

*Periodic DFT calculations for the solid state:  
Phonons and Vibrations in molecular crystals*

Mark JOHNSON  
Scientific Computing  
Institut Laue Langevin  
(<http://www.ill.fr/Computing/Club.html>)  
Grenoble, France

# Plan Of Talk

- I. Introduction to spectroscopy: IR, neutrons and X-rays
- II. *Hexamethyl benzene* - the importance of k-point sampling
- III. *Oligothiophenes* - from INS to IR
- IV. *Benzoic acid* - hydrogen bonded dimers, INS to IXS
- IV. *Urea* - multiphonons for small molecules
- V. *Kevlar* - new structural info
- VI. *Urea phosphoric acid* - short hydrogen bonds
- VI. Conclusion & perspectives (collagen, DNA ...)

# INS vs. IXS vs. IR

	INS	IXS	IR
Scattering by	Nuclei	Electrons	Electrons
Spectral intensities from eigenvectors and	Scattering lengths	Number of electrons and form factor	Variation of dipole moment via charge tensors
Selection rules	No	No	Yes
Phonon dispersion	Yes (K from $k_i$ , $k_f$ , $2\theta$ )	Yes (K from $2\theta$ , $k_i=k_f$ )	No (K=0)
Effect of isotopic substitution	Mass and scattering length	Mass only	Mass only
Resolution	Varies with energy transfer (> ~2%)	Constant (~meV)	Constant (~cm <sup>-1</sup> )
Counting times	Hours	Days	Seconds/minutes

## 3.46 Create/Neutron Scattering/Coherent Form Factor

## 3.49 Create/Neutron Scattering/Incoherent on Mono.

The  
exp

PHONON calculates the one-phonon double differential incoherent neutron scattering cross section as a sum of contributions from all atoms of the unit cell

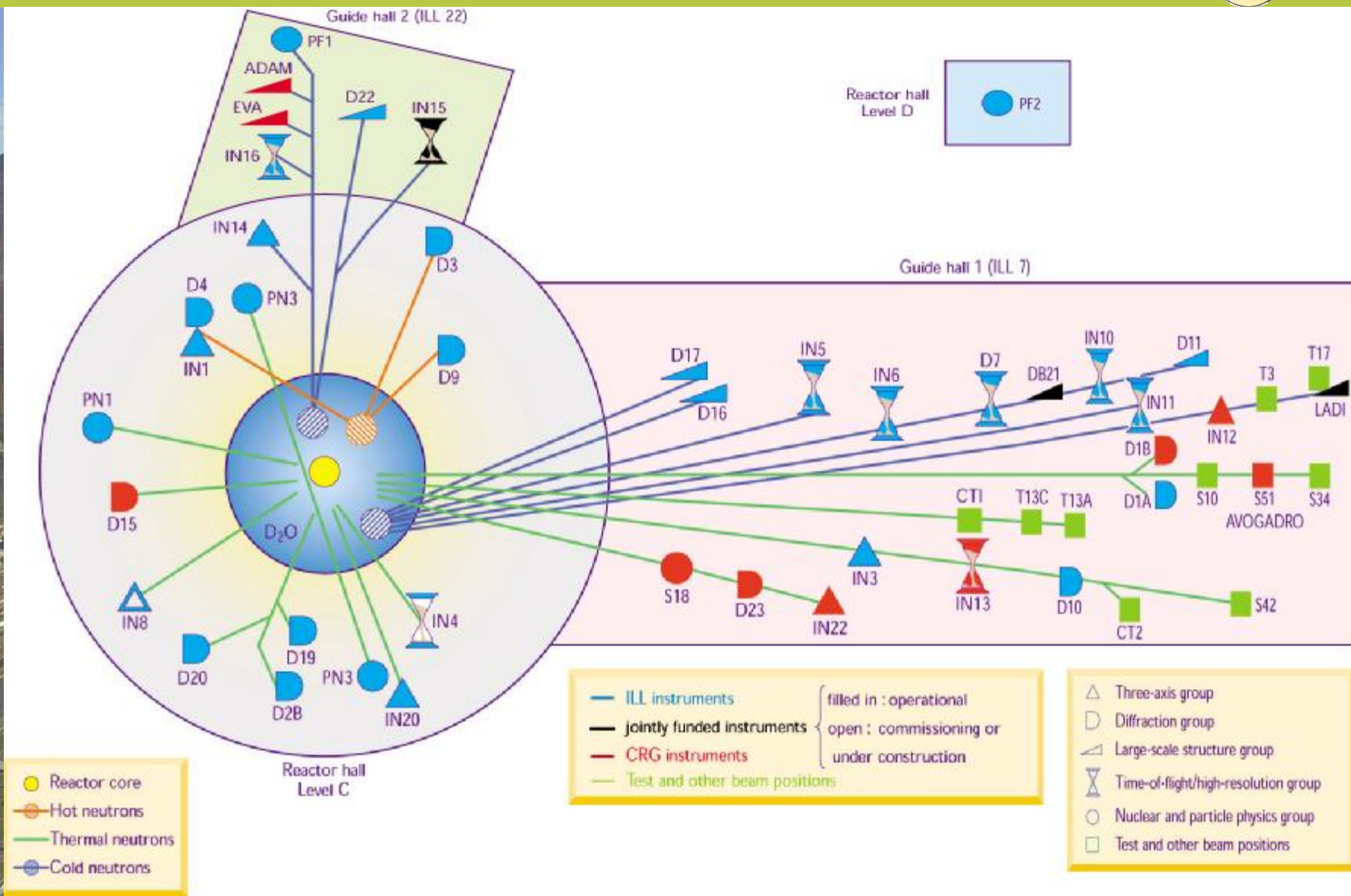
wh  
as

$$\frac{d^2\sigma_{inc}}{d\Omega dE} = \sum_{\mu} \frac{d^2\sigma_{inc}}{d\Omega dE}(\mu) \quad (88)$$

The contribution from atom  $\mu$  is

$$\begin{aligned} \frac{d^2\sigma_{inc}}{d\Omega dE}(\mu) &= \sigma_{inc}(\mu) \frac{K}{K_o} \sum_{\mathbf{k}, j} \frac{\hbar}{2M_{\mu}\omega(\mathbf{k}, j)} |\boldsymbol{\kappa} \cdot \mathbf{e}(\mathbf{k}, j; \mu)|^2 \\ &\times (n(\omega(\mathbf{k}, j)) + 1) \exp[-2W_{\mu}(\boldsymbol{\kappa})] \delta(\epsilon - \omega(\mathbf{k}, j)) \end{aligned} \quad (89)$$

$$IR: abs\_coeff(j) \sim \sum_g \left| \sum_{a,p} \frac{Z_{ga}^*(p)}{\sqrt{m_p}} e_a(p, j) \right|^2$$



## 2 ways to calculate a vibrational spectrum

### Eigenvalue method

Matrix of force constants  $\rightarrow$  dynamical matrix

DIAGONALISE  $\rightarrow$  Eigenvalues ( $\omega^2$ ) & eigenvectors (e)

$\rightarrow$  Vibrational density of states for all K  $\rightarrow$  INS, IXS, IR spectra

✓ Easy to visualise/understand modes, easy to calculate spectra for isotopomers

✗ But harmonic approximation, structure specific

### Fourier transform method

Molecular dynamics simulation  $\rightarrow$  velocity auto-correlation function *or*  $I(K,t)$

FOURIER TRANSFORM  $\rightarrow$  vDOS *or*  $S(K,\omega)$   $\rightarrow$  neutron spectrum

✗ More difficult to visualise modes, complete recalculation for isotopomers

✓ NO harmonic approximation

## *Structure:*

An ensemble of 100's atoms, ( $2000\text{\AA}^3$ )

*Was* single molecule or cluster (5-10 molecules),

*Now* unit cell (crystalline lattice) for  $K=0$ , supercell for  $K\neq 0$  (for phonons)

## *Potential energy calculation:*

VASP; *was* PW91 with USPP, *now* PBE with PAW

(key FLAGS; Prec=Accurate, Lreal=false, Ediff=1e-6, Addgrid=true,  
+/- displacements of  $\sim 0.05\text{\AA}$ )

✓ convergence; plane wave energy cut-off & k-point spacing ( $< 0.1\text{\AA}^{-1}$ )

✗ BUT DFT underestimates (no!) dispersive interactions & effect of functional

# Crystalline oligo-thiophenes (conducting polymers)

-From INS to IR

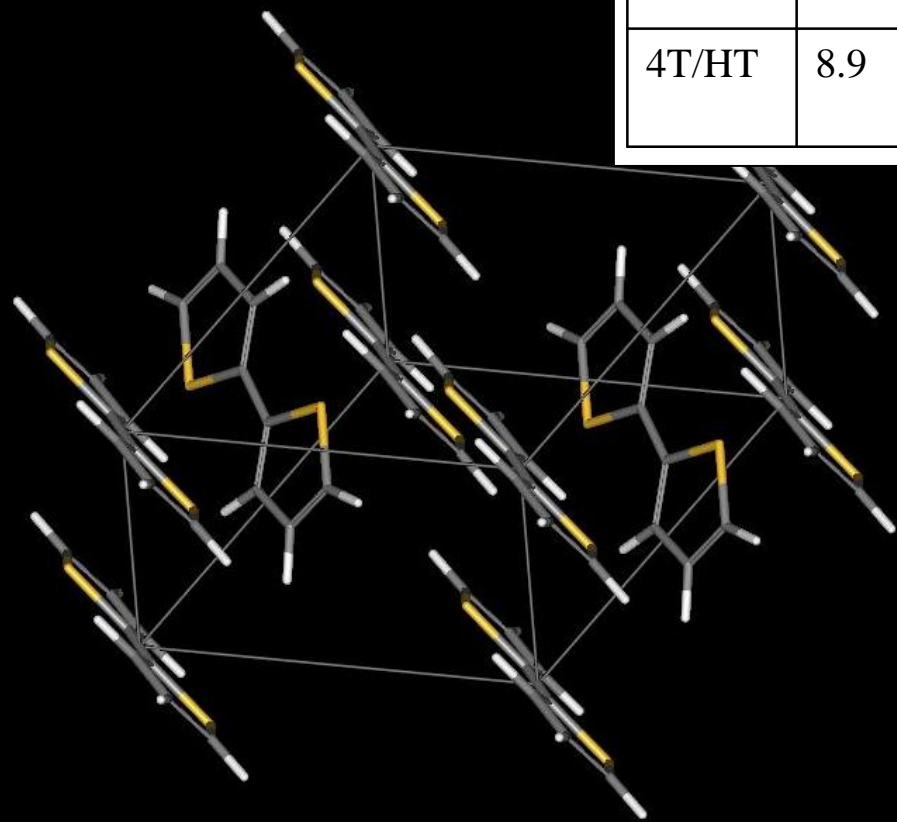
*(Patrick Hermet, Martijn Marsman - VASP)*

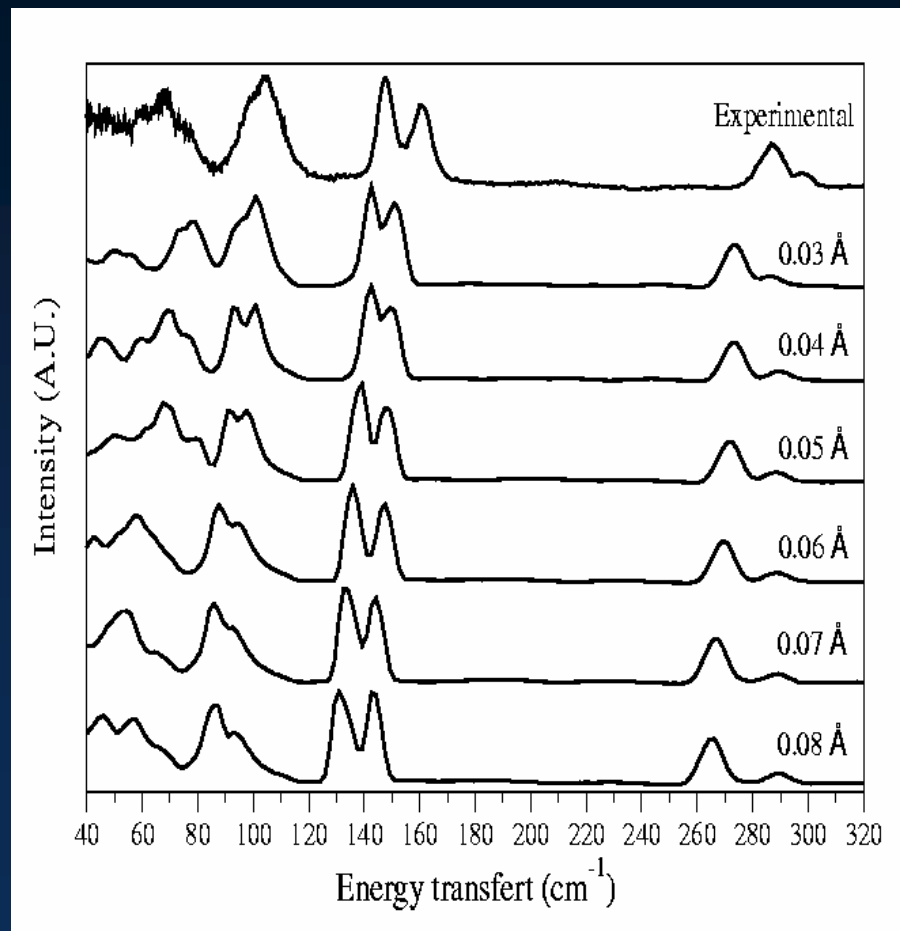
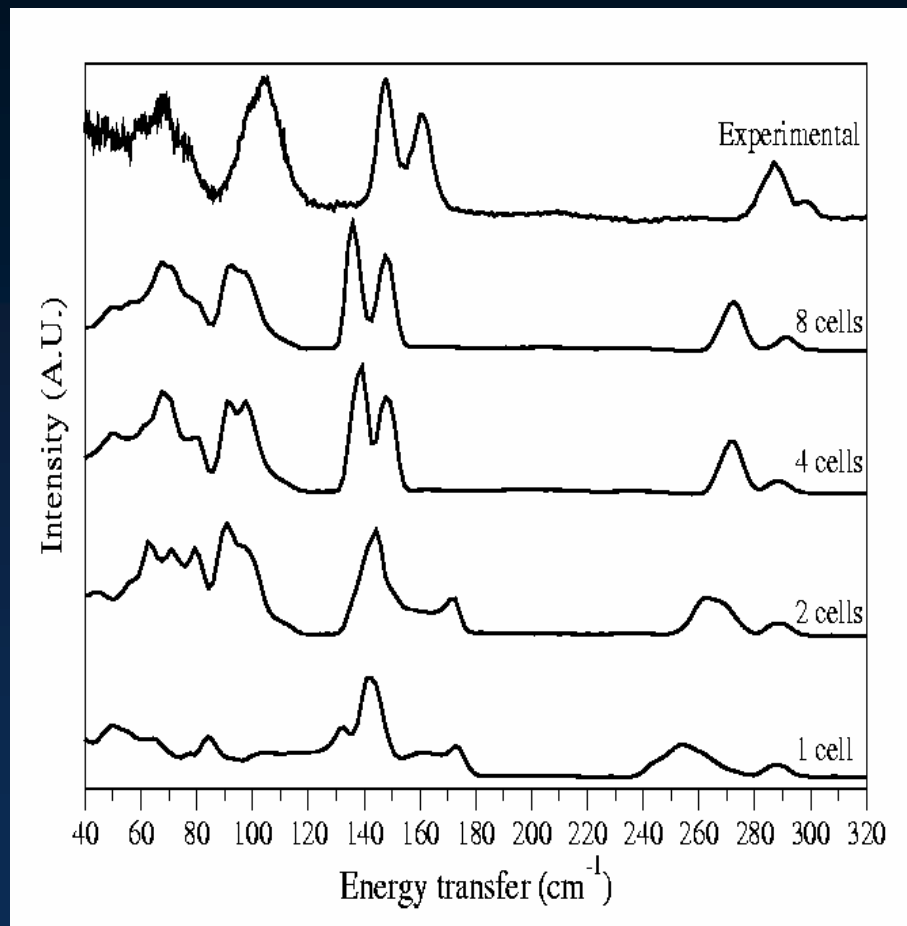
J.Phys:Cond.Matt 2004, J.Phys.Chem 2004

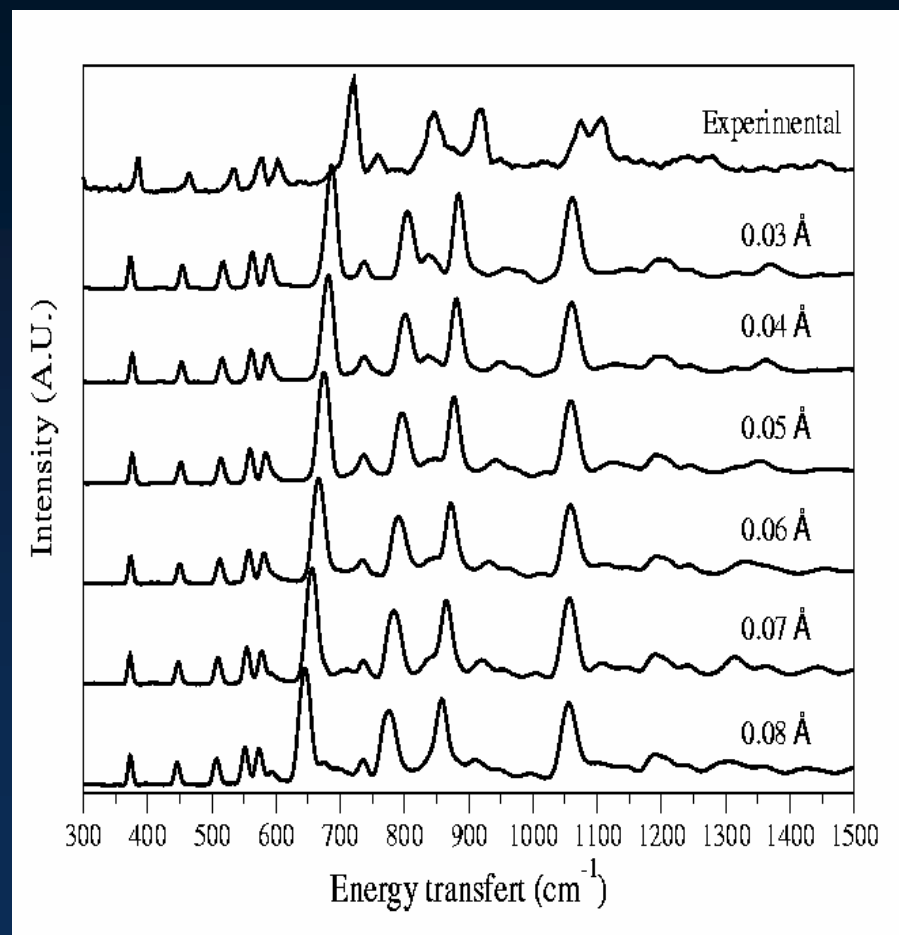
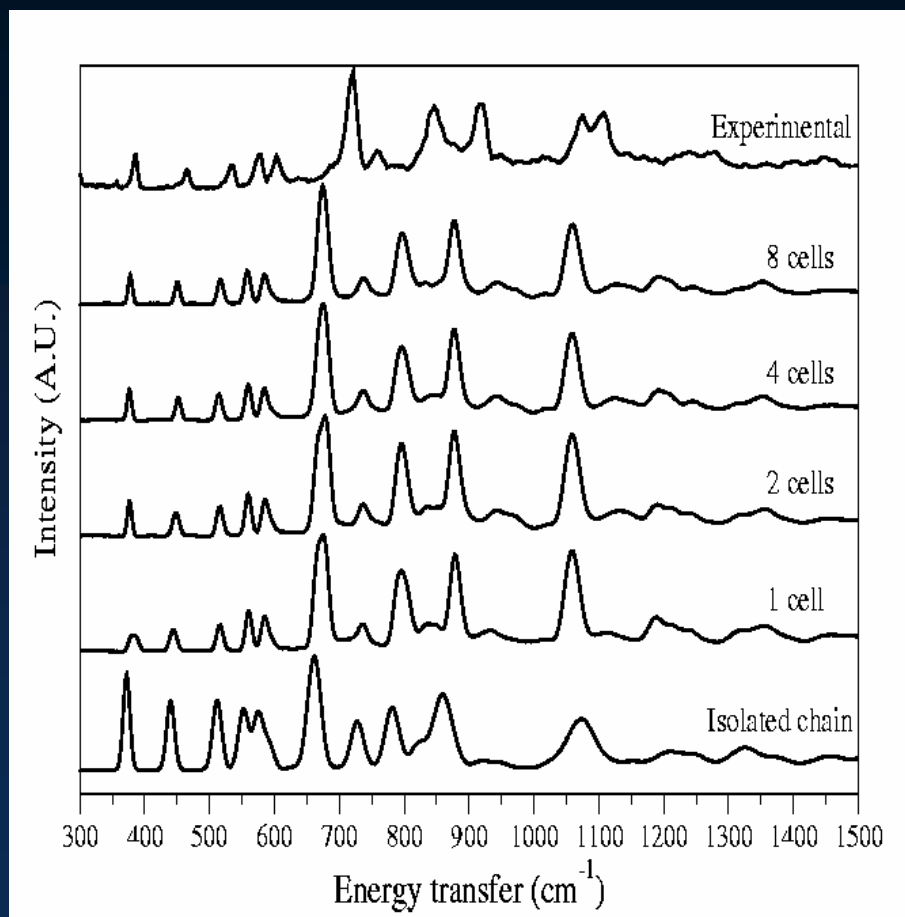


# Thiophene crystal structures (monoclinic-P21/c)

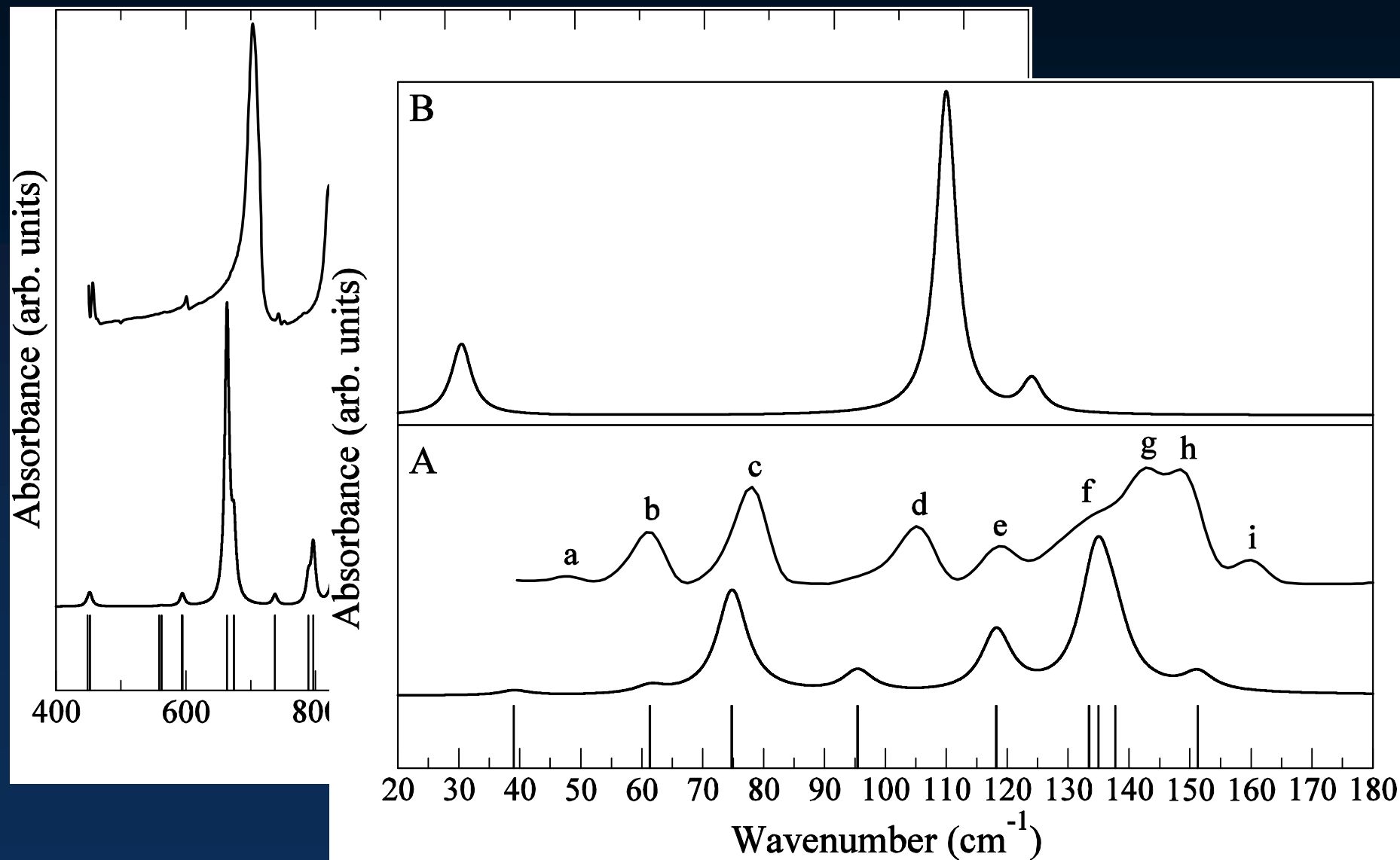
	a [Å]	b [Å]	c [Å]	$\beta$	Atoms/cell	Biggest supercell	Typical k-pts
2T	8.3	6.0	9.6	110	32 (2mol/cell)	2,2,2	2,2,2
4T/LT	6.1	7.9	30.5	92	120 (4mol/cell)	2,1,1	2,4,1
4T/HT	8.9	5.8	14.3	97	60 (2mol/cell)	1,2,1	2,2,2







# Bithiophene - INS vs IR



## Benzoic acid

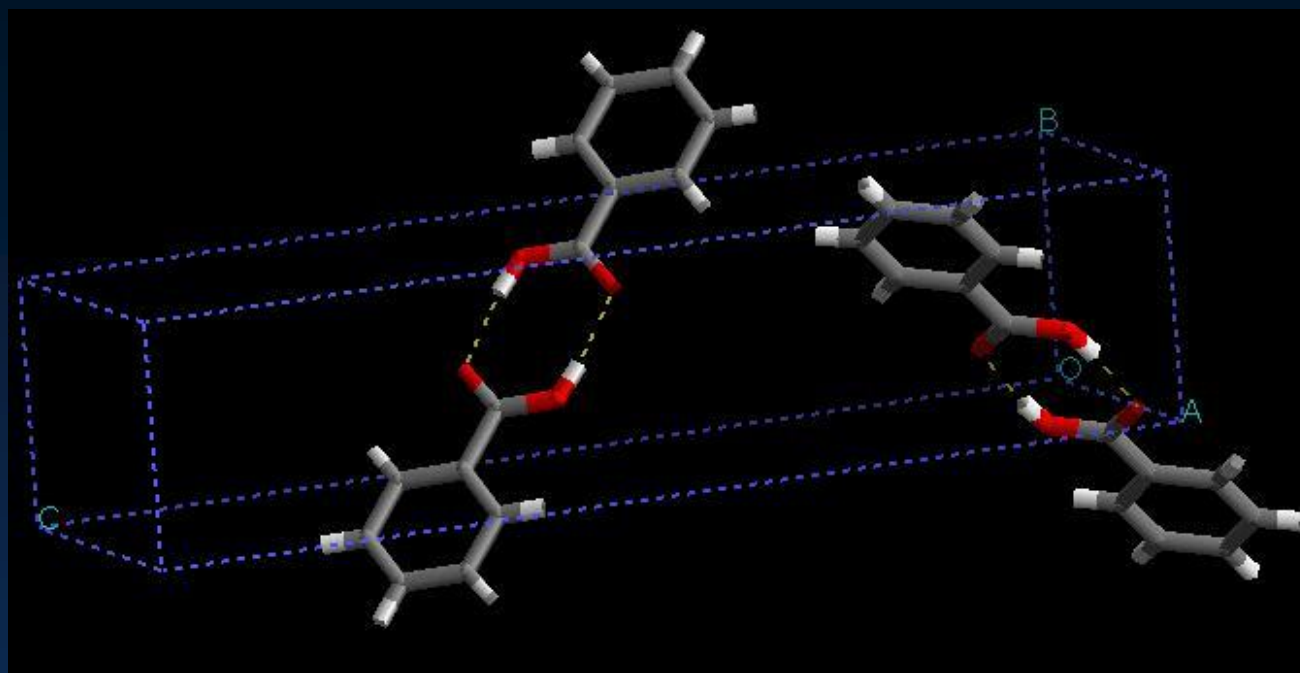
*vibrations and proton tunnelling*

- gamma point modes
- Gaussian vs. VASP
- a little bit of dispersion

*(Marie Plazanet, Tony Horsewill, Peter Trommsdorff)*

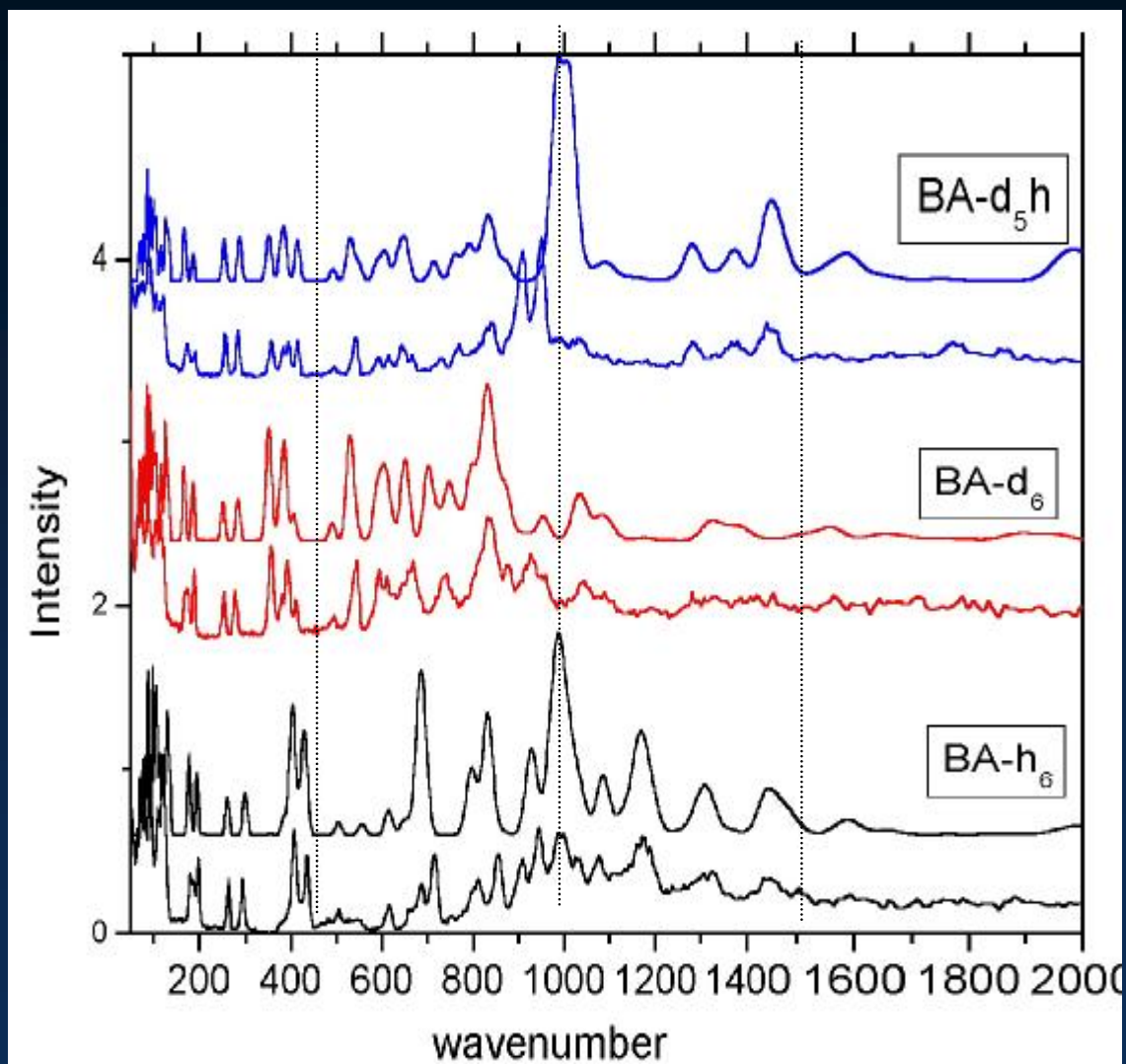
J.Chem.Phys 2001, Chem.Phys.Lett 2002

# Crystal Structure of Benzoic Acid



O-H ...O distance = 2.61Å (Chick  
Wilson et al., single-crystal, neutron  
diffraction at ~10 K - J. Chem. Soc.  
Faraday Transactions 92 (1996) 5051)

# Vibrations in Benzoic Acid Dimers

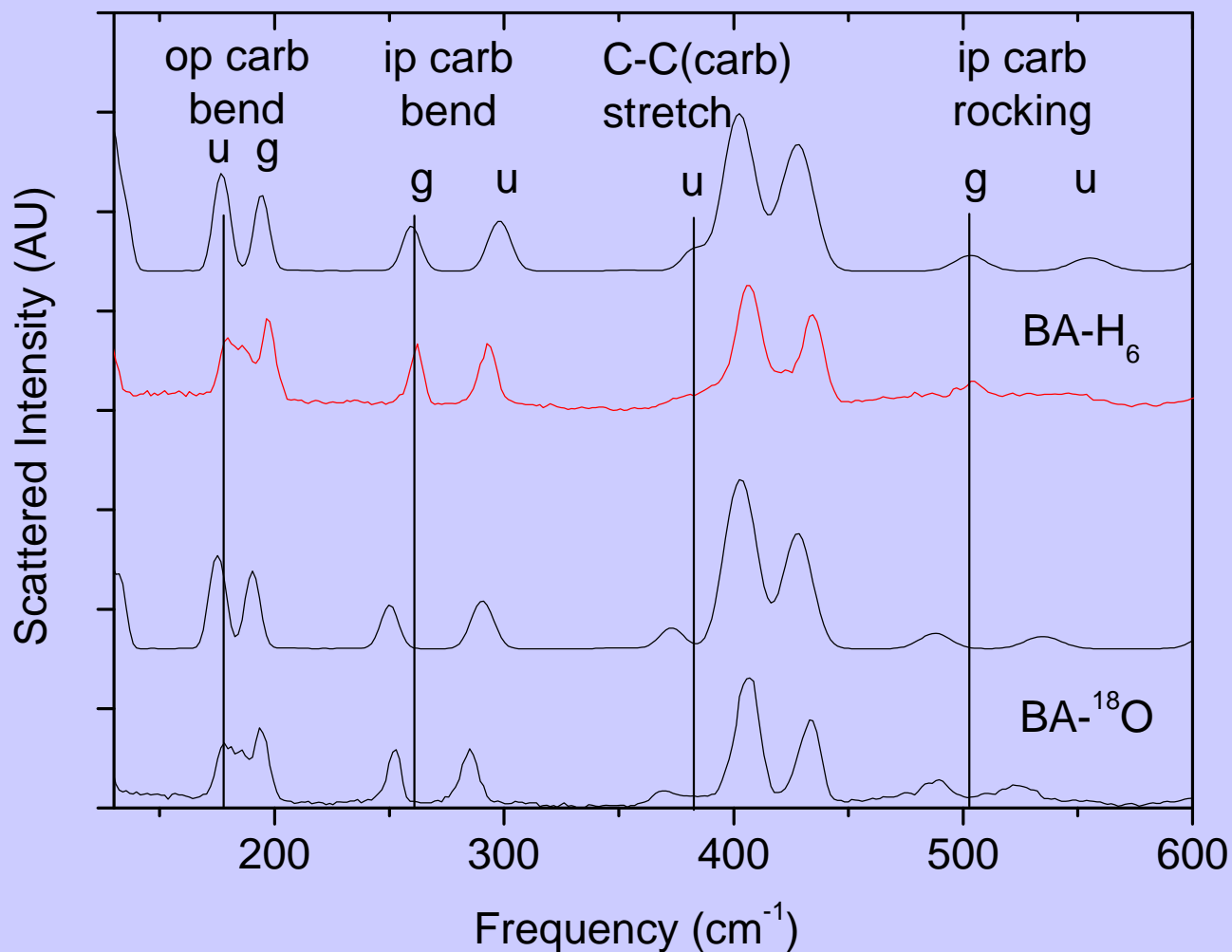


Dimer (Gaussian) gives excellent results, with only small overestimate of acid proton modes

Periodic DFT (VASP) is as good if not better

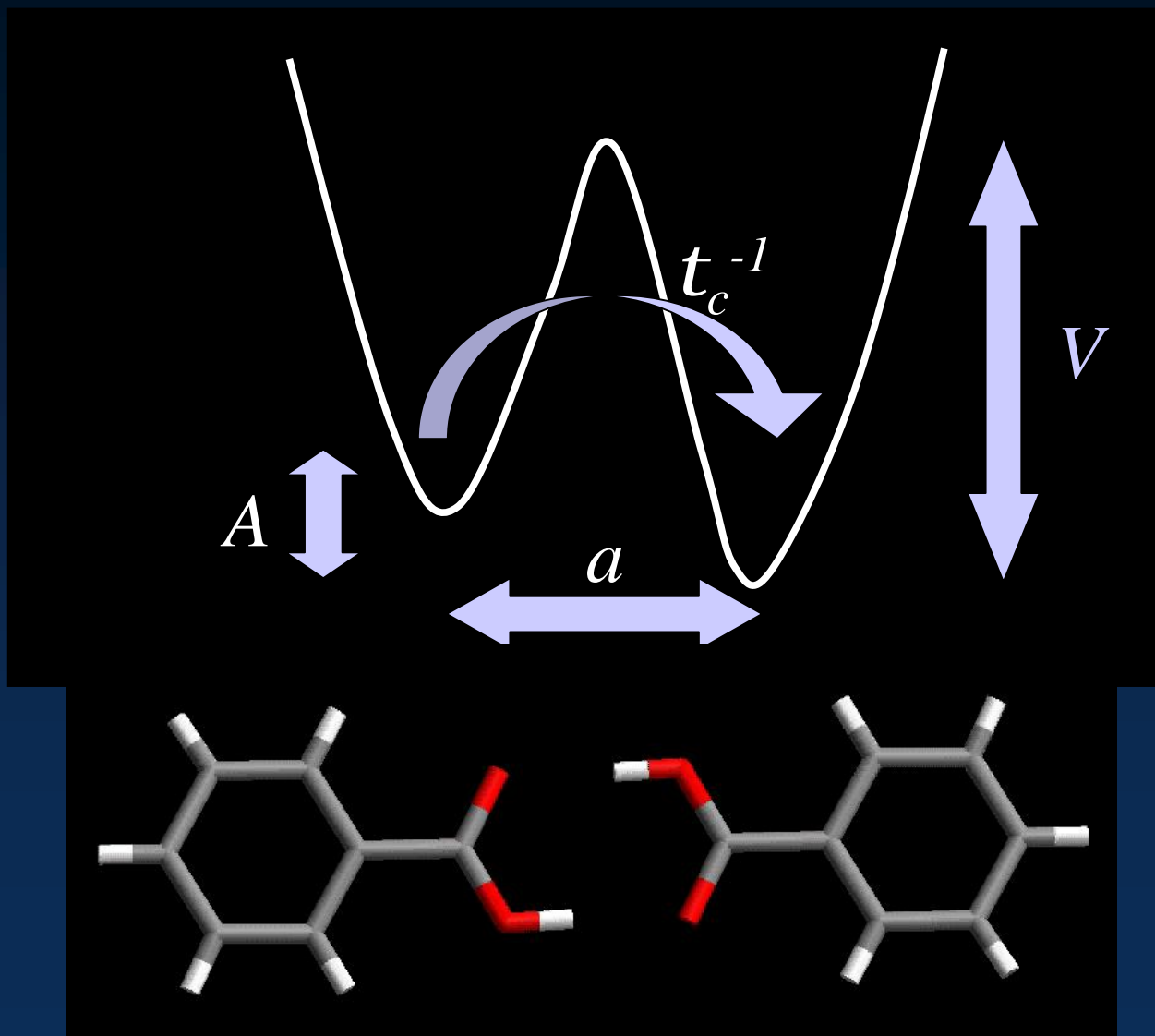
Overestimated h-bond modes: O-H ... O = 2.55Å & anharmonicities

# How good is PW-DFT? $^{16}\text{O}$ -BA $\otimes$ $^{18}\text{O}$ -BA





# Vibrations and Proton Transfer in BA

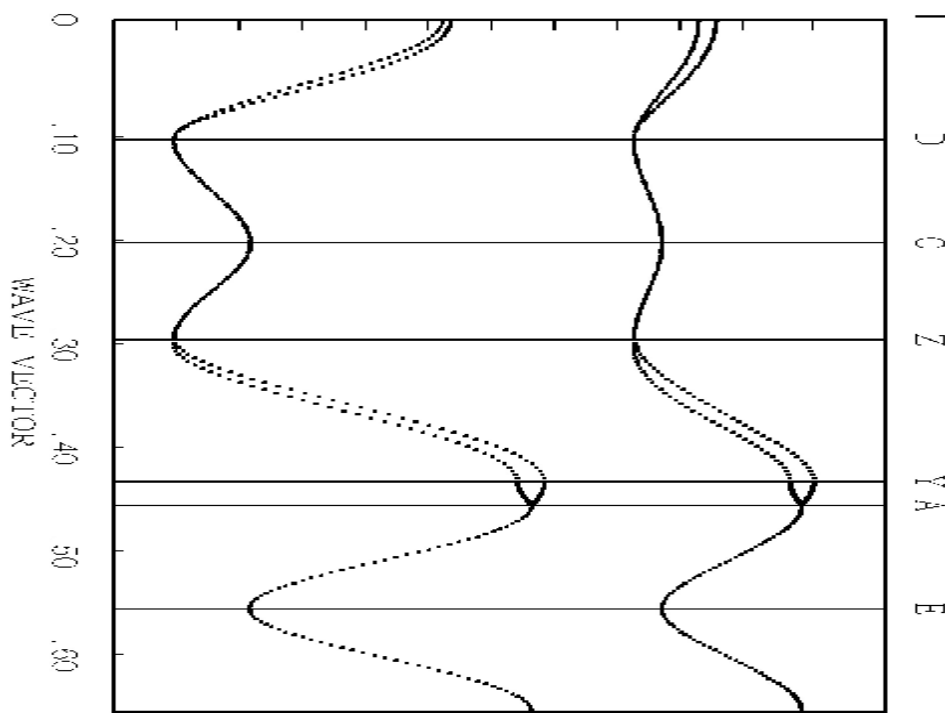
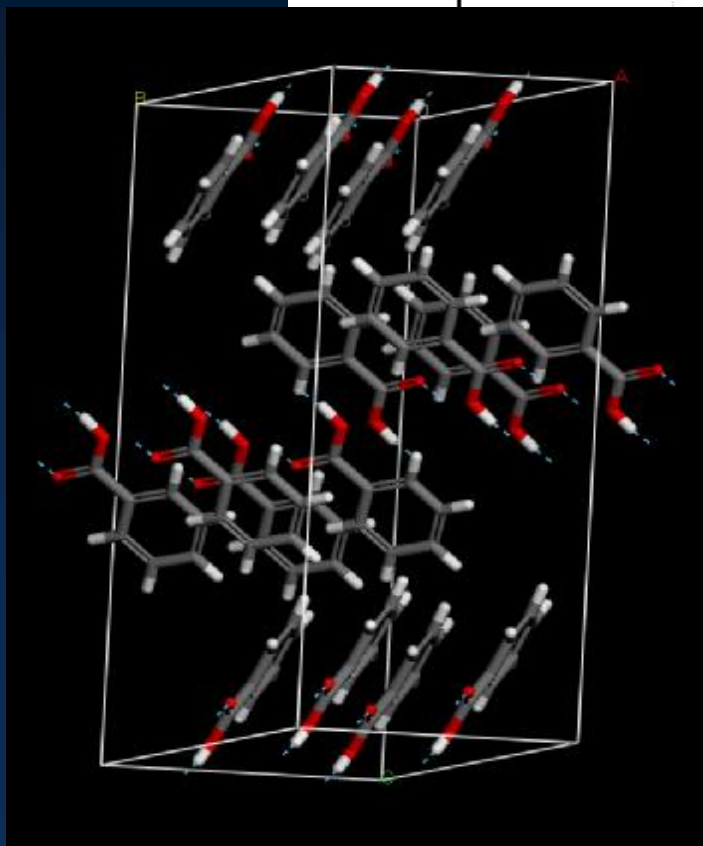
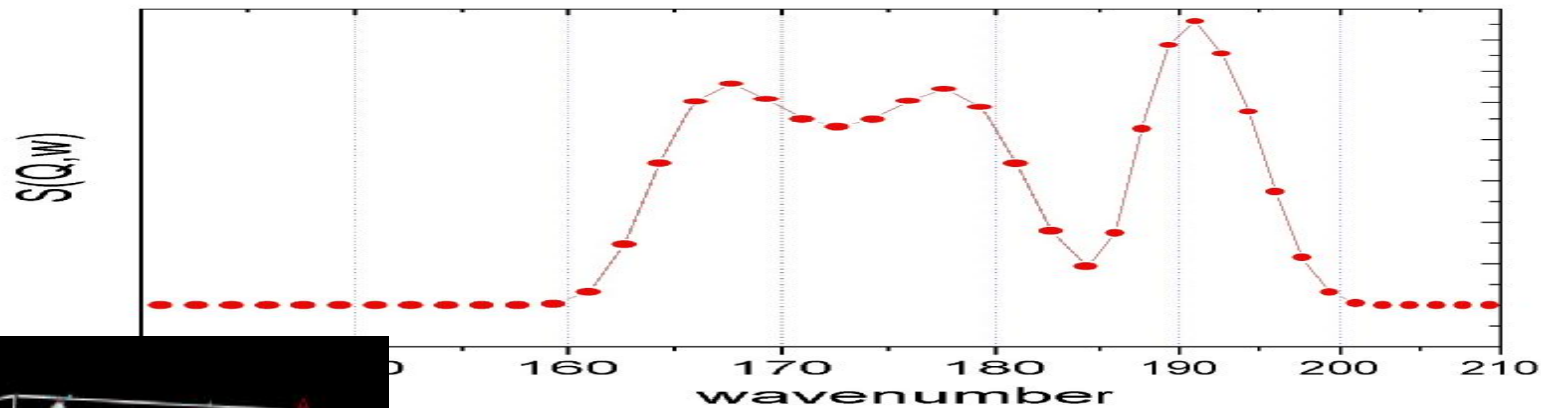


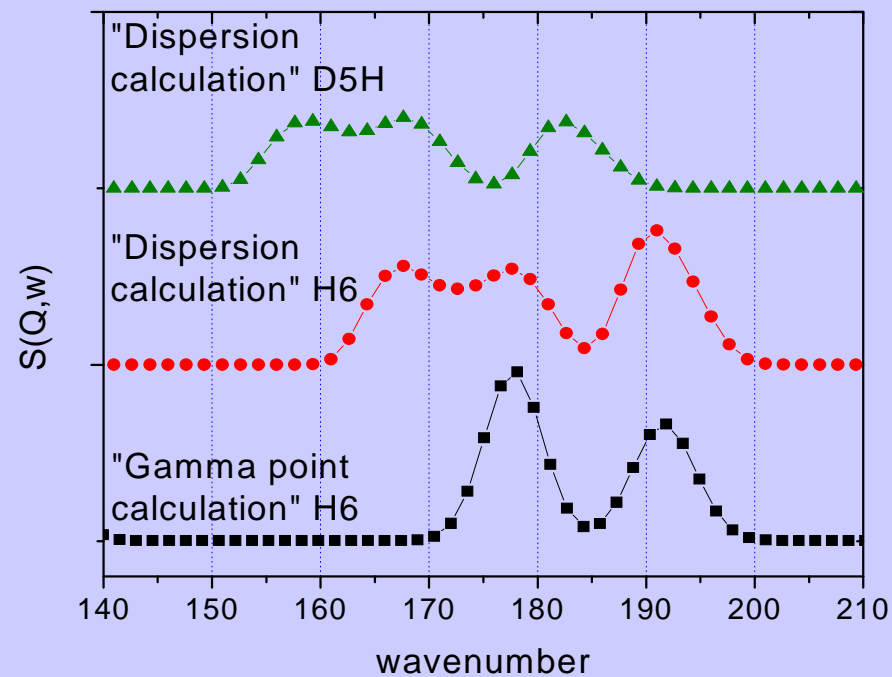
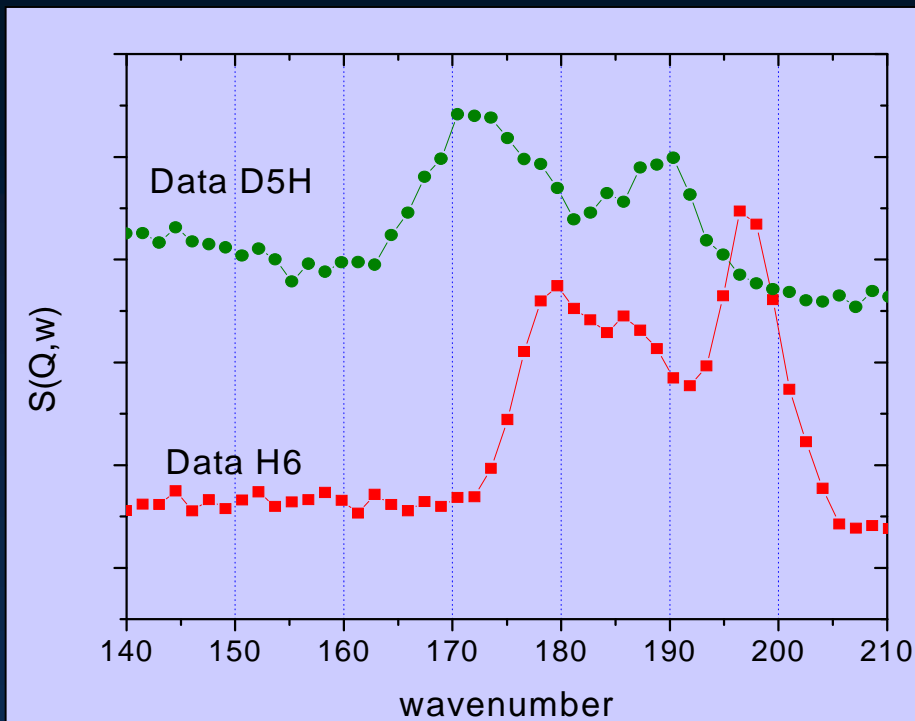
A 1D  
potential  
for a  
multi-D  
problem

Activation energy  
from NMR and  
QENS =  $125 \text{ cm}^{-1}$

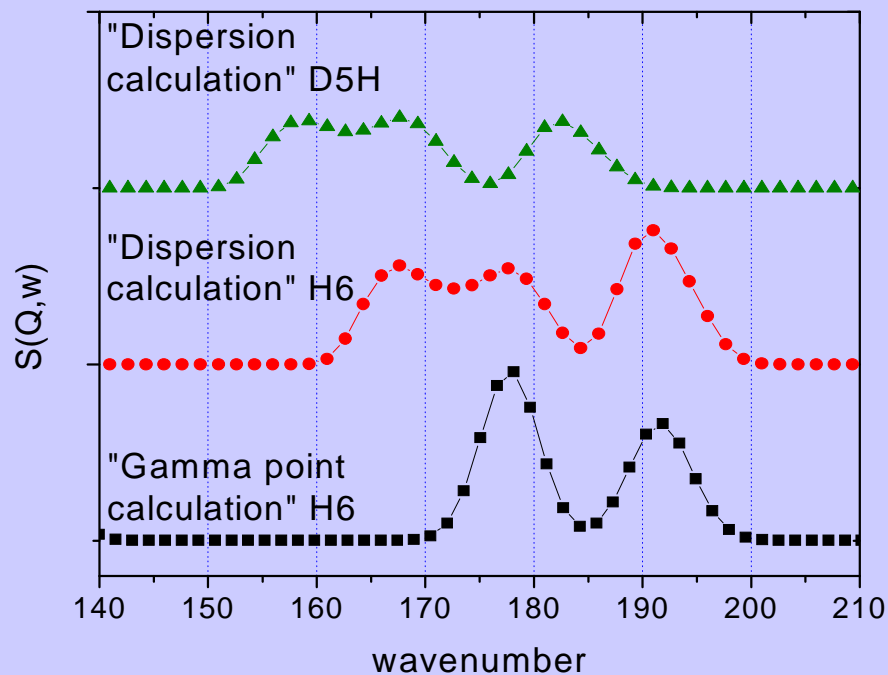
Active modes  
from VASP =  $129 \text{ cm}^{-1}$  &  $136 \text{ cm}^{-1}$

# ... AND LATTICE DYNAMICS CALCULATIONS



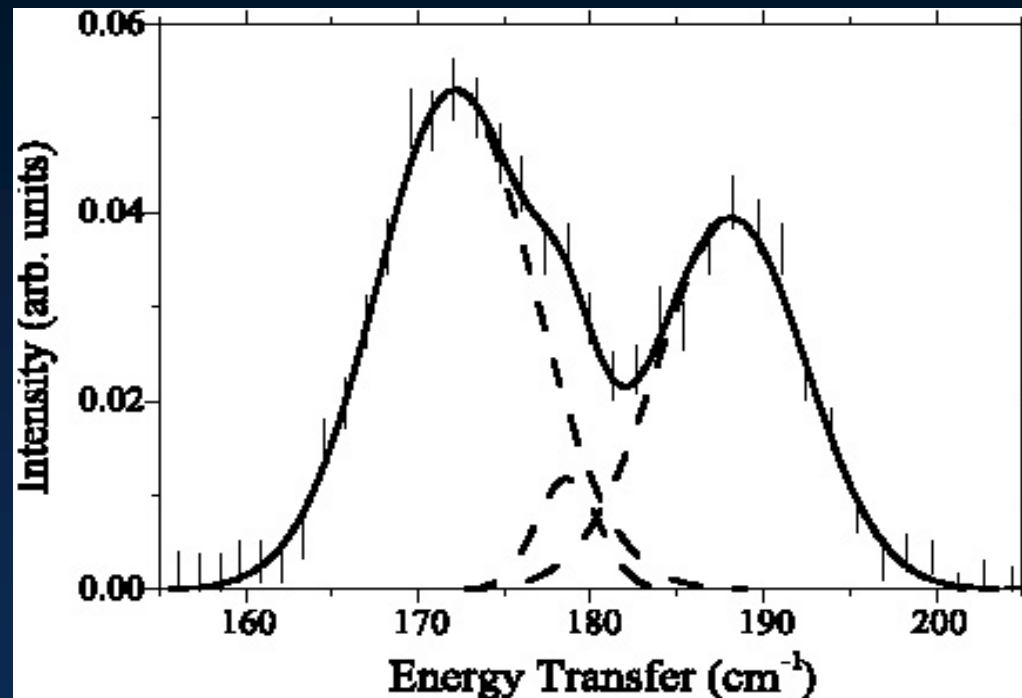


## SO ... DISPERSION OR TUNNELLING AT 180cm<sup>-1</sup>?



Tunnelling splitting  $\sim 0.25\text{cm}^{-1}$ , PRL 63 (1989) 1432

Dispersion at  $180\text{cm}^{-1}$ , Chem. Phys. Lett. 364 (2002) 34



Tunnelling peak at  $180\text{cm}^{-1}$ , F.Fillaux, Chem. Phys., 276 (2002) 181

# Urea

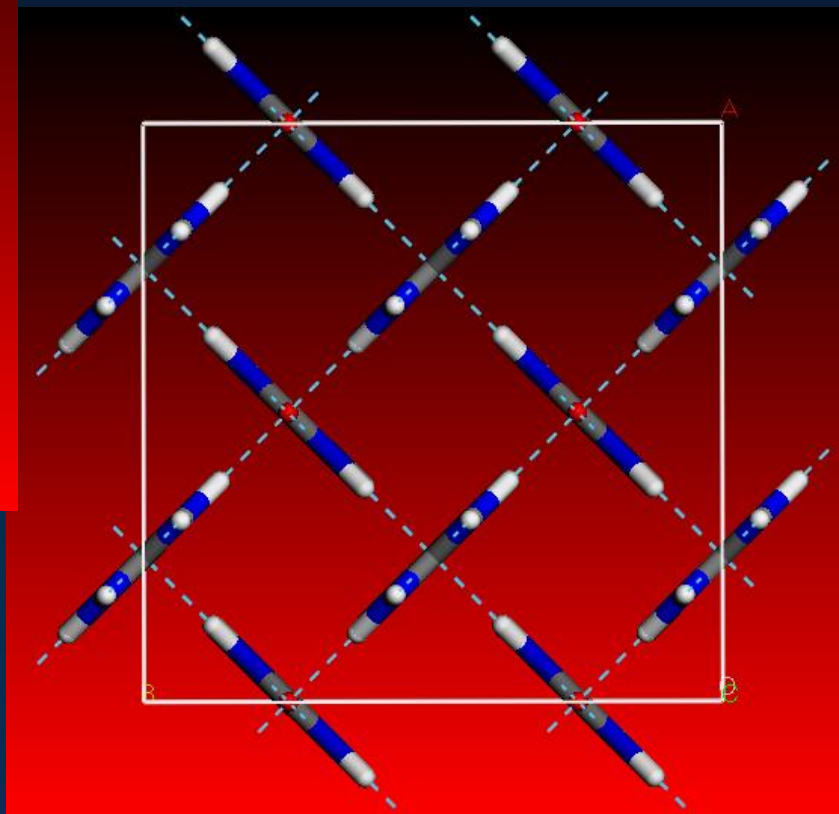
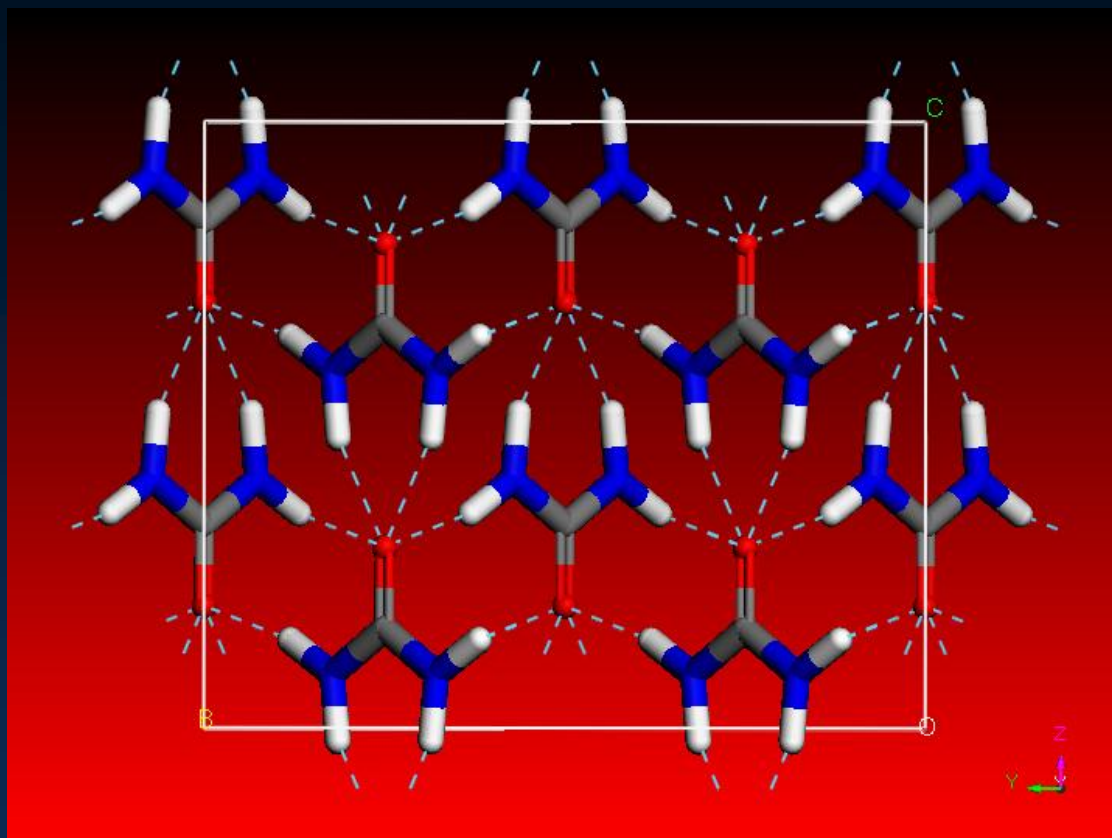
*extended 3D hydrogen bond network*

-multi-phonons

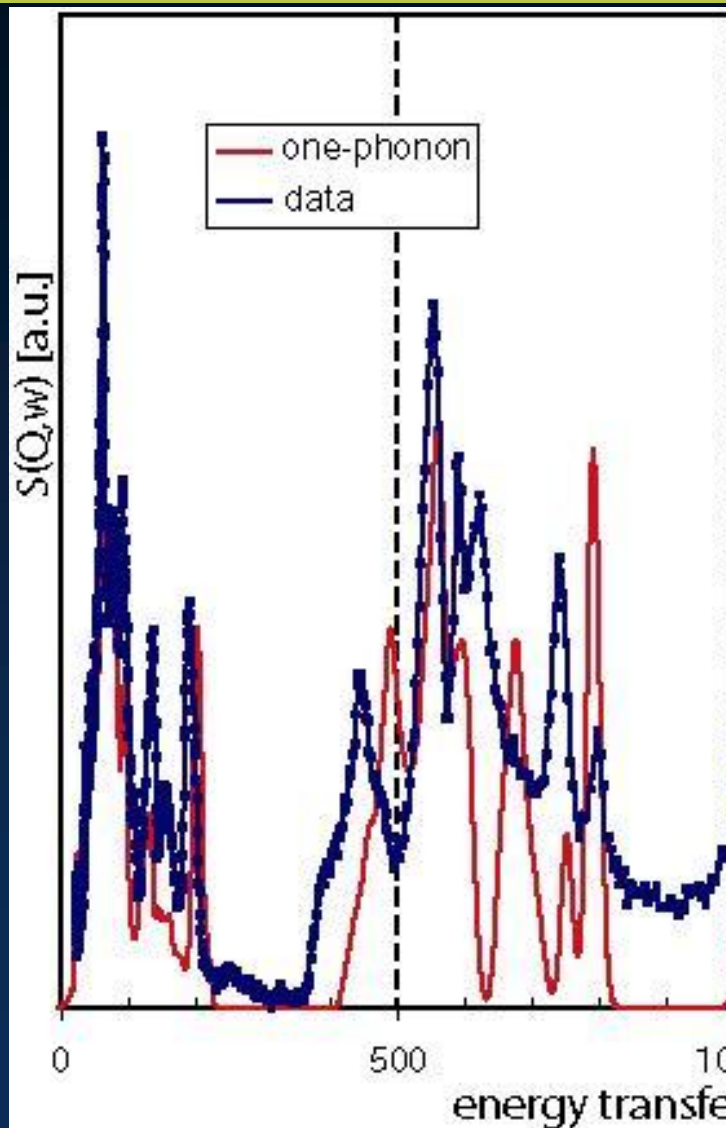
*(Krzysztof Parlinski)*

Chem.Phys 2002

# UREA - Dispersion in h-bond networks



# UREA - Dispersion in h-bond networks



PHONON 4.22

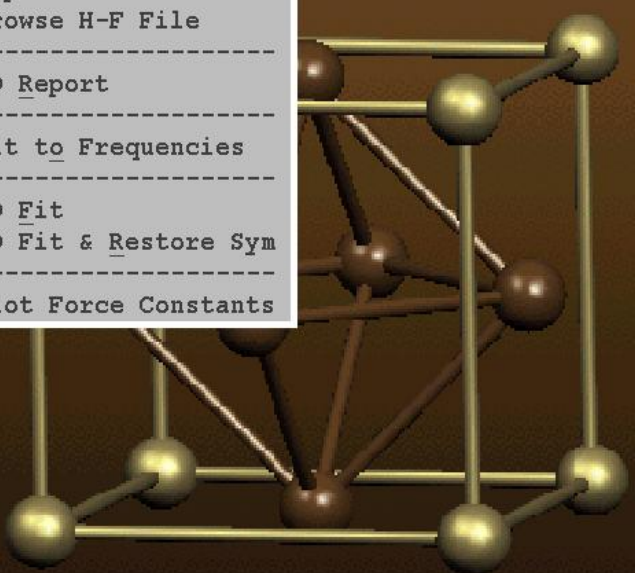
File Create Tools Help

glucose

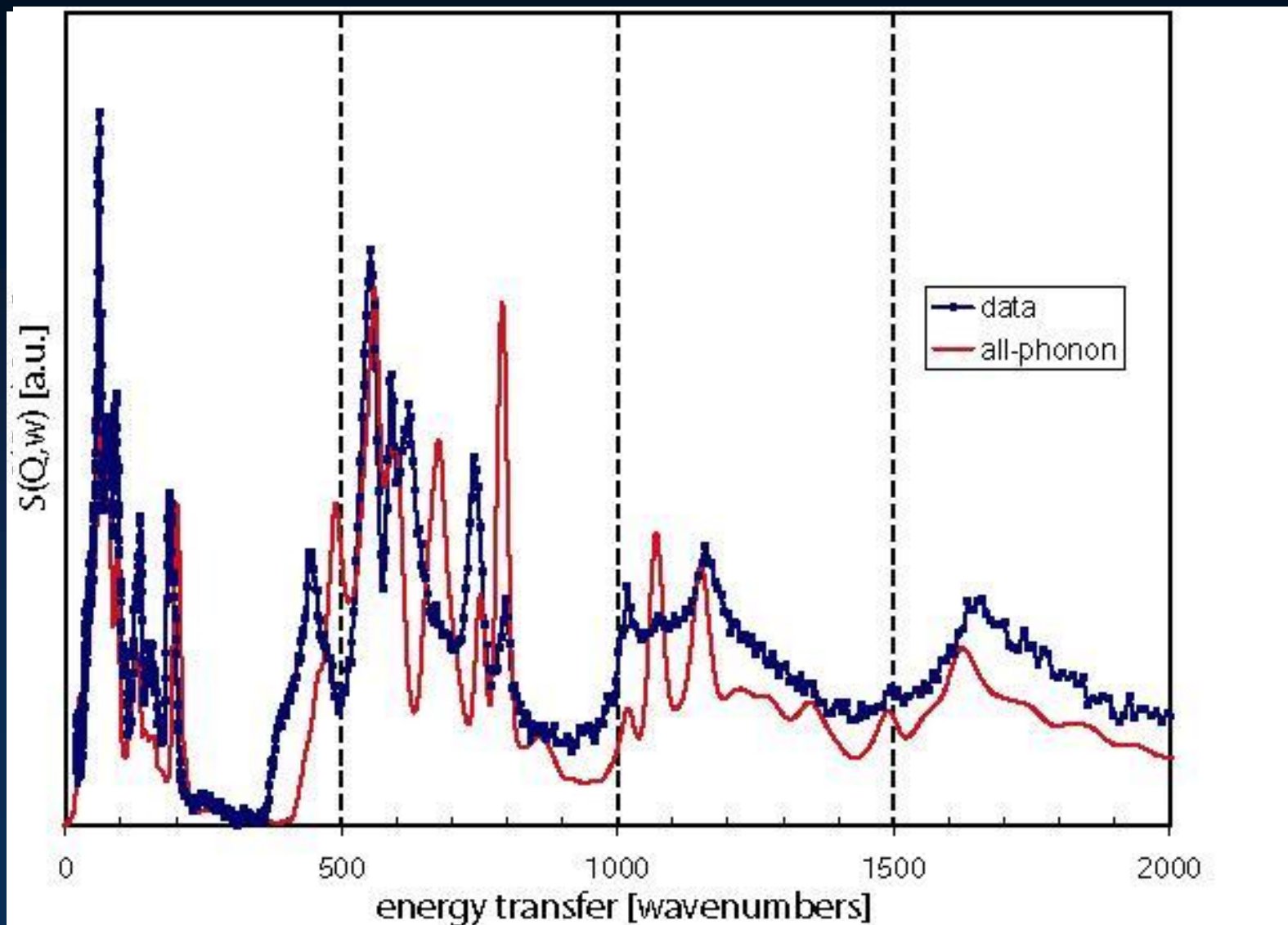
- Symmetry & Unit Cell
- Particles
- Interaction Range
- Hellmann-Feynman F.
- Potential Parameters
- 
- Dispersion Curves
- Density of States
- 
- Thermodynamic F.
- 
- Neutron Scattering

- Supercell
- Tran-Rot.Invariances
- Import H-F File
- Browse H-F File
- 
- DO Report
- 
- Fit to Frequencies
- 
- DO Fit
- DO Fit & Restore Sym
- 
- Plot Force Constants

**PHONON**



# UREA - multi-phonon spectra





# UREA - Dispersion in h-bond networks ( $400-800\text{cm}^{-1}$ )

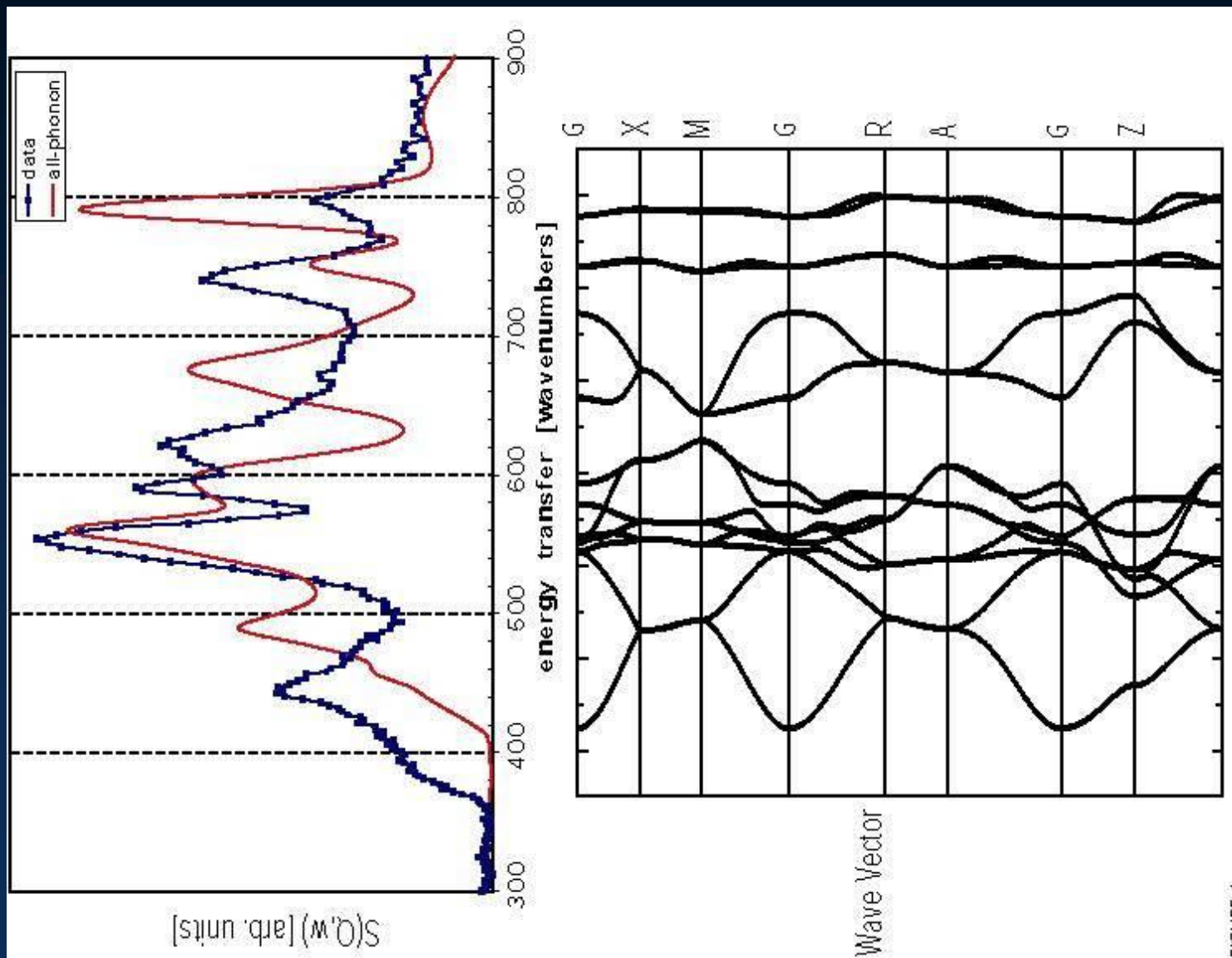
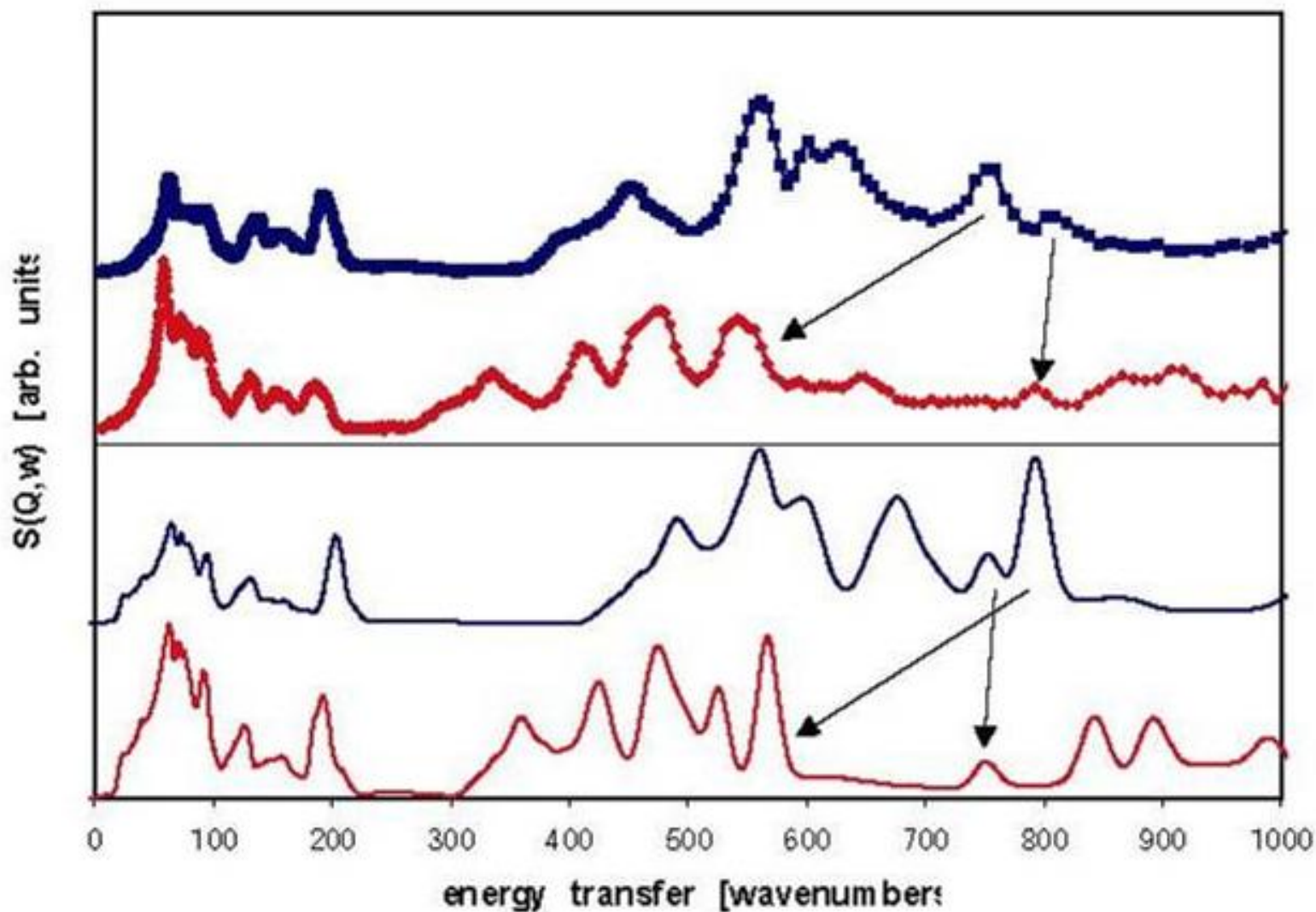


FIGURE 4

# UREA - H/D substitution



Good insight from VASP + PHONON approach

Continue to do this wherever possible

For more complex systems ...

1/ more inequivalent atoms (PHONON)

2/ often only vDOS data is available

3/ ~1000's steps of MD are more efficient than series of force calculations

4/ average over many structures

5/ no harmonic approximation in determining  $S(K, \omega)$

6/ better suited to liquid and amorphous systems

