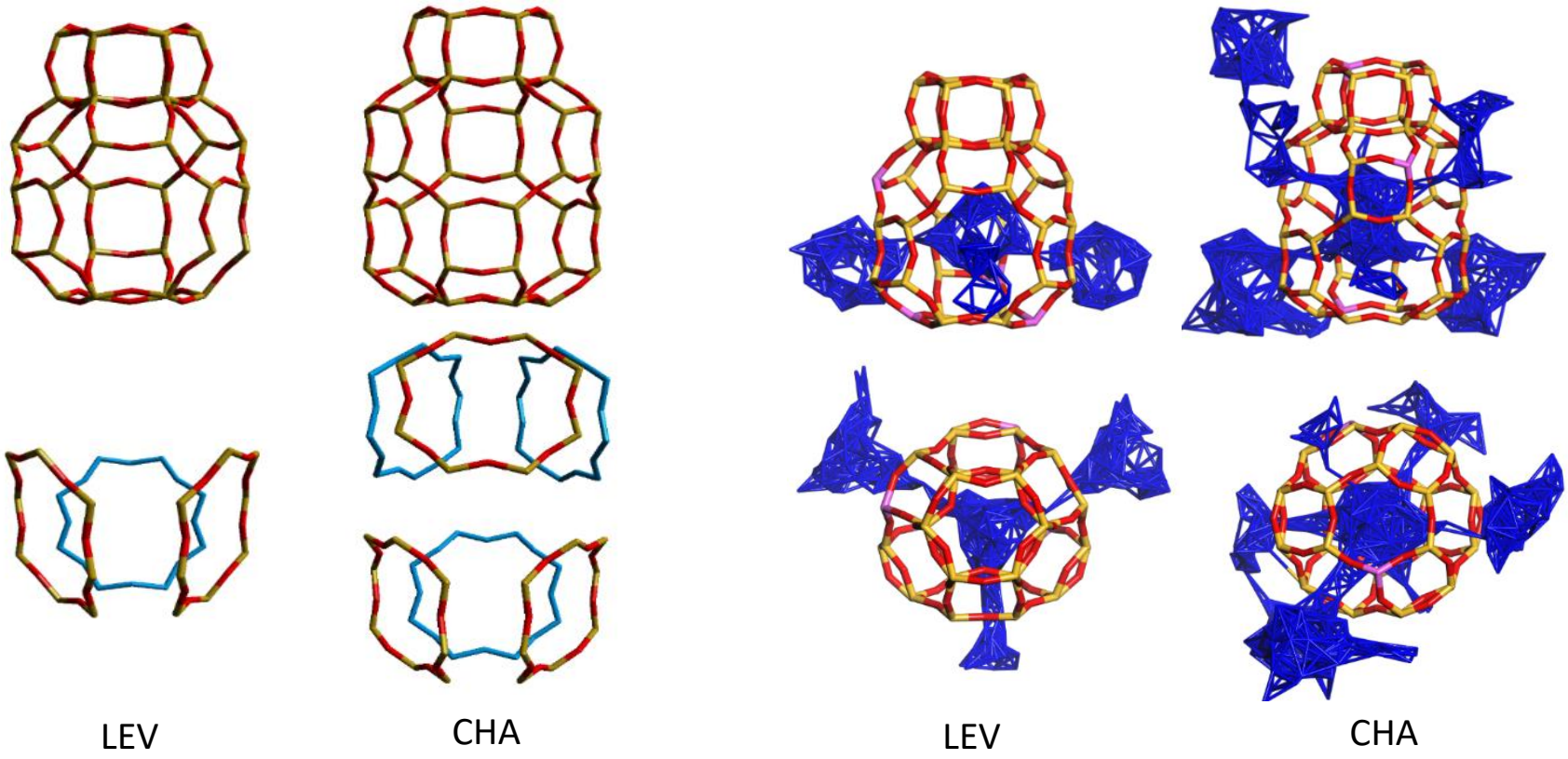


Figure 6. MSD plots of NH_3 along the three principle axes of CHA and LEV at 273 K.

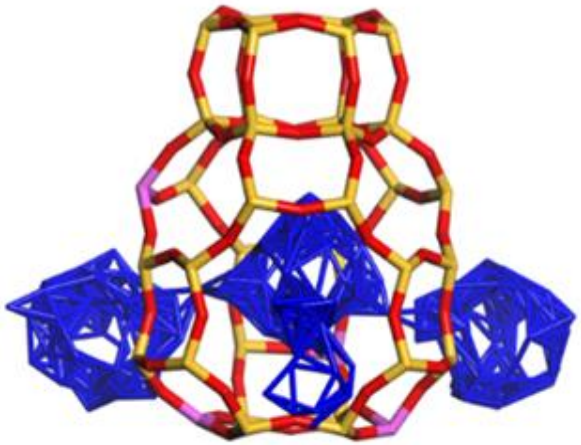
- Diffusion in the individual directions also illustrates anisotropy, however diffusion in the mobile directions is also significantly higher in CHA. Correlating with the 2x higher D_s
- Why?

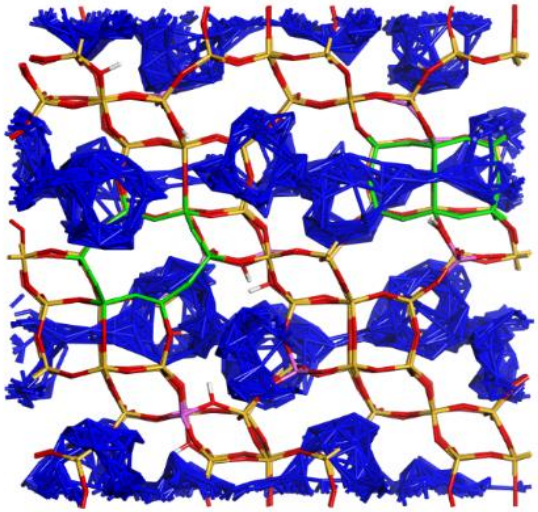
Comparing ammonia mobility in different NH_3-SCR catalysts

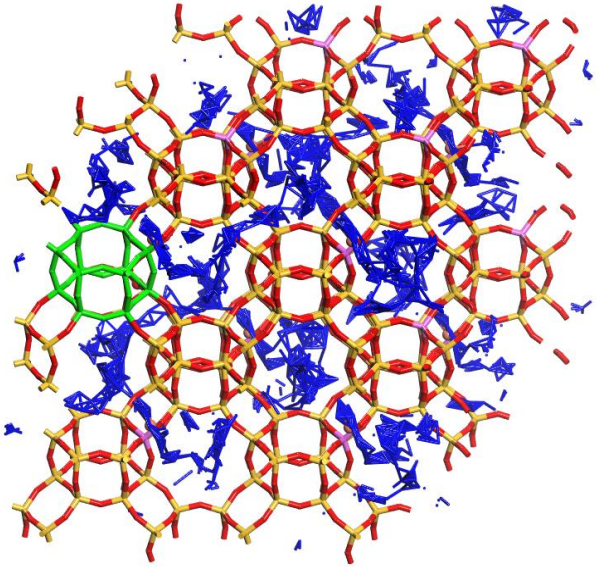


- Studying the building units (CHA and LEV cages) show that the CHA cage contains double the number of 8-rings.
- Double the number of geometric opportunities to perform jump diffusion between cages (as observed by QENS).

Comparing ammonia mobility in different NH_3-SCR catalysts



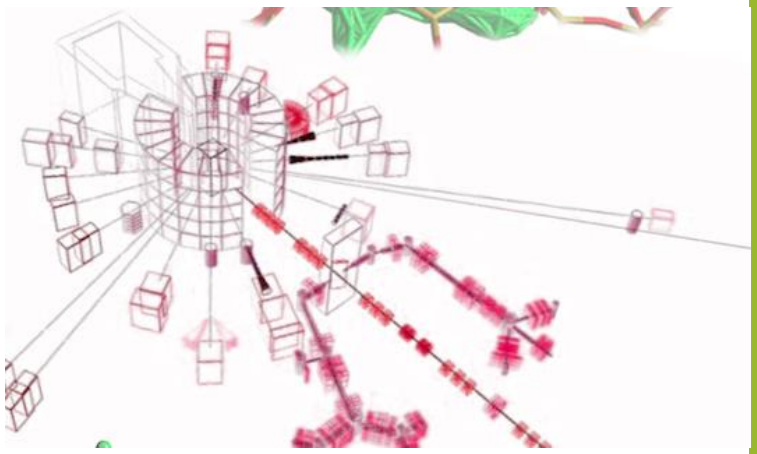


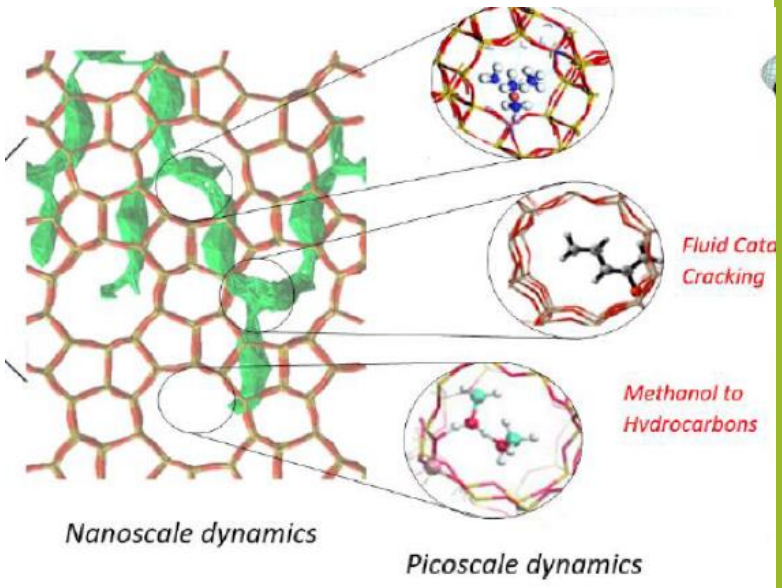


- Important synergy between the pico-scale sampled by the QENS and the nanoscale sampled by our MD simulations
- Interesting similarities and contrasts in the molecular behaviour between CHA and LEV zeolite catalysts, directly related to the structure.

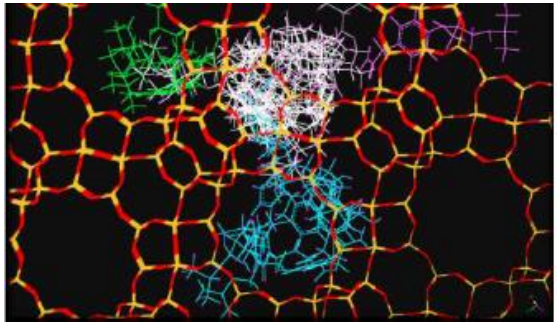
Summary and Conclusions

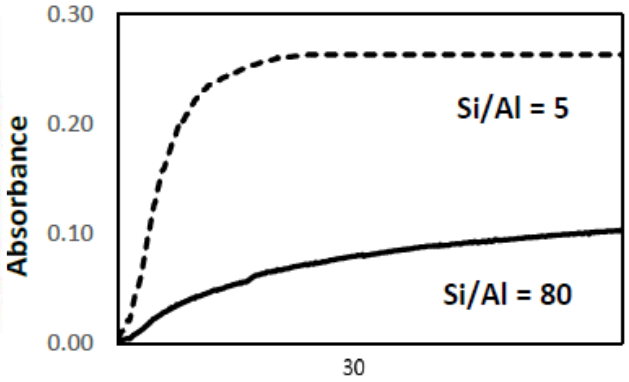
- Powerful experimental tools available for studying behavior in porous materials.
- Move from model systems to both established and developing catalytic systems now made!
- Combination of theory and experiment crucial!
- While detailed information can be obtained on this time/lengthscale, multiscale study is always necessary.





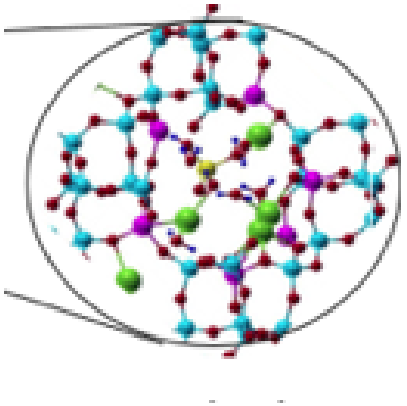
Current Work

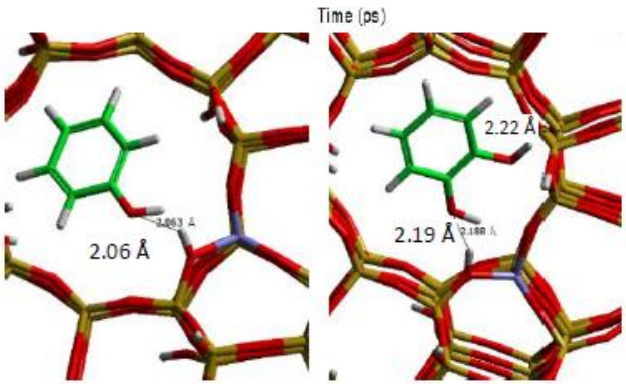




"The Effect of Framework Structure and Composition on Controlled Drug Release by Zeolites"
P. Cox et al.
University of Portsmouth

"Developing decontamination technologies through modelling water and toxic contaminant behaviour in zeolites"
B. Kwakye-Awuah
KNUST Kumasi, Ghana





"Mobility of Simple Phenolic Lignin Monomers for Model Development of Biomass Conversions in Zeolites"
C. Hernandez Tamargo, N. H. De Leeuw
Cardiff University

Acknowledgements

- Richard Catlow, Nora de Leeuw
- Carlos Hernandez-Tamargo, Herve Jobic
- Ian Silverwood, Stewart Parker
- Misbah Sarwar, Iain Hitchcock, Andrew York
- The Ramsay Memorial Trust
- The Roger and Sue Whorrod Fund

Thank You