The Power of Inelastic Neutron Scattering

Vibrational Spectroscopy of hydrogen, applications to catalysis

AJ (Timmy) Ramirez-Cuesta
ISIS Facility
Rutherford Appleton Laboratory
STFC

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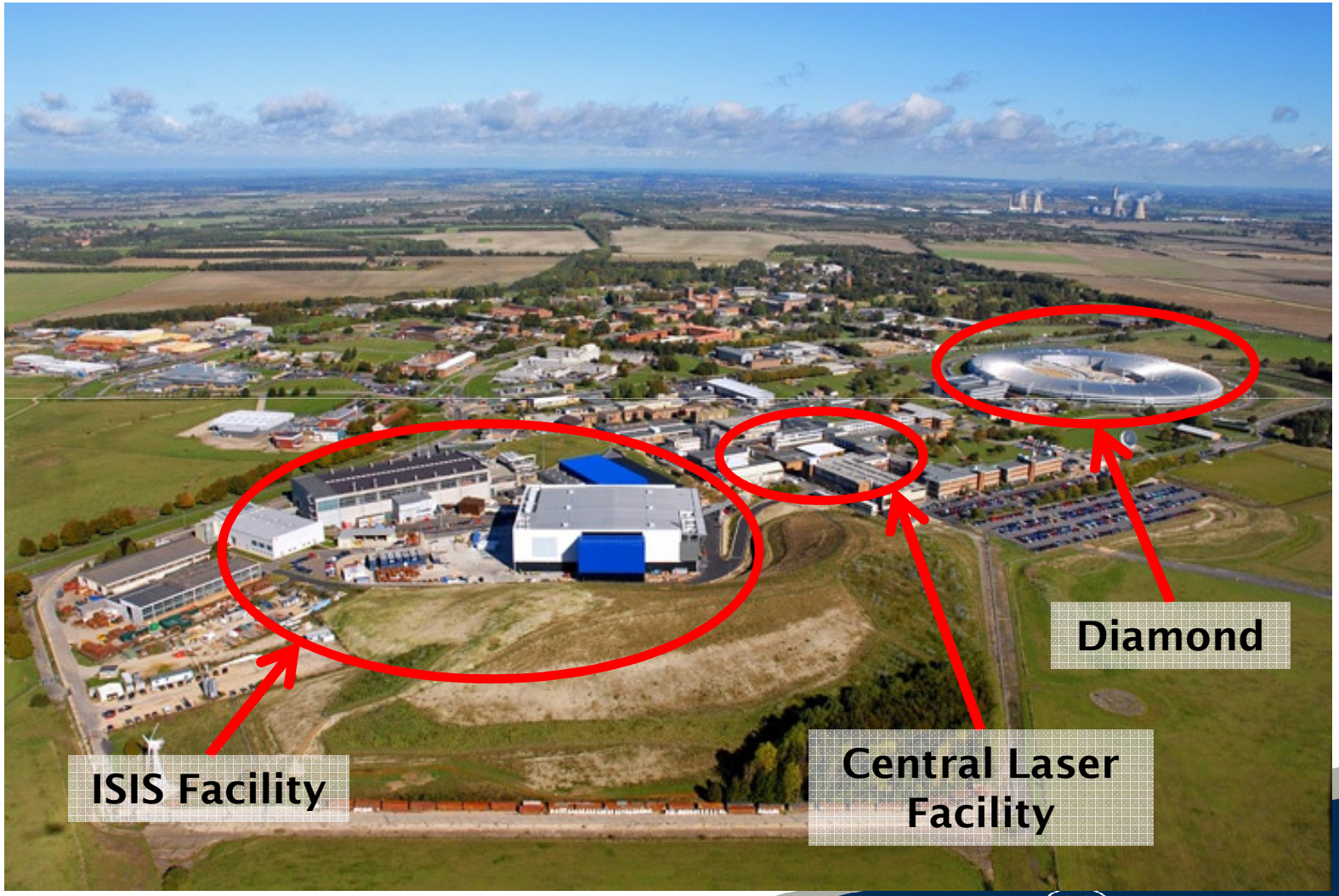
Rutherford Appleton Lab (on a sunny day!)



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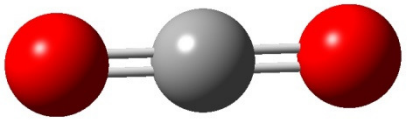
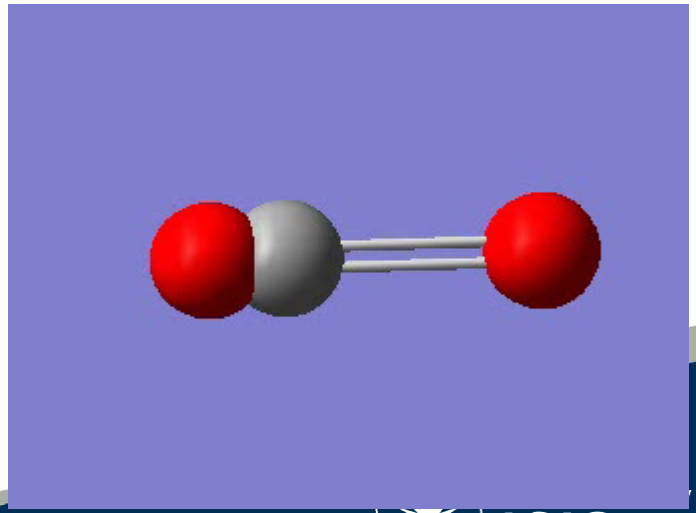
Why Vibrational Spectroscopy?

In chemistry we need the structure and dynamics of mater

- Where atoms are

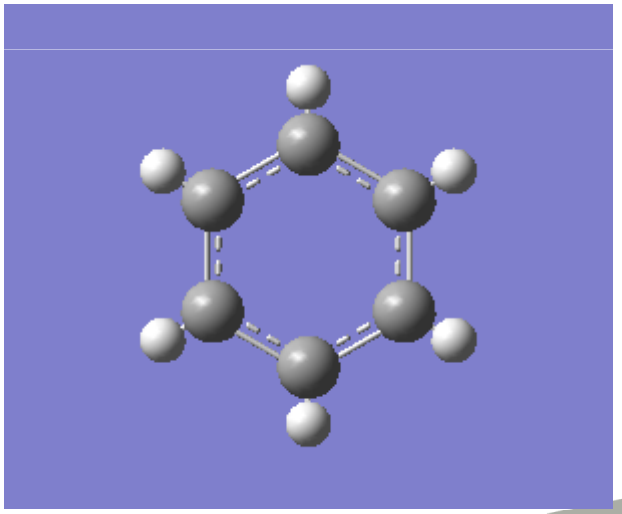


- What do they do



Why Vibrational Spectroscopy?

The way an object vibrates reflects it's structure



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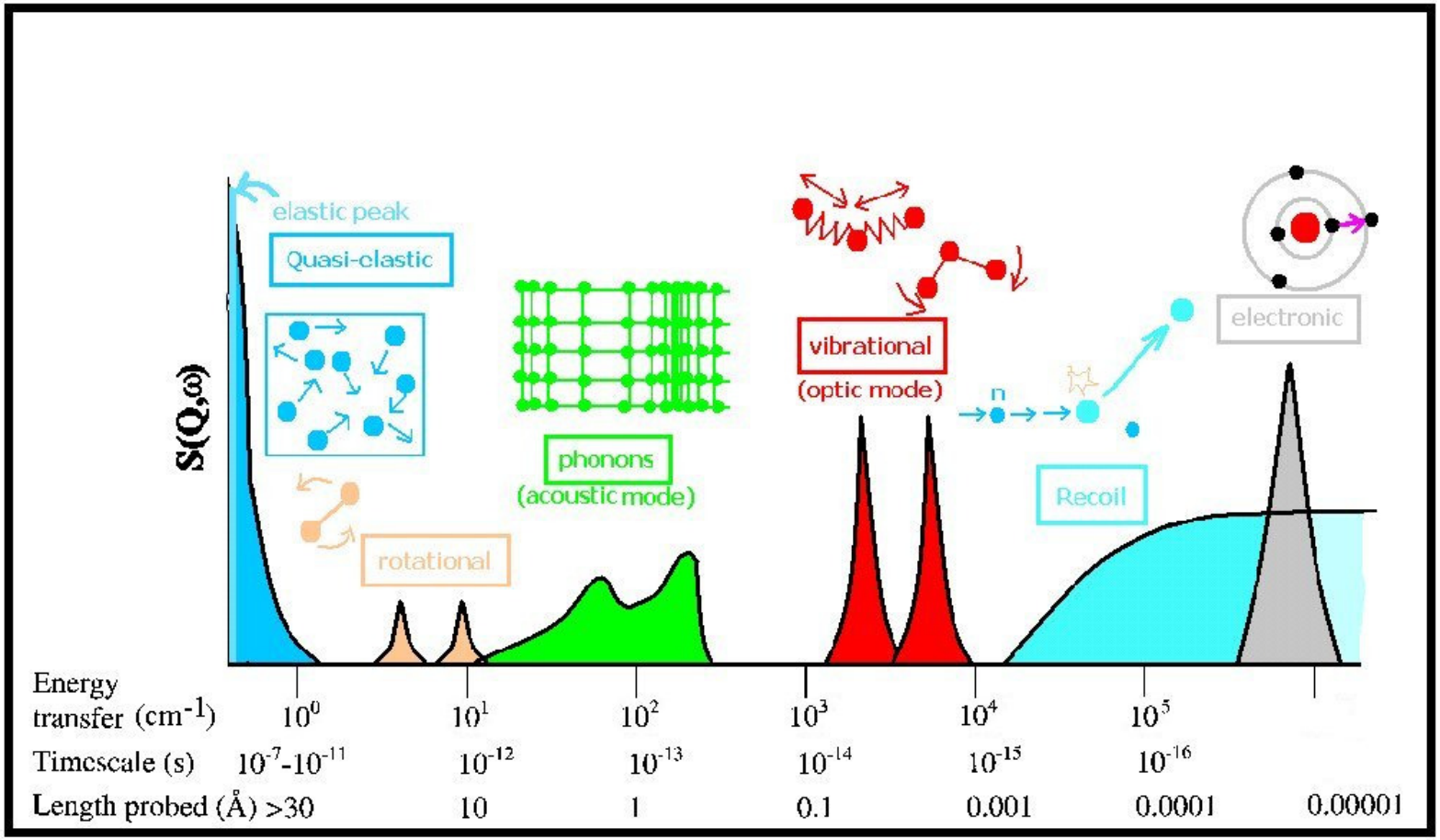
Inelastic neutron scattering



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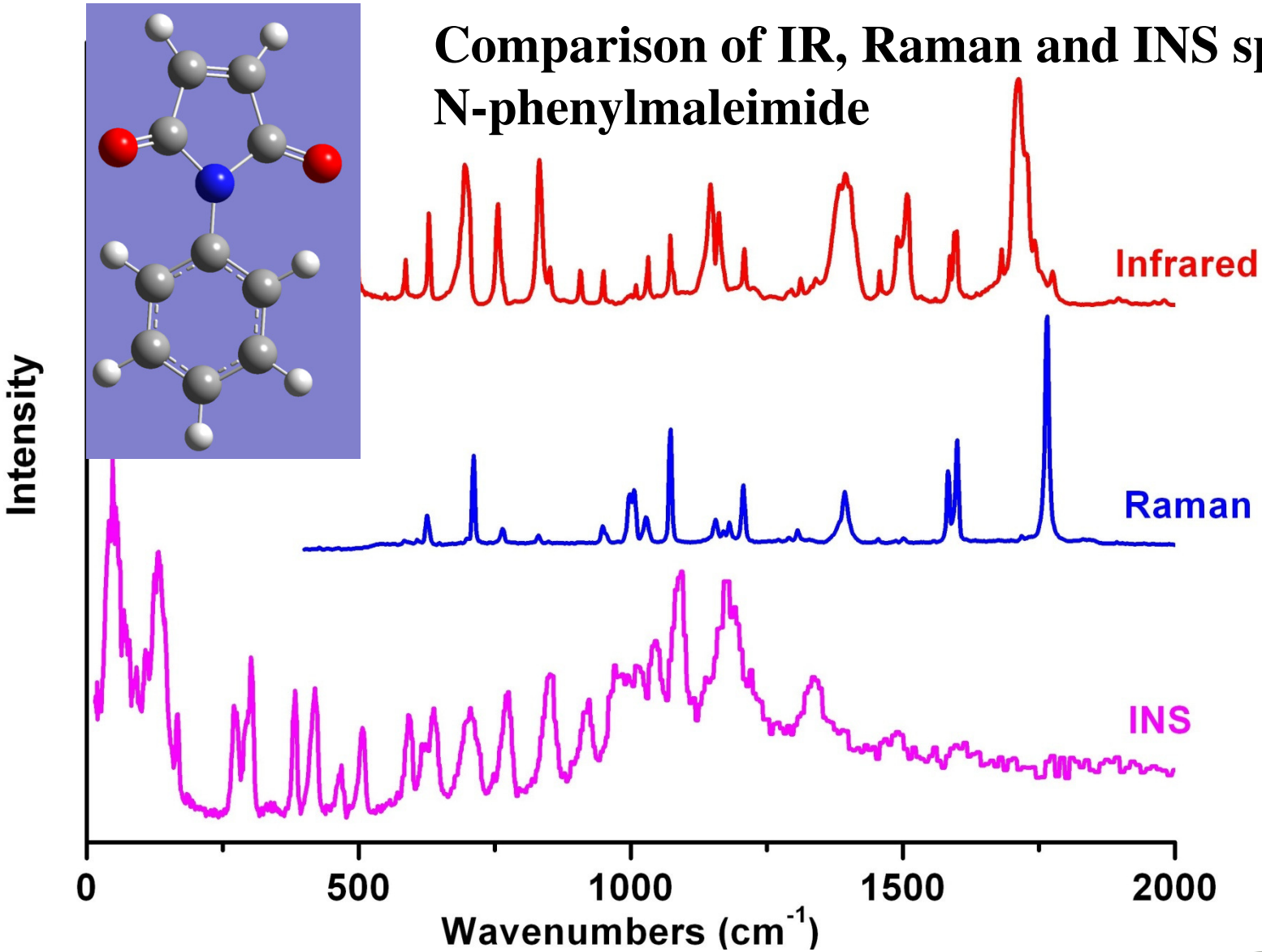
Comparison of IR, Raman and INS spectra of N-phenylmaleimide



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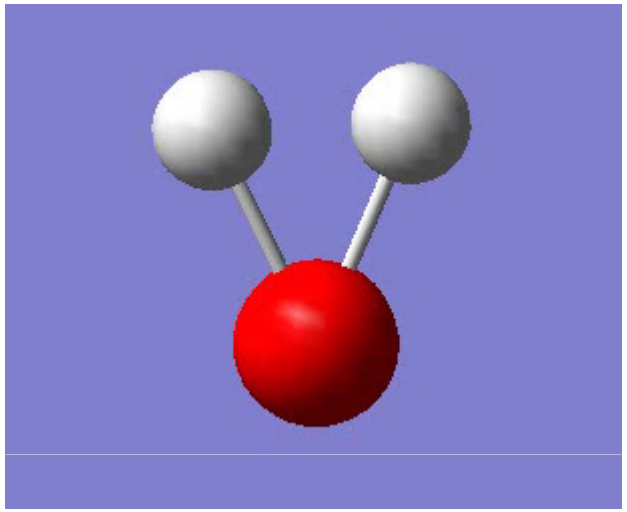
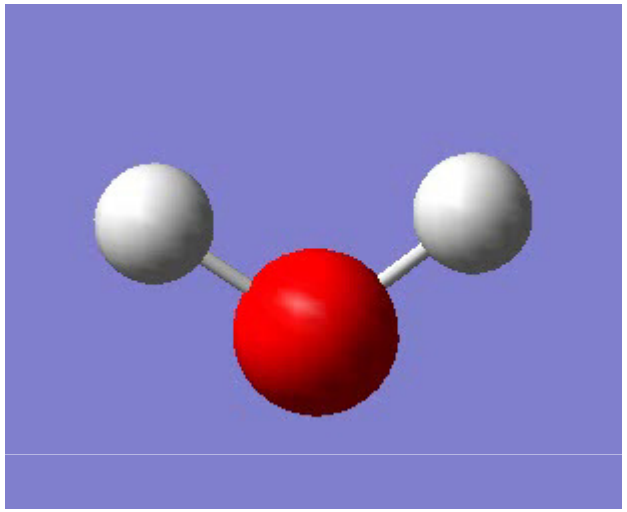
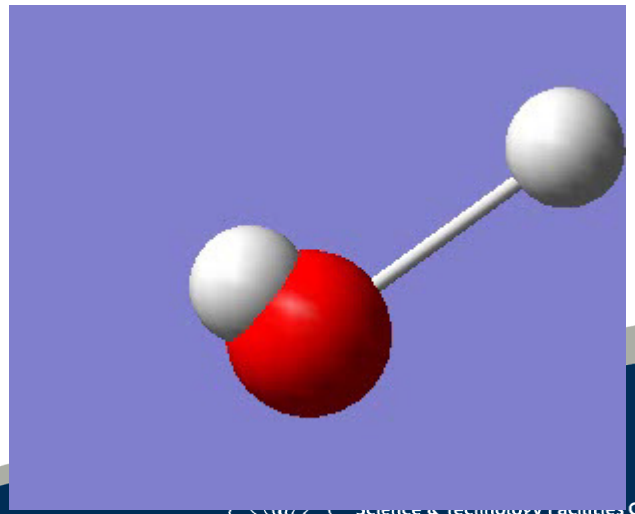
How do atoms move?

- In a molecule containing N atoms there are, in principle, 3N degrees of freedom.
- There are 3 translations and 3 rotations of the whole molecule
- Consequently there are 3N-6 motions that are not translations or rotations. (A linear molecule the number is 3N-5)

How do atoms move?







We call these motions the Normal Modes of vibration.

For example, in water there are:

$$n_{water} = 3 \times N_{atoms} - 6 = 3$$

What are Normal Modes

- In the harmonic approximation, a Normal Mode is a vibrational state in which atoms move in simple harmonic motion around their equilibrium positions.
- Any possible internal motion of the molecule can be described by a superposition of Normal Modes

How do we find the Normal Modes?

- At the energy minimum, and using mass weighted coordinates we can do a Taylor expansion:

$$V^{mol} = V_0^{mol} + \cancel{\sum_{i=1}^{3N_{atoms}} \left(\frac{\partial V^{mol}}{\partial q_i} \right) q_i} + \sum_{i,j=1}^{3N_{atoms}} \left(\frac{\partial^2 V^{mol}}{\partial q_i \partial q_j} \right) q_i q_j + \cdots$$

The term $$F_{ij} = \left(\frac{\partial^2 V^{mol}}{\partial q_i \partial q_j} \right)$$

Is called the force constant matrix

How do we find the Normal Modes? (2)

By diagonalising the force constant matrix we obtain the eigenvectors and the eigenvalues λ .

- The eigenvectors are the normal modes, ${}^{\nu}\mathbf{Q}$
- And the frequencies are $\lambda_{\nu} = \omega_{\nu}^{2}$

Why using the Normal Modes?

The quantum problem, the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Assuming separation of vibrational and rotational parts!

$$-\frac{\hbar^2}{2m}\sum_{\nu=1}^{3N-6}\frac{\partial^2\psi_{vib}}{\partial\,{}^{\nu}\mathbf{Q}^2} + \frac{1}{2}\sum_{\nu=1}^{3N-6}\lambda_{\nu}\,{}^{\nu}\mathbf{Q}^2\psi_{vib} = E^{mol}\psi_{vib}$$

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Why using the Normal Modes?

$$-\frac{\hbar^2}{2m}\sum_{\nu=1}^{3N-6}\frac{\partial^2\psi_{vib}}{\partial\,{}^{\nu}\mathbf{Q}^2}+\frac{1}{2}\sum_{\nu=1}^{3N-6}\lambda_\nu\,{}^{\nu}\mathbf{Q}^2\psi_{vib}=E^{mol}\psi_{vib}$$

This can be separated into 3N-6 equations, one for each normal mode. The energy and wavefunction can be written as:

$$E_{vib}^{mol}=\sum_{\nu}E_\nu \qquad \psi_{vib}=\prod_{\nu}\psi\left({}^{\nu}\mathbf{Q}\right)=\psi\left({}^{1}\mathbf{Q}\right)\psi\left({}^{2}\mathbf{Q}\right)\cdots\psi\left({}^{3N-6}\mathbf{Q}\right)$$

If each wavefunction and energy satisfy:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial\,{}^{\nu}\mathbf{Q}^2}+\frac{1}{2}\lambda_\nu\,{}^{\nu}\mathbf{Q}^2\psi=E^{\nu}\psi_{vib}$$

Why using the Normal Modes?(2)

The energy levels of the harmonic oscillator are

$$E_\nu = \left(n_\nu + \frac{1}{2} \right) \hbar \omega_\nu \quad n_\nu = 0,1,\ldots$$

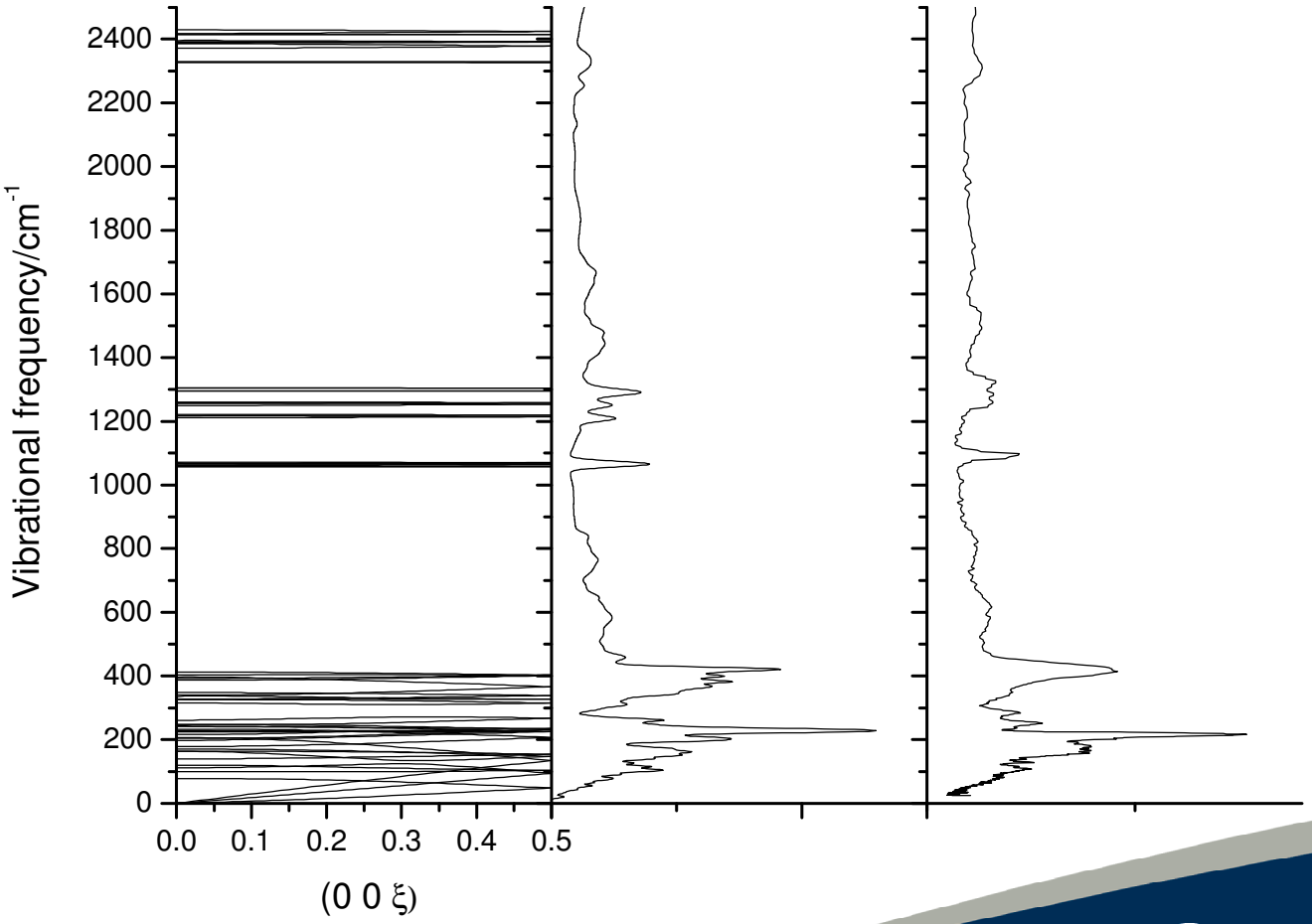
With n_ν the quantum vibrational number and ω_ν the classical frequency.

$$E_{vib}^{mol} = \sum_{\nu=1}^{3N-6} E_\nu = \sum_{\nu=1}^{3N-6} \left(n_\nu + \frac{1}{2} \right) \hbar \omega_\nu$$

The Vibrational Problem in the Solid State

- In the solid state, the periodicity of the lattice create phonon dispersion effects.
- The normal modes are now different on each point of the first Brillouin zone
- The total number of vibrations is 3N, of which, 3 are acoustic modes and 3N-3 are called optical modes.
- DFPT allows the calculation of the normal modes for an arbitrary point in the Brillouin zone by interpolation.

Dispersion, sampling



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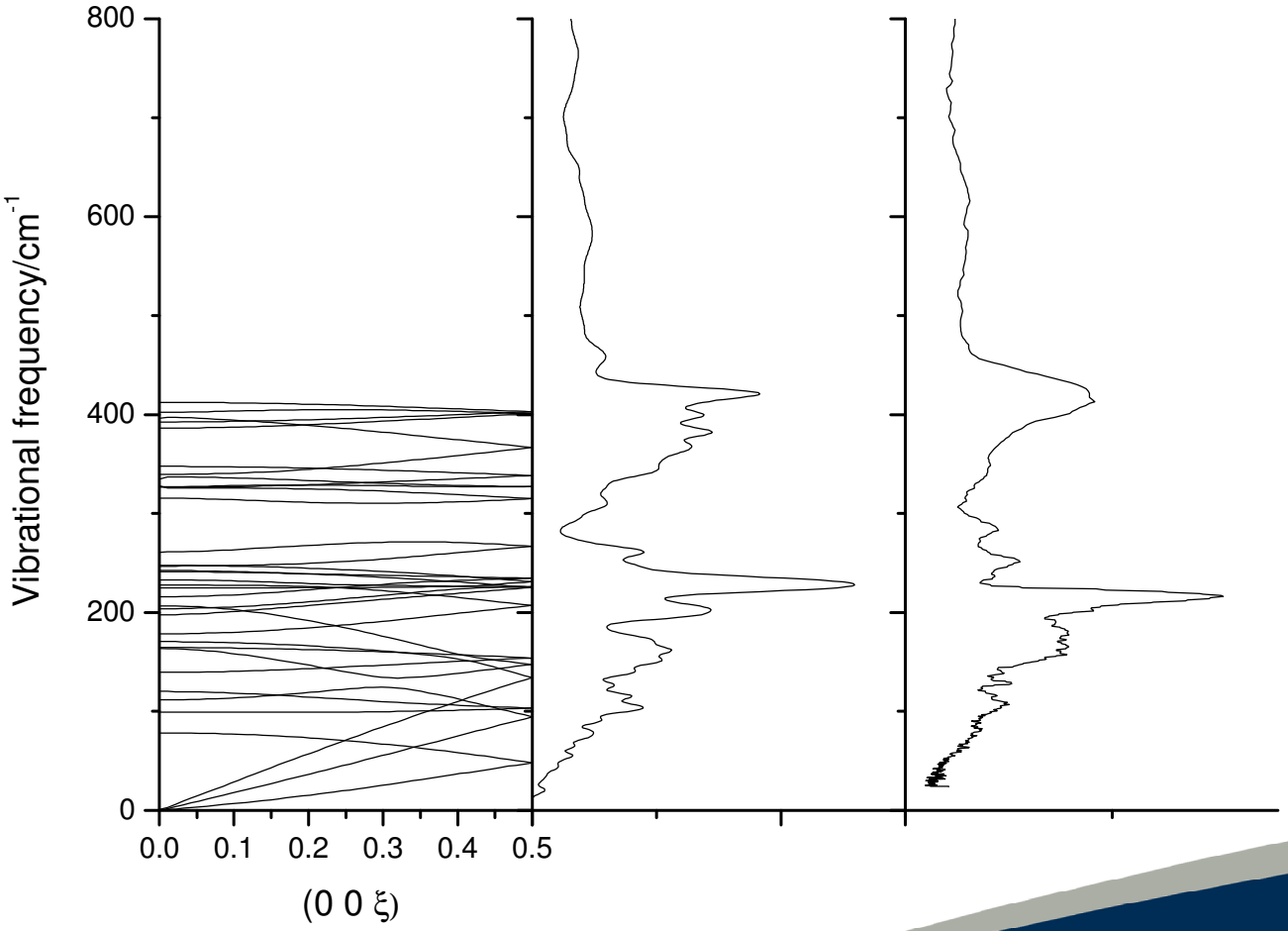
Dispersion, sampling



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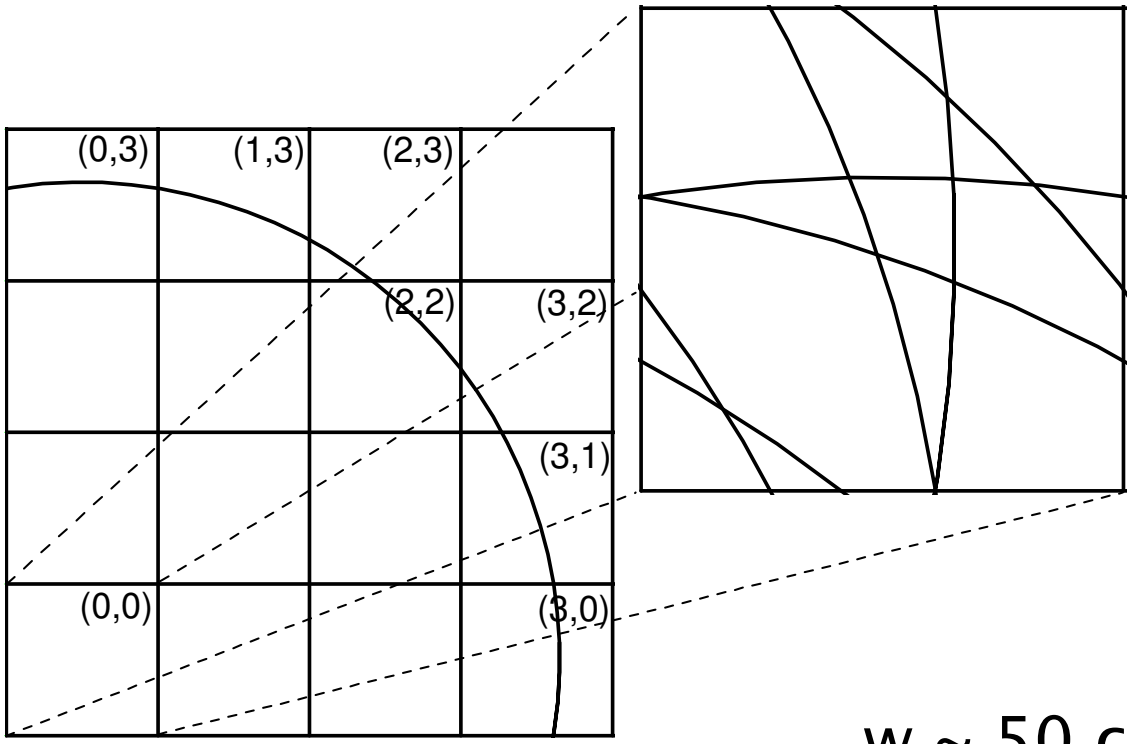
Powder Average



w ~ 50 cm^{-1}

Uniform sampling of the Brillouin zone

Lattice dynamics

- Quasihamonic lattice dynamics is the most efficient approach to carry out atomistic calculations at low temperature (approx half melting point temperature)
- The quantity to minimise is the Helmholtz Free Energy (not always possible):

$$F_H(\mathbf{r},T) = \Phi(\mathbf{r}) + F_{vib}(\mathbf{r},T)$$

$$F_{vib}(\mathbf{r},T) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \left\{ \frac{1}{2}\hbar\omega_{\mathbf{k}} + k_B T \left[\ln\left(1 - e^{-\frac{\hbar\omega_{\mathbf{k}}}{k_B T}} \right) \right] \right\}$$

Chemical Physics **2005**, *317*, 119-129

How do we probe the vibrations?

- We need a probe to excite one of the vibrational energy levels.
- We can use photons and neutrons
  - Using photons we have IR and Raman spectroscopy
  - Using neutrons we have Inelastic Neutron Scattering INS

Inelastic Neutron Scattering

- Transitions are proportional to the amplitude of motion and the cross section of the nuclei.
- Interaction between probe and nucleus
- Simultaneous transfer of energy and momentum.
- No selection rules.

$$S^{\bullet}(\mathbf{Q},\omega_{\nu})_l^n = y\,\sigma_l \frac{\left[\left(\mathbf{Q}.\,{}^{\nu}\mathbf{u}_l(\mathbf{Q})\right)^2\right]^n}{n!}\exp\left(-\frac{1}{3}\left(\mathbf{Q}.\sum_{\nu}{}^{\nu}\mathbf{u}_l(\mathbf{Q})\right)^2\right)$$

Mitchell, P. C. H.; Parker, S. F.; Ramirez-Cuesta, A. J.; Tomkinson, J. *Vibrational Spectroscopy with Neutrons: with applications in Chemistry, Materials Science and Catalysis*; World Scientific: **London**, 2005

Why low temperature?
Amplitude of vibration

$$S^{\bullet}(\mathbf{Q},\omega_\nu)_l^n = y\,\sigma_l \frac{\left[\left(\mathbf{Q}.\,{}^{\nu}\mathbf{u}_l(\mathbf{Q})\right)^2\right]^n}{n!}\exp\left(-\frac{1}{3}\left(\mathbf{Q}.\sum_{\nu}{}^{\nu}\mathbf{u}_l(\mathbf{Q})\right)^2\right)$$

For atom i in mode ν

$${}^{\nu}\mathbf{u}_i^2 \propto \frac{1}{{}^{\nu}\mu_i\omega_\nu}\coth\left(\frac{\alpha\cdot\omega_\nu}{T}\right)$$

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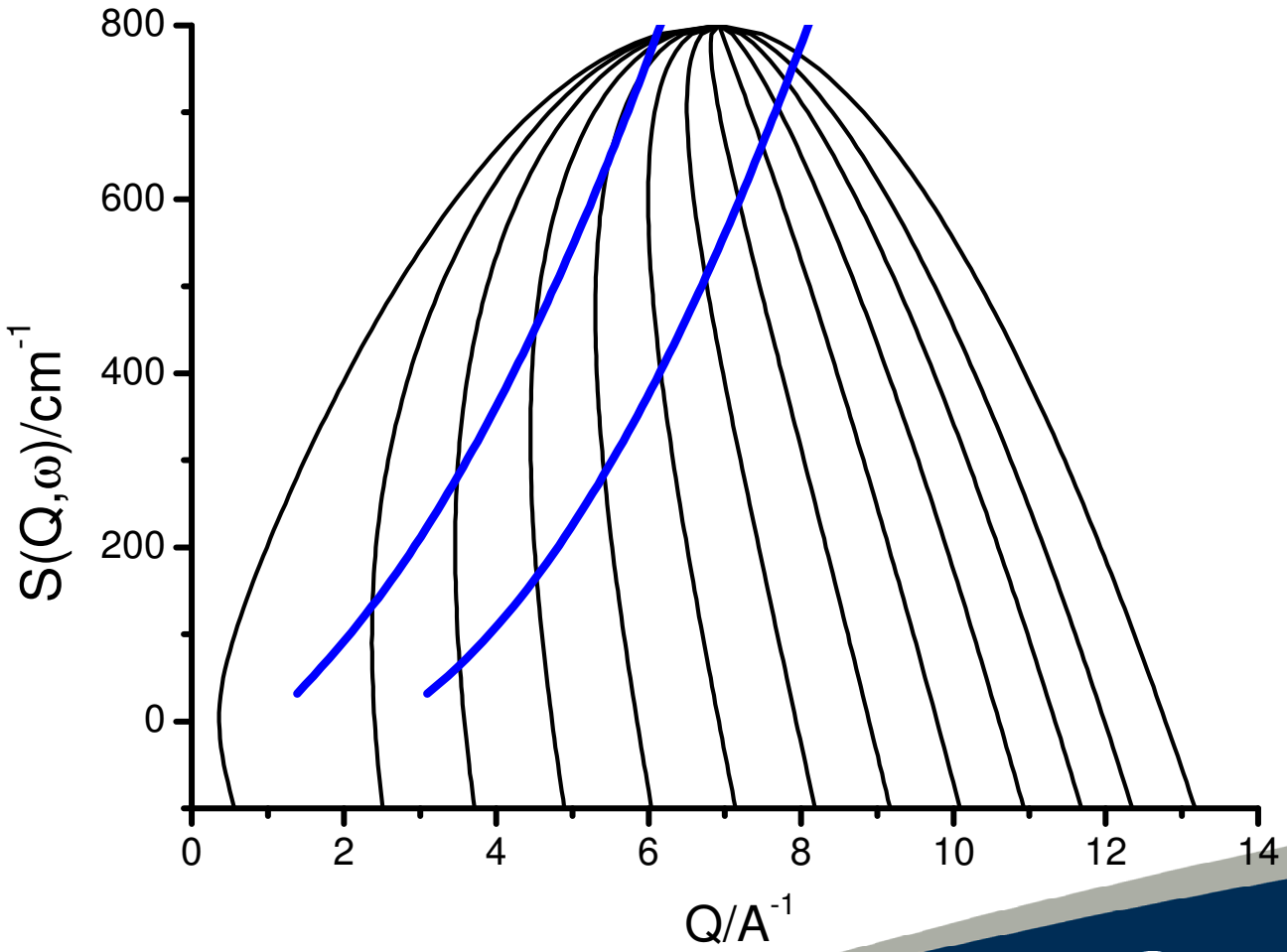
The TOSCA/VISION trajectory in S(Q,ω) Map



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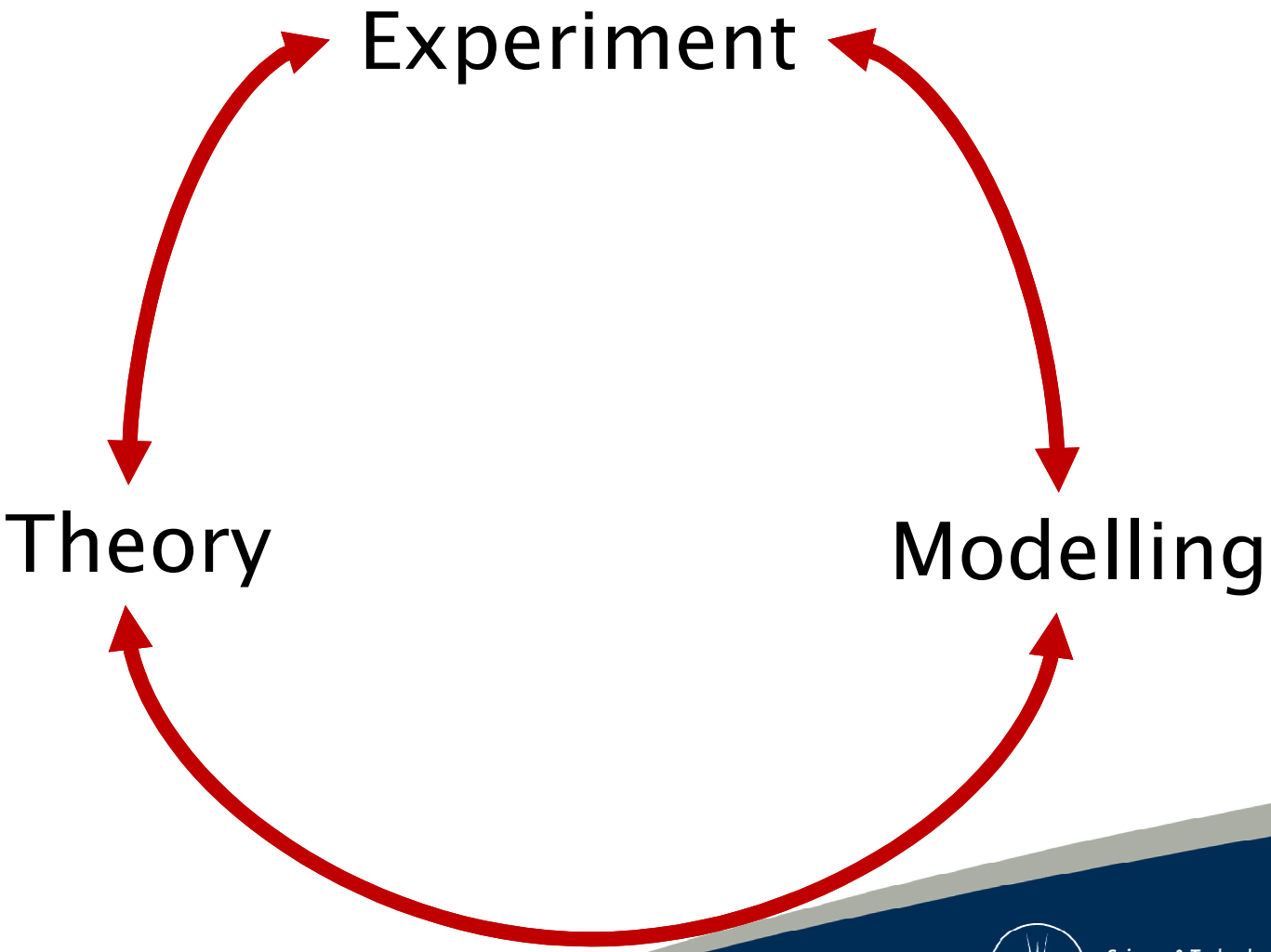
Why low temperature?

- In an indirect geometry instrument (VISION), fixed trajectories, most of the time need low temperature

- In a chopper machine (SEQUOIA,ARCS) you can change the incident energy and that determines your lower Q at given energy. You trade having to stitch spectra of different energy resolutions

Playing the game



DFT calculations

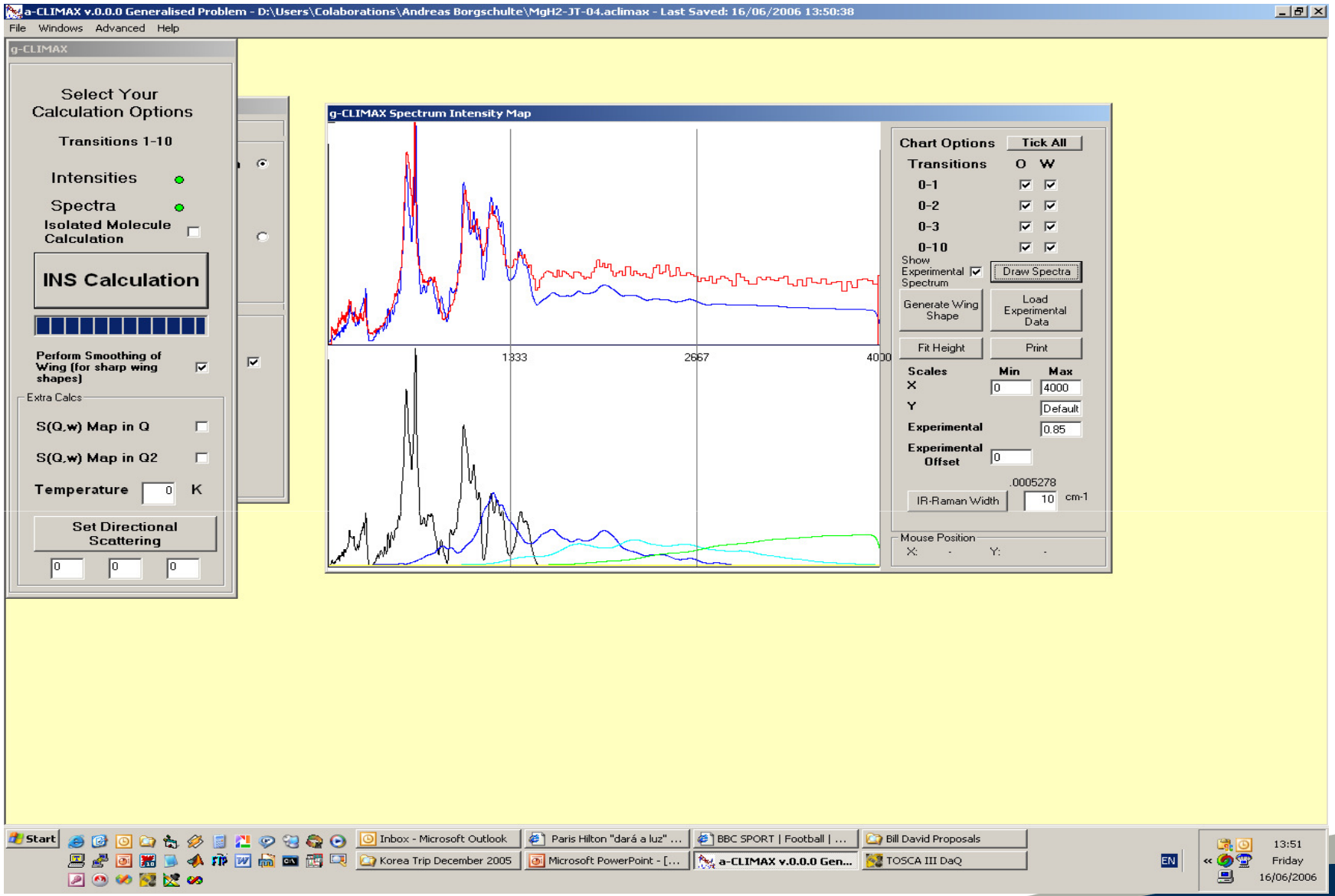
- For the calculations shown in this talk I have used CASTEP from Accelrys
- Interpolation algorithms of the dynamical matrix allow the sampling of the Brillouin zone with different grid sizes.
- In principle any calculation that gives the eigenvactors and frequencies can be used to determine the INS spectrum

Calculation of INS spectra

a-CLIMAX

- It uses the isolated molecule approach for the study of molecular solids.
- For extended solid calculations, with a fine sampling of the Brillouin zone the approximation is not longer necessary since there is no distinction between external and internal modes.

Computer Physics Communications **2004**, *157*, 226-238


a-CLIMAX v.0.0.0 Generalised Problem - D:\Users\Colaborations\Andreas Borgschulte\MgH2-JT-04.aclimax - Last Saved: 16/06/2006 13:50:38
File Windows Advanced Help
g-CLIMAX
Select Your Calculation Options
Transitions 1-10
Intensities
Spectra
Isolated Molecule Calculation
INS Calculation
Perform Smoothing of Wing (for sharp wing shapes)
Extra Calcs
S(Q,w) Map in Q
S(Q,w) Map in Q2
Temperature 0 K
Set Directional Scattering
g-CLIMAX Spectrum Intensity Map
1333
2667
4000
Chart Options
Tick All
Transitions O W
0-1
0-2
0-3
0-10
Show Experimental Spectrum
Draw Spectra
Generate Wing Shape
Load Experimental Data
Fit Height
Print
Scales Min Max
X 0 4000
Y Default
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Korea Trip December 2005
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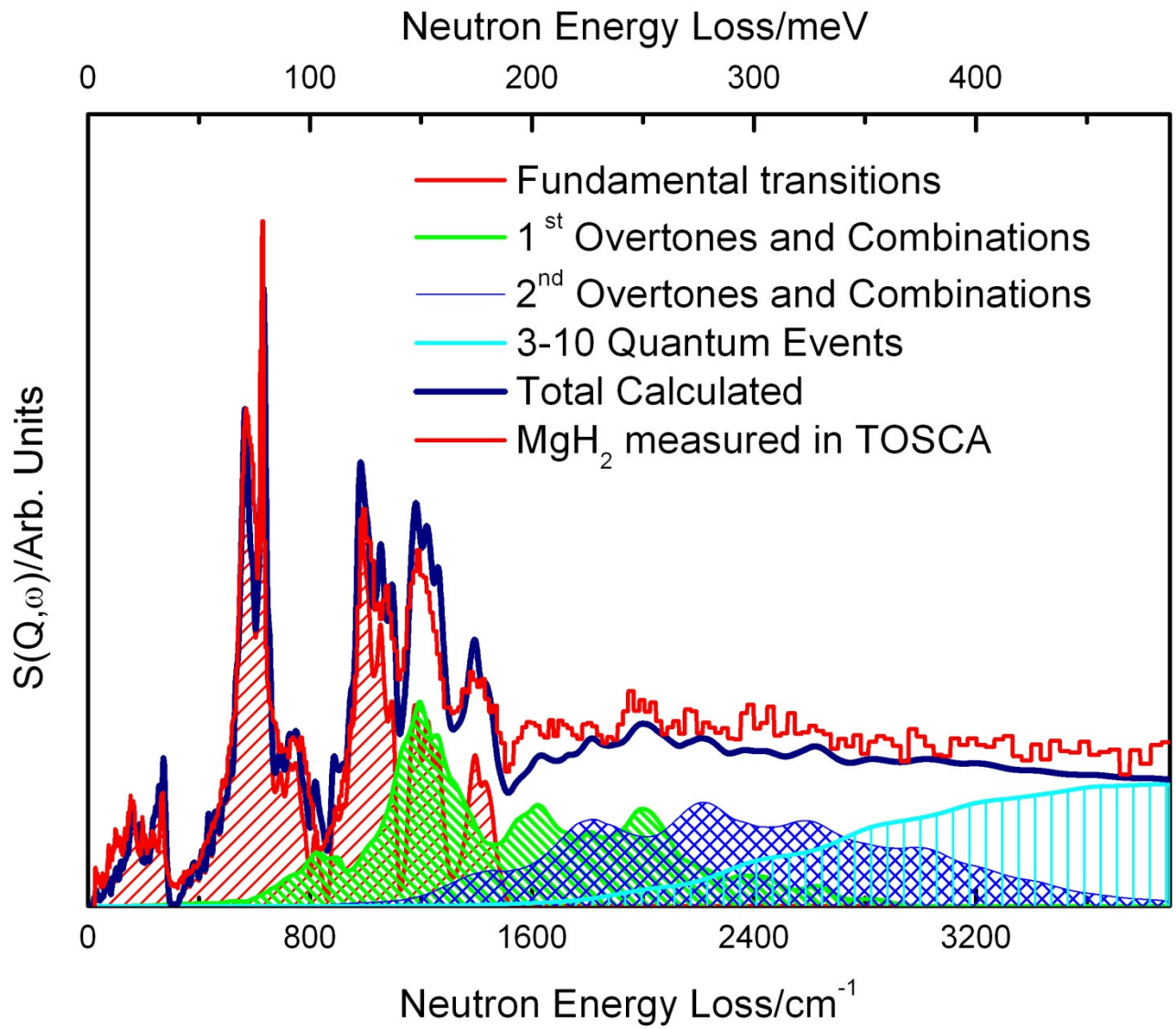
Friday
16/06/2006

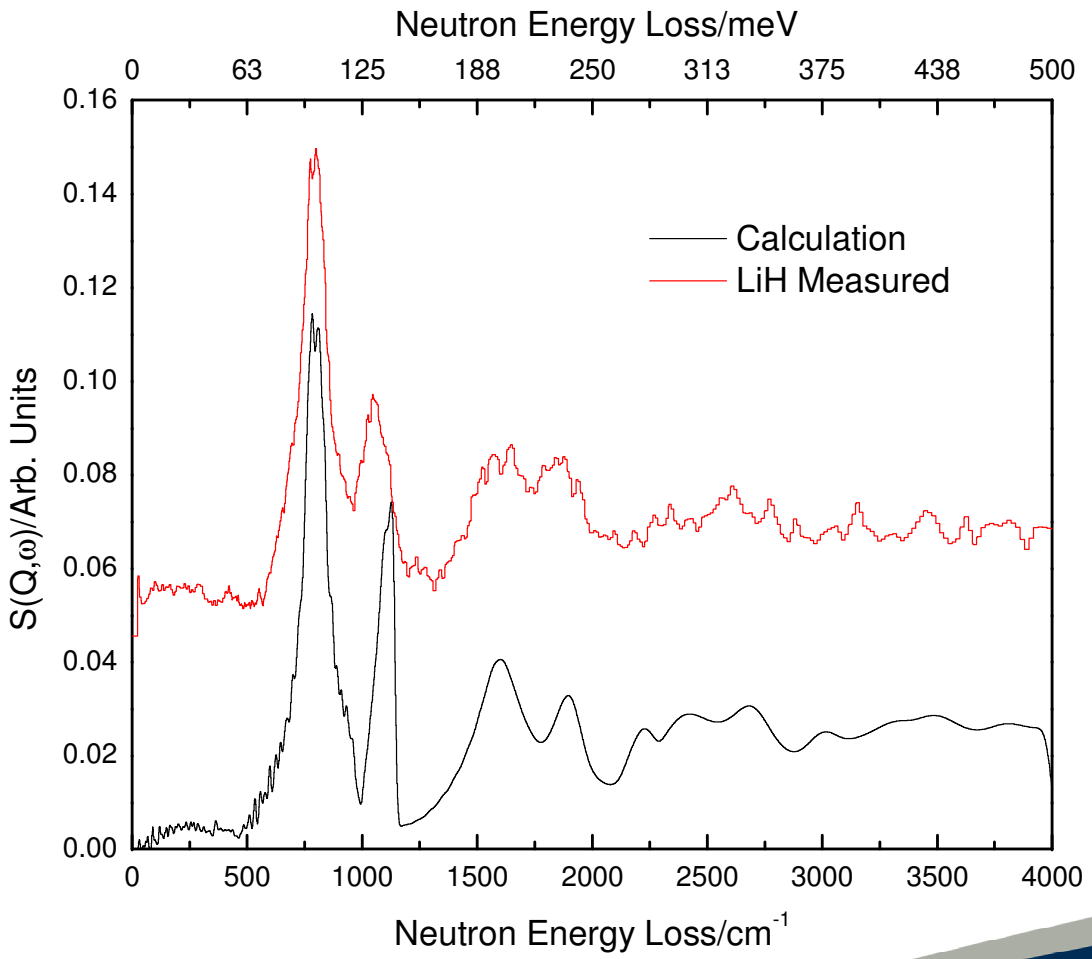
Calculation of INS spectra

- The normal modes are calculated for a large grid of points in the reciprocal space. In the example we mention here the lattice was sampled as a 16x16x32 grid (the symmetry of the system makes that number substantially smaller).
- The INS spectra is generated from the eigenvectors and eigenvalues on every point in the grid.

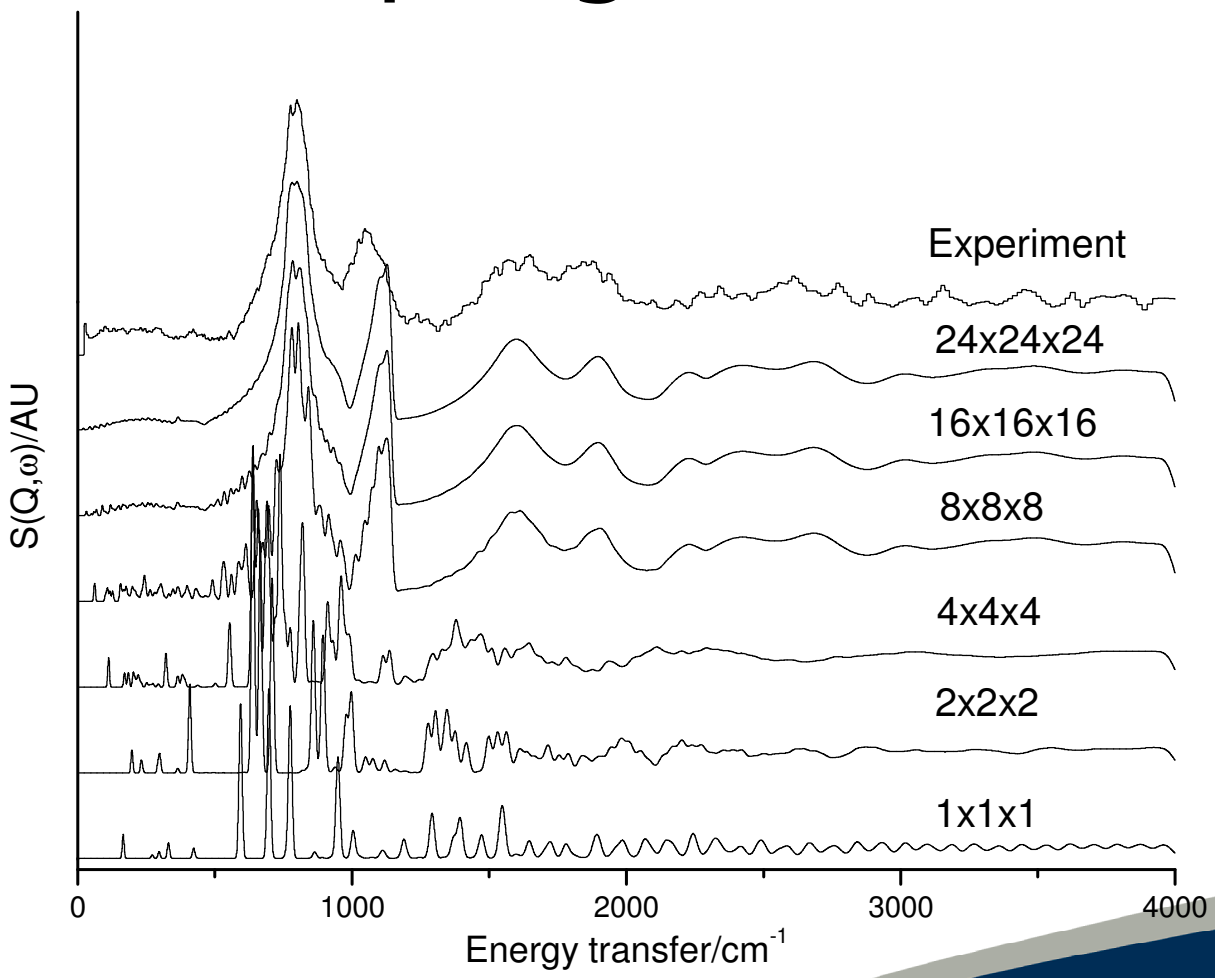
Example MgH_2



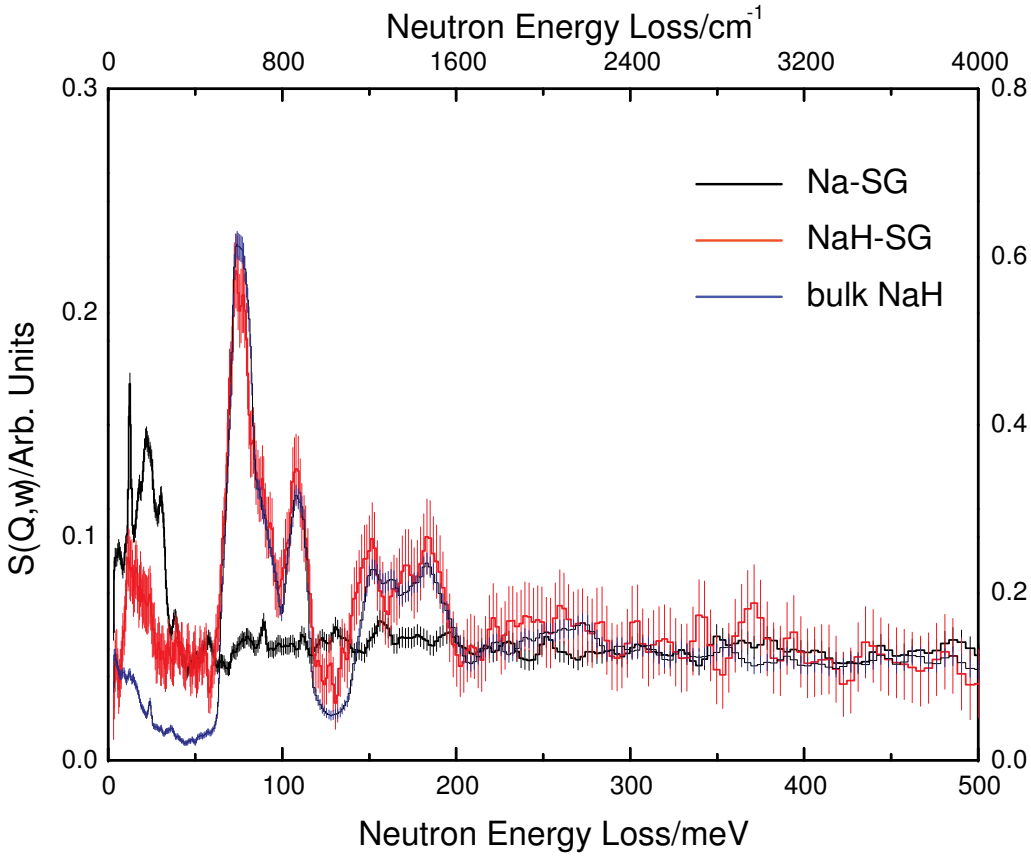
LiH an example of k-space sampling effects (extreme case)



LiH an example of k-space sampling effects



Na Silica Gel/NaH SG



The size of the nanoparticles has to be larger than 16x16X16

Journal of Cluster Science, **21**,543-549, 2010

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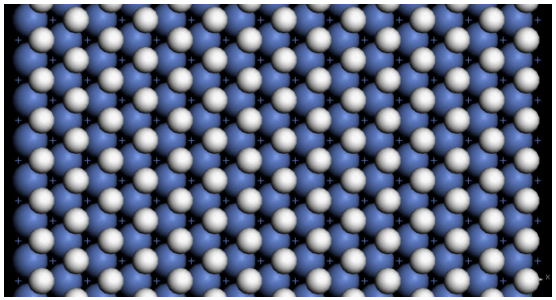
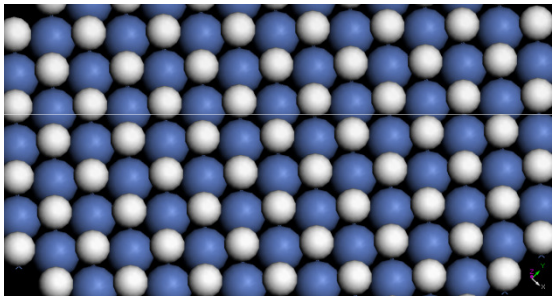
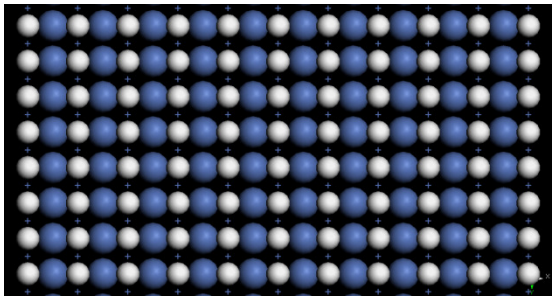
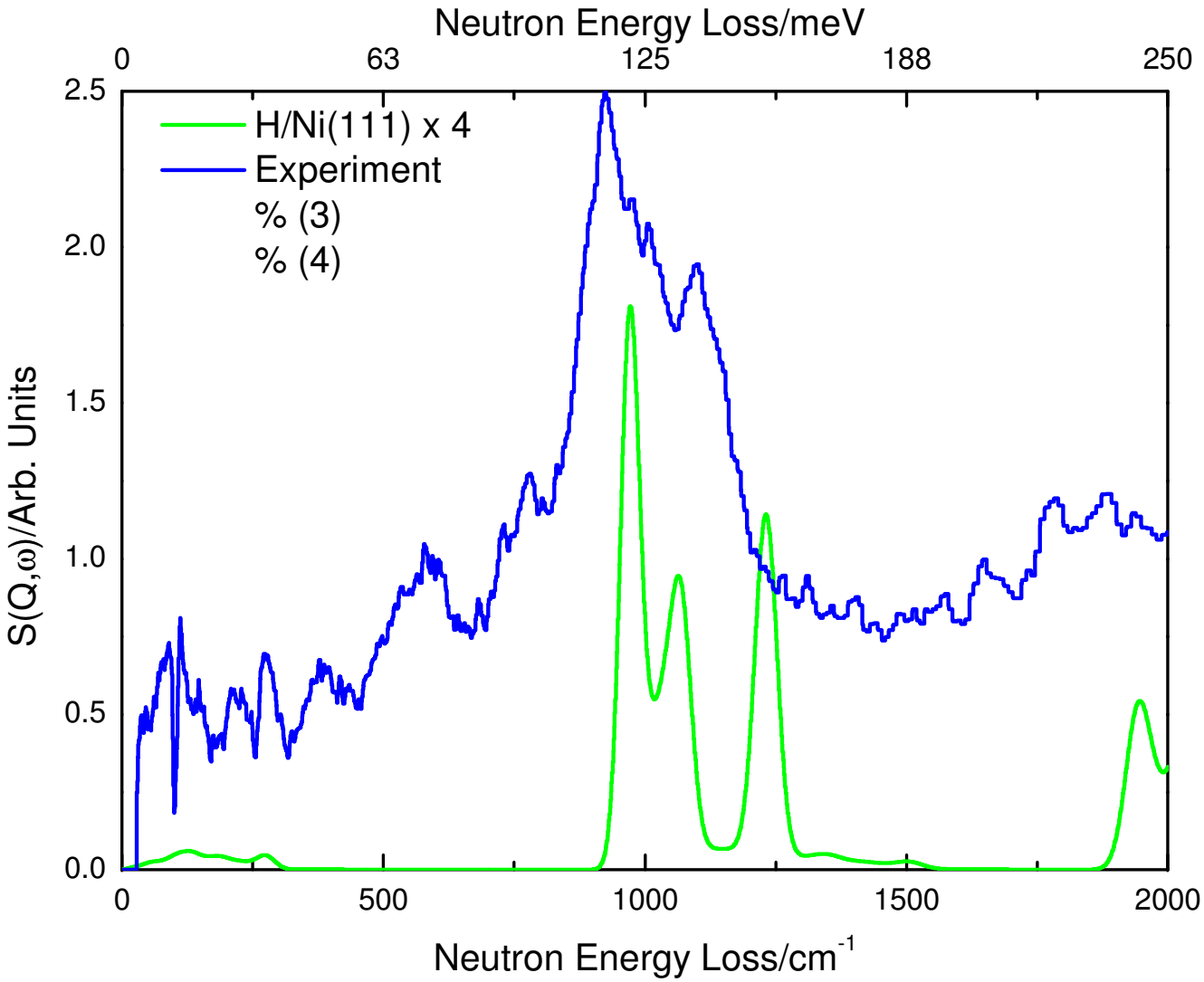
Raney Ni





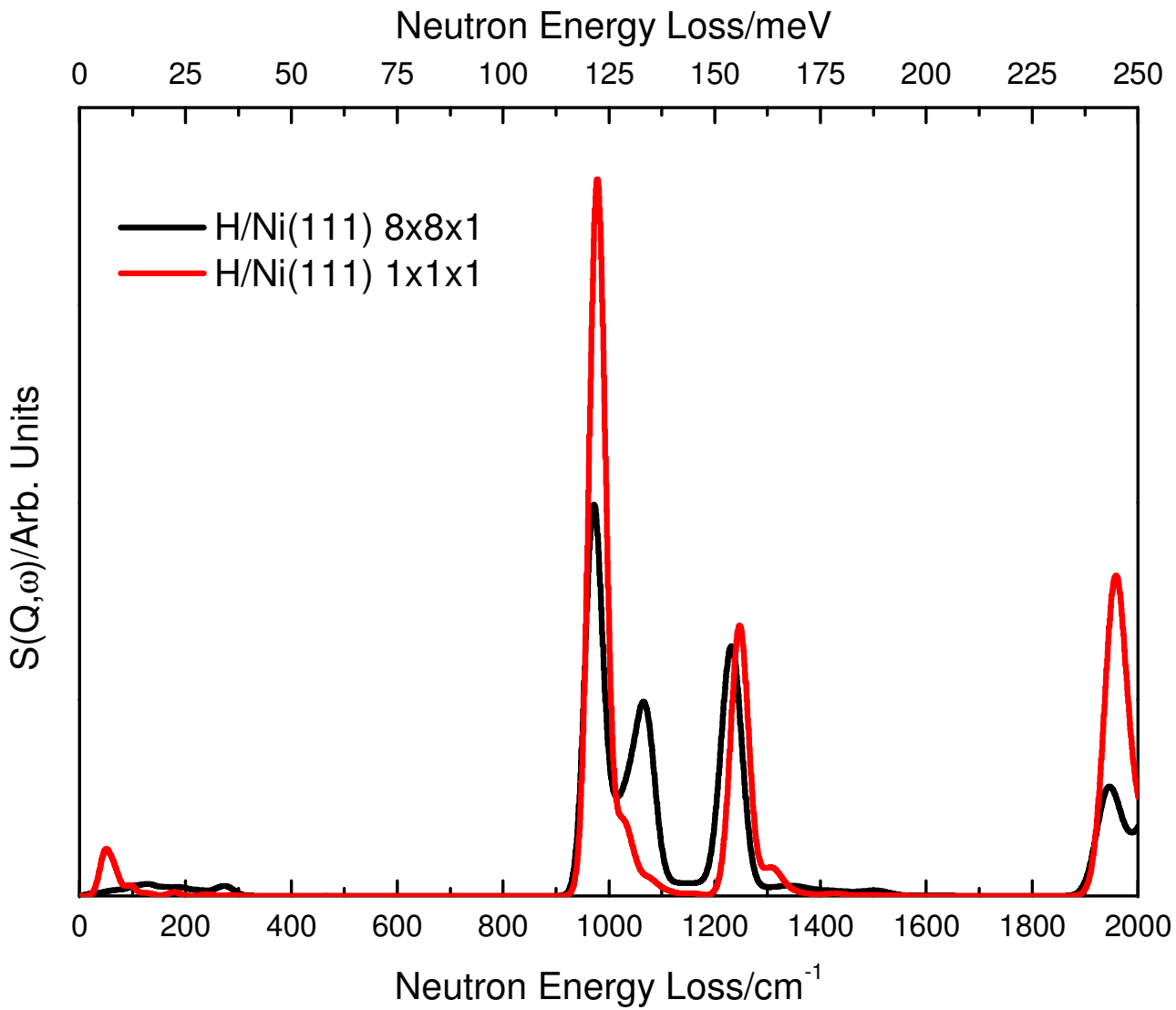


Raney Ni



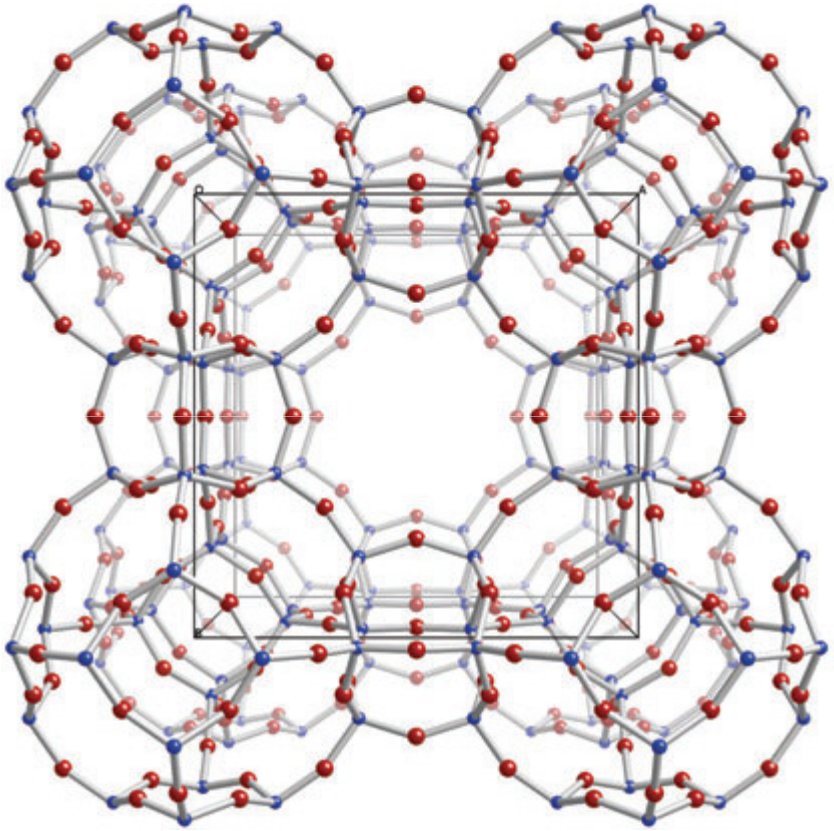
Chem. Commun., 2010, **46**, 2959-2961

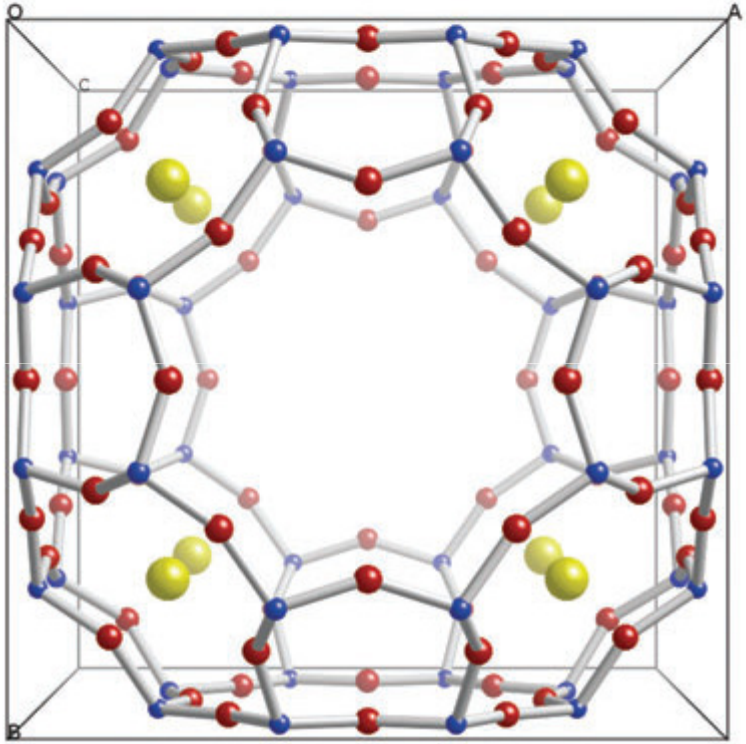
Effect of Brillouin sampling on surface modes



Council

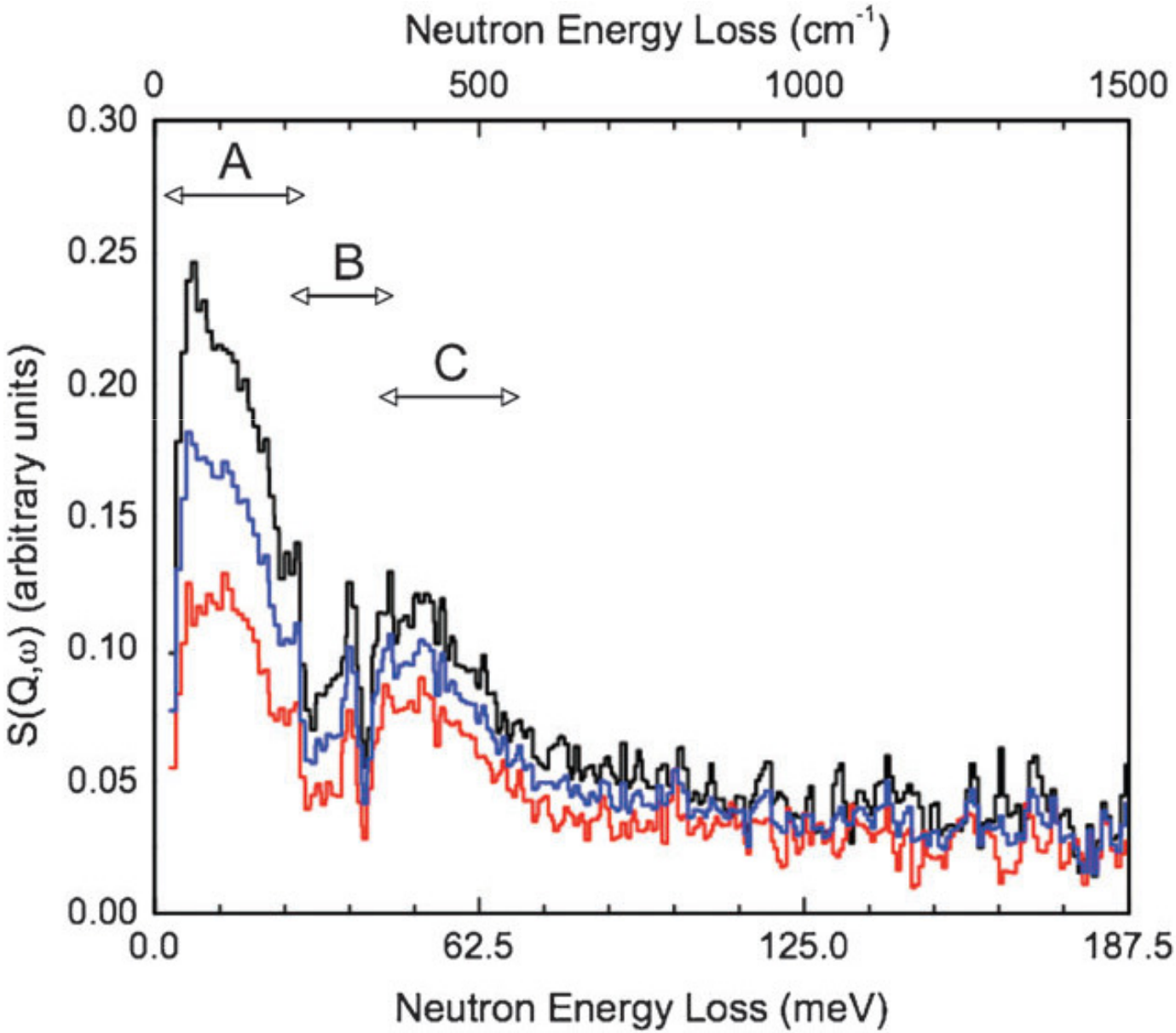
Zeolite A





PCCP *(33) 9661-9666, 2010*

Ammonia in Zeolite A



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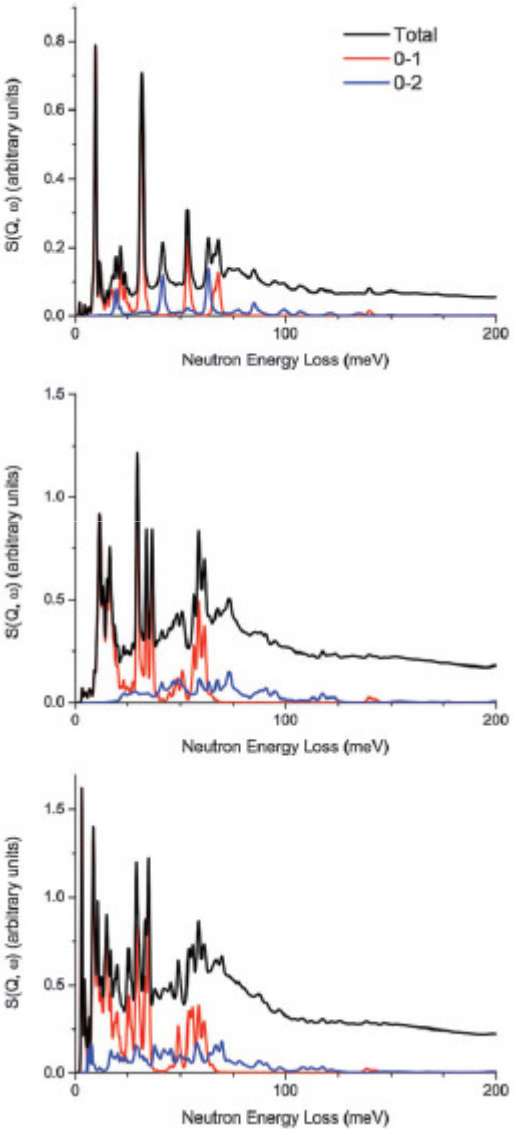
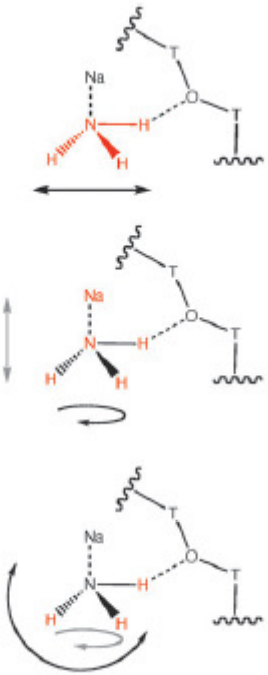
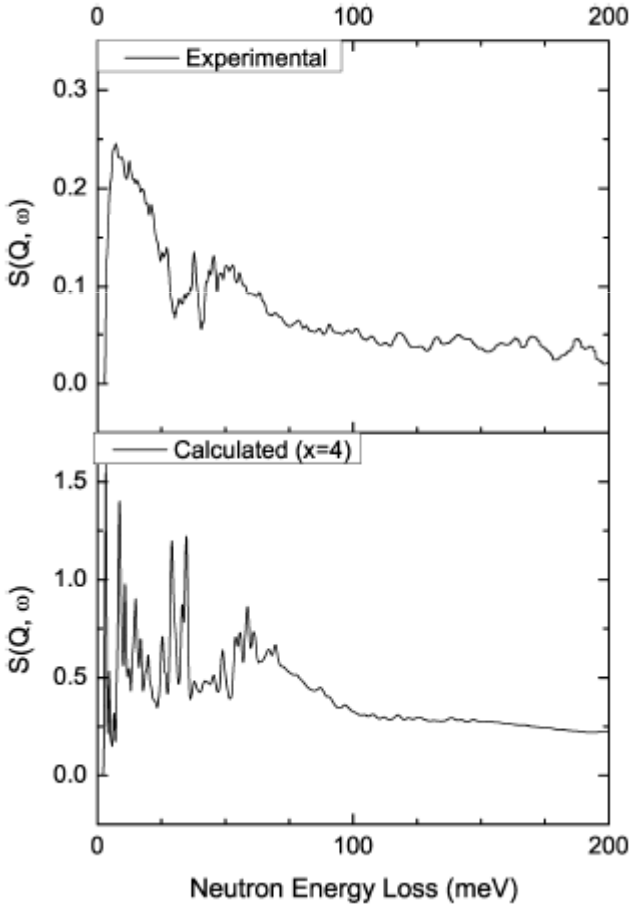
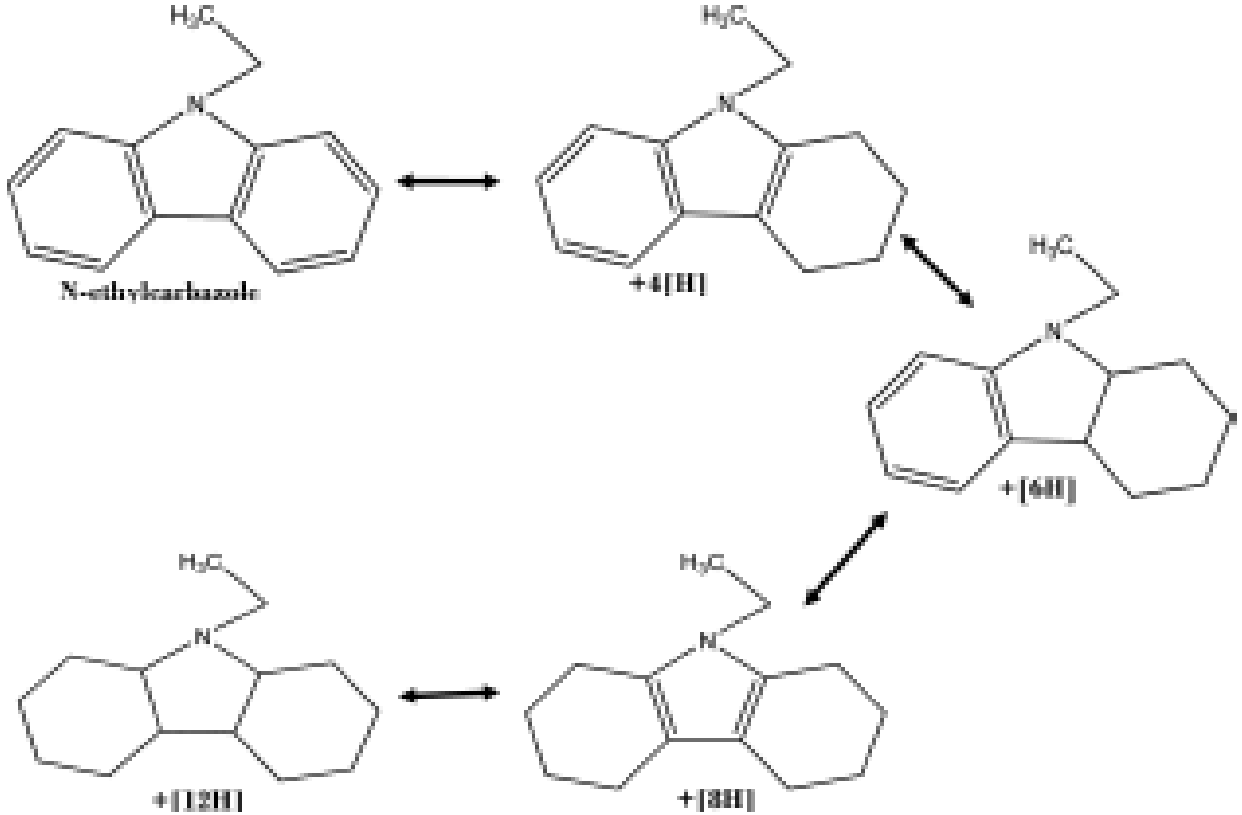

Total
0-1
0-2
S(Q, ω) (arbitrary units)
Neutron Energy Loss (meV)


Na
N
H
O
T


Experimental
Calculated (x=4)
S(Q, ω)
Neutron Energy Loss (meV)

Catalytic Hydrogenation of Organic Molecules as Hydrogen Storage Vectors

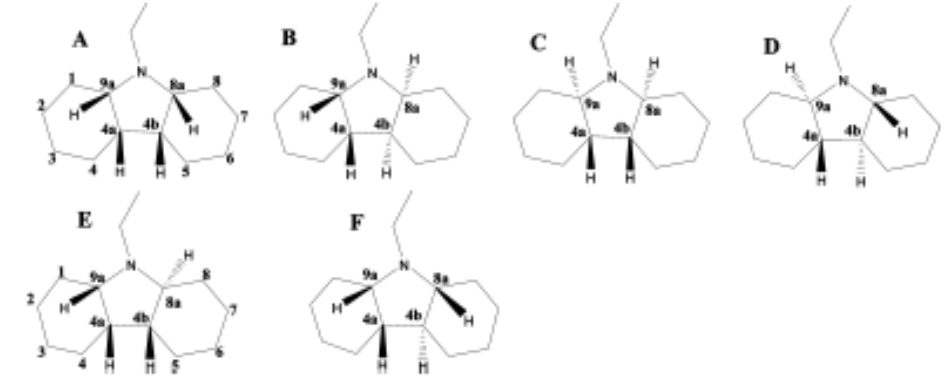
SCHEME 1: Stepwise Hydrogenation of *N*-Ethylcarbazole to Perhydro-*N*-ethylcarbazole over Noble Metal Catalysts (the Structures of the Starting Material, +4[H], and +8[H] Come from Experimental Assignments from NMR Experiments)[a]



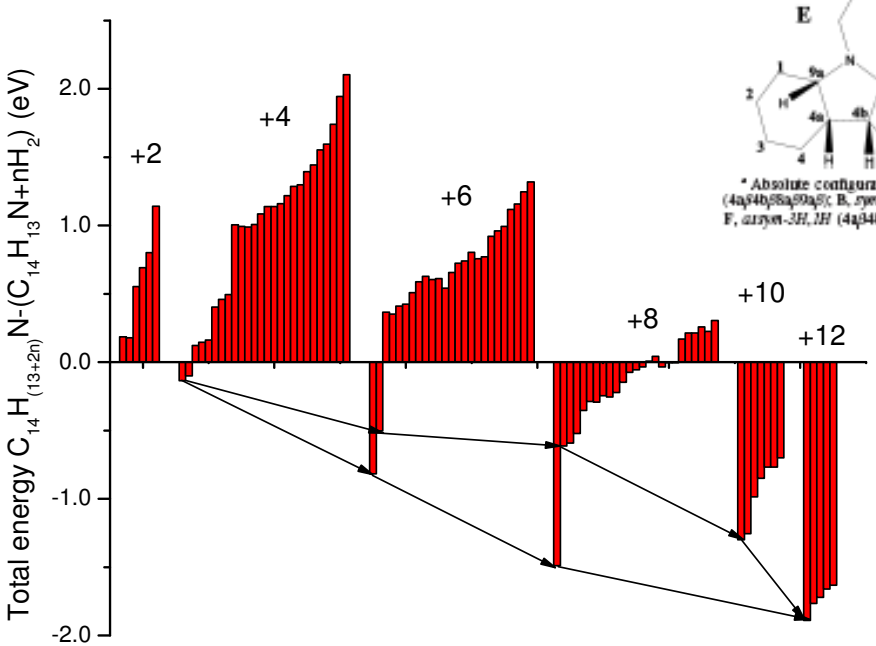
[a] The reactants and intermediates are named as follows: starting material, *N*-ethylcarbazole; +4[H]- *N*-tetrahydroethylcarbazole; +6[H]- *N*-hexahydroethylcarbazole; +8[H]- *N*-octahydroethylcarbazole; and +12[H]- *N*-perhydroethylcarbazole.

Catalytic Hydrogenation of Organic Molecules as Hydrogen Storage Vectors

SCHEME 2: Chemical Structures of All Six Possible Stereoisomers of the *N*-Perhydroethylcarbazole That Are Theoretically Distinguishable by Means of NMR[a]



[a] Absolute configuration shown arbitrarily with partial numbering of carbon atoms used for signal assignments. From upper left: A, *syn-4H* (4aβ4bβ8aβ9aβ); B, *syn-2H,2H* (4aβ4bα8aα9aβ); C, *syn-2H,2H* (4aβ4bβ8aα9aα); D, *syn-2H,2H* (4aβ4bα8aβ9aα); E, *anti-syn-3H,1H* (4aβ4bβ8aα9aβ); F, *anti-syn-3H,1H* (4aβ4bα8aβ9aβ).[24]



International Journal of Hydrogen Energy, ***In Press***

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Catalytic Hydrogenation of Organic Molecules as Hydrogen Storage Vectors

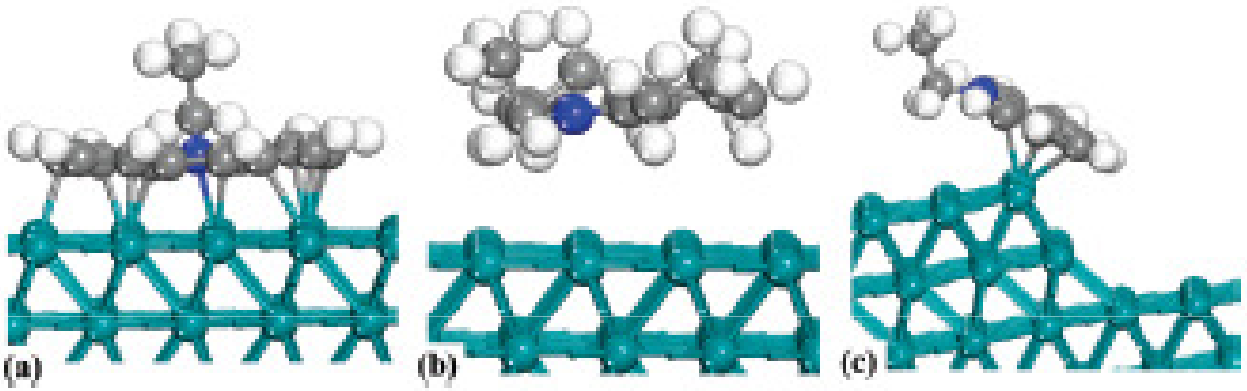

Figure 6. (a) Calculated structure of ethylcarbazole adsorbed on terrace of Ru(001); (b) energetically favorable desorption of +8[H] intermediate from Ru(001); (c) ethylcarbazole adsorbed on the stepped Ru(109) with two atomic height. $E(a) = 2.56$ eV $E(b) = 0.32$ eV, $E(c) = 1.61$ eV.

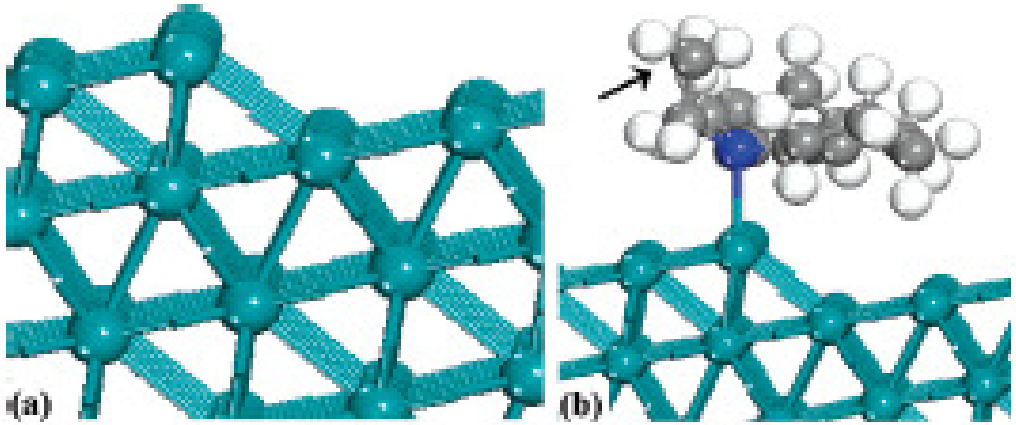

Figure 7. (a) Calculated structure of one-atom-height step of Ru(109); (b) calculated structure of adsorbed +8[H] intermediate at the step edge. The arrow in black specifies the ethyl group.

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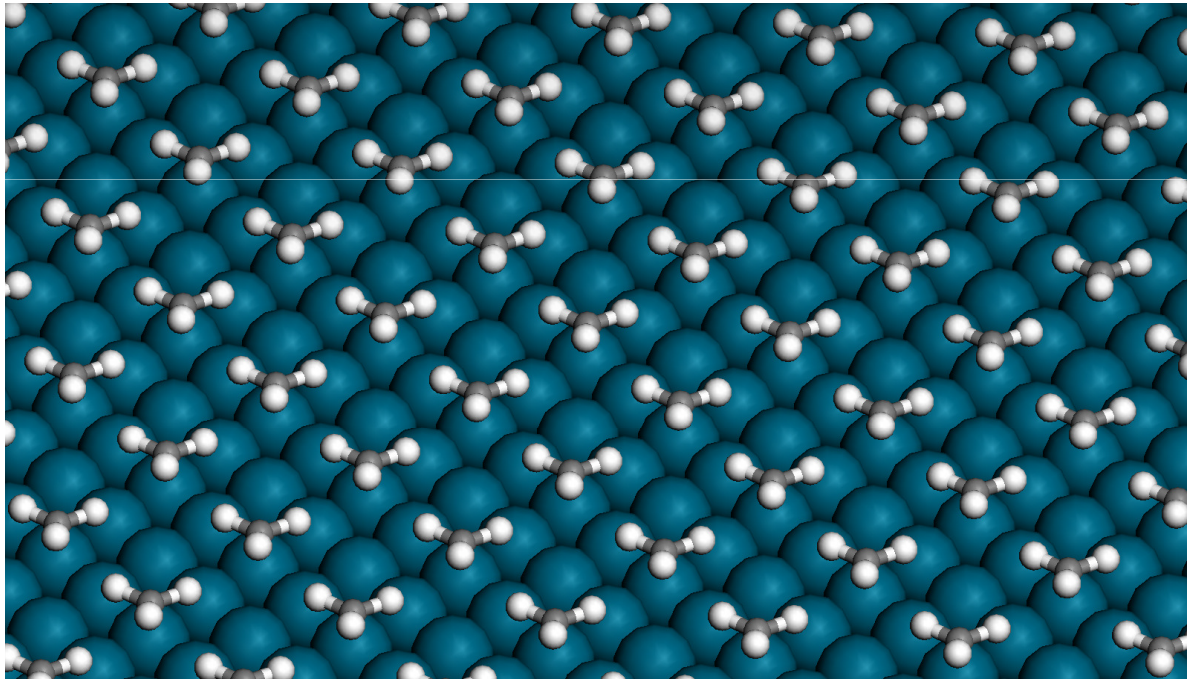
Revisiting CH3/Pd(111)
(how things changed in 10 years)



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Force field fitting

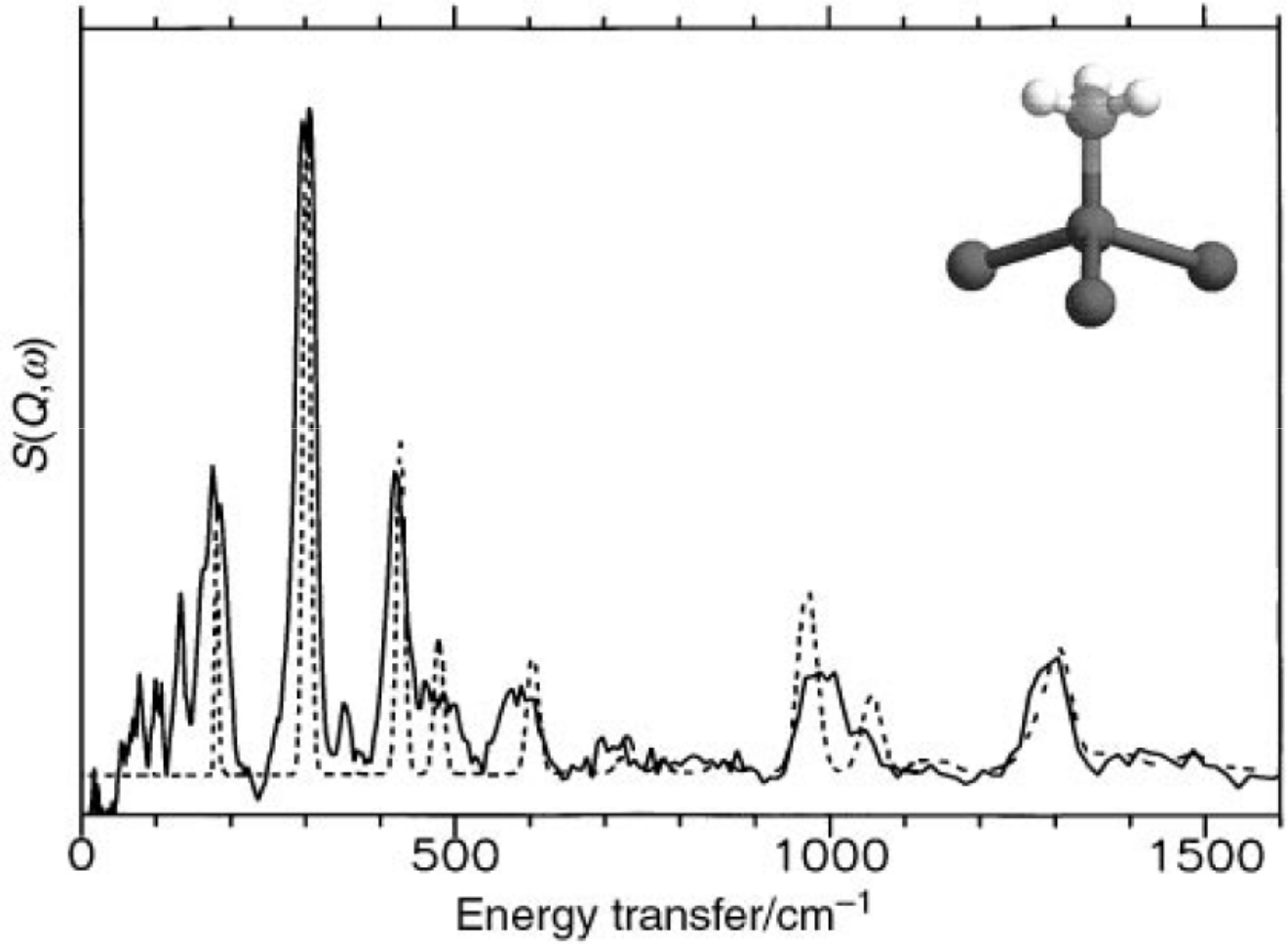

Fig. 2 Comparison of the INS spectrum of the deactivated catalyst (solid line) and the results from the CLIMAX analysis of the spectrum (dashed line).

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Final thoughts

- Modelling is a vital part in the interpretation of catalysis studies with INS.
- Without modelling there is less or even little understanding of INS spectra

However:

- Catalysis experiments with neutrons are particularly demanding and difficult.
- Sample environment is also very important.
- But above all, it is the experimental design, the know how, what will give you a successful experiment!

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