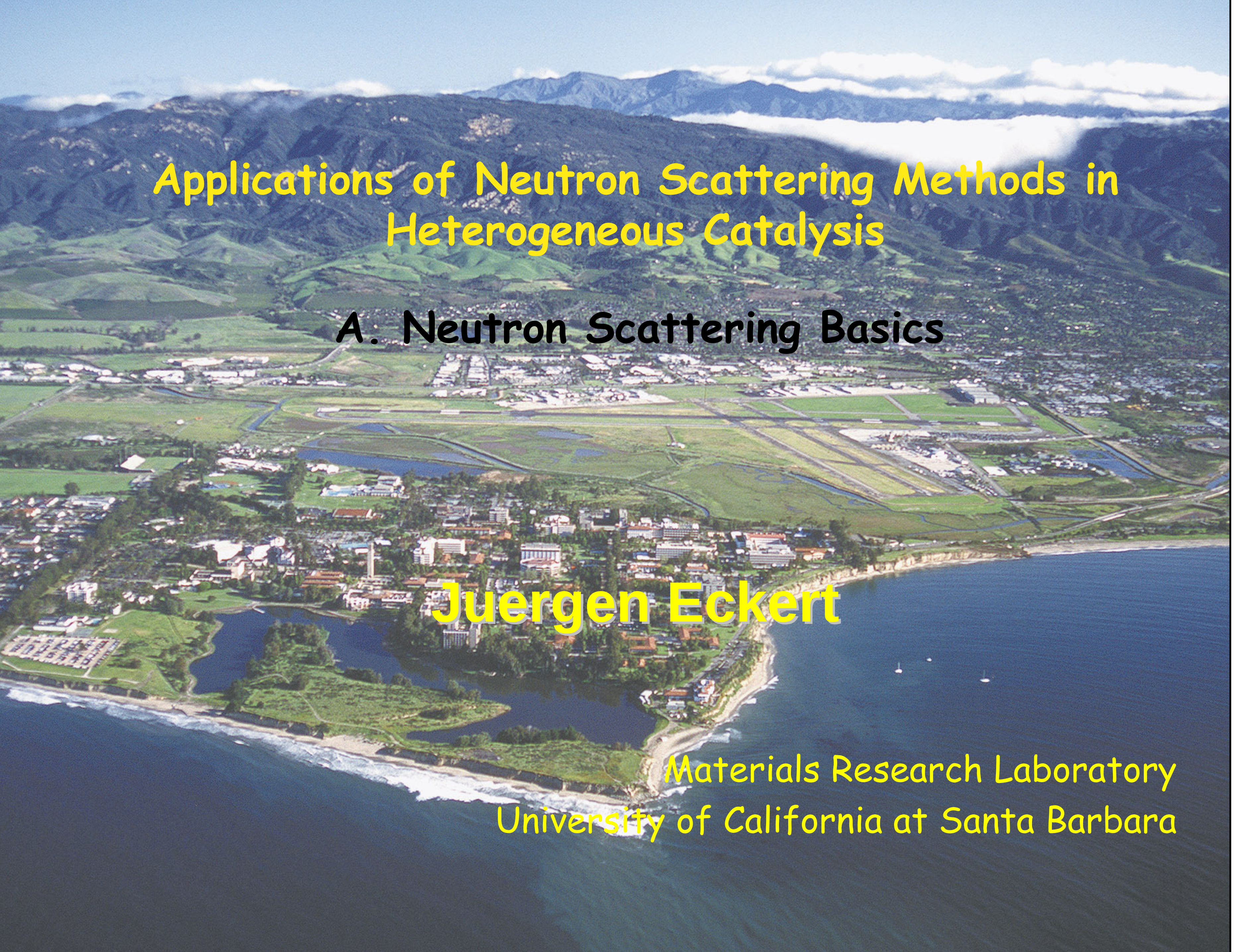


Applications of Neutron Scattering Methods in Heterogeneous Catalysis

A. Neutron Scattering Basics

Juergen Eckert

Materials Research Laboratory
University of California at Santa Barbara

and

Los Alamos Neutron Science Center,

Los Alamos, New Mexico

Why Neutrons ?

Wavelengths ~ Å's

- comparable to interatomic and intermolecular distances
- similar to x-rays

=> interference effects - diffraction

Energies ~ meV's (1 meV =8 cm^{-1} = 11 K)

- comparable to the time scale of many motions in materials

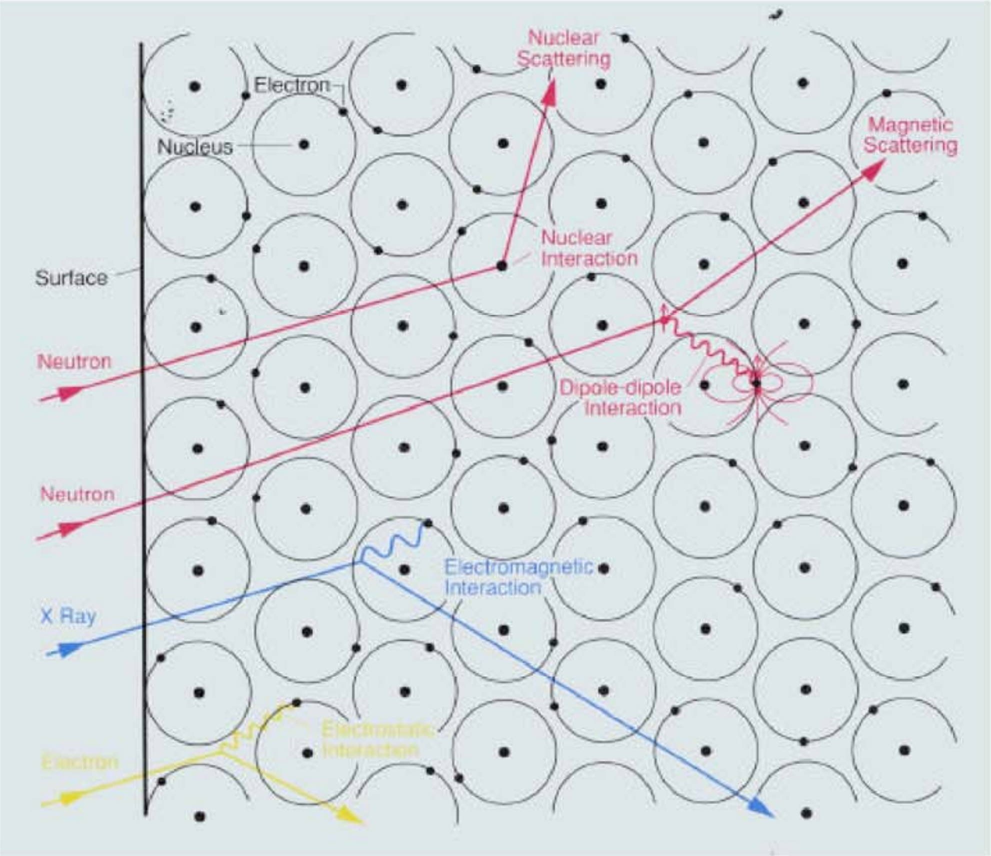
=> inelastic scattering from vibrations, diffusion, reorientations, and relaxational processes can be observed

=> this scattering also has angular dependence:

=> geometry of the motion

- light E ~ eV's λ ~ 1000 Å's (selection rules)(=> spectroscopy)
- x-rays E ~ keV's λ ~ Å's (=> diffraction)

Interaction Mechanisms



- Neutrons interact with atomic nuclei via very short range (~fm) forces.
- Neutrons also interact with unpaired electrons via a magnetic dipole interaction.

Why Neutrons

Neutron-Nuclear Interaction

- strong but very short ranged: point interaction
  => computational ease
- no electrostatic interaction: overall interaction is weak =>
  scattering cross sections and absorption is small
  => neutrons easily penetrate experimental apparatus
- scattering power varies "randomly" from isotope to isotope
  => isotopic labeling
- nuclear spin dependence of the interaction
  ⇒neutrons can scatter coherently (diffraction, lattice modes)
  ⇒or incoherently (disorder, diffusive motions)

Neutrons as microscopic probes in heterogeneous catalysis

Utilize the special properties of neutron interaction with materials for select problems in Catalysis.

Neutrons are scattered by atomic nuclei, not electrons

- isotope-dependent scattering (H/D; Fe, Ti, others)
- intensities (very different) are governed by this interaction

Both elastic and inelastic scattering of neutrons can be detected: -

structure AND dynamics

Structure

Light atoms: H, Li
Si vs. Al
molecular and/or adsorbate complexes

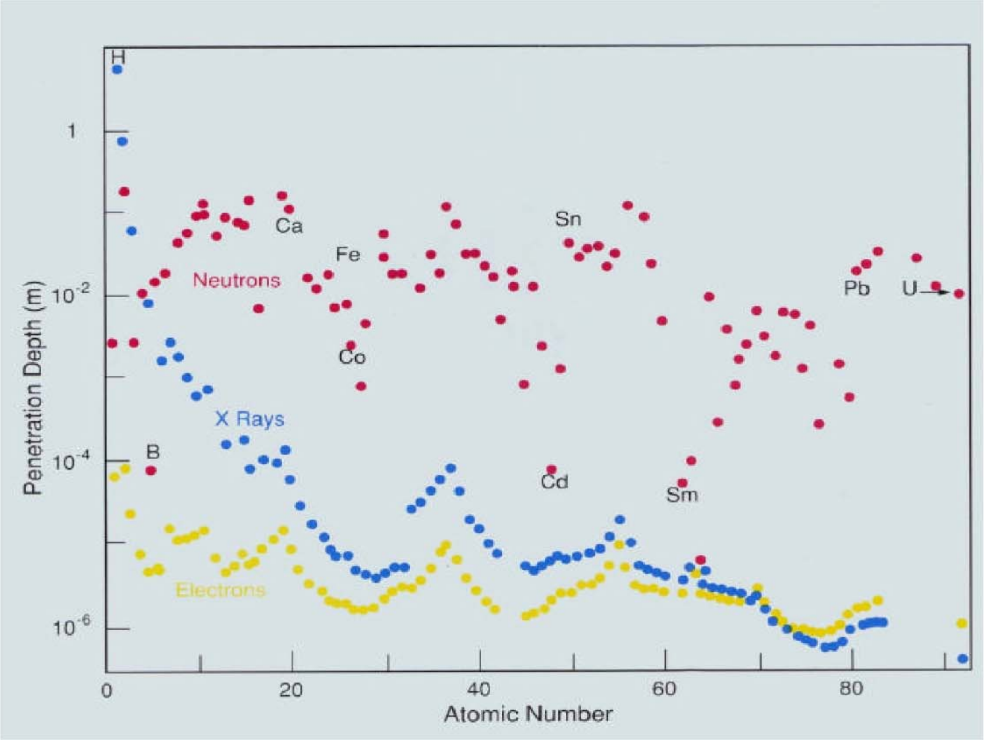
Dynamics

vibrational spectra – framework and/or adsorbate
microscopic diffusion
close connection with computer simulations

In-situ studies

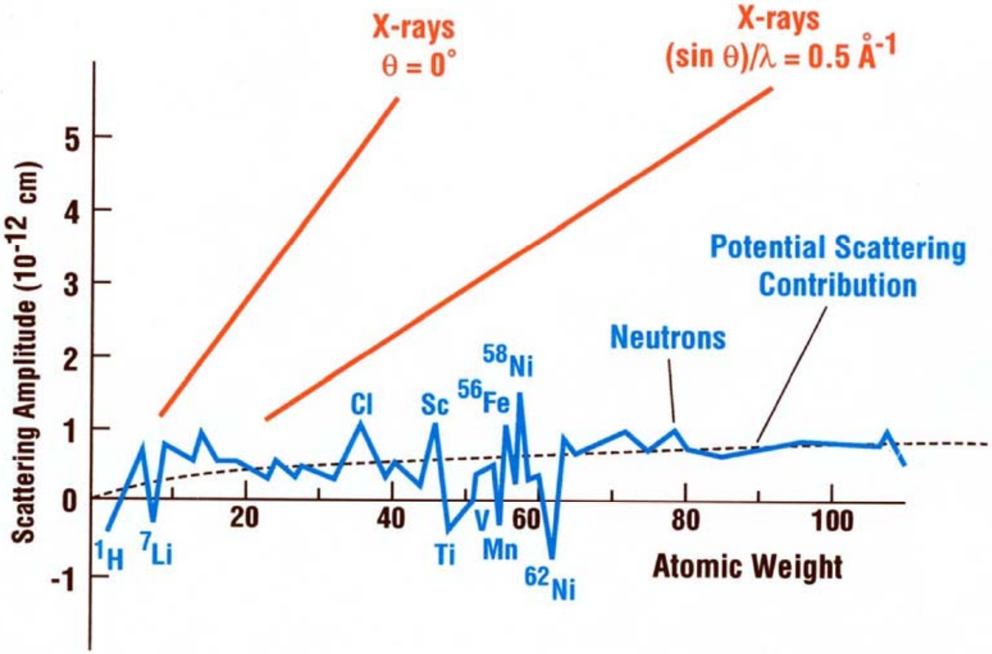
low absorption cross-sections
bulk probe - surface sensitivity by scattering contrast
virtually no technical impediment to use under reaction conditions – except: LOW SOURCE INTENSITIES.

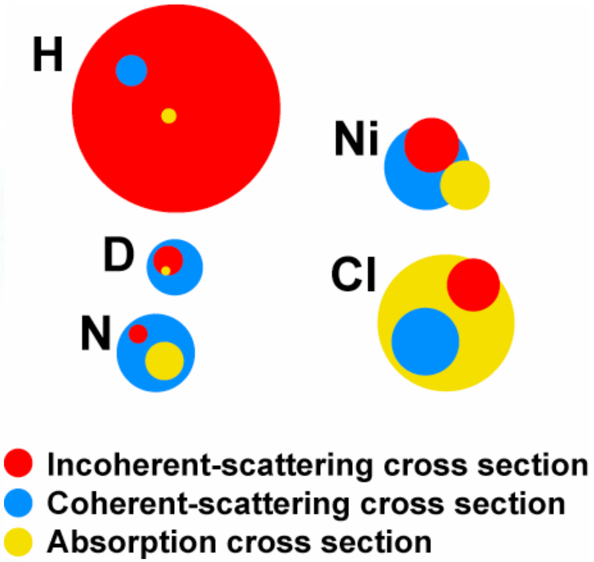
Thermal Neutrons, 8 keV X-Rays & Low Energy Electrons:- Absorption by Matter



Note for neutrons:

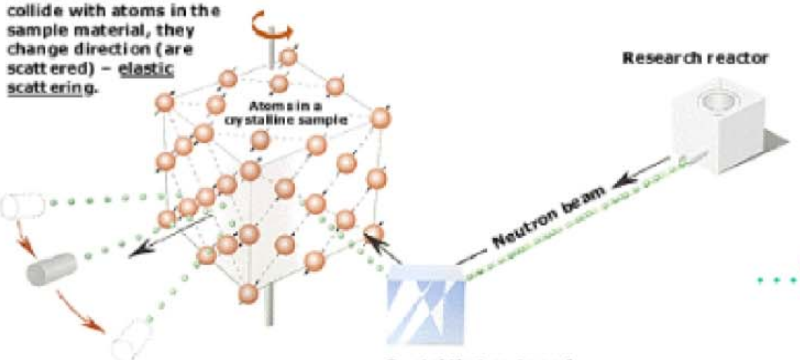
- H/D difference
- Cd, B, Sm
- no systematic A dependence


X-rays
θ = 0°
X-rays
(sin θ)/λ = 0.5 Å⁻¹
Potential Scattering Contribution
Neutrons
Scattering Amplitude (10⁻¹² cm)
5
4
3
2
1
0
-1
20
40
60
80
100
Atomic Weight
¹H
⁷Li
Cl
Sc
⁵⁶Fe
⁵⁸Ni
Ti
V
Mn
⁶²Ni


H
Ni
D
N
Cl
● Incoherent-scattering cross section
● Coherent-scattering cross section
● Absorption cross section

The 1994 Nobel Prize in Physics – Shull & Brockhouse

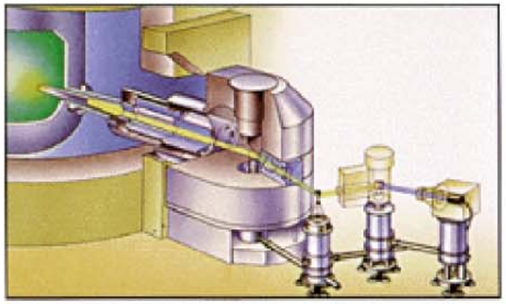
Neutrons show where the atoms are….



When the neutrons collide with atoms in the sample material, they change direction (are scattered) – elastic scattering.

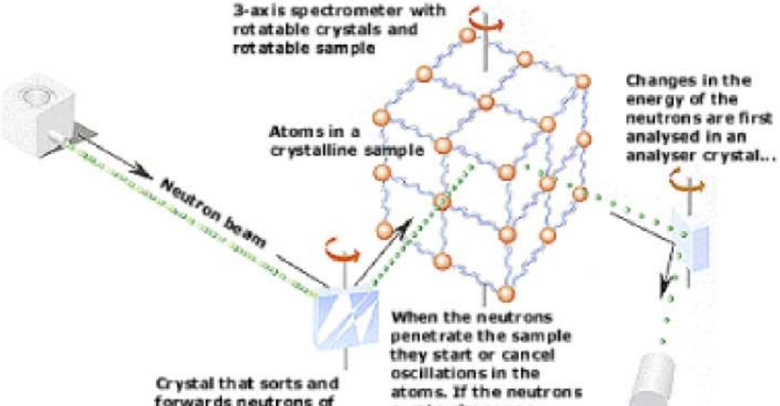
Detectors record the directions of the neutrons and a diffraction pattern is obtained.
The pattern shows the positions of the atoms relative to one another.

Crystal that sorts and forwards neutrons of a certain wavelength (energy) – monochromatized neutrons



3-axis spectrometer

…and what the atoms do.



3-axis spectrometer with rotatable crystals and rotatable sample

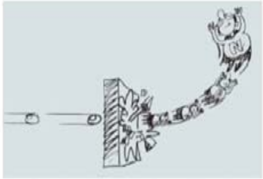
Changes in the energy of the neutrons are first analysed in an analyser crystal...

Crystal that sorts and forwards neutrons of a certain wavelength (energy) – monochromatized neutrons

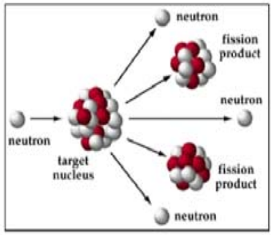
When the neutrons penetrate the sample they start or cancel oscillations in the atoms. If the neutrons create phonons or magnons they themselves lose the energy these absorb – inelastic scattering

...and the neutrons then counted in a detector.

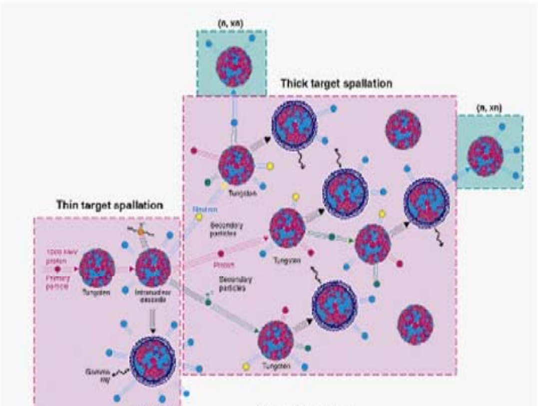
Neutron Production



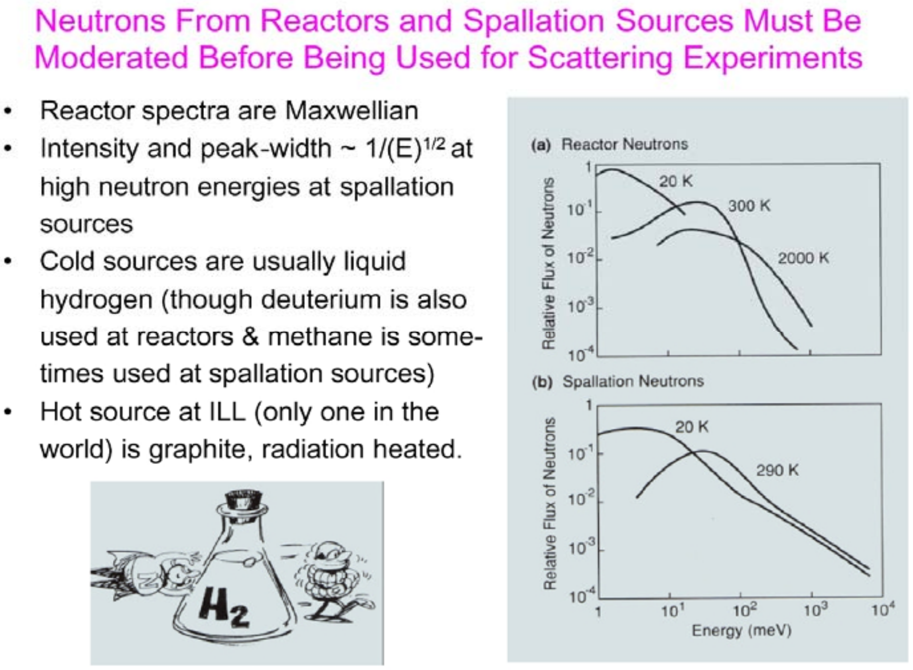
Artist's view of spallation



Nuclear Fission

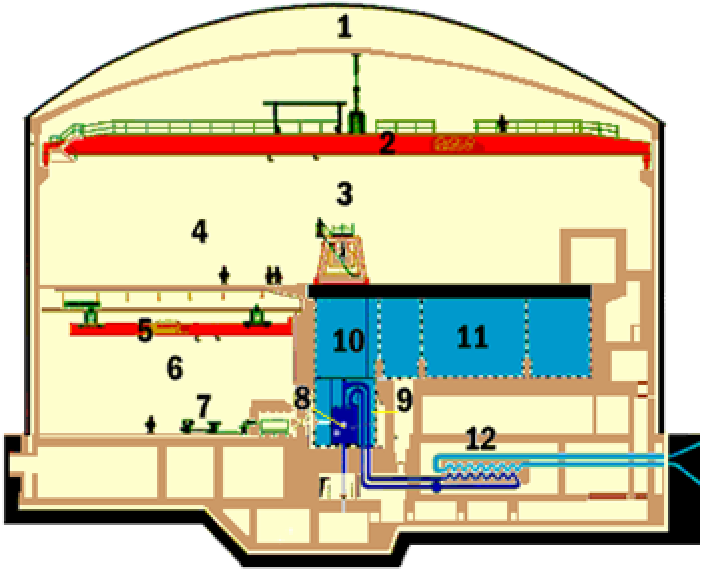


Spallation



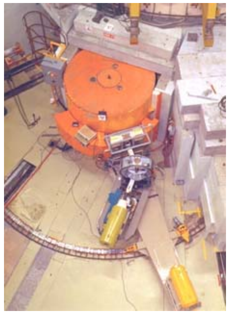
Neutrons From Reactors and Spallation Sources Must Be Moderated Before Being Used for Scattering Experiments

- Reactor spectra are Maxwellian
- Intensity and peak-width ~ $1/(E)^{1/2}$ at high neutron energies at spallation sources
- Cold sources are usually liquid hydrogen (though deuterium is also used at reactors & methane is sometimes used at spallation sources)
- Hot source at ILL (only one in the world) is graphite, radiation heated.



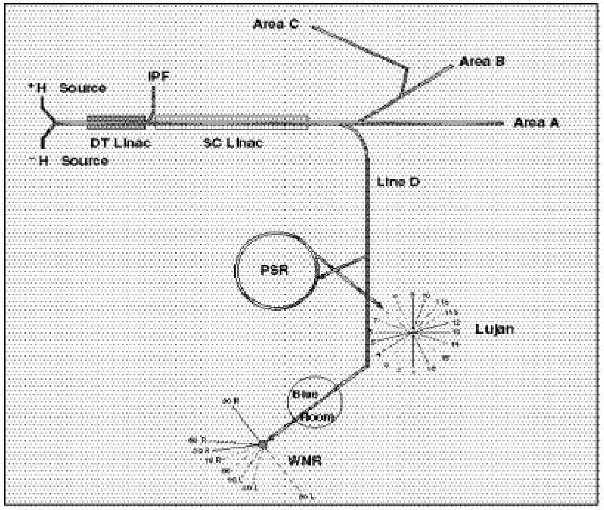
High Flux Reactor at the Institut Laue-Langevin

Grenoble, France

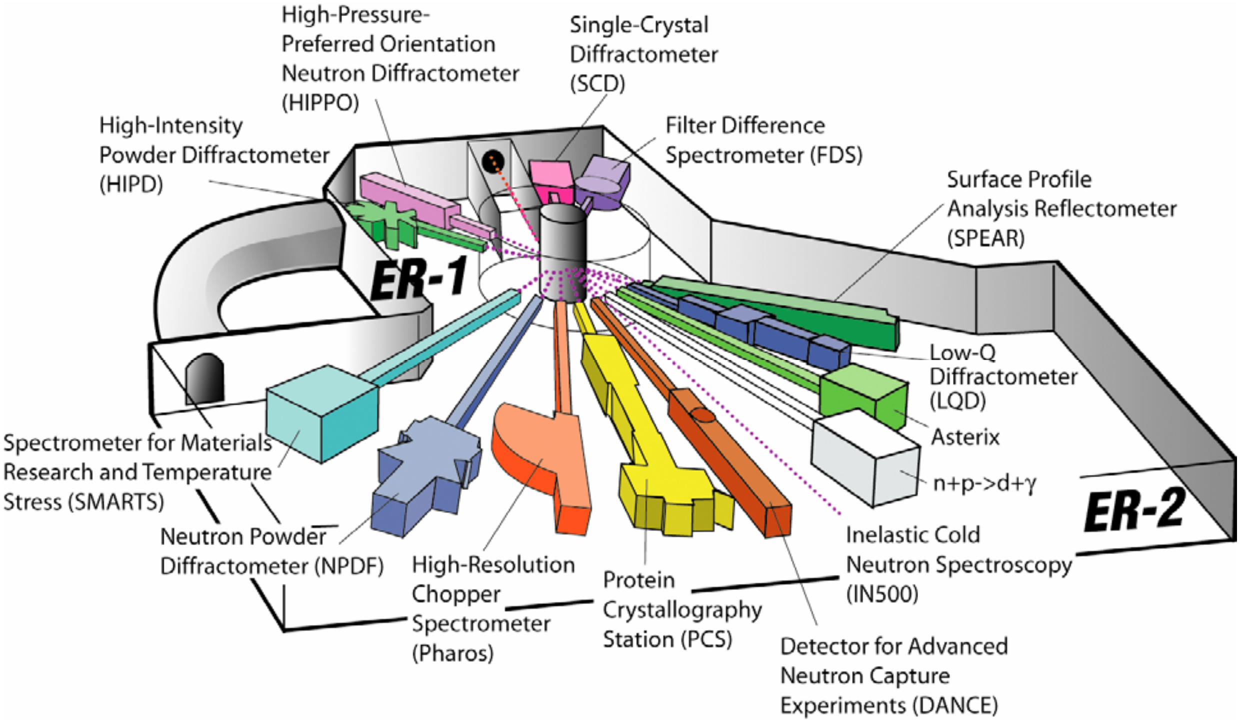


Neutron Production at LANSCE

- Linac produces 20 H^- (a proton + 2 electrons) pulses per second
  - 800 MeV, ~800 μsec long pulses, average current ~100 μA
- Each pulse consists of repetitions of 270 nsec on, 90 nsec off
- Pulses are injected into a Proton Storage Ring with a period of 360 nsec
  - Thin carbon foil strips electrons to convert H^- to H^+ (I.e. a proton)
  - ~3 x 10^{13} protons/pulse ejected onto neutron production target



Neutron Scattering Instruments at the Lujan Center of Los Alamos National Laboratory

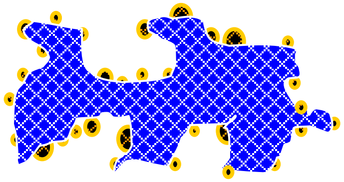


LANSCE
Los Alamos Neutron Science Center

Brightness & Fluxes for Neutron & X-Ray Sources

	Brightness *(s^{-1} m^{-2} $ster^{-1}$)*	*dE/E* *(%)*	*Divergence* *($mrad^2$)*	*Flux* *(s^{-1} m^{-2})*
Neutrons	10^{15}	2	10 x 10	10^{11}
Rotating Anode	10^{16}	3	0.5 x 10	5×10^{10}
Bending Magnet	10^{24}	0.01	0.1 x 5	5×10^{17}
Wiggler	10^{26}	0.01	0.1 x 1	10^{19}
Undulator (APS)	10^{33}	0.01	0.01 x 0.1	10^{24}

>> Neutron scattering methods are intensity limited: large samples, high surface areas, “long” counting times; time-dependent measurements: yes, but…



Surface Area = ~100 m^2/g

e.g.: high Surface area oxide-supported metal catalysts

Synchrotron- and Neutron Scattering Places

Neutron Sources in Asia and Australia:

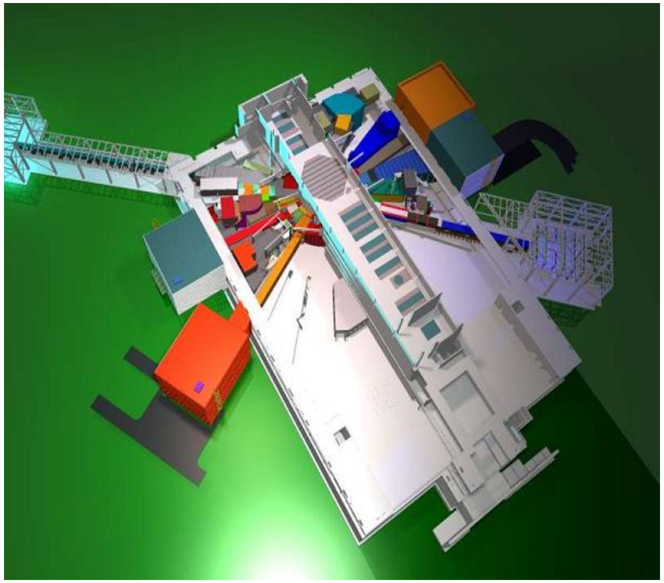
Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia
High-flux Advanced Neutron Application Reactor (HANARO), Korea
Japan Atomic Energy Research Institute (JAERI), Tokai, Japan
KENS Neutron Scattering Facility, KEK, Tsukuba, Japan
Kyoto University Research Reactor Institute (KURRI), Kyoto, Japan
Malaysian Institute for Nuclear Technology Research (MINT), Malaysia
NEW: Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan

SNS A U.S. Department of Energy multilaboratory project
Spallation Neutron Source

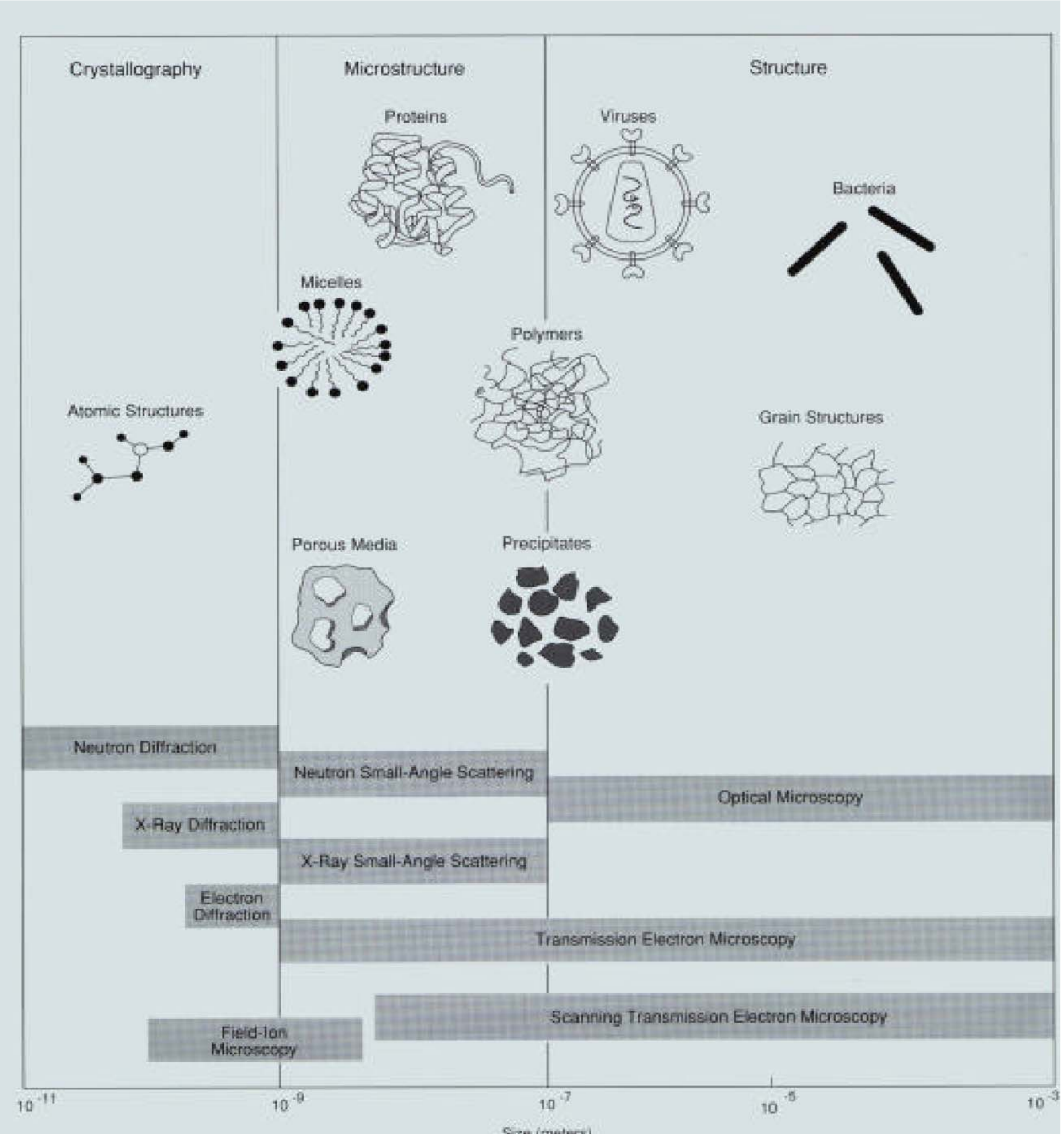
The Future is Now:

SNS at Oak Ridge National Laboratory, the world’s most intense neutron source

First neutrons produced April 28, 2006



Summary of Structural Probes



X-rays and Neutrons for Diffraction Experiments

Wavelengths must match typical d-spacings in crystals:

X-rays (electromagnetic waves): $E = hc/\lambda$ or $E(\mathrm{keV}) = 1.2398/\lambda(\mathrm{nm})$

Neutrons are heavy particles, have wave properties:

(de Broglie): $\lambda = h/mv$,

kinetic energy $E = h^2/2m\lambda^2$ or $E = 0.81787/\lambda(\mathrm{nm})^2$

	Energy (meV)	Temp (K)	Wavelength (nm)
Cold	0.1 - 1	1 -120	0.4 - 3
Thermal	5-100	60 -1000	0.1 - 0.4
Hot	100-500	1000-6000	0.04-01

Note: Neutrons have appropriate wavelengths AND energies - and a magnetic moment

Where do we get X-rays, neutrons from?

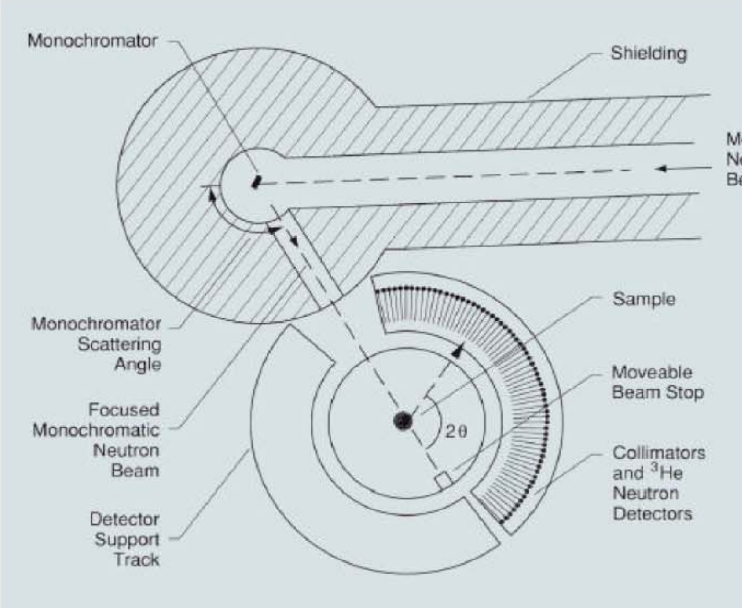
X-rays

- Laboratory X-ray generator
- Synchrotron Radiation

Neutrons

- Research Reactor (fission)
- Pulsed (accelerator-based) source (spallation)

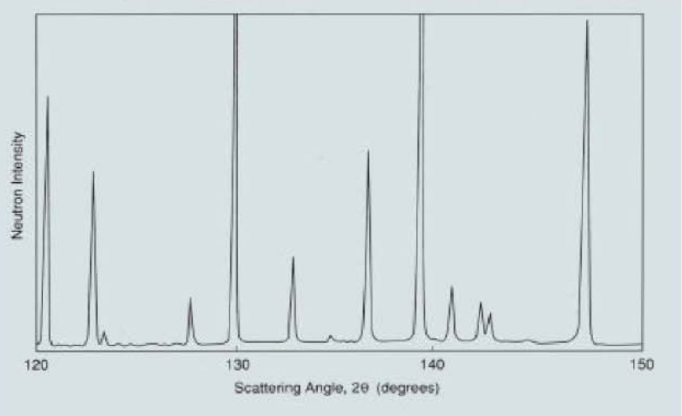
Measuring Neutron Diffraction Patterns with a Monochromatic Neutron Beam



POWDER DIFFRACTION AT A REACTOR SOURCE

Use a continuous beam of mono-energetic neutrons.

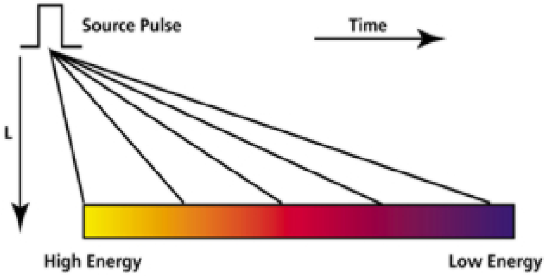
Since we know the neutron wavevector, k, the scattering angle gives G_{hkl} directly:
$G_{hkl} = 2\ k \sin\theta$



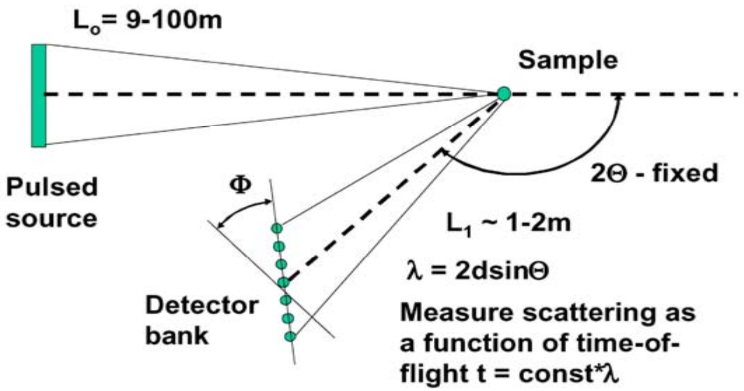
A POWDER DIFFRACTION PATTERN RECORDED AT A REACTOR

Neutron Powder Diffraction at a Pulsed (Spallation) Neutron Source:

Source produces bursts of neutrons
Most efficient use is by T-O-F methods



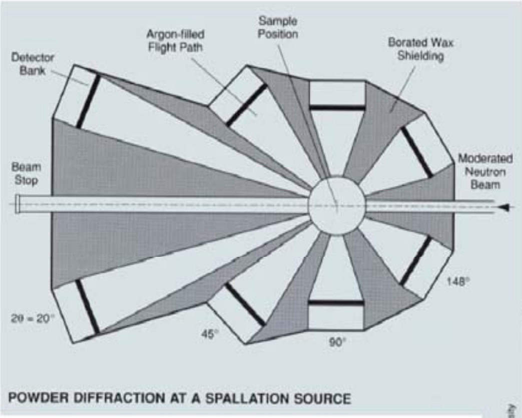
Neutron Powder Diffraction using Time-of-Flight



$\lambda = 2d\sin\Theta$

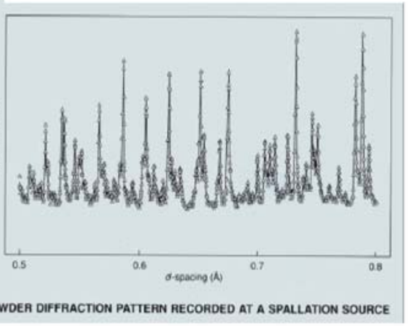
Measure scattering as a function of time-of-flight t = const*λ

Time-of-Flight Powder Diffraction



POWDER DIFFRACTION AT A SPALLATION SOURCE

Use a pulsed beam with a broad spectrum of neutron energies and separate different energies (velocities) by time of flight.

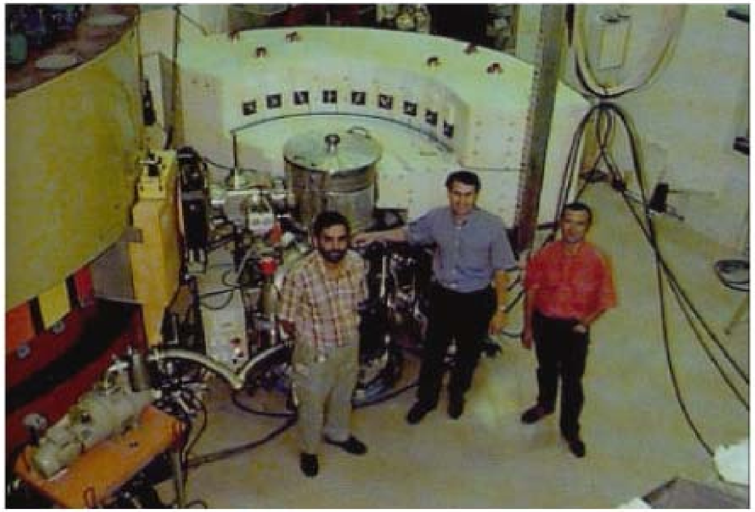


A POWDER DIFFRACTION PATTERN RECORDED AT A SPALLATION SOURCE

Spallation source:
All of the neutrons some of the time

Reactor source:
Some of the neutrons all the time

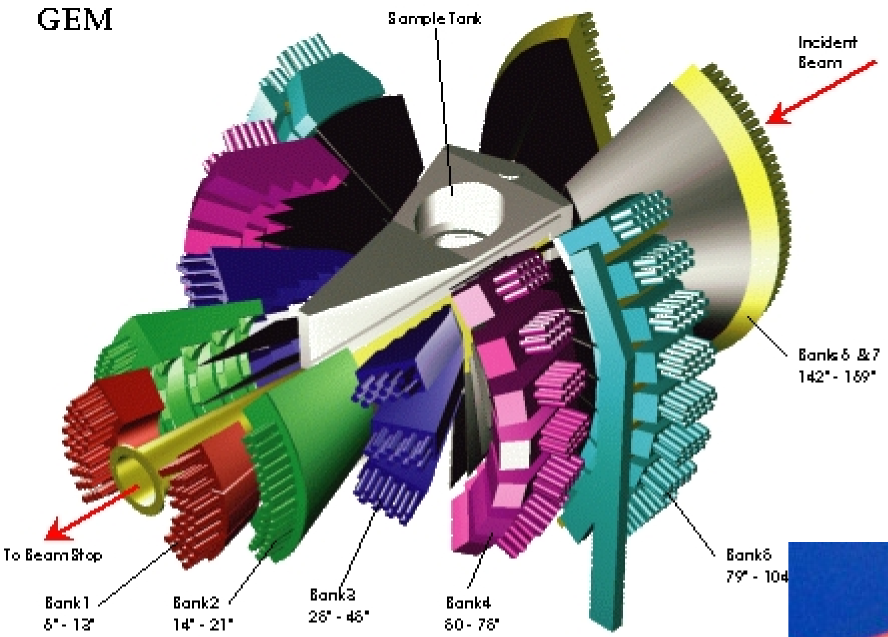
What do Neutron Powder Diffractometers look like?

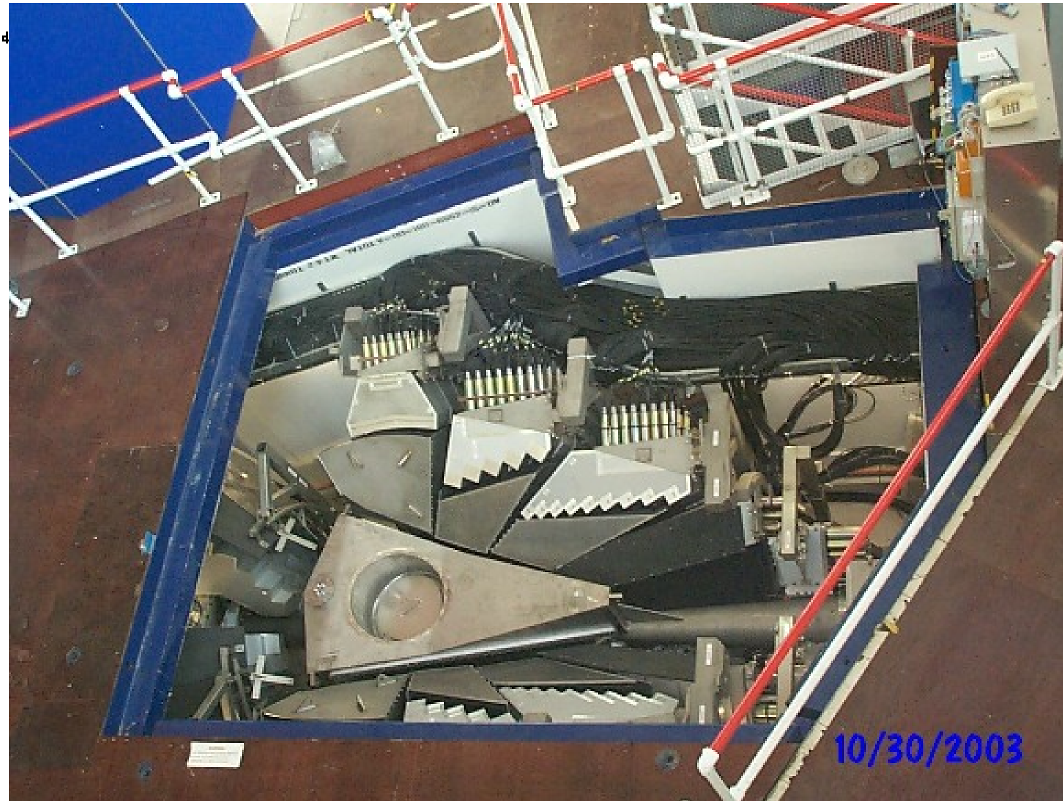


Note: relatively massive shielding; long flight paths for time-of-flight spectrometers; many or multi-detectors on modern instruments

General Materials Diffractometer

ISIS (Rutherford Appleton Lab, UK)



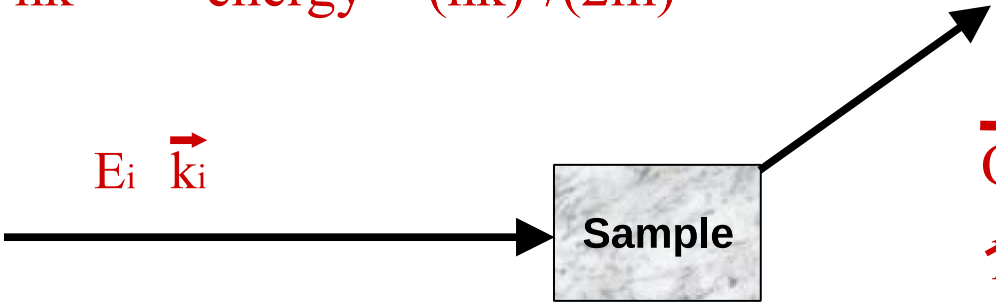


Neutron wavelengths ~□Å's and energies ~ meV's

: angular dependence of scattering always gives spatial information, not just in the case of $\Delta E = 0$ (diffraction)

---

momentum = $\hbar\vec{k}$ energy = $(\hbar k)^2/(2m)$



E_f $\vec{k}_f$

E_i $\vec{k}_i$

$\vec{Q} = \vec{k}_i - \vec{k}_f$

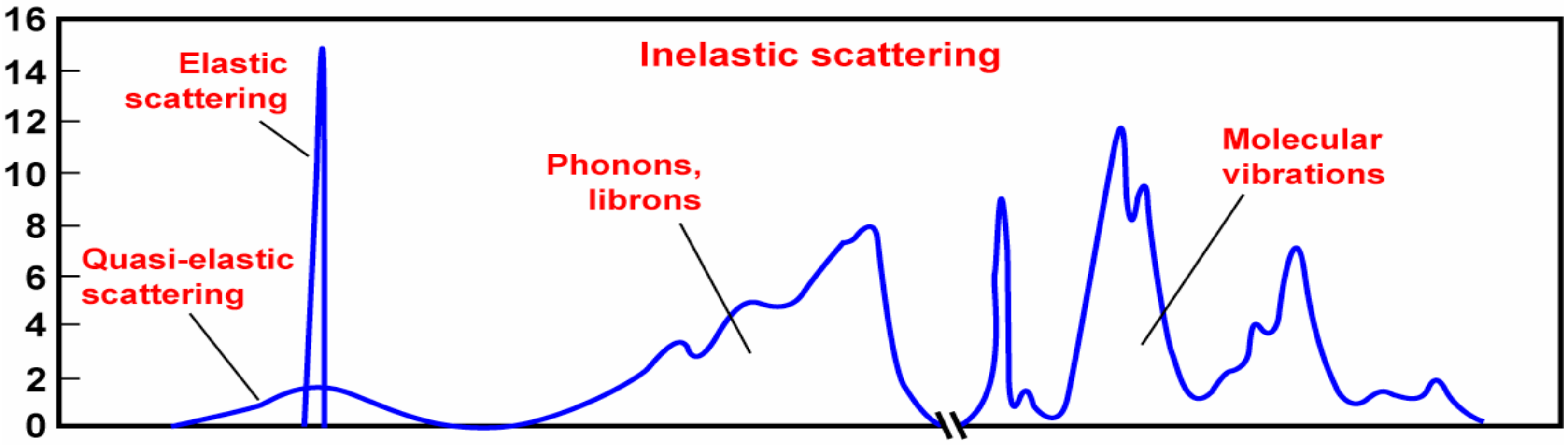
$\hbar\omega = E_i - E_f$

Measure the number of scattered neutrons
as a function of Q and ω

=> $S(Q,\omega)$ (the scattering function)

Consequence of neutron momentum: particle recoil!

“Generic” Neutron Scattering Spectrum



Frequency (10^8 - 10^{15} s^{-1})

Example: for an adsorbate molecule

elastic: structural information

quasielastic scattering:

diffusive motions (rotational, translational, transport)

external modes:

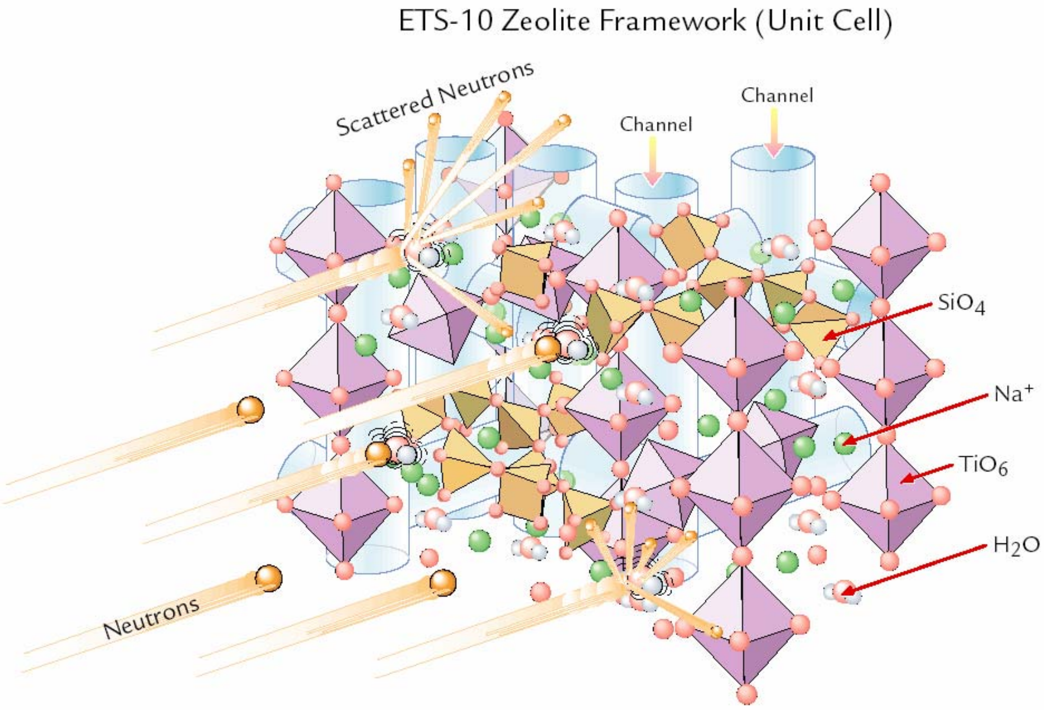
whole-body librations, translations

(internal) molecular vibrations

What Molecules "Do" in/on Catalytic Materials: Dynamics

Types of dynamics, or motions, molecules experience
Why are these importance?
How can we observe these motions?
What will you learn from their observation?

Example(below): water in zeolite ETS-10



Water molecule (in zeolite): dynamics

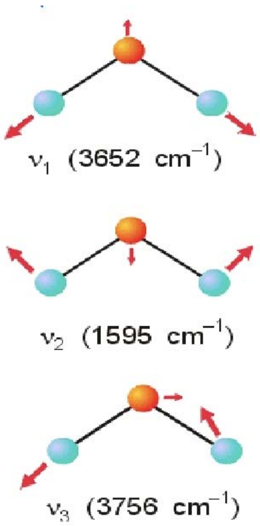
1. Internal vibrations (e.g. O-H bond stretching)
2. Whole-body vibration, libration (e.g. H_2O bounces up and down on the surface)
3. Diffusion: molecules moves through the structure

What Molecules “Do” in/on Catalytic Materials: Dynamics

1. Internal, or molecular, vibrations:
    - change when the molecule binds to the surface
    - magnitude of the change depends on the nature of binding, e.g. physisorption, hydrogen-bonding, chemisorption, dissociative, reactive binding*

Identify reaction products by

- “fingerprinting” (vibrational signatures)
- computation of spectra from proposed reaction products



The three vibrational modes for water. Each mode is listed with a ν (Greek letter ‘nu’) and a subscript and the energy of the vibration is given in parentheses. ν_1 is called the “symmetric stretch”, ν_2 is called the “anti-symmetric stretch” and ν_1 is called the “symmetric bend”.

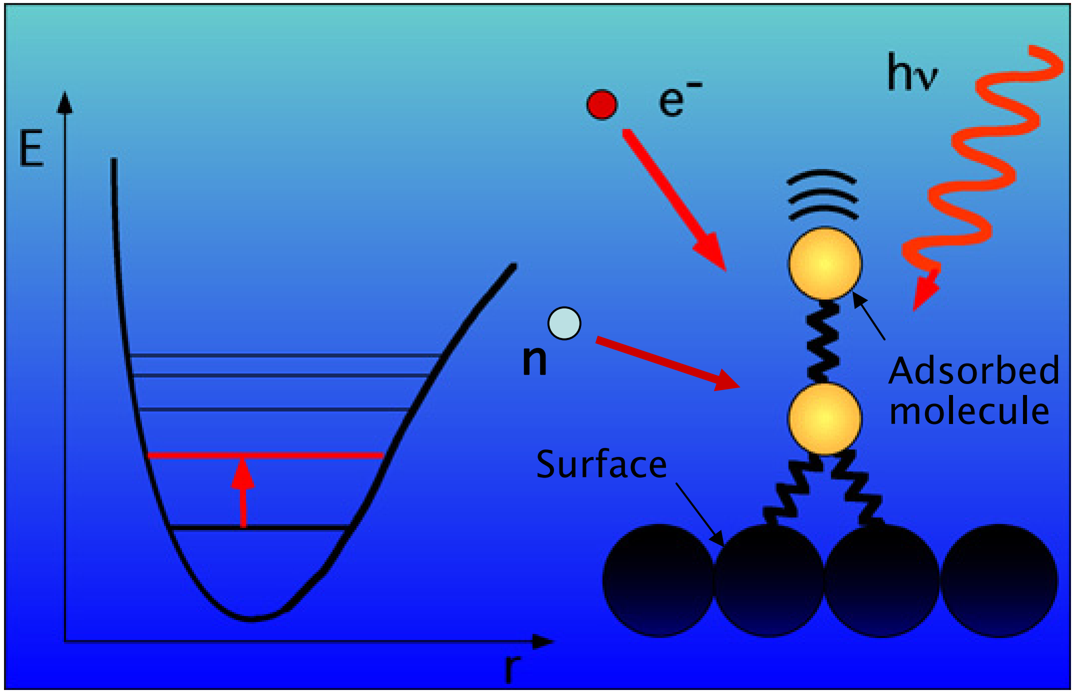
What can we learn from a study of molecular vibrations?

- **Vibrational frequencies** depend on interactions between atoms and groups of atoms. They tell us about intra- and intermolecular interactions.

- **Vibrational modes** vary with the nature of atoms in the bond and chemical environment. They give us information about chemical bonding and the chemical environment.

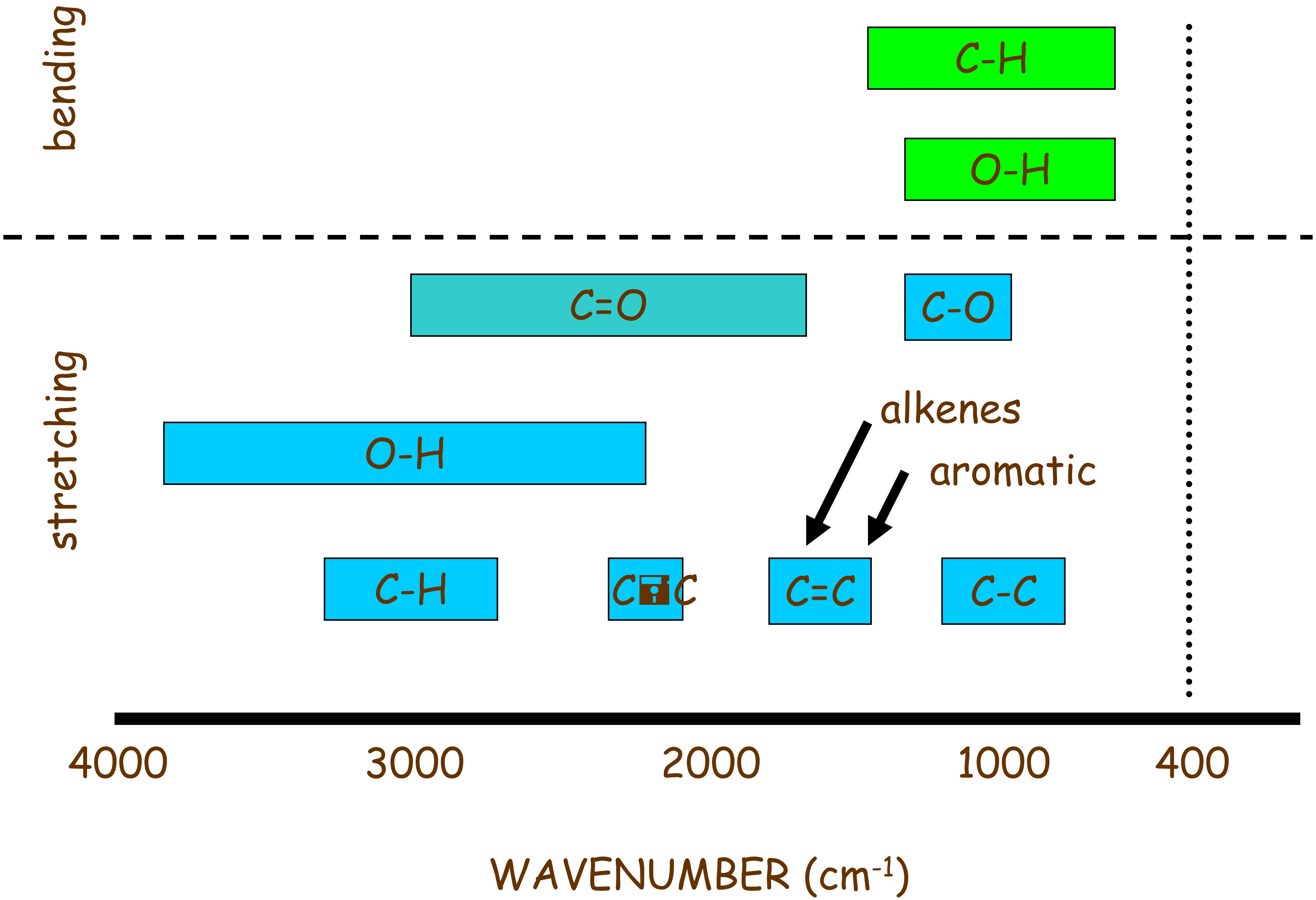
- Many **bond types** exhibit characteristic ("fingerprint") vibrational frequencies that allow us to establish the presence of certain functional groups, or products in a catalytic reaction.

MOLECULAR VIBRATIONAL SPECTROSCOPY



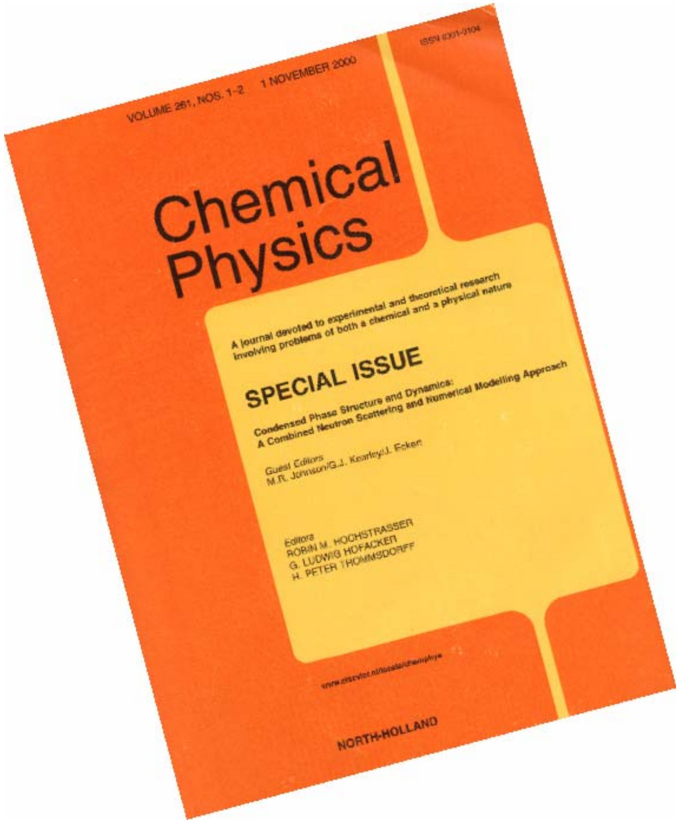
- ☐ Vibrational spectra in the mid- to far-infrared are fingerprints for molecular species identification.
- ☐ Surface molecular vibrational spectra -in conjunction with modern computational tools-provide information of adsorption sites, orientations, surface bonding, and local chemical environment of adsorbed species on surfaces.
- ☐ Raman, FTIR and HREELS are standard vibrational spectroscopy techniques
- ☐ What about neutrons? How are they a surface-specific scattering probe?

Basic Functional Groups



MOLECULAR VIBRATIONAL SPECTROSCOPY

Inelastic Neutron Scattering vibrational spectroscopy in conjunction with numerical modeling is a powerful technique that has several advantages over optical techniques:



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A journal devoted to experimental and theoretical research involving problems of both a chemical and a physical nature

SPECIAL ISSUE

Condensed Phase Structure and Dynamics:
A Combined Neutron Scattering and Numerical Modelling Approach

Guest Editors
M.R. Johnson/G.J. Kearley/J. Eckert

Editors
ROBIN M. HOCHSTRASSER
G. LUDWIG HOFACKER
H. PETER TROMMSDORFF

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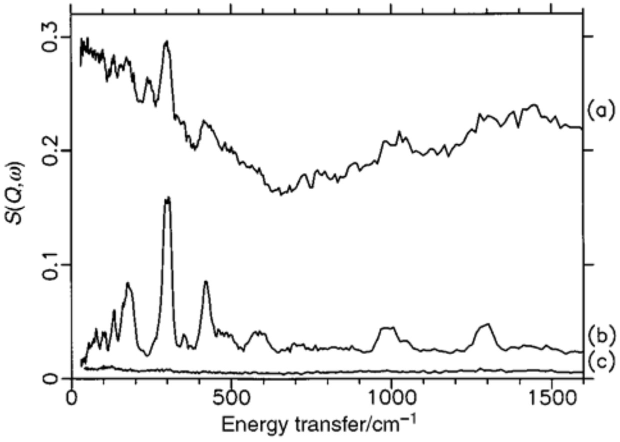
NORTH-HOLLAND

- High sensitivity to H (large incoherent neutron scattering cross section)
- No selection rules;
- No complicated electron/photon interactions: computational ease
- Enhanced contrast from the large difference in H and D cross section;
- “Real” surfaces (no need for ultraclean, single-crystal surfaces).

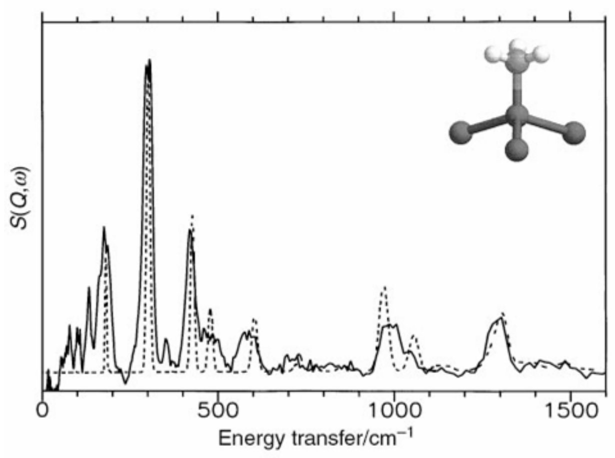
Poisoning of a Pd Catalyst Studied by INS*

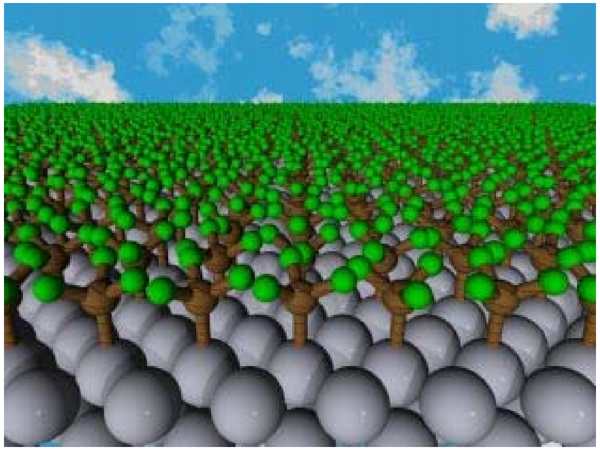
ISIS Facility (UK): Albers (Degussa-Huls) et al., Chem. Com. **1999**, 1619



Deactivated catalyst before (a) and after (b) solvent extraction. Active catalyst after extraction (c)

Identification of species poisoning the catalyst
Comparison of observed and calculated INS spectrum for on-top methyl group





* and computations

Incoherent inelastic neutron scattering cross section: molecular vibrational spectra

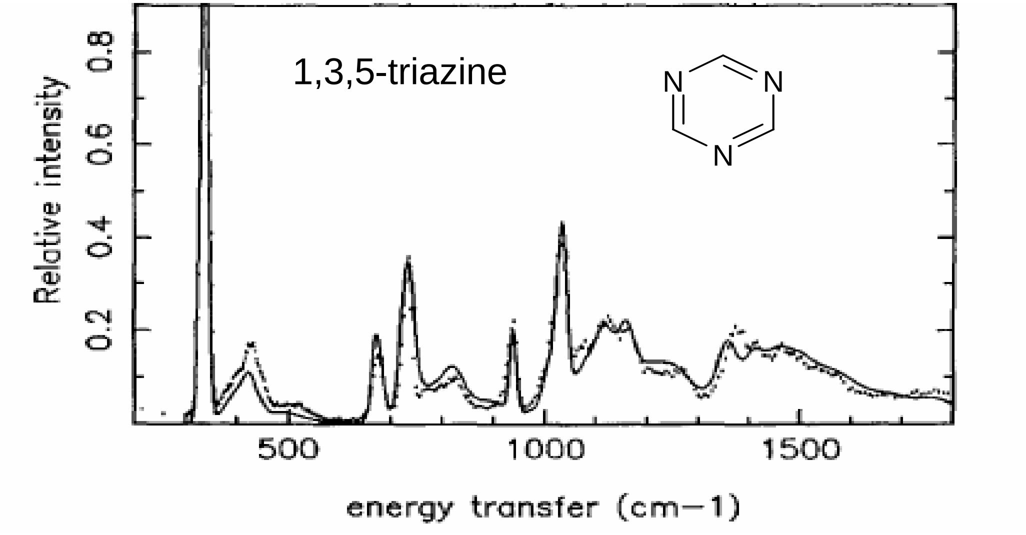
A normal mode of vibration with frequency ω_s in a polycrystalline sample contributes a term

$$\frac{Q^2\langle U^2\rangle}{\mu\omega_s}\exp\left(-Q^2\langle U^2\rangle\right)$$

to S, the scattering cross section, mulitplied by the scattering lengths b for atom involved

where μ is the effective oscillator mass and Q the momentum transfer.

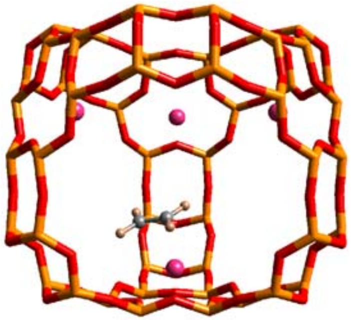
Frequencies and amplitudes alone determine the INS spectrum; can be readily calculated any number of ways (NCA, ab-initio, etc.). **Complete spectral profile** is calculated and compared with experiment.



What Molecules "Do" in/on Catalytic Materials: Dynamics

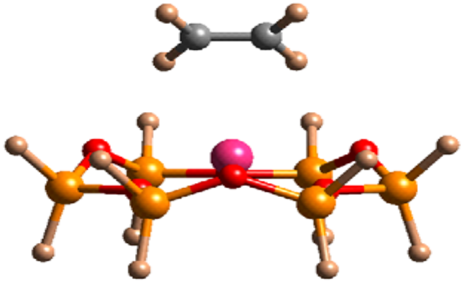
2. [illegible] librations/translations of sorbate molecule relative to surface:
very high sensitivity to guest-host interaction

INS and Computation: External (suface-specific) adsorbate vibrational modes



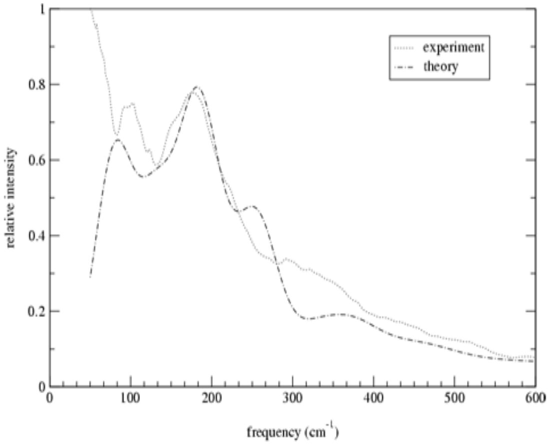
[illegible] calculation (emprirical forces) to **determine location** of the sorbate molecule

QM cluster calculation yields **minimum energy structure** of sorption complex



Compute INS spectrum and compare with experiment

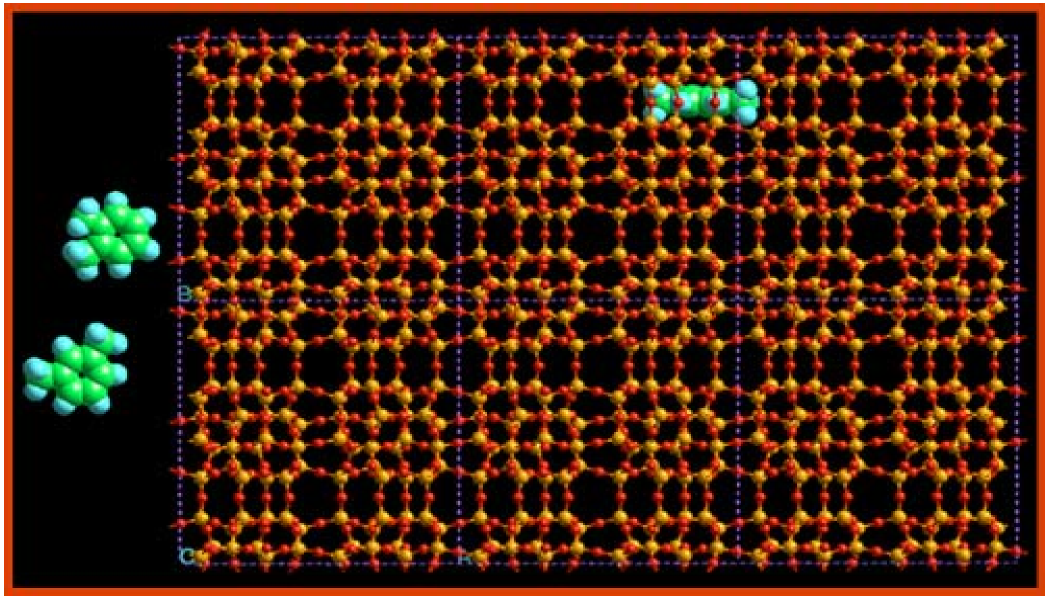
[illegible] agreement with force-field: whole system



J. [illegible], P. J. Hay and A. Redondo, Chem. Phys., **261**, 111 (2000)

What Molecules “Do” inon Catalytic Materials: Dynamics

3. Diffusion: molecules move through the structure (if they can),
pores and channels;
also: random changes of orientation (“rotational diffusion”)



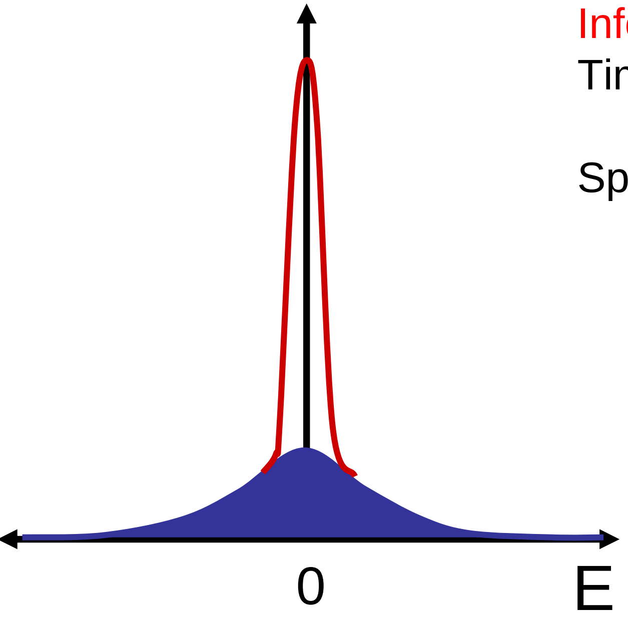
Observation does not contain much information about the molecule, but…

Importance: separation (here p-xylene from o- and m-xylenes)
catalysis: reactants need to move rapidely to the
active site, desired products have to move out

Quasielastic Neutron Scattering

Quasielastic neutron scattering spectrum: one or more Lorentzians centered at E=0

Origin: atomic or molecular motions subject to random and/or fluctuating potentials:
- translational diffusion, e.g. continuous(=Brownian Motion) or jumps
- stochastic molecular reorientation



Information obtained:

Time scale of motion: L width ~ $1/\tau$

($< 10^8\ s^{-1}$)

Spatial description of motion:

: angular (=Q) dependence of width and intensity

Example: ➔

continuous diffusion

$1/\tau = 2DQ^2$

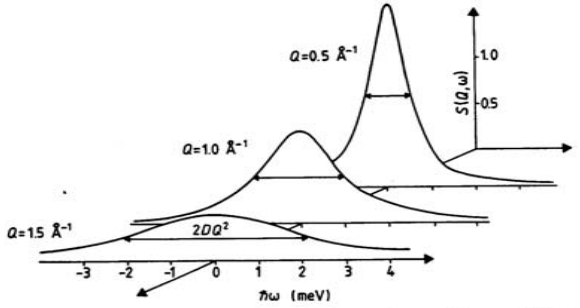
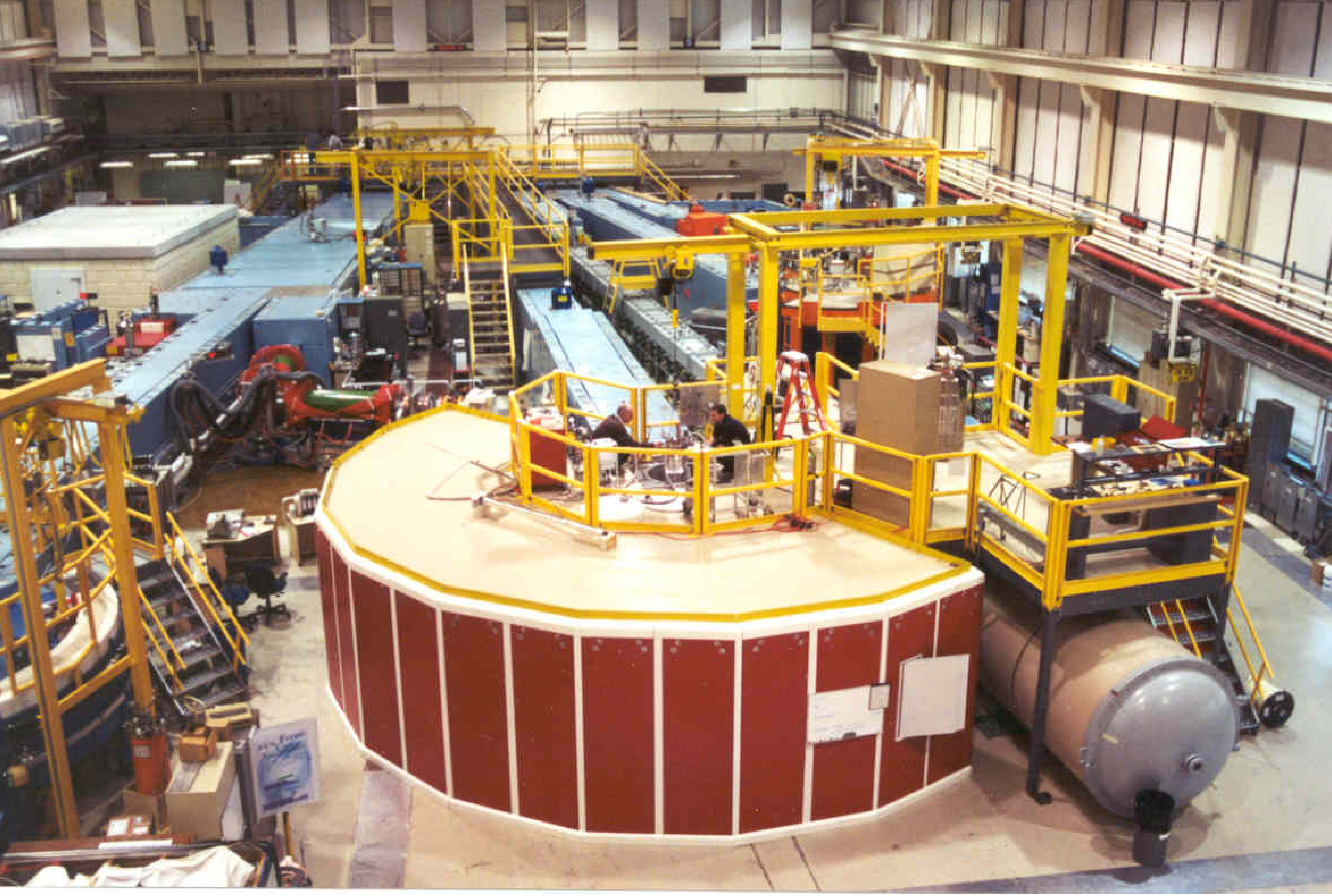
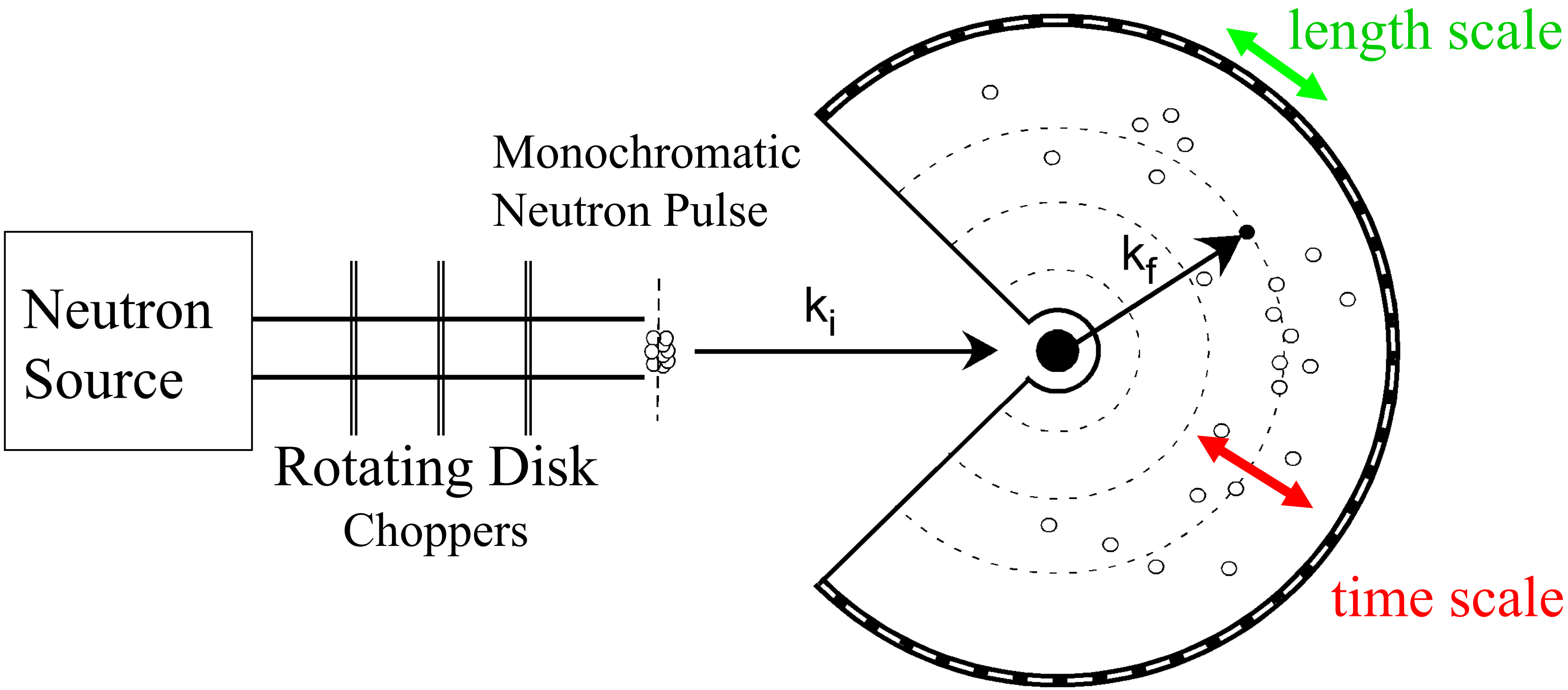


Figure 5.2 Scattering law corresponding to the continuous diffusion model.

spectrum may be a convolution of L's for several diffusive motions: slow process (red), fast process (blue)



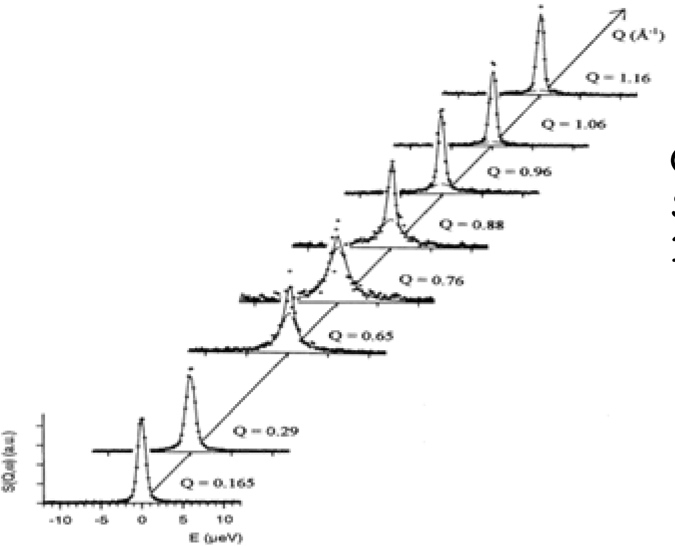
Dynamics by Neutron Scattering



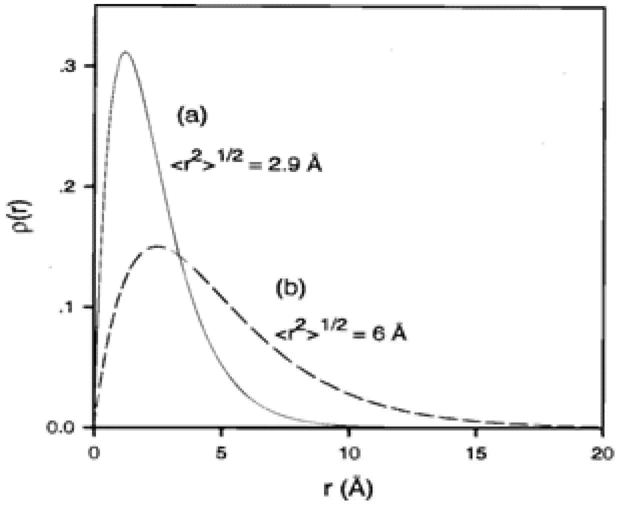
$q=k_i-k_f$ [=]$Å^{-1}$ **$d=2\pi/q$**

Diffusion of Benzene by Quasielastic Neutron Scattering

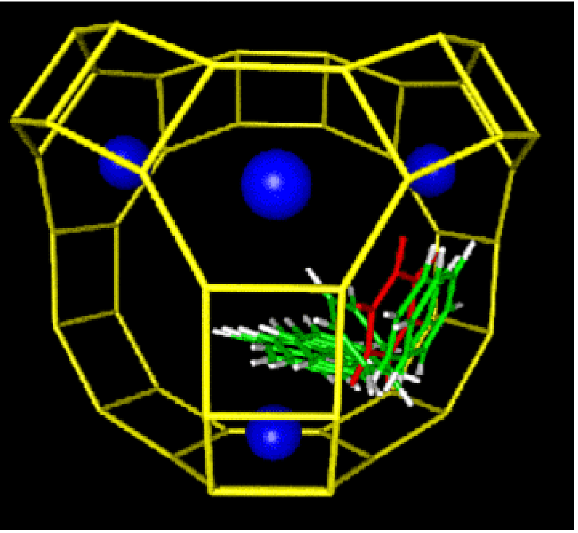
ILL: Jobic et al. J. Phys. Chem. B 2000, 104,

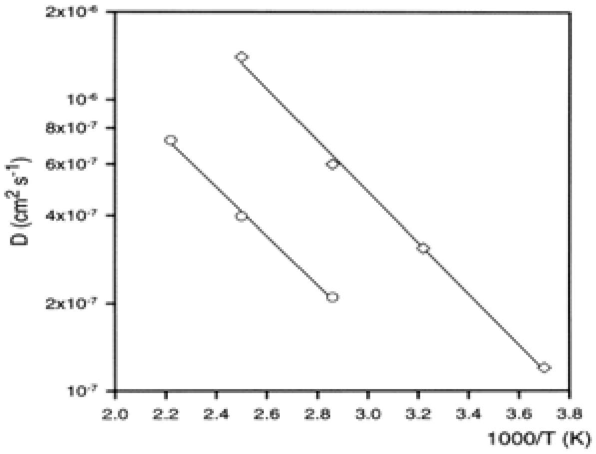


Quasielastic Neutron
Scattering Spectra, 350K
1.5 Benzene/supercage



QENS provides both
time and spatial
information:
jump distance distributions
(top) and
diffusion constants
(bottom)

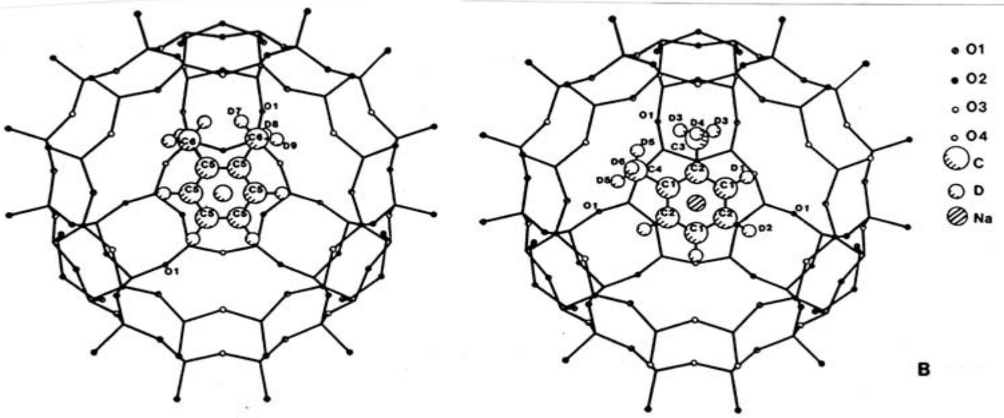




Simulations: Auerbach et al.,

Xylenes in Yb,Na-Y

(M. Czjzek, H. Fuess and T. Vogt, J. Phys. Chem. 95, 5255, 1991)



(Neutron powder diffraction; p-complexes; "liquid-like" phase at higher coverages)

Translational Diffusion of Xylenes in Na, Ba-Y (Hervé Jobic)

Time scale of 10^{-9} s^{-1} requires IN16 at the ILL

Random jump diffusion: length ~ 5.5Å between type II cation sites

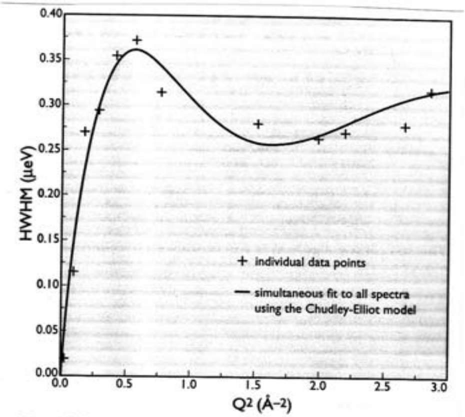
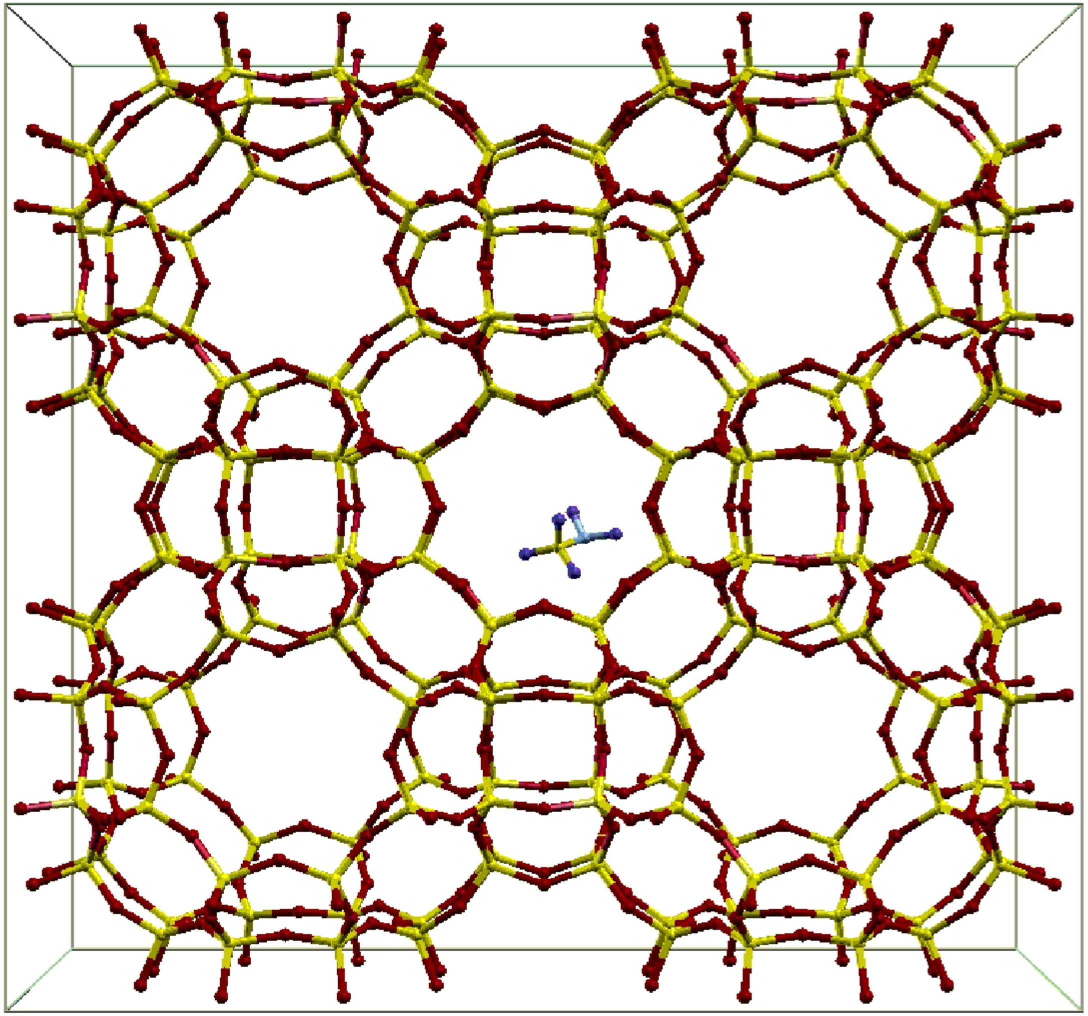
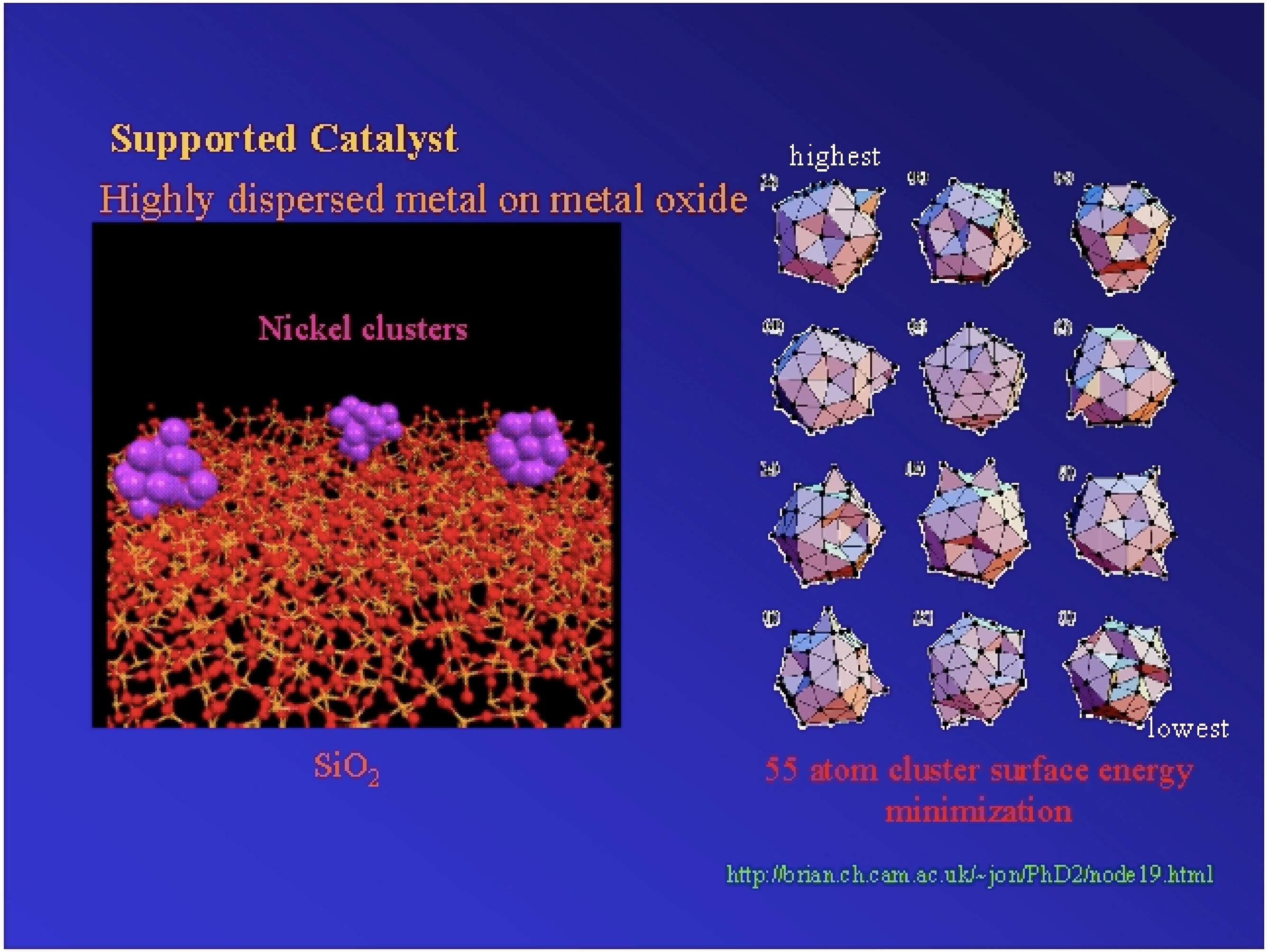


Figure 2: *Broadenings measured for para-xylene in NaX zeolite, at 355 K.*

□Can you find the sorbate molecule ?



Example: metal clusters (various sizes, locations) on a (disordered) amorphous support - no Bragg!!



Supported Catalyst

Highly dispersed metal on metal oxide

55 atom cluster surface energy minimization

http://brian.ch.cam.ac.uk/~jon/PhD2/node19.html

Binding of Chloroform in Faujasite Type Zeolites

Sorbate molecules may be difficult to locate in/on catalytic materials by normal diffraction techniques - why?

crystalline hosts/supports:

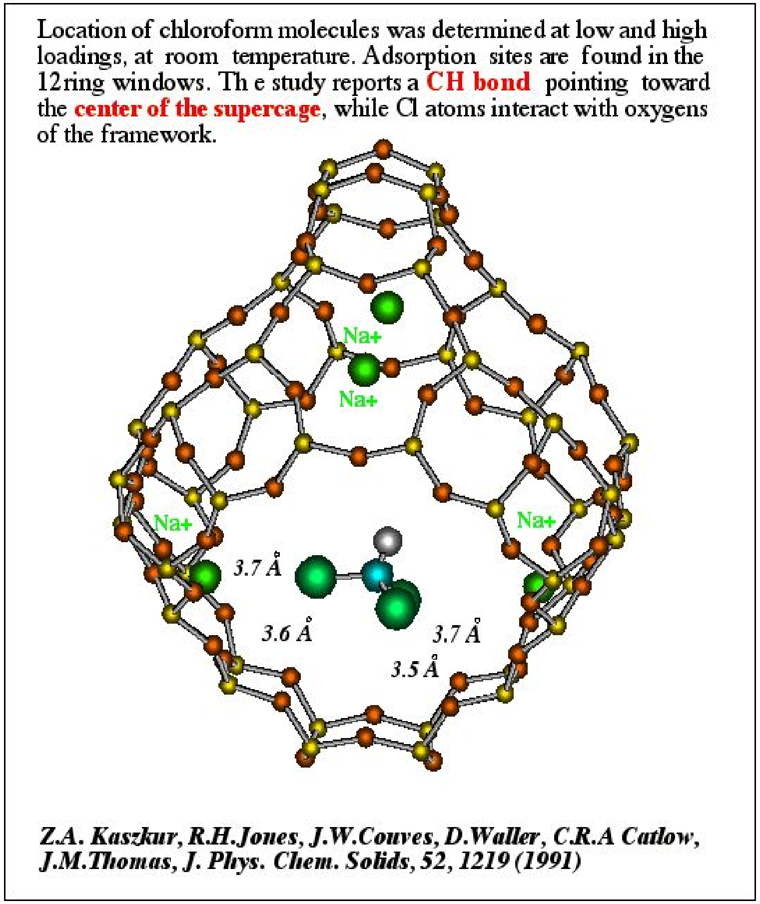
- multiple binding sites
- weak "corrugation" of surface
- no long-range coherence of siting
- orientational disorder
- scattering contrast

host/support may not be crystalline

\>> Combine:

- spectroscopy
- computation
- diffraction (in a different way)

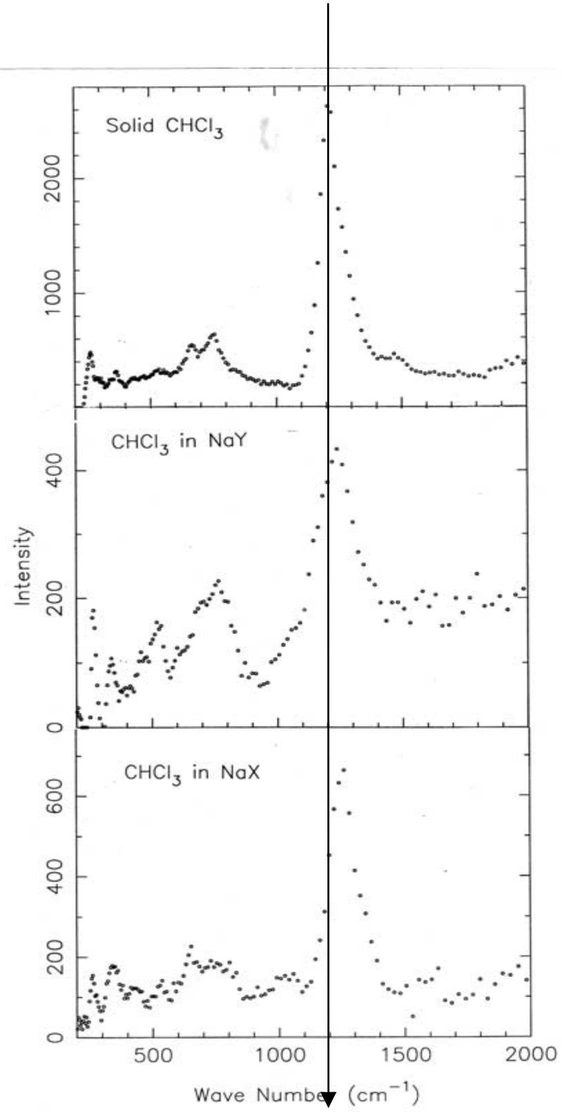
Previous Work:
Synchrotron XRay D iffraction study of $CHCl_3$ in NaY



Location of chloroform molecules was determined at low and high loadings, at room temperature. Adsorption sites are found in the 12ring windows. Th e study reports a **CH bond** pointing toward the **center of the supercage**, while Cl atoms interact with oxygens of the framework.

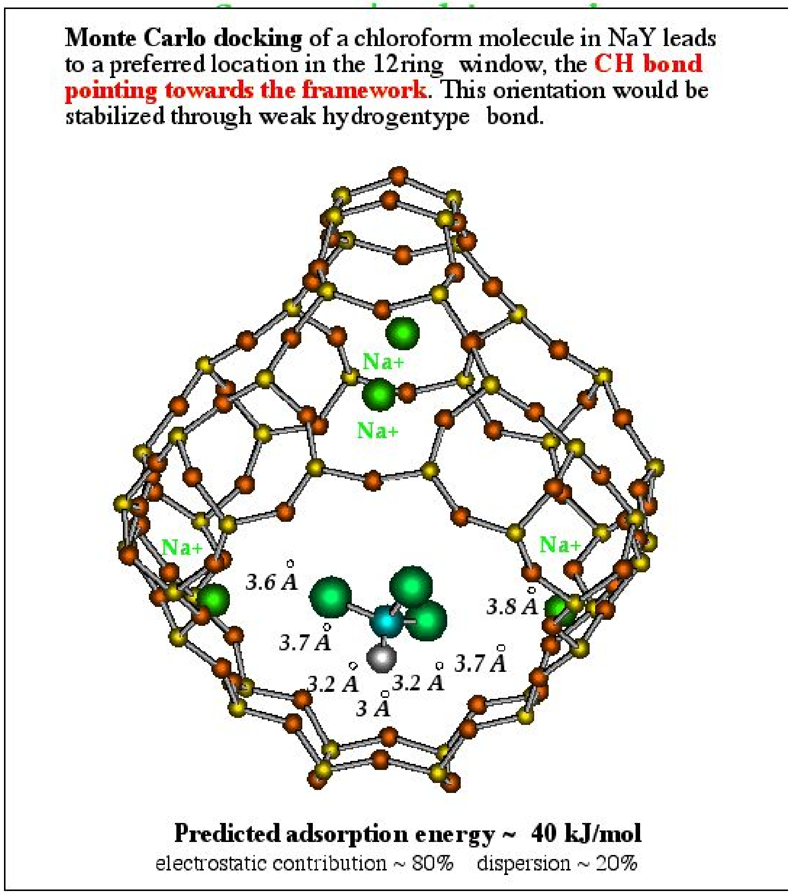
Z.A. Kaszkur, R.H. Jones, J.W.Couves, D.Waller, C.R.A Catlow, J.M.Thomas, J. Phys. Chem. Solids, 52, 1219 (1991)

Internal vibrations of sorbed chloroform molecule can suggest how the molecule binds to the zeolite host



Note shift of C-H bending mode frequency

Molecular Mechanics approach:
Monte Carlo Docking

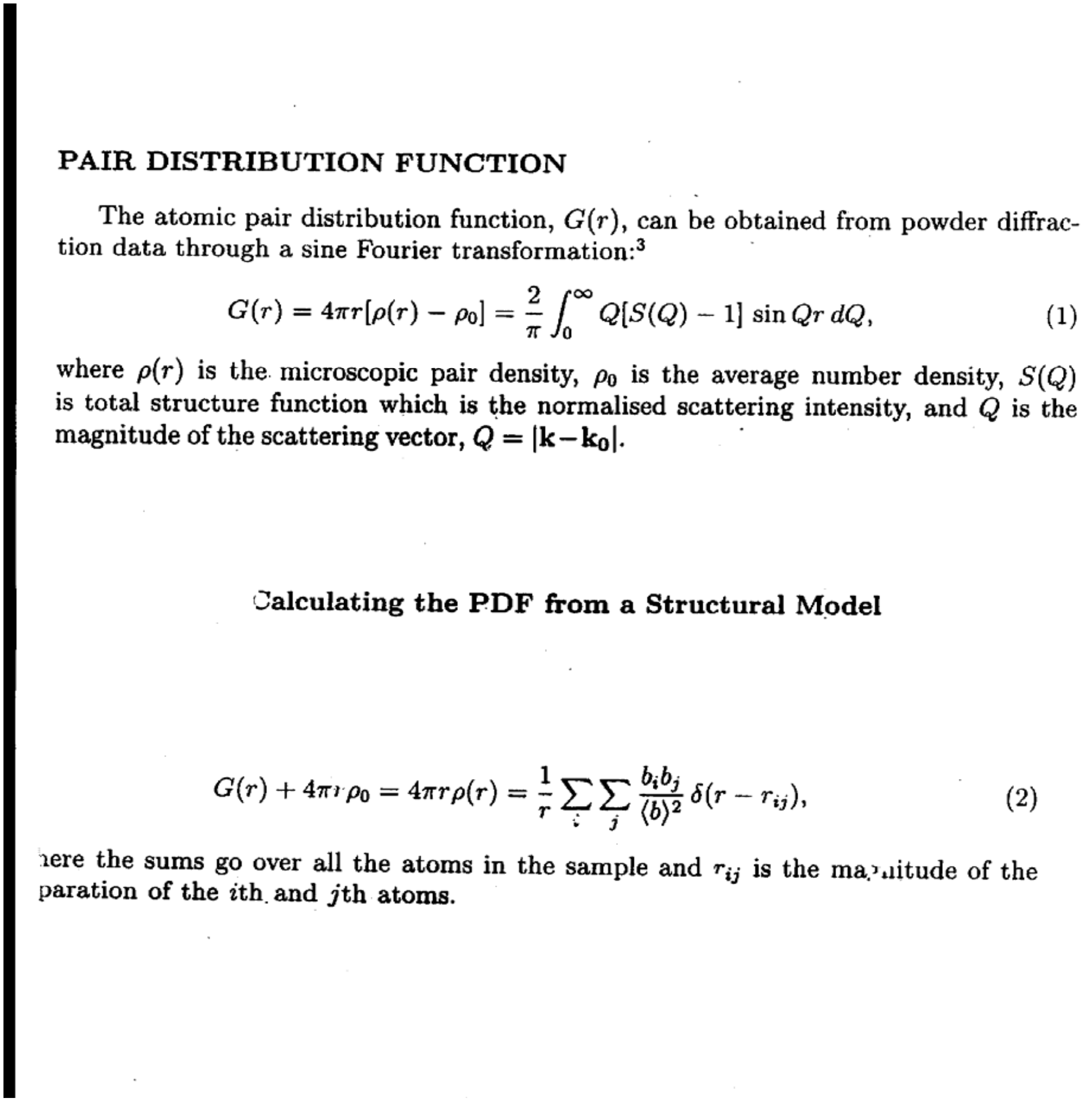


Monte Carlo docking of a chloroform molecule in NaY leads to a preferred location in the 12ring window, the **CH bond pointing towards the framework**. This orientation would be stabilized through weak hydrogentype bond.

Predicted adsorption energy ~ 40 kJ/mol
electrostatic contribution ~ 80% dispersion ~ 20%

Use computations to provide more detail

Information on structural disorder of all (?) kinds: Pair Distribution Function Analysis



PAIR DISTRIBUTION FUNCTION

The atomic pair distribution function, $G(r)$, can be obtained from powder diffraction data through a sine Fourier transformation:[3]

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr\,dQ, \tag{1}$$

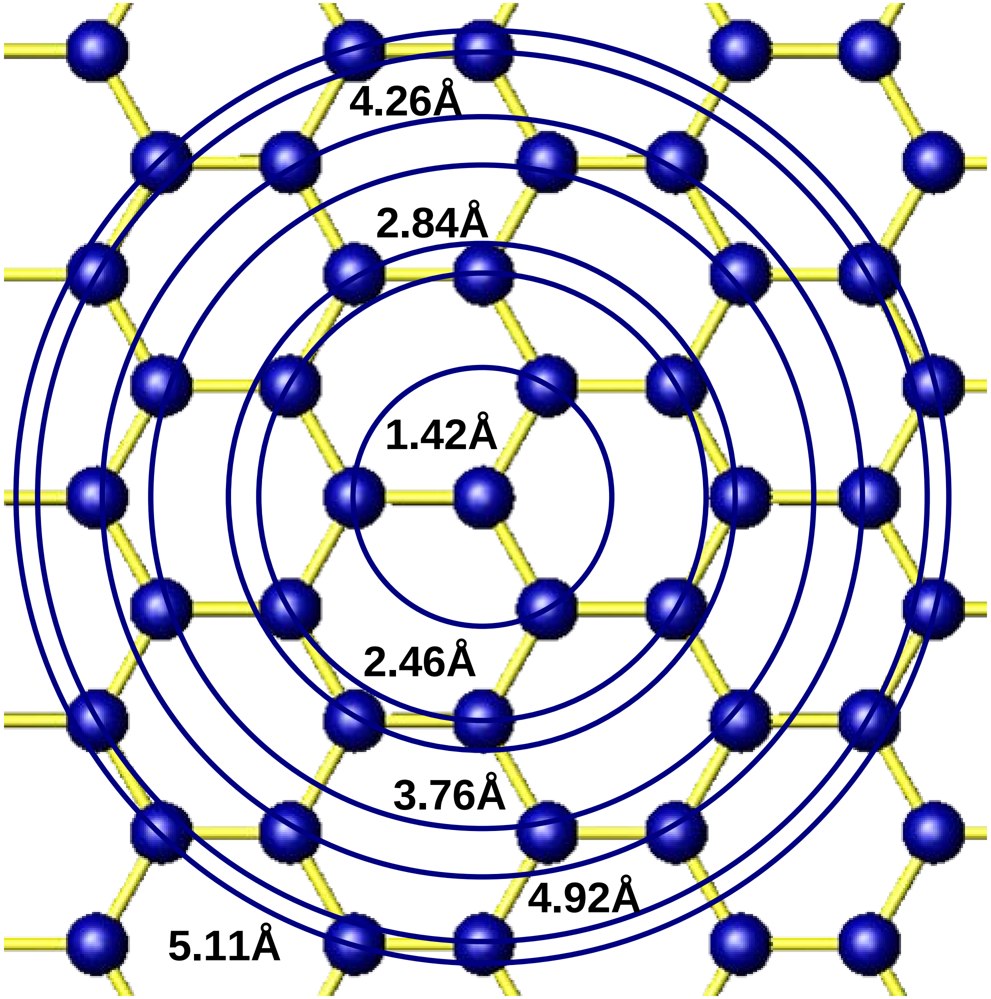
where $\rho(r)$ is the microscopic pair density, ρ_0 is the average number density, $S(Q)$ is total structure function which is the normalised scattering intensity, and Q is the magnitude of the scattering vector, $Q = |\mathbf{k} - \mathbf{k}_0|$.

Calculating the PDF from a Structural Model

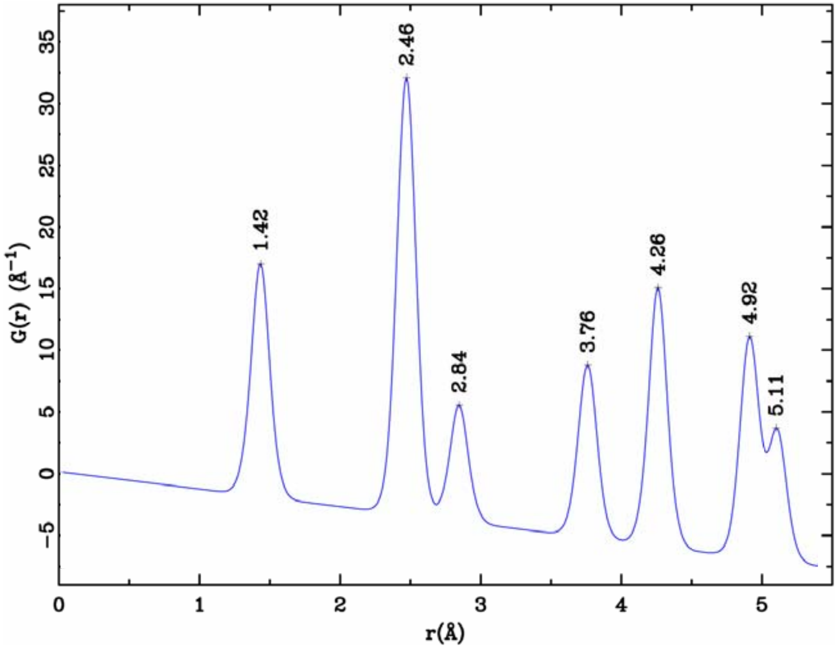
$$G(r) + 4\pi r\rho_0 = 4\pi r\rho(r) = \frac{1}{r}\sum_i\sum_j \frac{b_i b_j}{\langle b\rangle^2}\delta(r - r_{ij}), \tag{2}$$

here the sums go over all the atoms in the sample and r_{ij} is the magnitude of the paration of the ith and jth atoms.

What is a PDF?

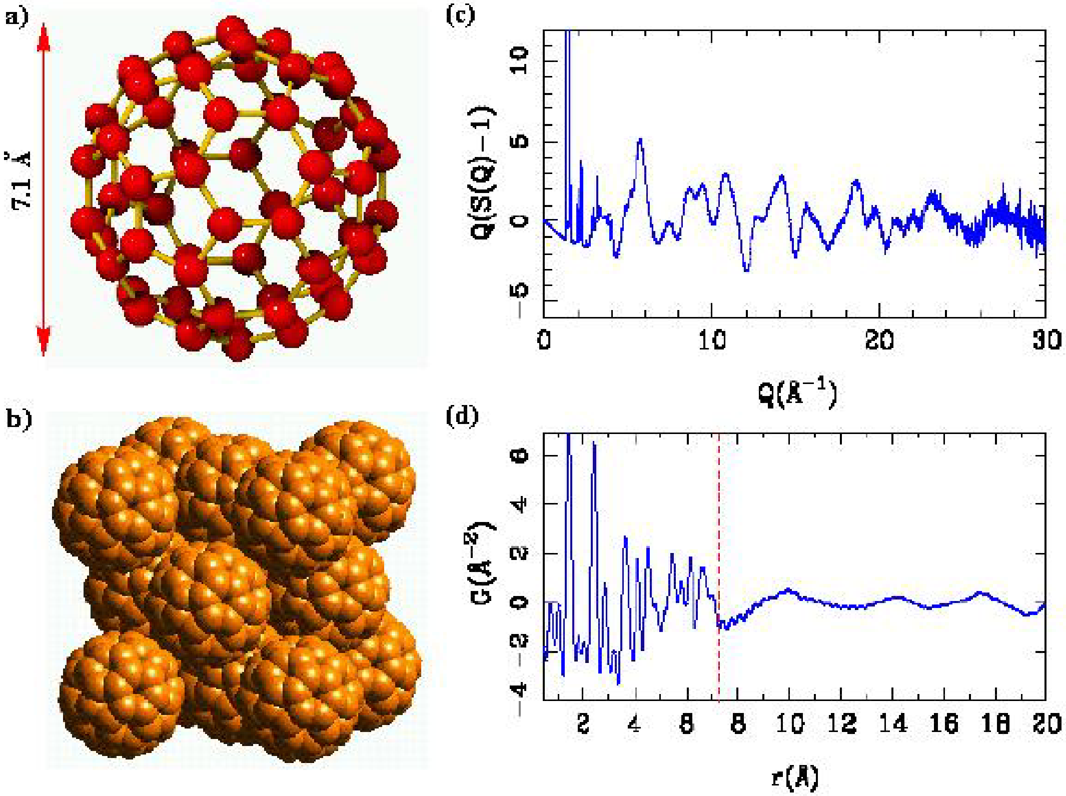


Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.

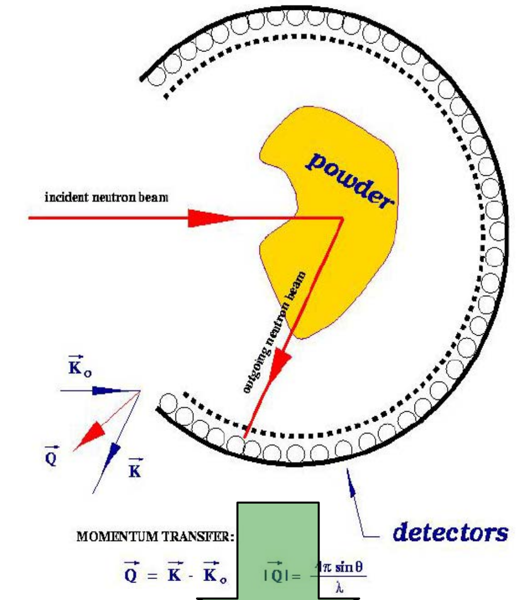


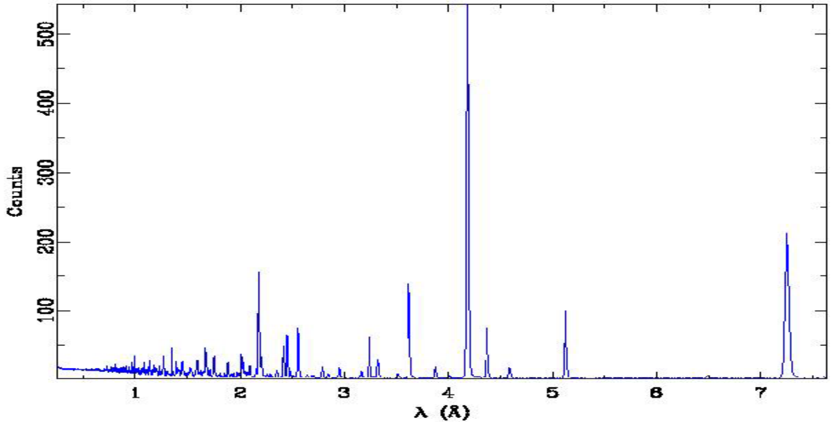
What is the PDF?

- . (a) The red ball is a C_{60} molecule. C_{60} forms a solid by the molecules clustering (b). The scattering and PDF are shown in (c) and (d) respectively.
- Sit on an atom and look at your neighborhood. The nearest neighbor is at 1.4A distance, the second neighbor at 2.2A and so on. There are sharp peaks in G(r) at these positions. This is the structural information in the PDF.
- There are no sharp peaks beyond 7.1A, the diameter of the ball because the balls are spinning with respect to each other. The PDF can see this



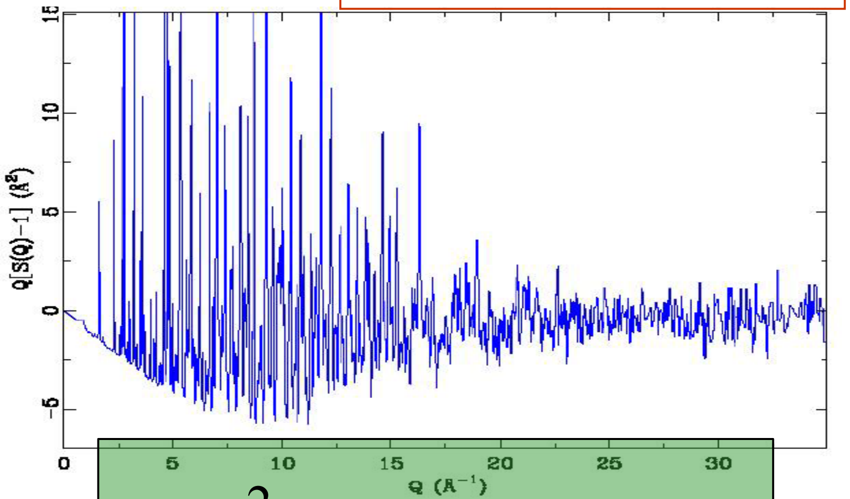
Obtaining the PDF



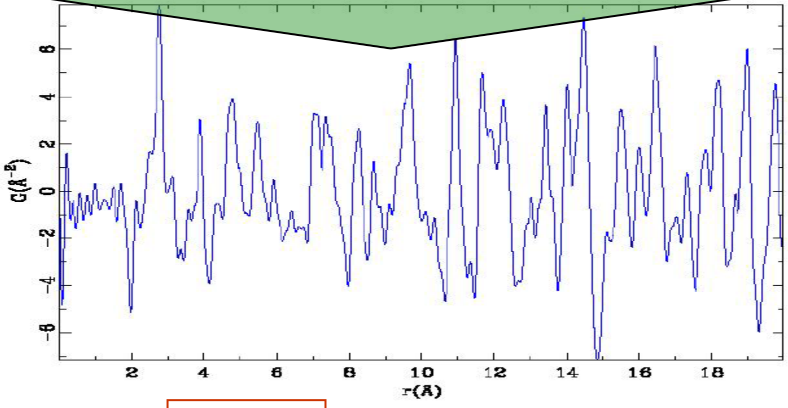


Raw data

Structure function

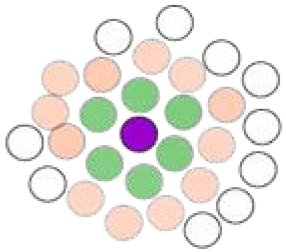


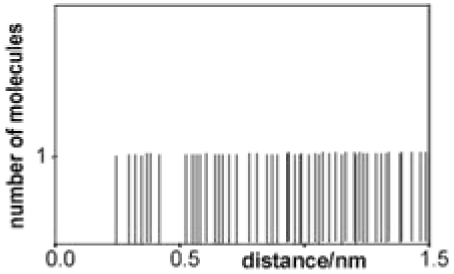
$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr\,dQ$$



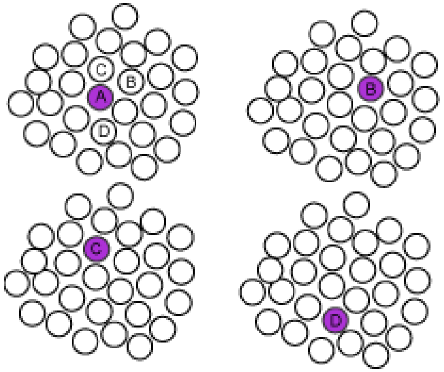
PDF

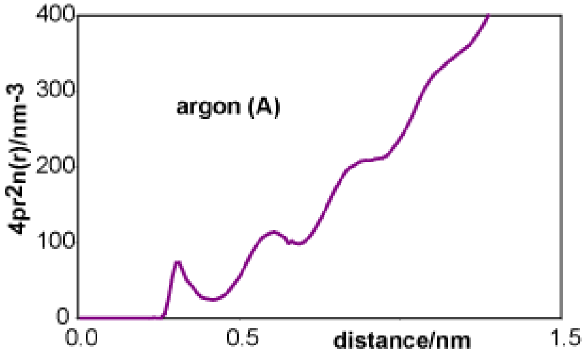
Radial Distribution Function in a Liquid



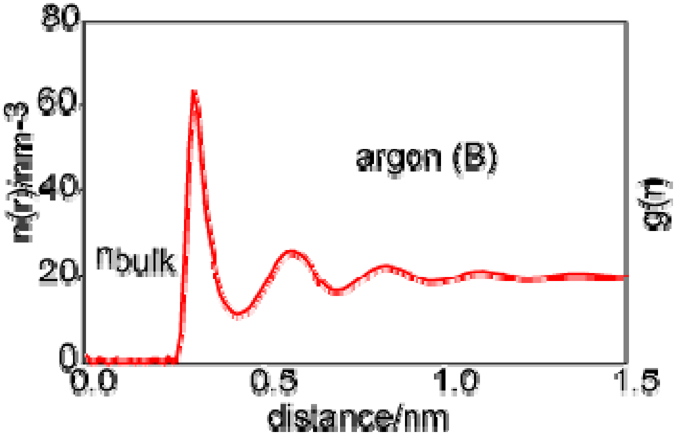


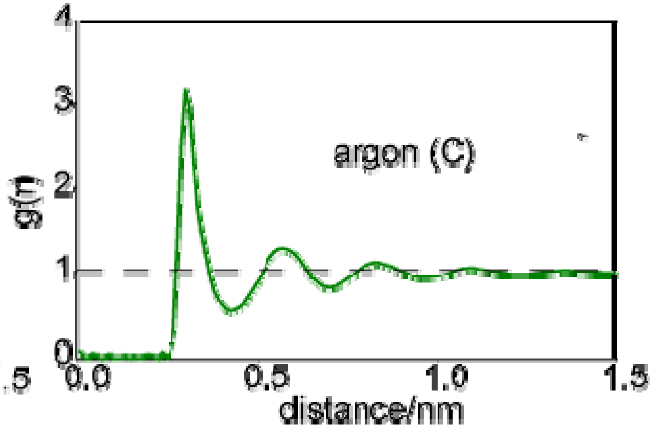
How far is each atom from purple?





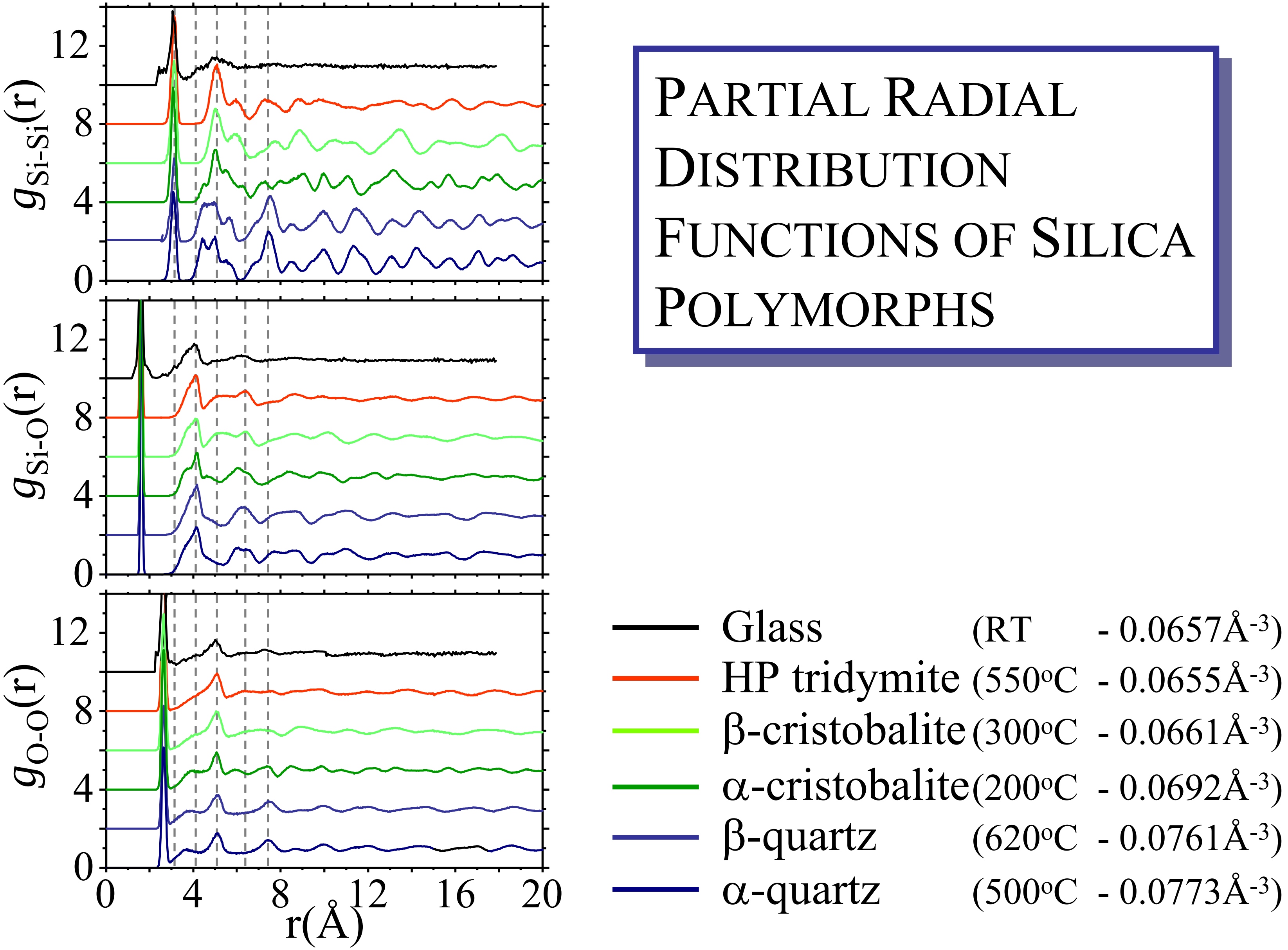
remove factor $4\pi r^2$ from A to get average number density n(r) (B)





Divide B by bulk number density to get g(r) (C).

Partial Radial Distribution Functions of Silica Polymorphs



One approach to modeling of the PDF

Reverse Monte Carlo Method

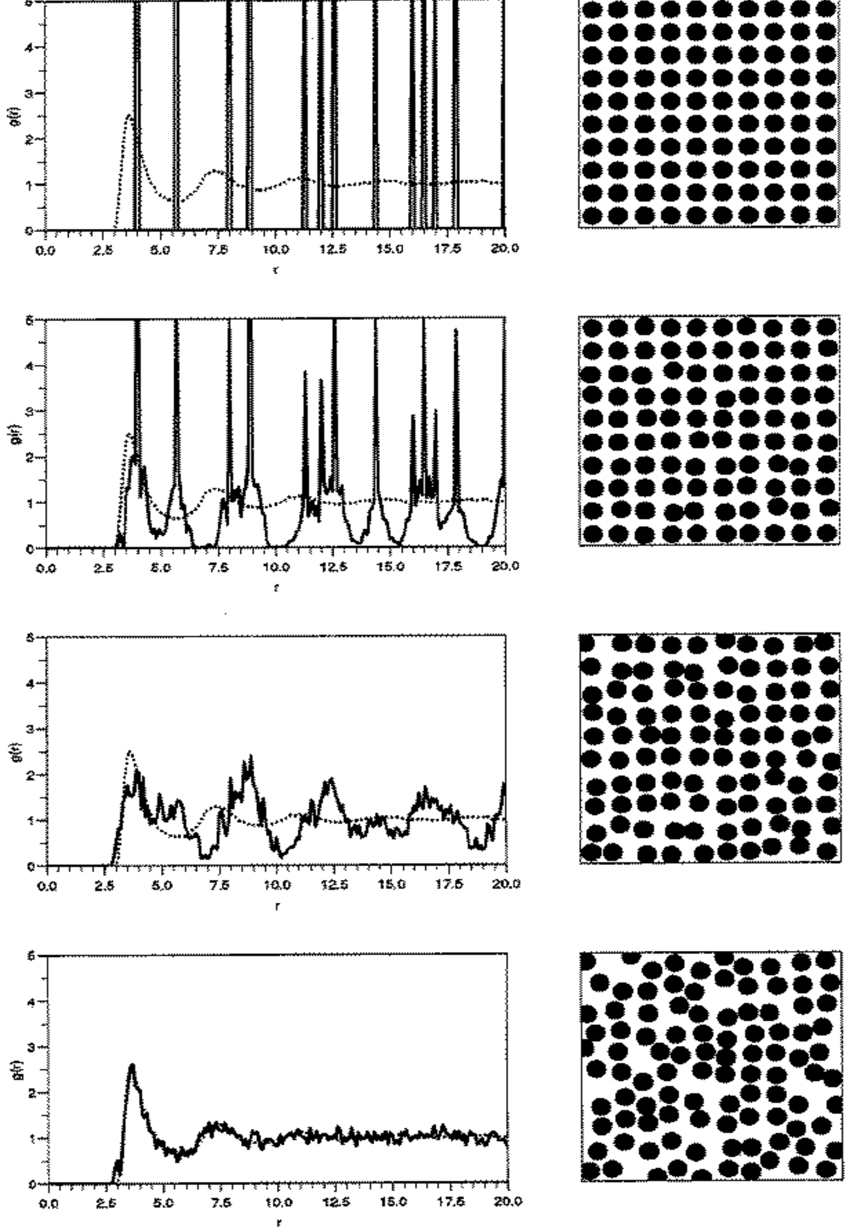
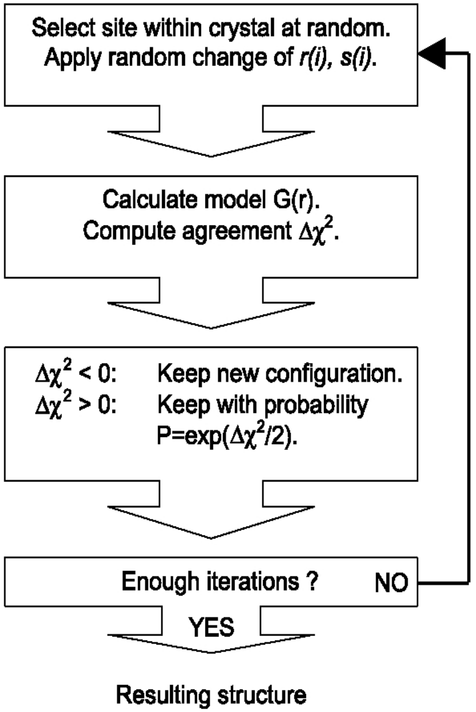


Figure 1. An example of RMC modelling of a simple test system. The configuration (two-dimensional) is shown on the right and on the left $g^C(r)$ (solid curve) is compared to the target data, $g^E(r)$ (broken curve), obtained by Metropolis Monte Carlo simulation using a Lennard-Jones potential. The starting configuration is at the top, the final configuration at the bottom and two intermediate configurations in between. In this example a total of 2500 accepted moves were made. Note that $g^C(r)$ is statistically noisy due to the small model size.



Select site within crystal at random.
Apply random change of *r(i), s(i)*.

Calculate model G(r).
Compute agreement $\Delta\chi^2$.

$\Delta\chi^2 < 0$: Keep new configuration.
$\Delta\chi^2 > 0$: Keep with probability $P=\exp(\Delta\chi^2/2)$.

Enough iterations ? NO

YES

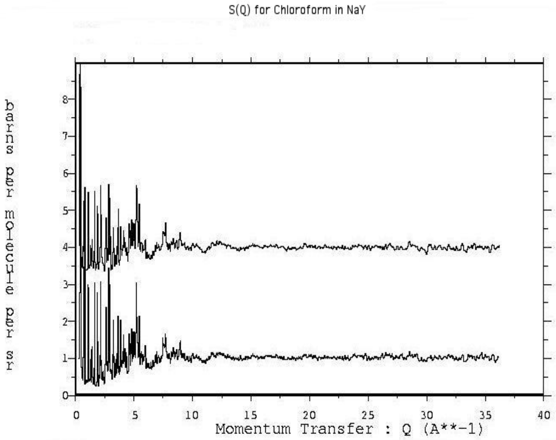
Resulting structure

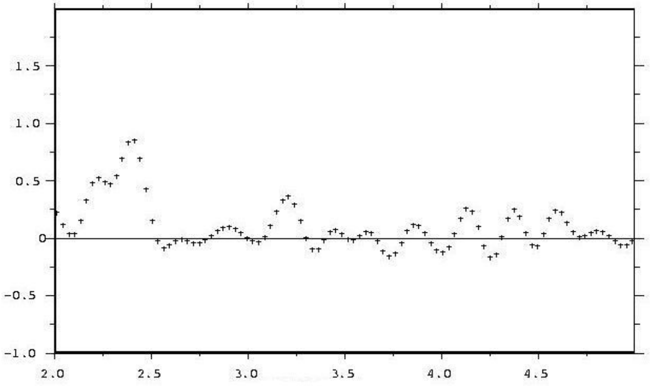
Fig. 2. Schematic flow diagram of RMC simulation.

Chloroform Adsorption in Faujasite

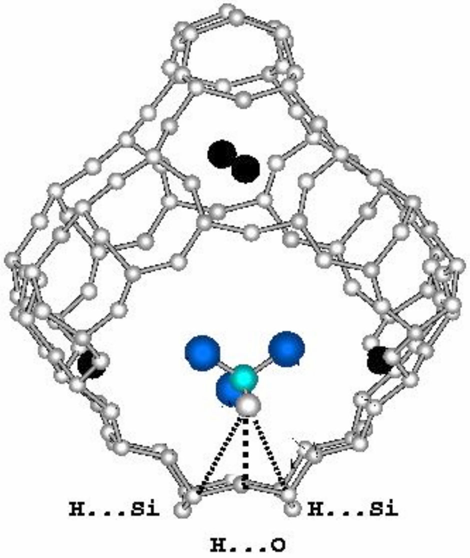
Spectroscopic (INS, Raman) evidence points towards formation of a $Cl_3CH\cdots O$(framework) H-bond when chloroform is adsorbed in Faujasite

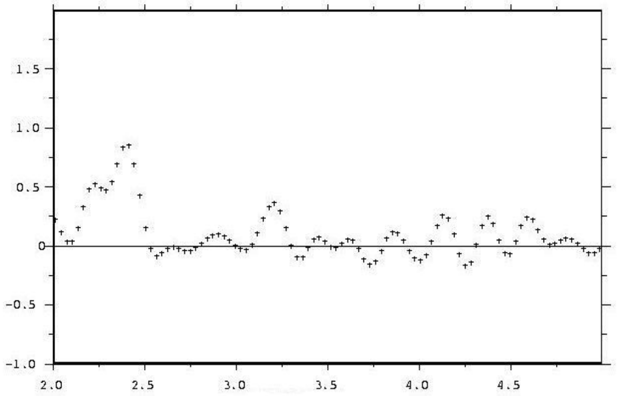
Diffraction data (left: S(Q) of $CHCl_3$ and $CDCl_3$ in Faujasite; right: differential pdf gives H pair correlations) gives direct evidence for the H-bond formation: peak at 2.25 Å (next to intramolecular H-Cl peak).





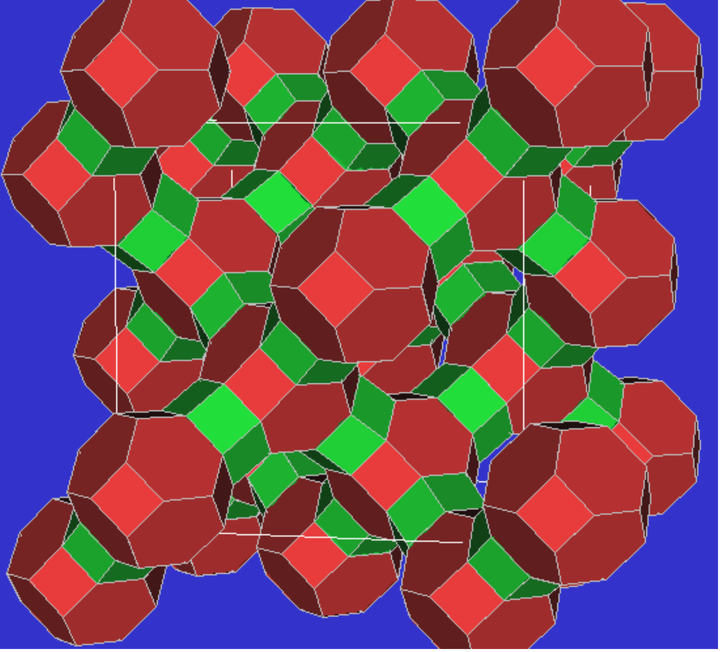
Binding of Chloroform in Faujasite NaY

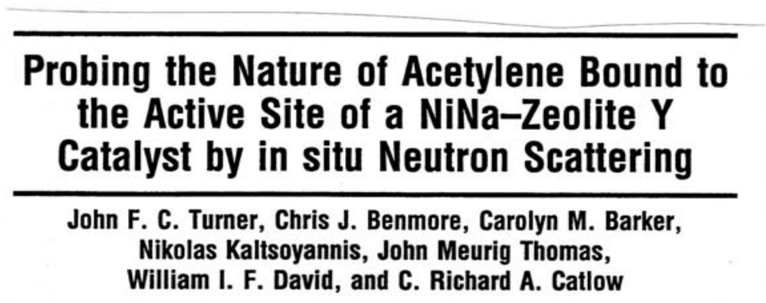




Schematic (left) showing guest-host distances observed in H-pdf(top) : H…O at 2.25 Å and H….Si at 3.5 Å. Peak at 2.4 Å is the intramolecular H…Cl distance.

(J. Eckert, C. Mellot-Draznieks and A. K. Cheetham, J. Am. Chem. Soc. **2002**, *124*, 170)





Probing the Nature of Acetylene Bound to the Active Site of a NiNa–Zeolite Y Catalyst by in situ Neutron Scattering

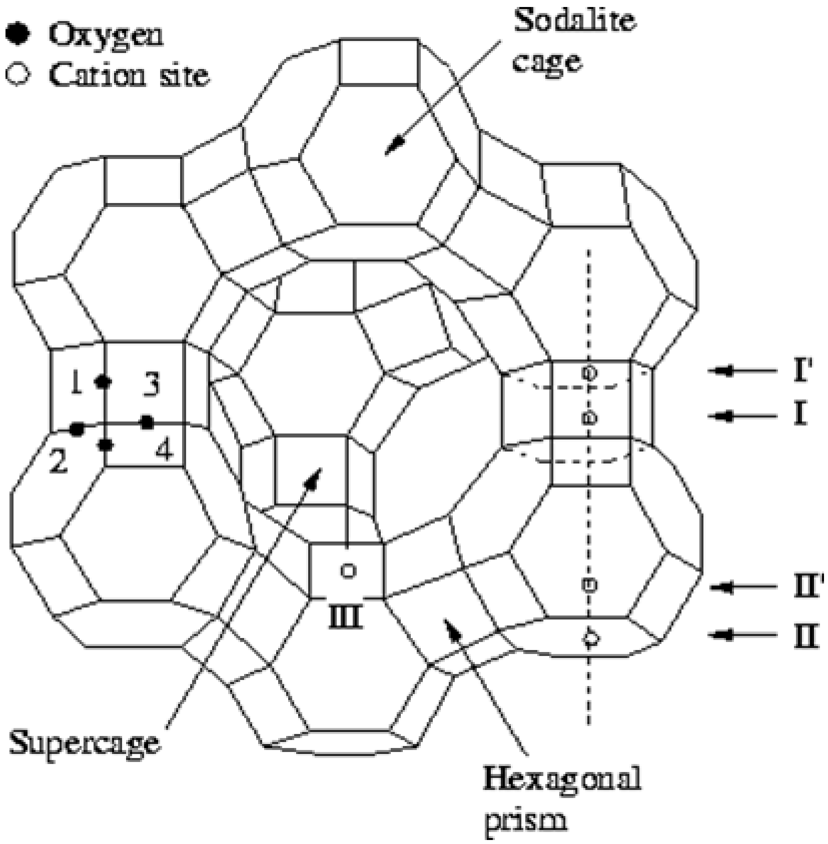
John F. C. Turner, Chris J. Benmore, Carolyn M. Barker,
Nikolas Kaltsoyannis, John Meurig Thomas,
William I. F. David, and C. Richard A. Catlow

NiNa-Y has both Ni and Na cations for charge compensation (of Al in the Framework)

Ni sites are likely to be much more active

Where and how does acetylene bind?

Small molecule can get lost in a large cavity!



Use Neutron Diffraction and PDF analysis

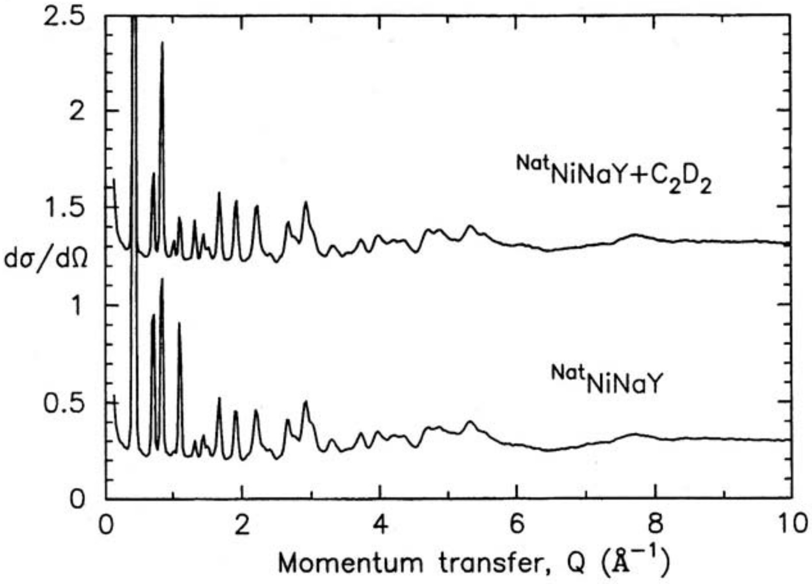
Collect diffraction data on

^{Nat}NiNa-Y

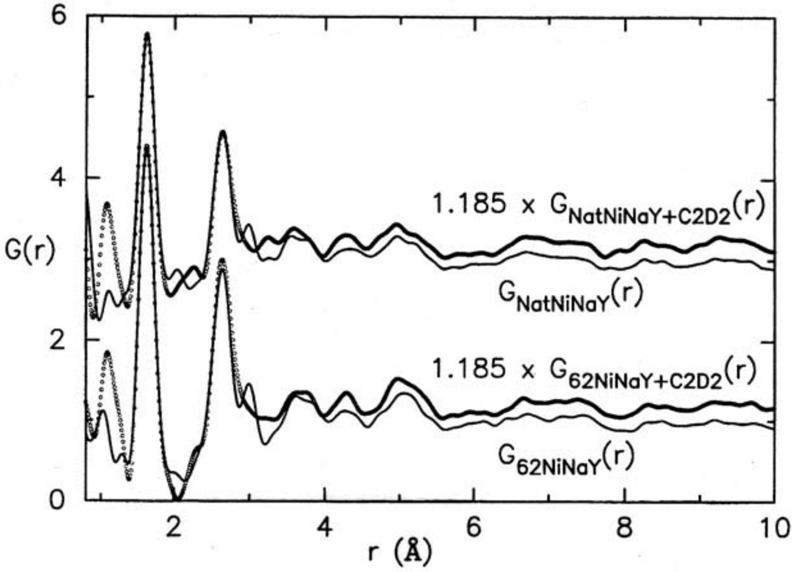
^{Nat}NiNa-Y + C_2D_2

^{62}NiNa-Y

^{62}NiNa-Y + C_2D_2



Take various differences to obtain partial PDF's



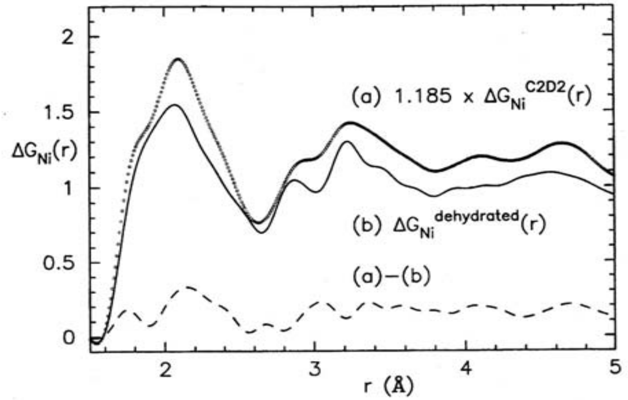


Figure 4. Real space Ni environment in NiNaY, measured with (circles), and without (solid line) the presence of acetylene (the NiNaY + C_2D_2 difference has been scaled by a factor of 1.185, see text).

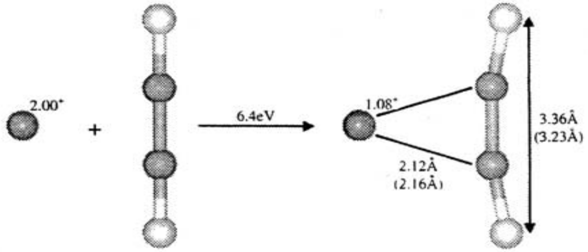
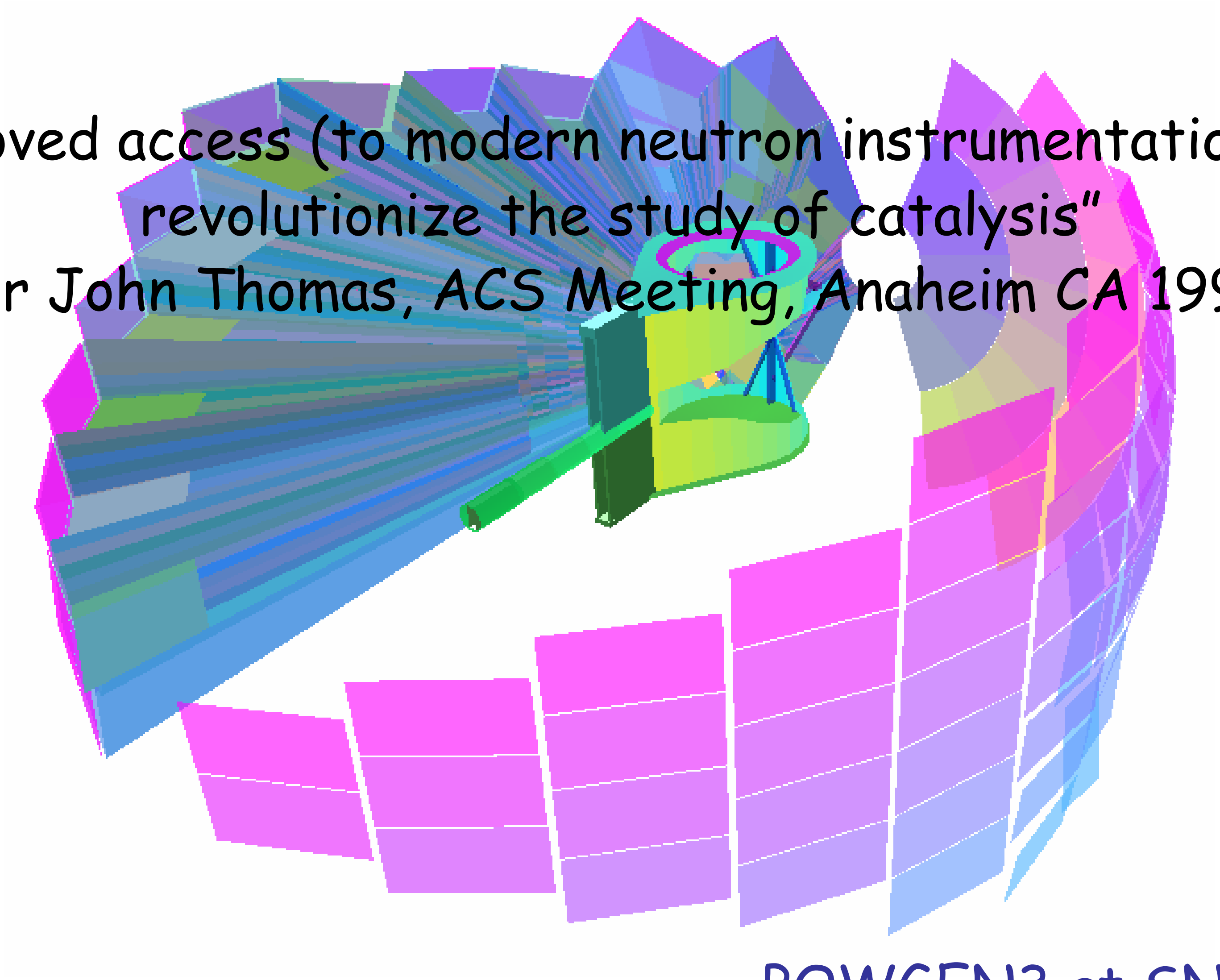


Figure 5. BLYP/DNP optimized geometries, Ni charge, and binding energy for the interaction of one molecule of acetylene with a bare Ni^{II} ion. Distances obtained from neutron scattering data in brackets.

TABLE 1: Bond Lengths (in Å) and Angles (in degrees) of Acetylene Unbound and Bound to Ni^{II} as Calculated by the BLYP Nonlocal Density Functional and *VWN Local Density Functional

	C−C	C−H	H−H	Ni−C	Ni−H	C−C−H
C_2H_2	1.21	1.07	3.36			180.0
	1.21	1.08*	3.35*			180.0*
Ni^{II}−	1.26	1.10	3.44	2.12	2.81	169.0
$\eta^2(C_2H_2)$	1.25	1.11*	3.42	2.05*	2.76*	169.4*



“Improved access (to modern neutron instrumentation) will revolutionize the study of catalysis”
(Sir John Thomas, ACS Meeting, Anaheim CA 1999)

POWGEN3 at SNS

This is all well and good - but what has it to do with the SURFACES of amorphous silica?

This is where simulation uses results verified by comparison with the bulk to model the surface

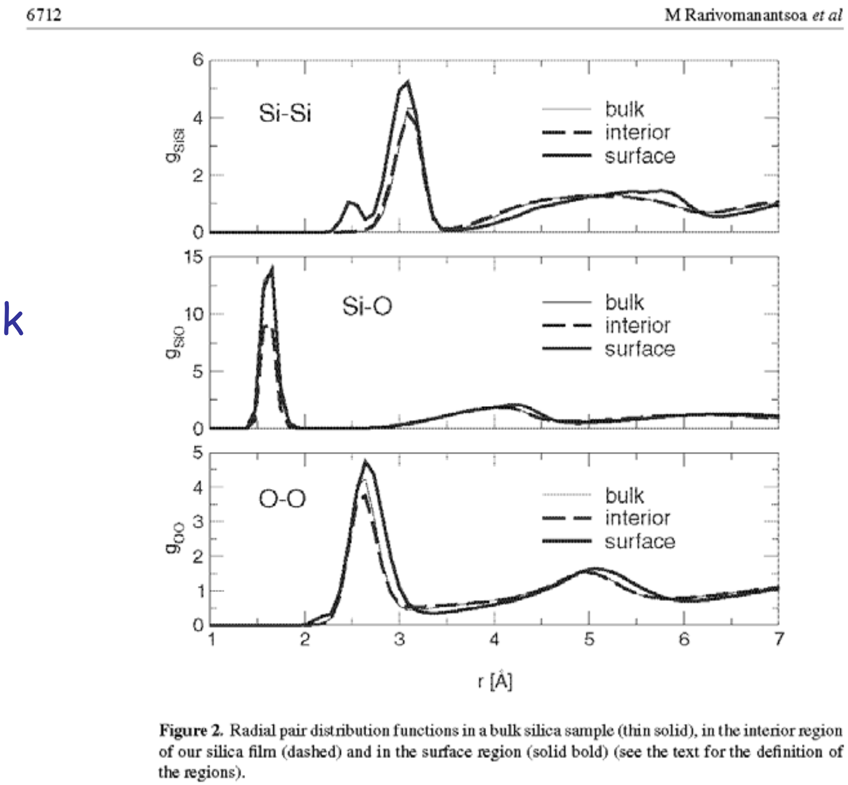


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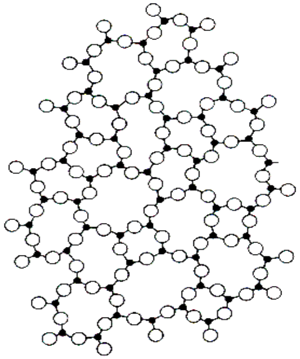
Figure 2. Radial pair distribution functions in a bulk silica sample (thin solid), in the interior region of our silica film (dashed) and in the surface region (solid bold) (see the text for the definition of the regions).

Note the surface peak
at about 2.5□□Å
What could it be?

This is all well and good - but what has it to do with the SURFACES of amorphous silica?

This is where simulation uses results verified by comparison with the bulk to model the surface



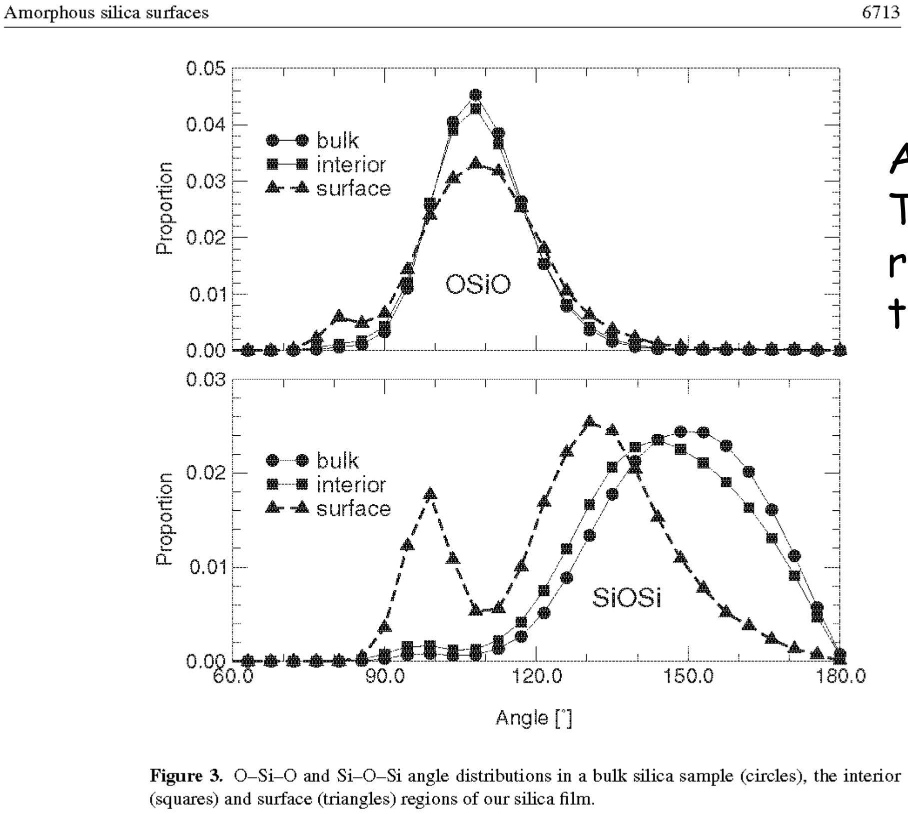


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Figure 3. O–Si–O and Si–O–Si angle distributions in a bulk silica sample (circles), the interior (squares) and surface (triangles) regions of our silica film.

Answer:
Two-membered
rings may be possible on the silica surface.