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First-Principles Vibrational spectroscopy and lattice dynamics of materials in the solid state

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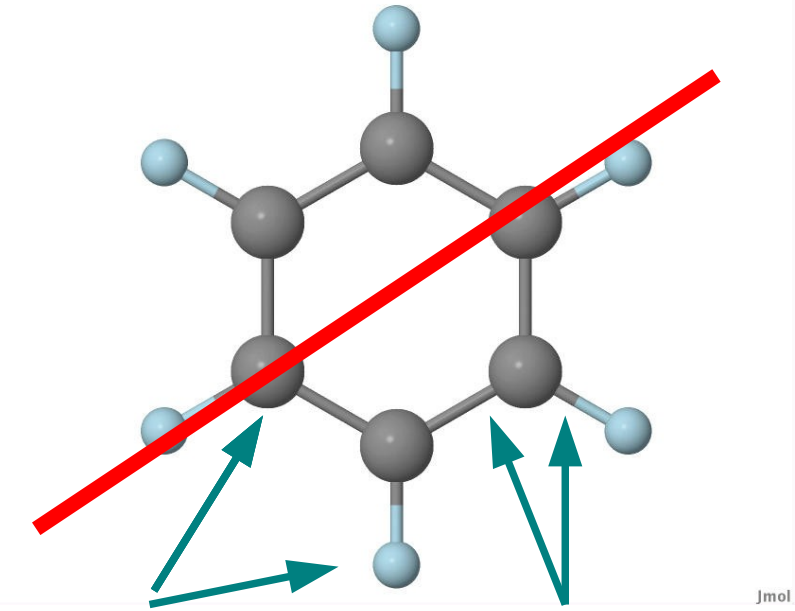
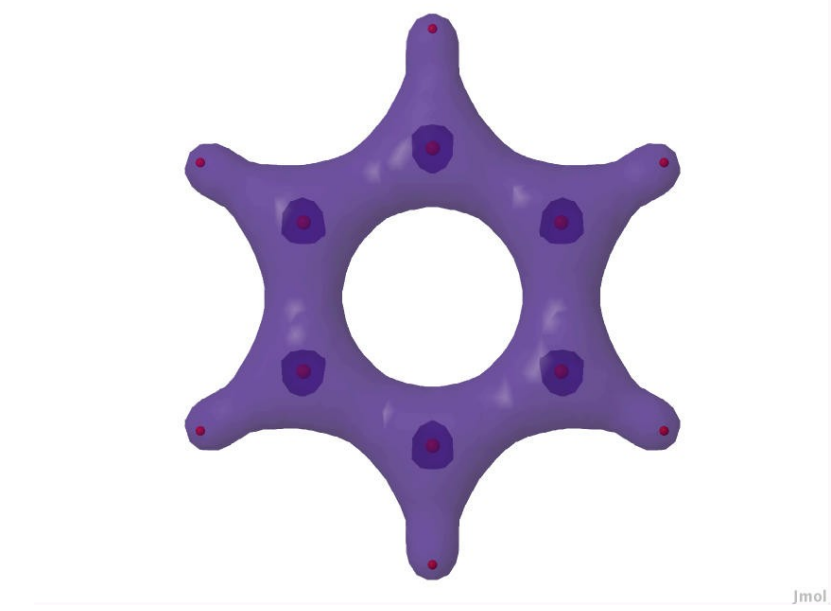
First principles modelling



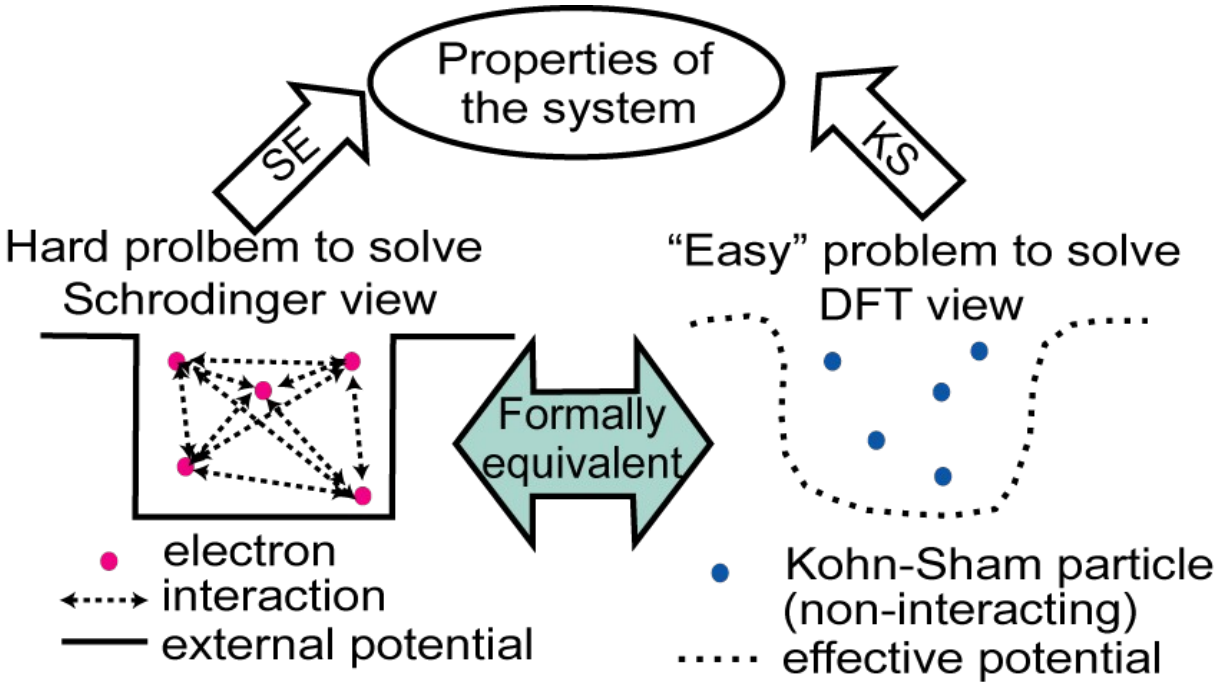
Atoms Bonds



Nuclei Electrons

$$\frac{-\hbar^2}{2m_e}\Psi + \hat{V}\Psi = E\Psi$$

Density Functional Theory



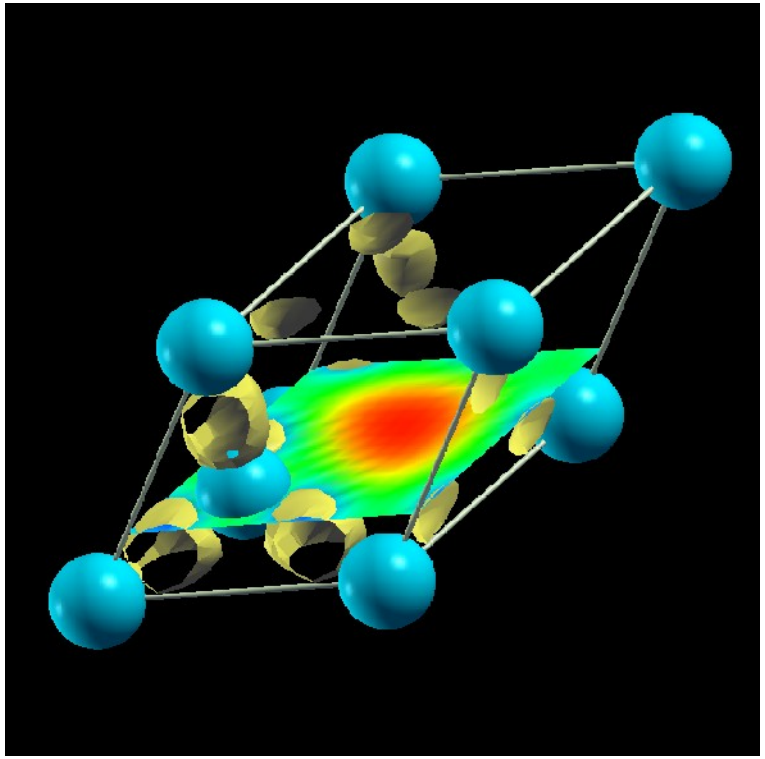
Approximations to exchange and correlation

- Local Density Approximation (LDA)
- Generalised Gradient Approximation (GGA)

Modified from Mattsson et al., (2005) *Modeling. Simul. Mater. Sci. Eng.* **13**, R1.

DFT with a Plane-wave basis

- Periodic boundary conditions applied to ions orbitals, electron densities.
- Electron density represented on *grid*.
- Basis coefficients of orbitals also stored on grid in **G**-space.
- Use FFTs to evaluate terms in Hamiltonian.
- Never construct Hamiltonian, only compute effect of operator.
- Kohn-Sham equations solved using SCF
- PW basis is efficient, accurate, robust.
- PW basis requires pseudopotentials.
- Mature technology – good algorithms.
- Robust in use, even by non experts.



The CASTEP project

- Original 1990s CASTEP code by Mike Payne/Accelrys reached end of life.
- Complete re-engineering of a new plane-wave code from scratch beginning 1999.
- Core "Developer Group" of P. Hasnip, S. Clark, M. Probert, C. Pickard, M. Segall, P. Lindan, (Payne) and in 2002, K. Refson.
- Commercialised by Accelrys and integrated into Materials Studio
- Aim: build a flexible, well-engineered development platform for new physics using modular software practices and documented API specification.
- Parallel/HPC use built in from start.Release 1 in late 2001.
- Now at release 6.0.
- Excellent "Core" functionality with many additional capabilities; Structure, dynamics and many properties.

CASTEP Capabilities

CASTEP has a variety of Hamiltonians and XC functionals

- *Pure local DFT (LDA,LSDA, PBE, RPBE, WC,...)*
- *Hybrid HF exchange methods (HF, Screened HF, PBE0, B3LYP*
- *Model methods (LDA+U)*
- *More under development (TDDFT, GW,..).*

CASTEP can perform many spectroscopic calculations

- *IR and raman spectroscopy (vibrational/phonon)*
- *INS and IXS spectroscopy (vibrational phonon)*
- *Conduction-band optical dielectric spectra (EELS etc)*
- *Core level spectroscopy (ELNES, XANES)*
- *NMR chemical shifts*

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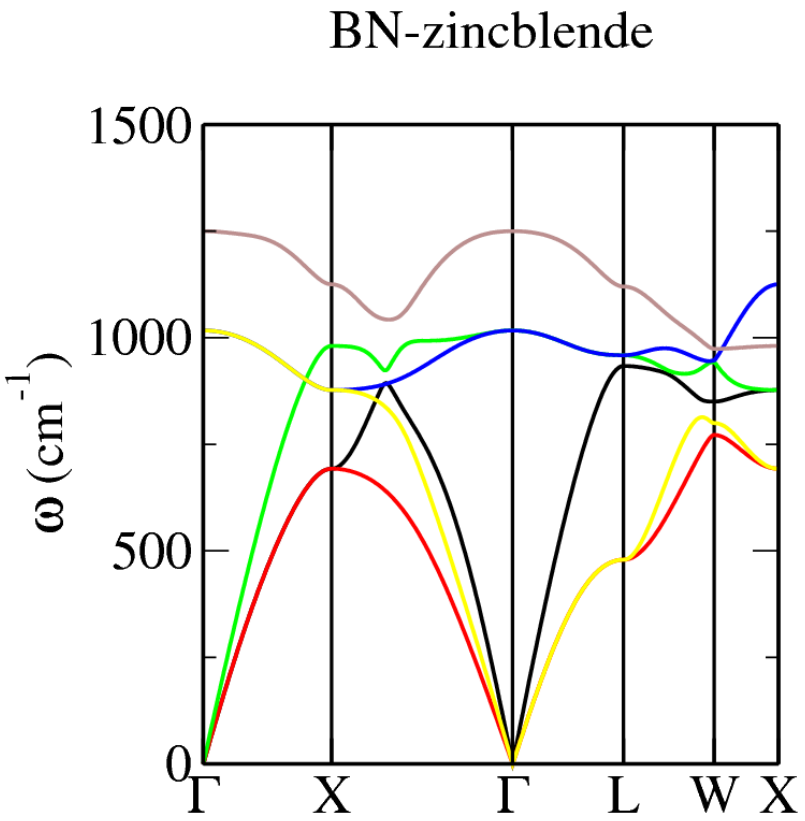
Vibrational Spectroscopy in CASTEP

- Full *ab-initio* lattice dynamics code
- Plane-wave basis w pseudopotentials
- DFPT and supercell methods
- Phonons across full BZ by interpolation
- Symmetry analysis of eigenvectors
- Highly parallel for HPC use (can use 1000's of cores)



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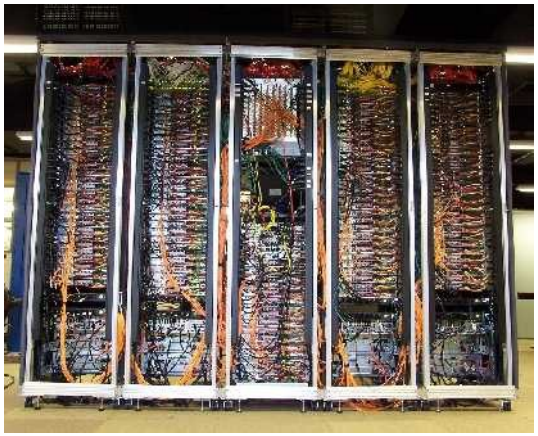
Parallel Supercomputing

Parallel supercomputing enables large calculations and high throughput.



http://www.hector.ac.uk

http://hpcsg.esc.rl.ac.uk/scarf/

Approaches to first principles Lattice Dynamics

Density-Functional Perturbation Theory

- Works with LDA/GGA Hamiltonians
- Only primitive cell calculations required
- Fourier interpolation of dynamical matrices to entire BZ from grid of q-points.
- Can compute dielectric permittivity and Born effective charges
- LO/TO splitting included.
- IR absorptivity or Raman activity included

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Modelling the spectrum

Orientationally averaged infrared absorptivity

$$I_m = \left| \sum_{\kappa,b} \frac{1}{\sqrt{(M_\kappa)}} Z^*_{\kappa,a,b} u_{m,\kappa,b} \right|^2$$

Raman cross section

$$I^m_{\text{raman}} \propto \left| \boldsymbol{e_i} \cdot \boldsymbol{A^m} \cdot \boldsymbol{e_s} \right|^2 \frac{1}{\omega_m} \left(\frac{1}{\exp(\hbar \omega_m / k_B T) - 1} + 1 \right)$$

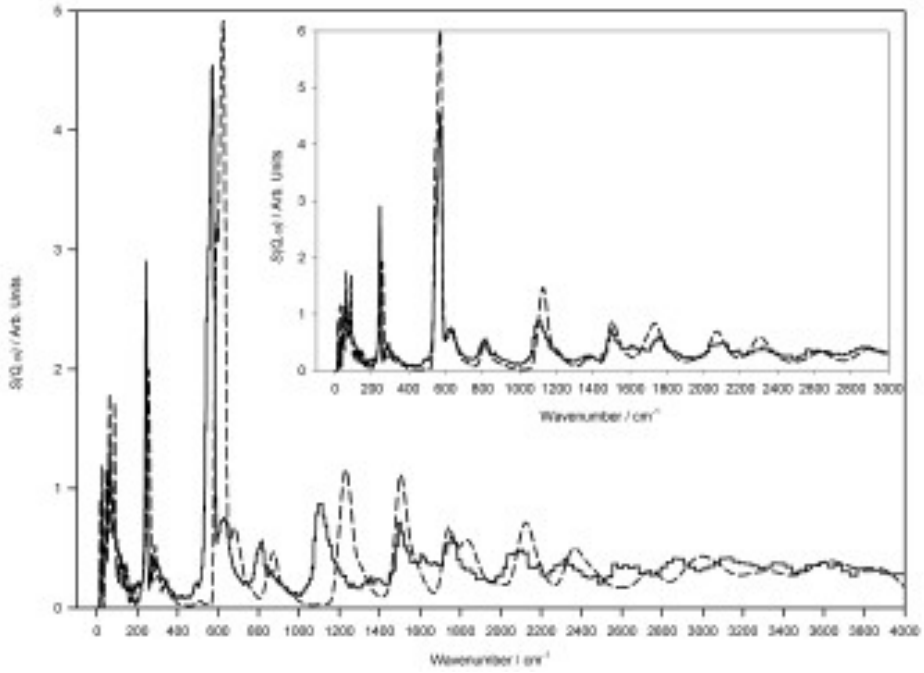
$$A^m_{\alpha,\beta} = \sum_{\kappa,\gamma} \frac{\partial^3 E}{\partial \boldsymbol{\mathcal{E}}_\alpha \partial \boldsymbol{\mathcal{E}}_\beta \partial u_{\kappa,\gamma}} u_{m,\kappa,\gamma} = \sum_{\kappa,\gamma} \frac{\partial \epsilon_{\alpha\beta}}{\partial u_{\kappa,\gamma}} u_{m,\kappa,\gamma}$$

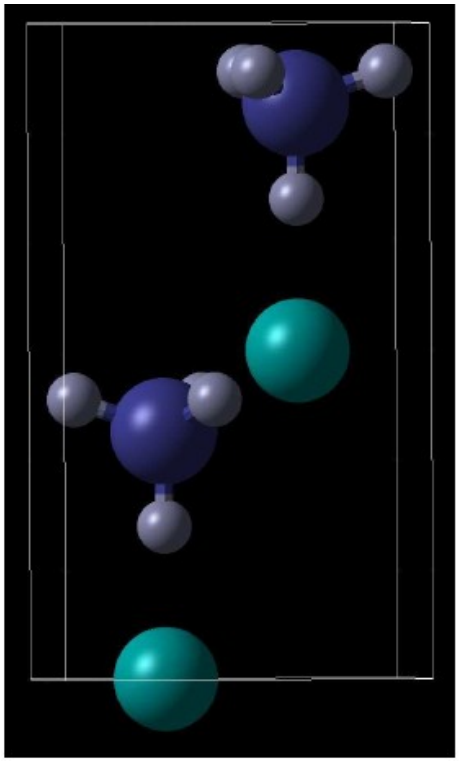
Inelastic neutron cross section

$$S^n(\omega_m) = \int d\boldsymbol{Q} \sum_\kappa \sigma_\kappa \left\langle \frac{(Q \cdot u_{m,\kappa})^{2n}}{n!} \exp(-(Q \cdot u_{m,\kappa})^2) \right\rangle$$

Spectral response to light depends on response of electrons; for neutrons only nuclei.

INS Spectrum of Ammonium Fluoride

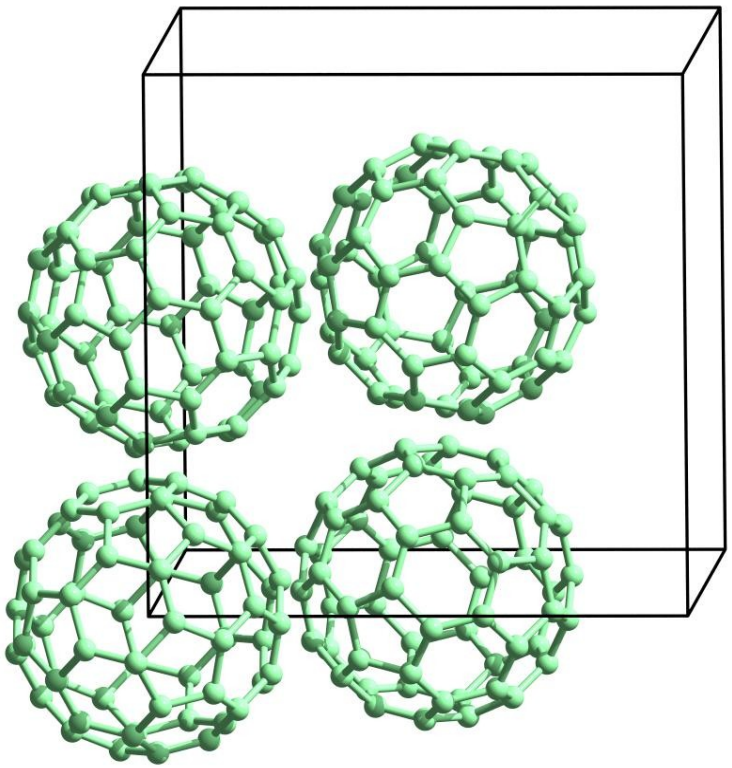




- NH4F studied in the ISIS TOSCA spectrometer.
- Collaborator: Mark Adams (ISIS)
- Structurally isomorphic with ice ih
- INS spectrum modelled using ACLIMAX software (A. J. Ramirez Cuesta)
- Predicted INS spectrum agrees with experiment
- NH4 libration modes in error by ? 5%.
- Complete mode assignment achieved.

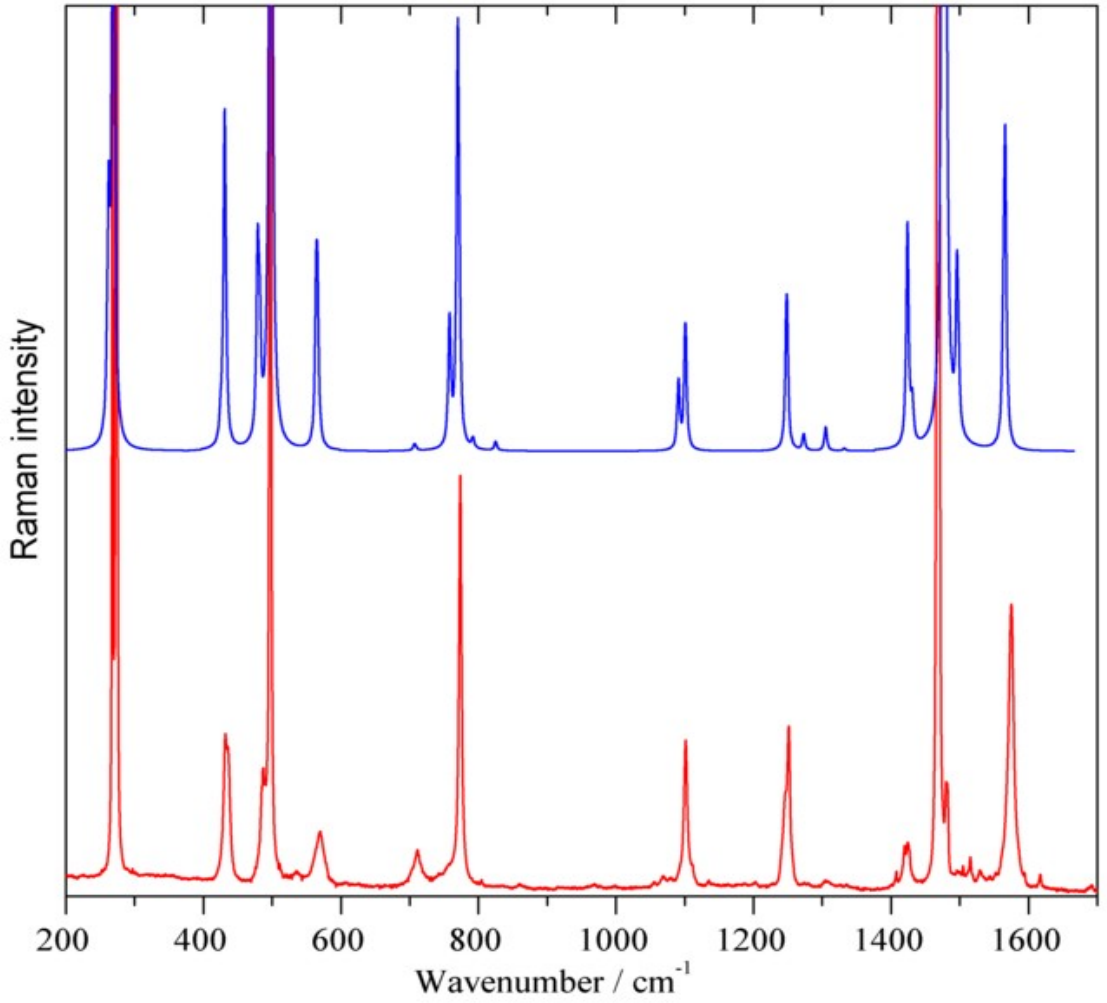
Adams, Refson & Gabrys, Phys. Chem. Chem. Phys 7, 3685 (2005)

Raman and ir spectroscopy of C_{60}



- Above 260K takes Fm3m structure with dynamic rotational disorder
- m3m point group lower than I_h molecular symmetry
- Selection rules very different from gas-phase.
- Intramolecular modes and factor group splitting seen.
- Try ordered Fm3 model for crystal spectral calculation.
- Full CASTEP DFPT lattice dynamics calculation on Fm-3 and Pa3 phases
- Complete assignment of vibrational modes [Phys Chem Chem Phys (2011).]

GGA Raman spectrum of C_{60}



INS

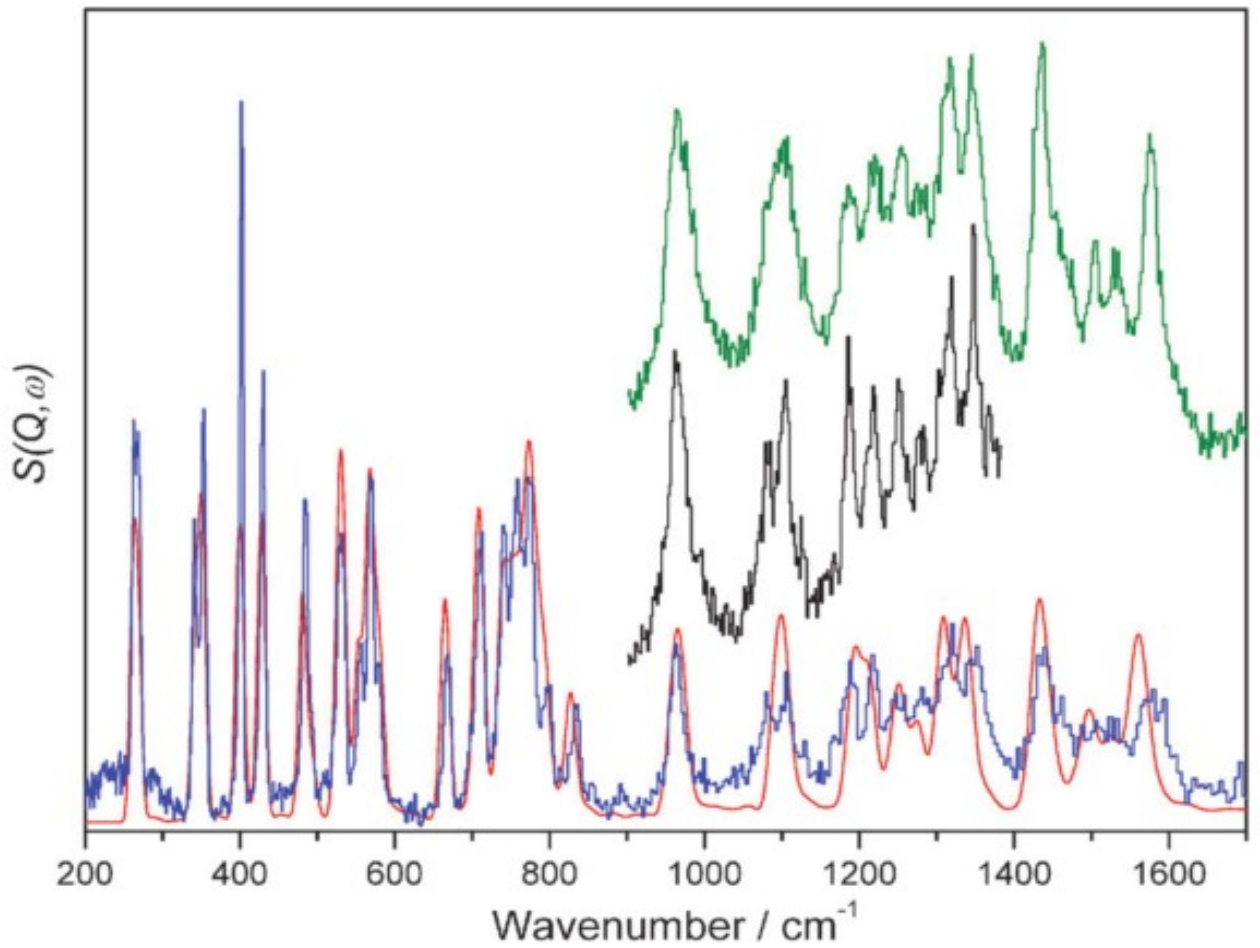
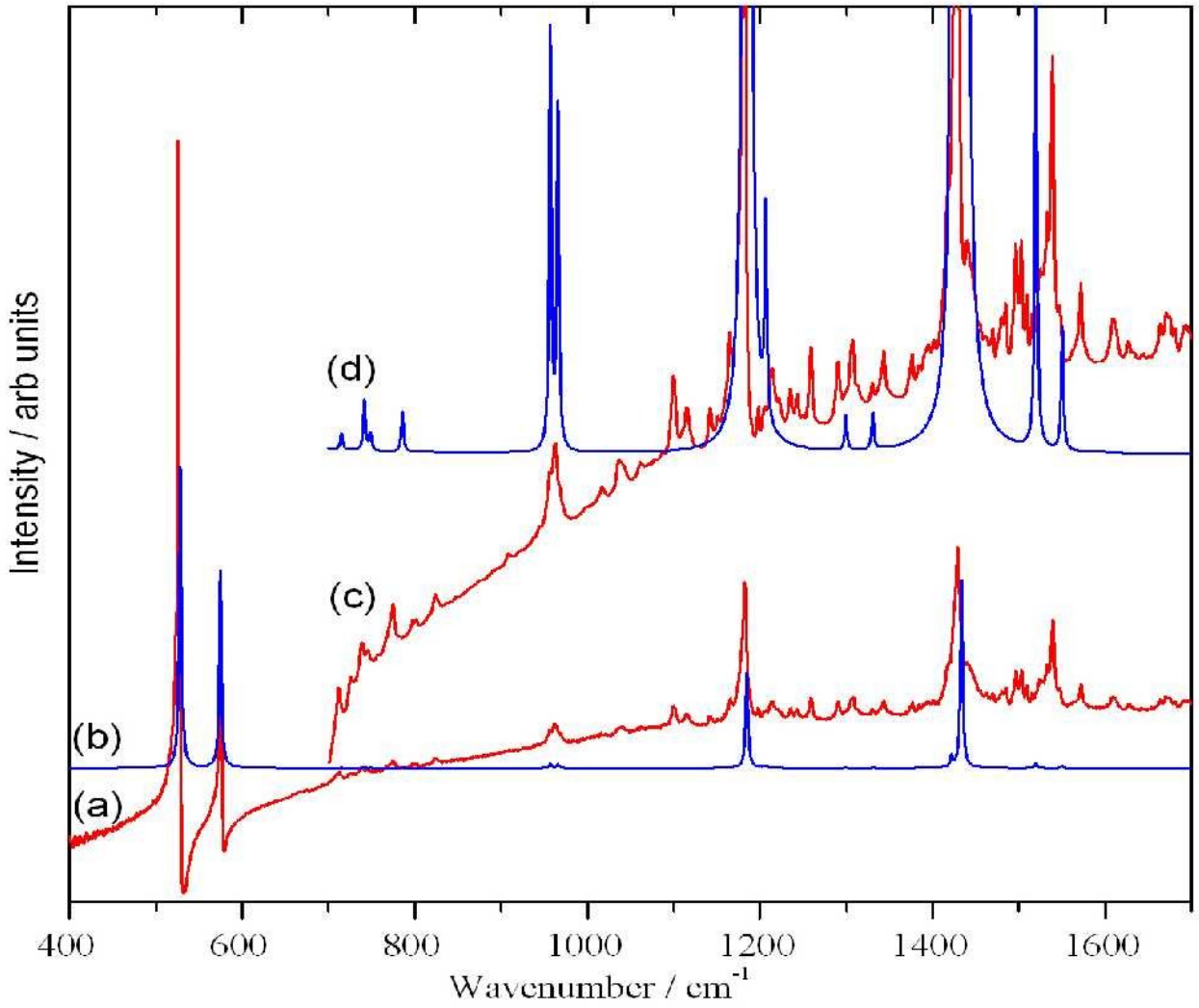


Fig. 6 INS spectra of the internal modes of C_{60} in the $Pa\bar{3}$ phase: recorded on TOSCA at 20 K (blue), recorded on MARI at 5 K with 1815 cm^{-1} (olive green) and 1452 cm^{-1} (black) incident energy compared with that generated from the CASTEP calculation (red).

GGA infrared spectrum of C_{60}

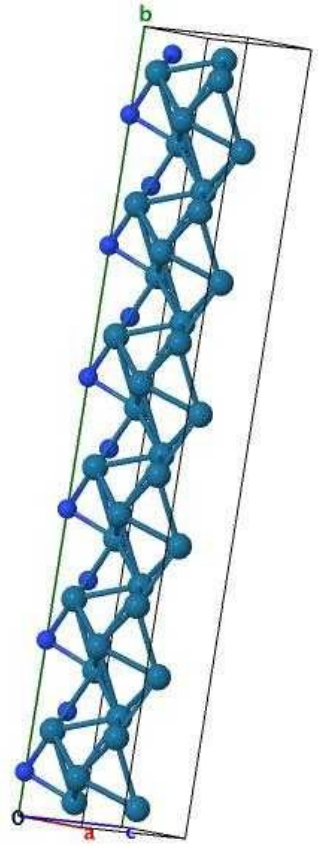


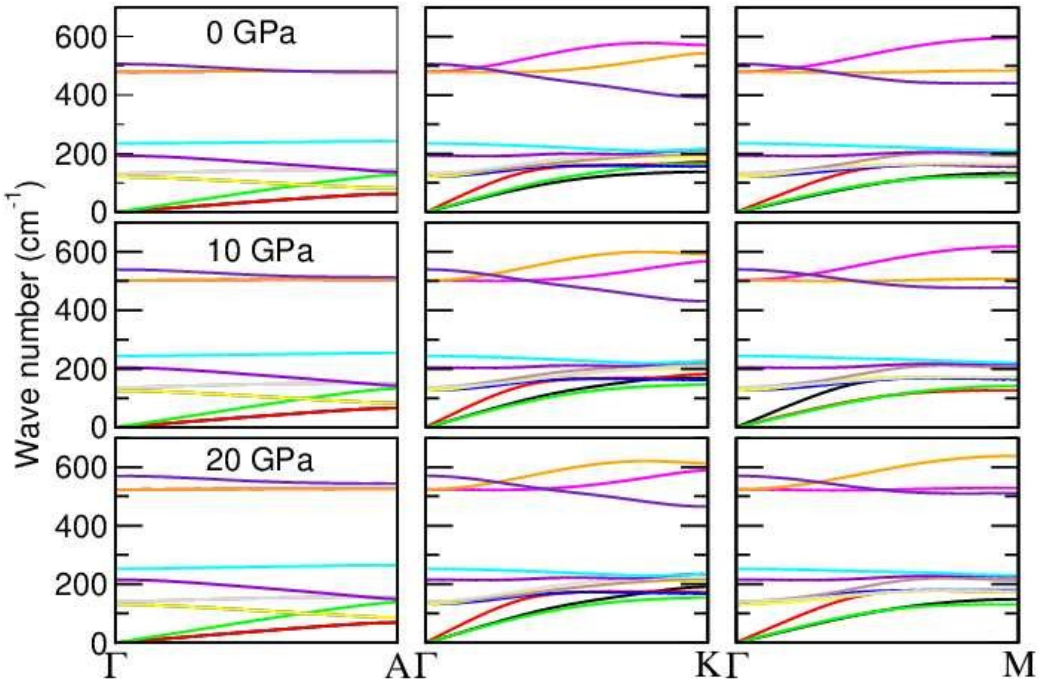
Approaches to first principles Lattice Dynamics

Finite displacement and supercells

- Works with most general Hamiltonians (PBE0/B3LYP, LDA+U, DFT+D, USPs)
- Accurate, but computationally expensive
- Can not compute dielectric permittivity or Born effective charges
- Can not include LO/TO splitting.
- Can not compute IR or Raman absorptivity/activity

Re3N at high pressure





Friedrich,et al Phys. Rev. ***B*** *82, 224106 (2010).*

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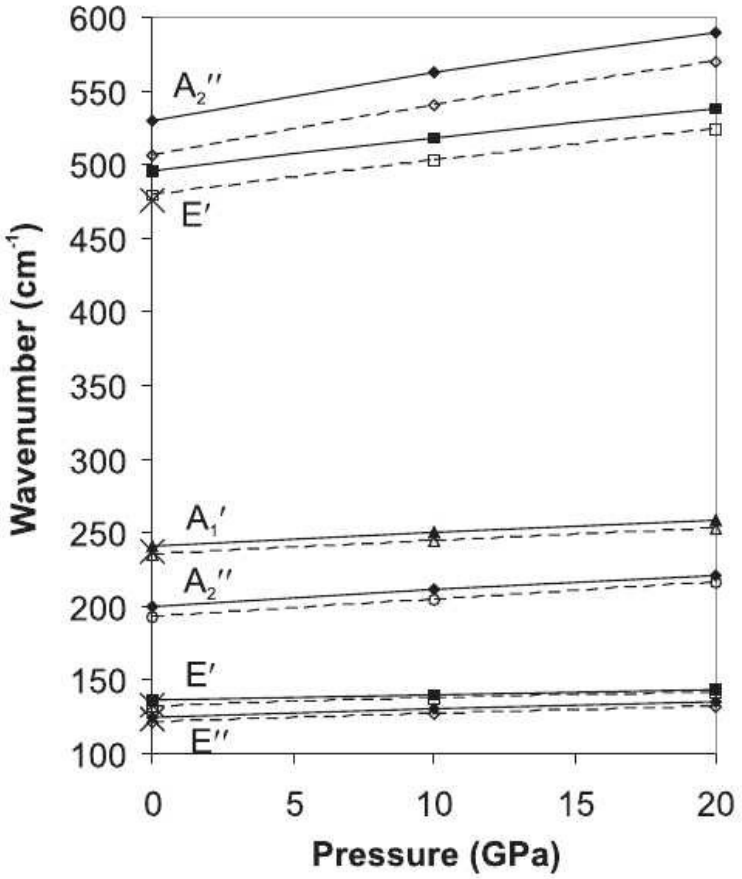
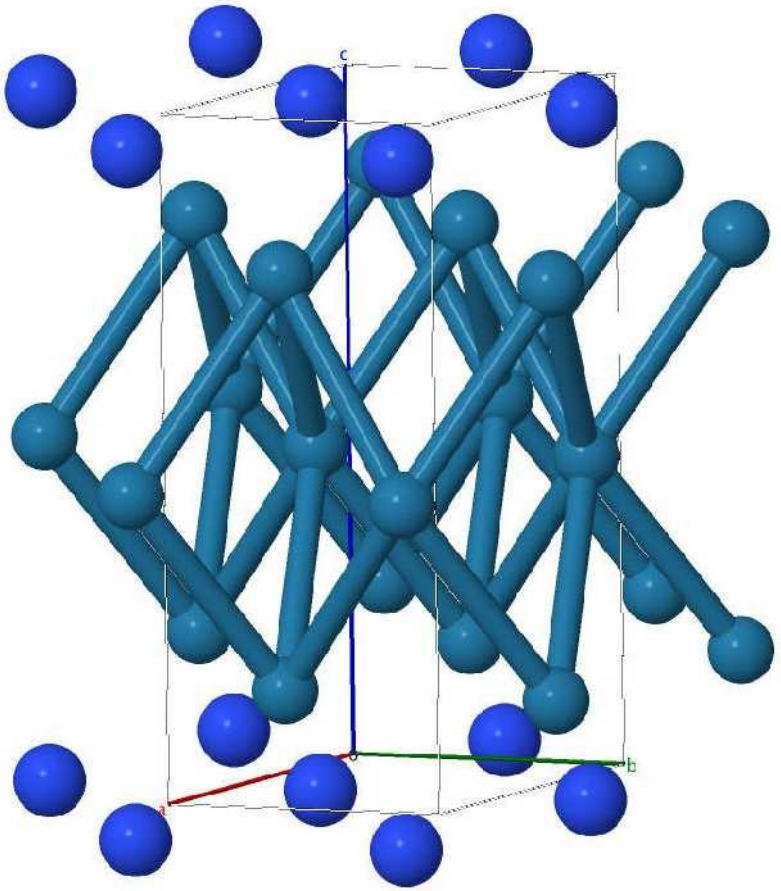
High Pressure – Re_3N





Phys Rev B 82, 244106 (2010)

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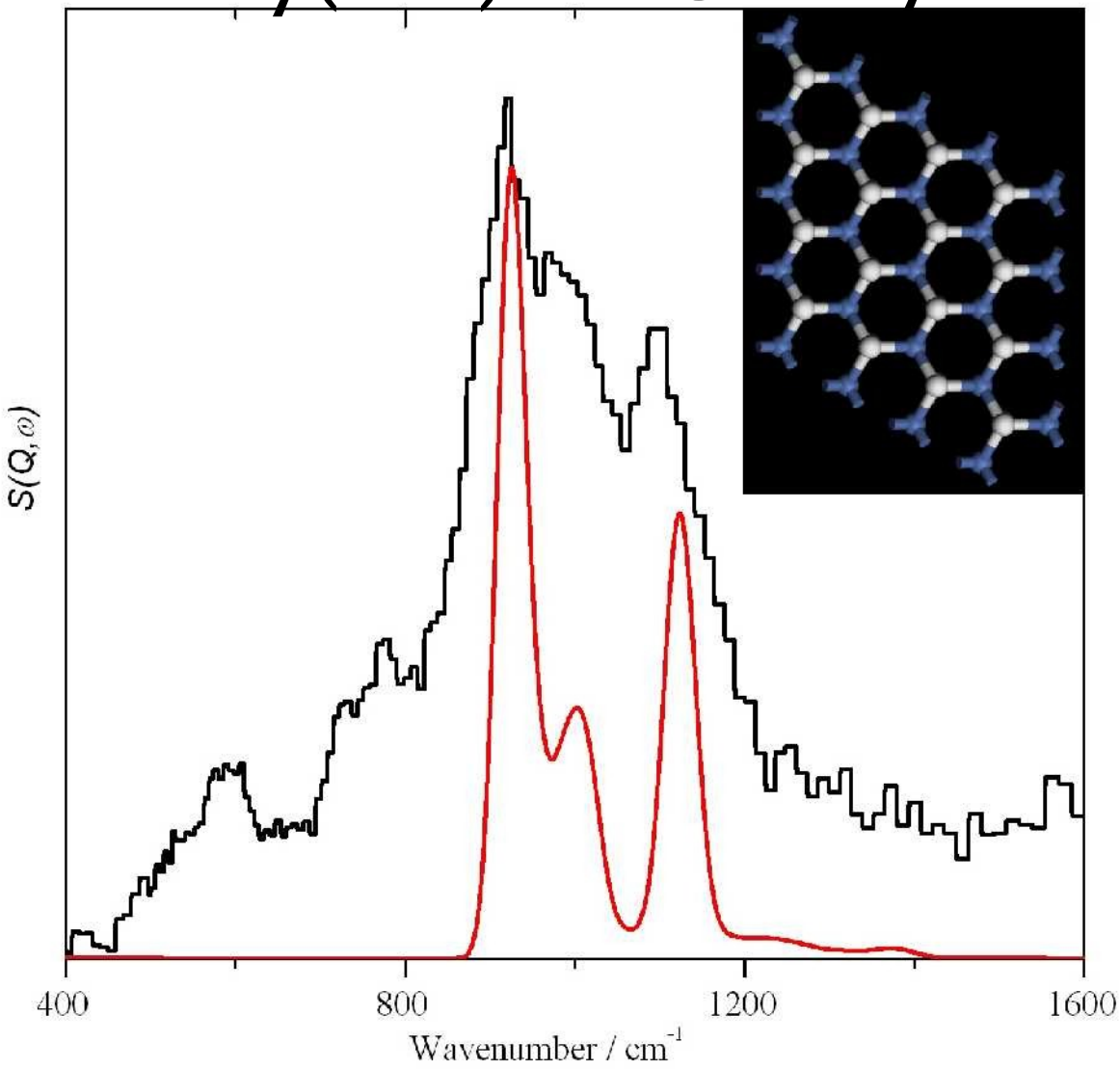
Raney(TM) Ni Catalyst

INS spectrum of hydrogen on Raney Ni.

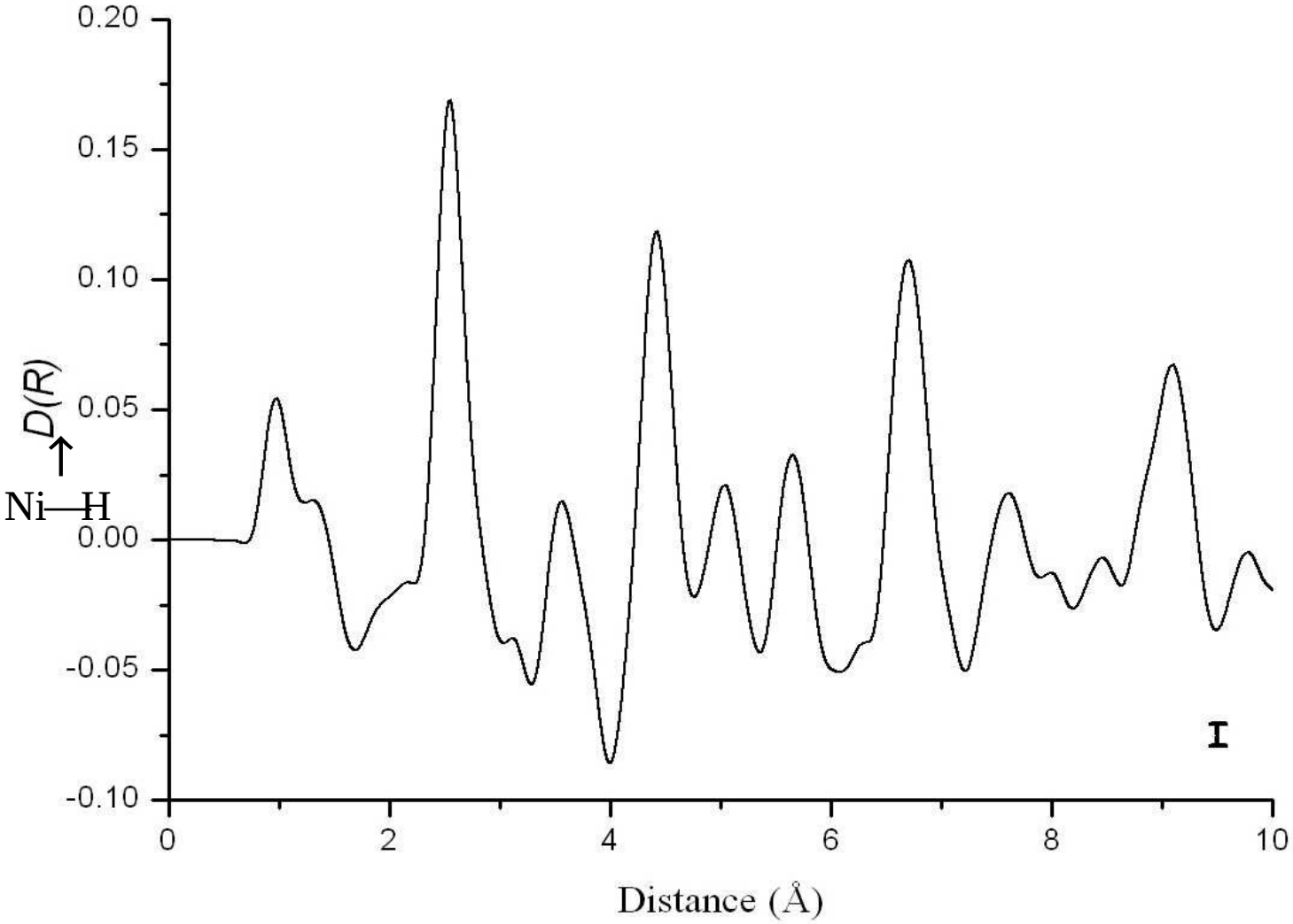
expt (TOSCA)

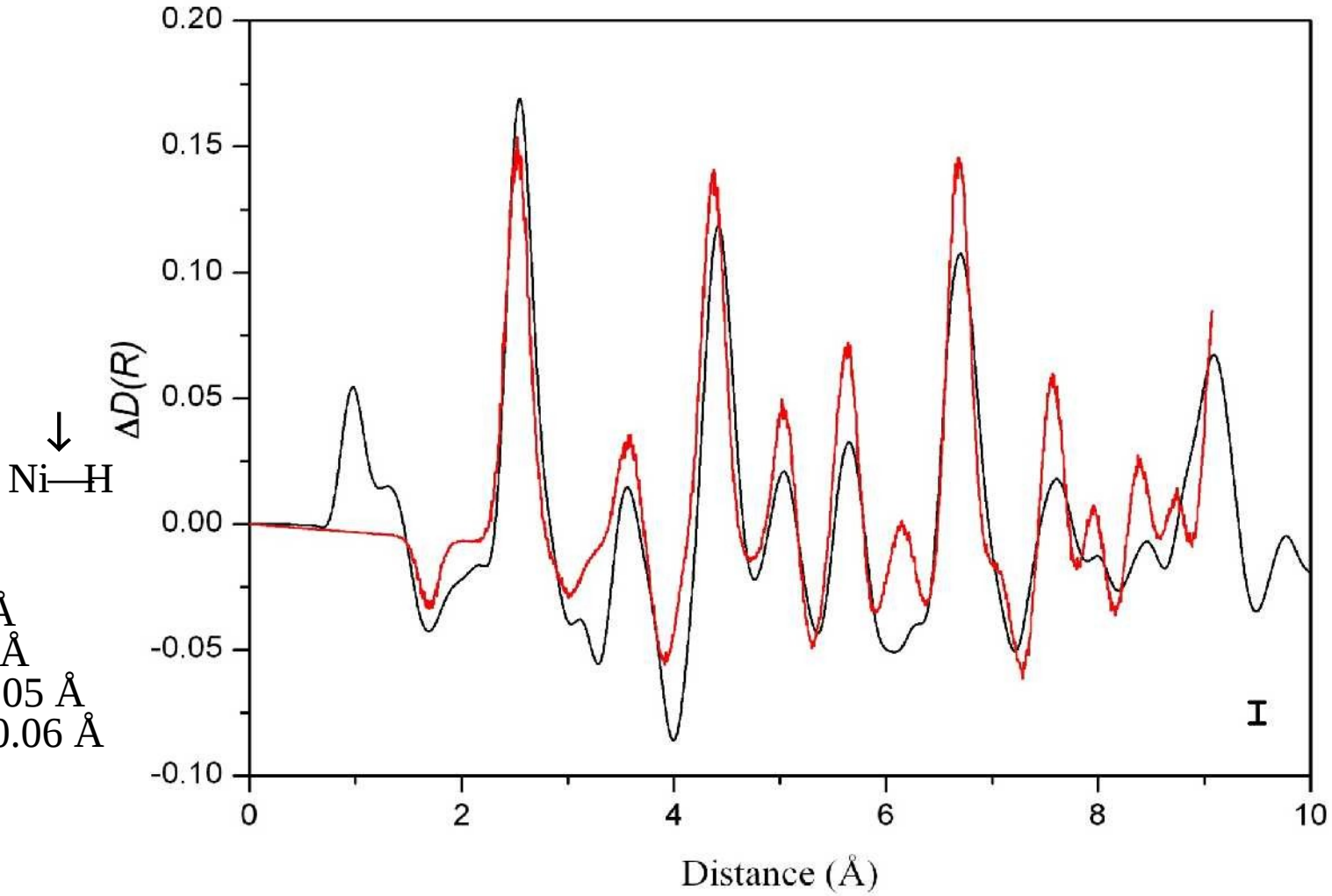
Full dispersion calc. for Ni(111)/H (scaled by 0.93).



Stewart Parker, *et al* Chem. Comm. **46**, 2959-61 (2010).

Pair distribution function, *D(R)*, for hydrogen on Raney nickel.
Fourier transform of the normalised difference between the two *S(Q)*.





Ni—H

Ni—H
Neutron: 1.68 Å
Ab initio: 1.68 Å
LEIS: 1.65 ± 0.05 Å
LEED: 1.84 ± 0.06 Å

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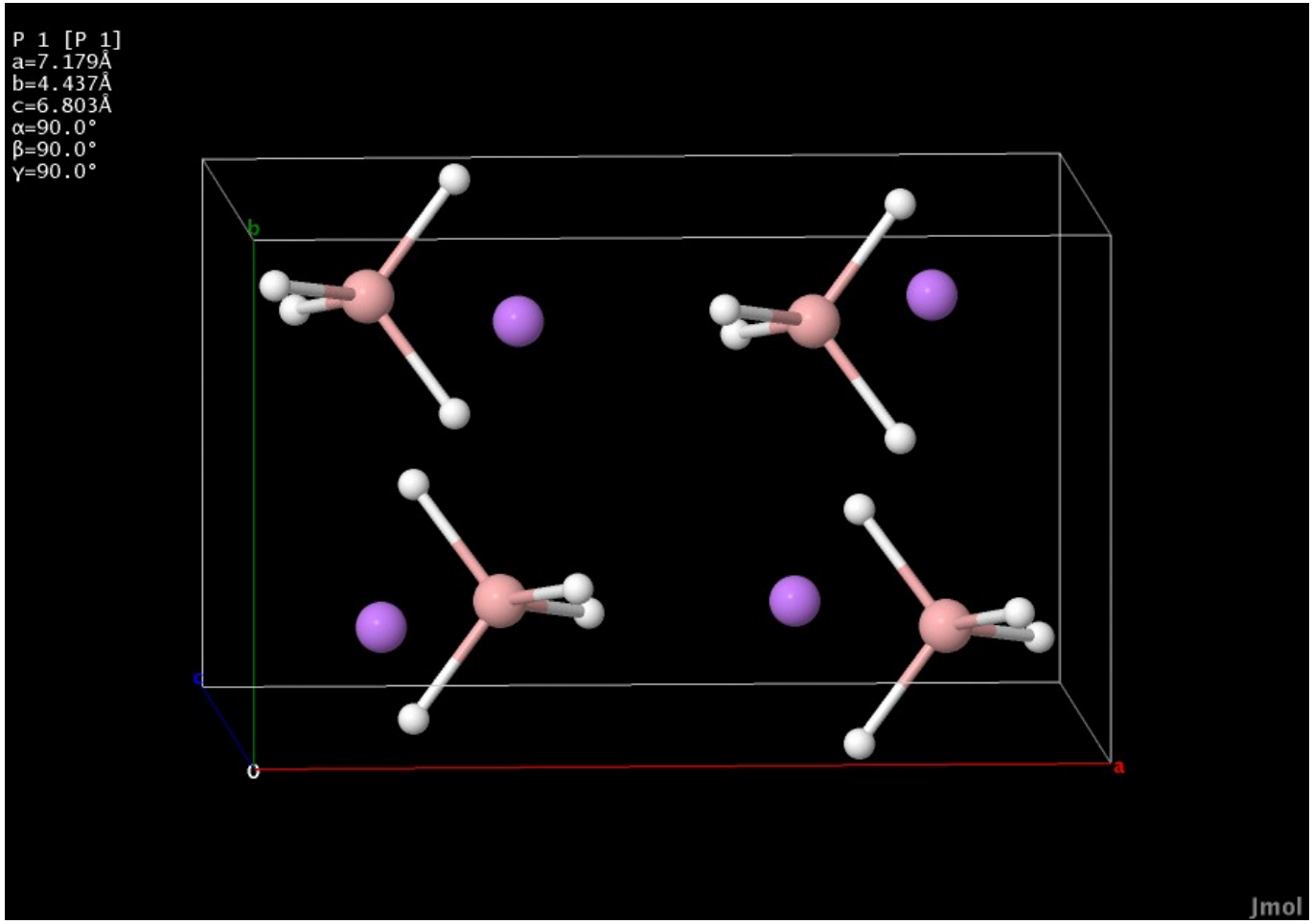
H-storage materials

H transport in LiBH4



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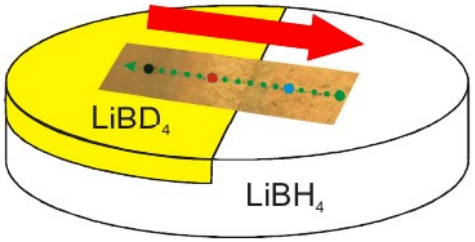
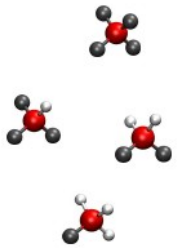
Raman studies of H transport

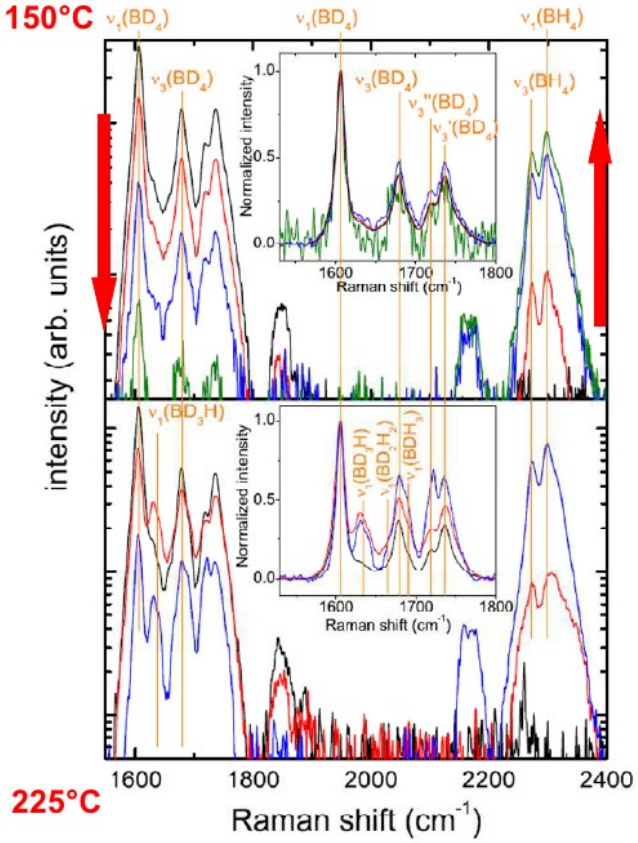
Expts: A. Borgschulte, EMPA
With A.J. Ramirez Cuesta, ISIS



@ low temperature
transport of intact BH_4 units

@ >225°C
all isotopomeres are present





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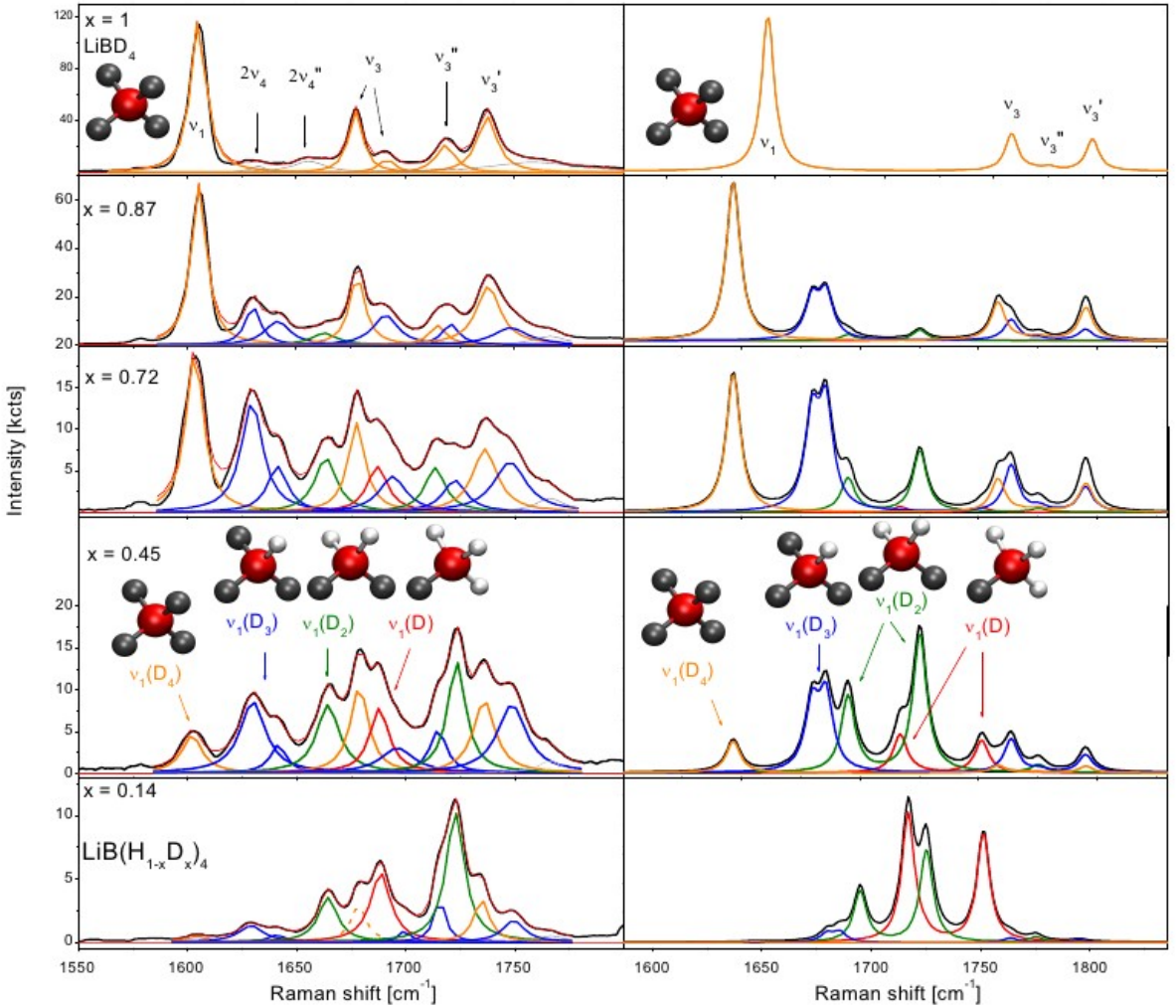
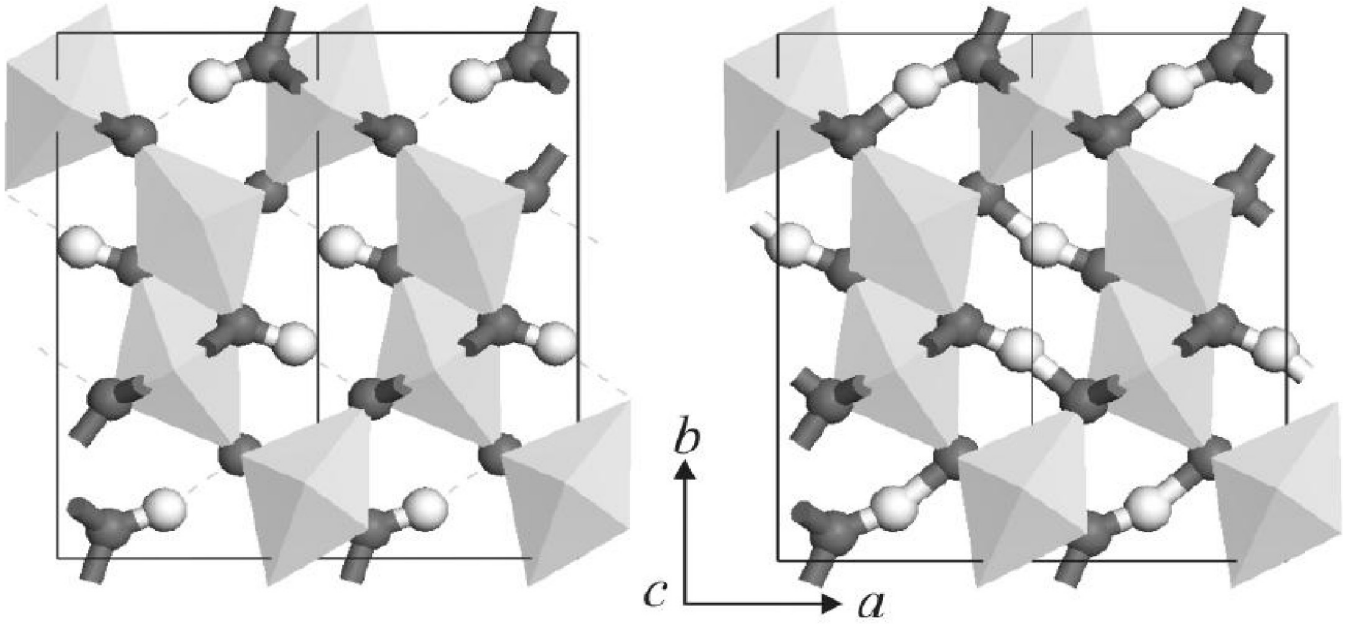
CASTEP Raman calculation

Measurement Calculation



R. Gremaud et al, PRB 80 100301(R) (2009)

Diaspore (AlOOH)



Canonical example of hydrous mineral

A. Friedrich, D. J. Wilson, E. Hausshl, B. Winkler, W. Morgenroth, K. Refson, and V. Milman, Phys. Chem. Miner. 34, 145 (2007).

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Inelastic X-Ray scattering of diaspore

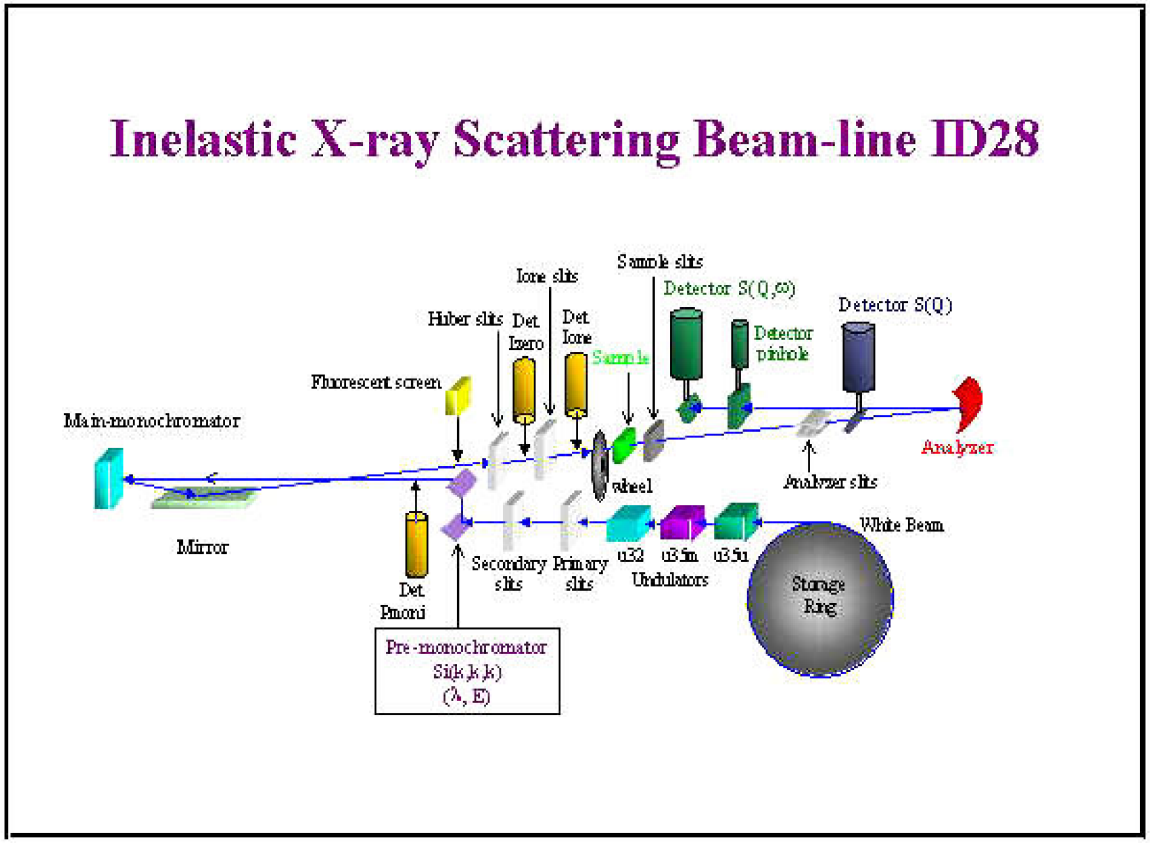
Conventional wisdom: OH groups interact weakly and modes show little dispersion.

Ab-initio calculations frequently show significantly dispersive OH stretch modes.

INS is not feasible in OH stretch range of 3000-4000 cm^{-1}.

First IXS measurement of OH stretch dispersion ever performed at ID28 at ESRF

B. Winkler, *et. al.* Physical Review Letters, 101, 065501 (2008).



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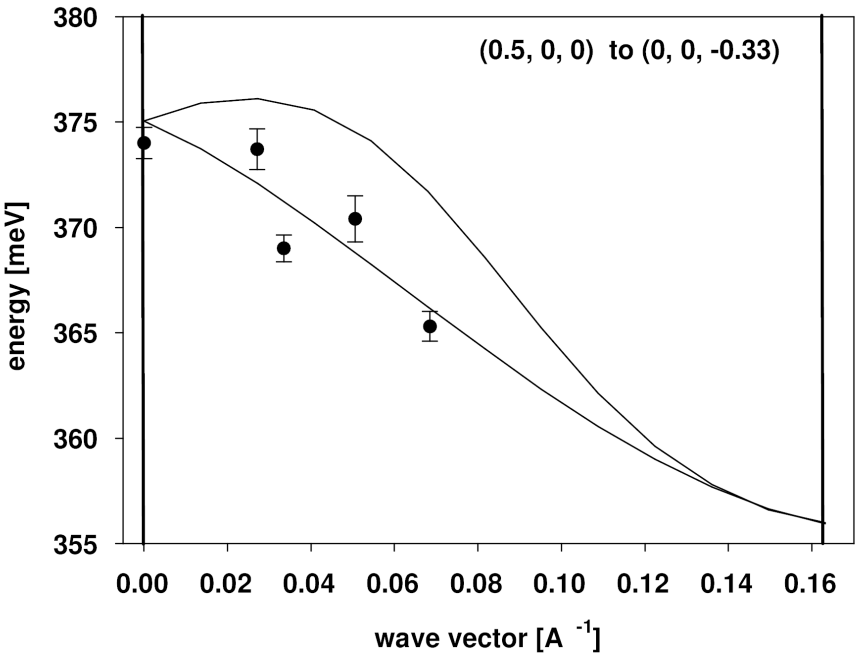
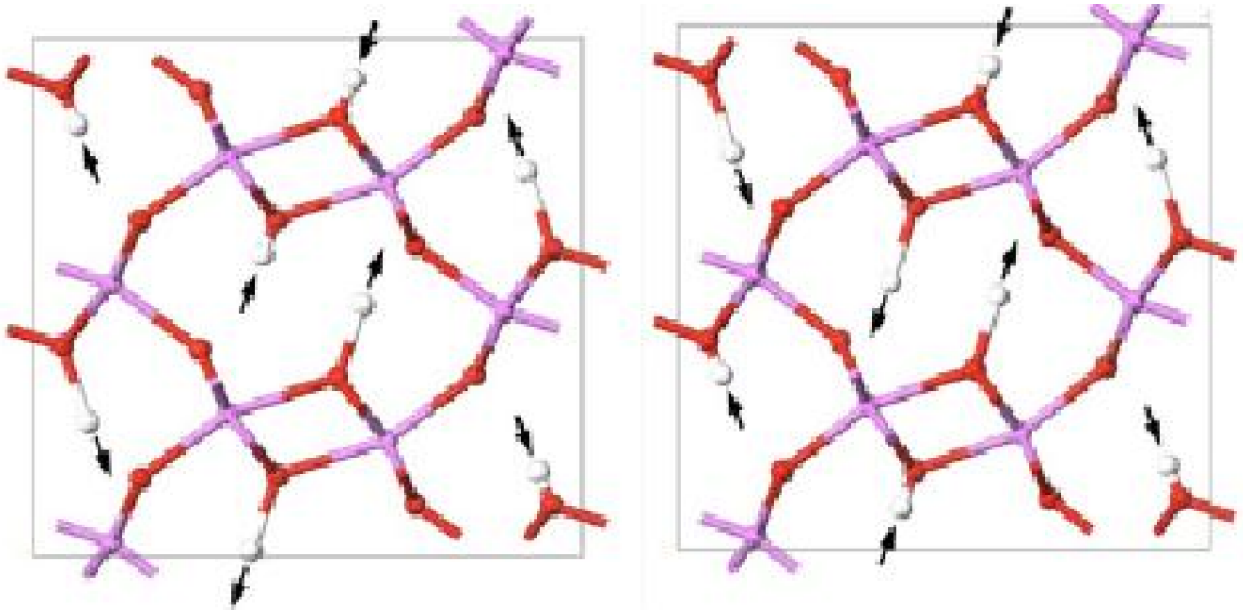
OH dispersion in diaspore





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Developments in CASTEP

HPC performance and scaling

- Band parallelism
- Shared-memory node optimizations of FFT
- Wavefunction read/write optimizations
- Memory optimization
- Distributed $\langle \beta | \phi \rangle$

Recently added properties and capabilities

- DFT+D
- Hirshfeld atomic Charges
- NMR Hyperfine Coupling
- New GGAs (PBEsol, WC)
- Hybrid functionals (PBEh, B3LYP), SX
- LDA+U
- EELS and XANES with d core-hole final states
- Raman and infrared intensity/spectroscopy
- Electron localization functions (ELF)
- DFPT phonons for metallic systems

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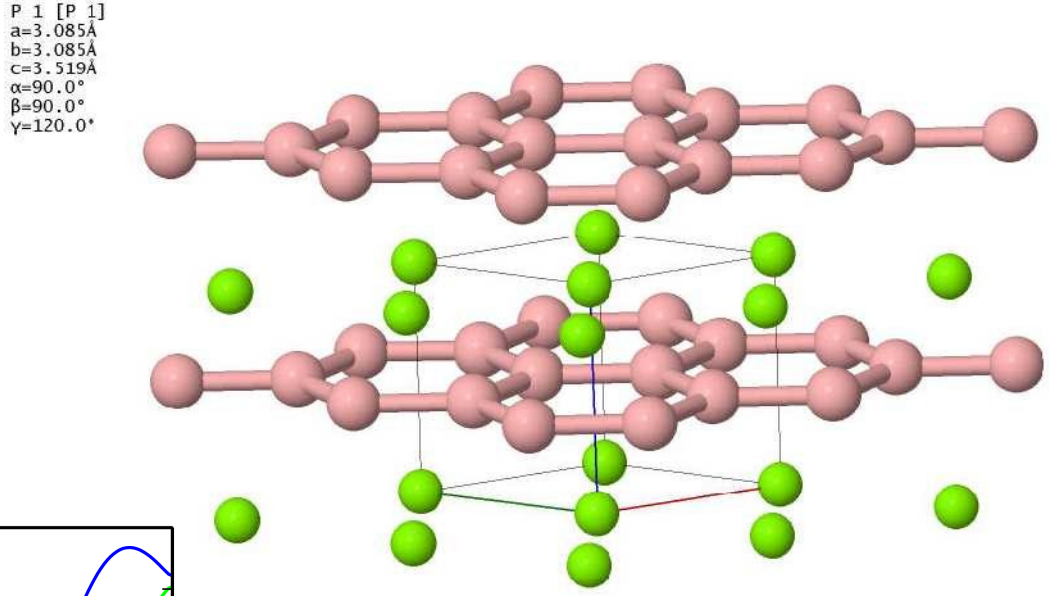
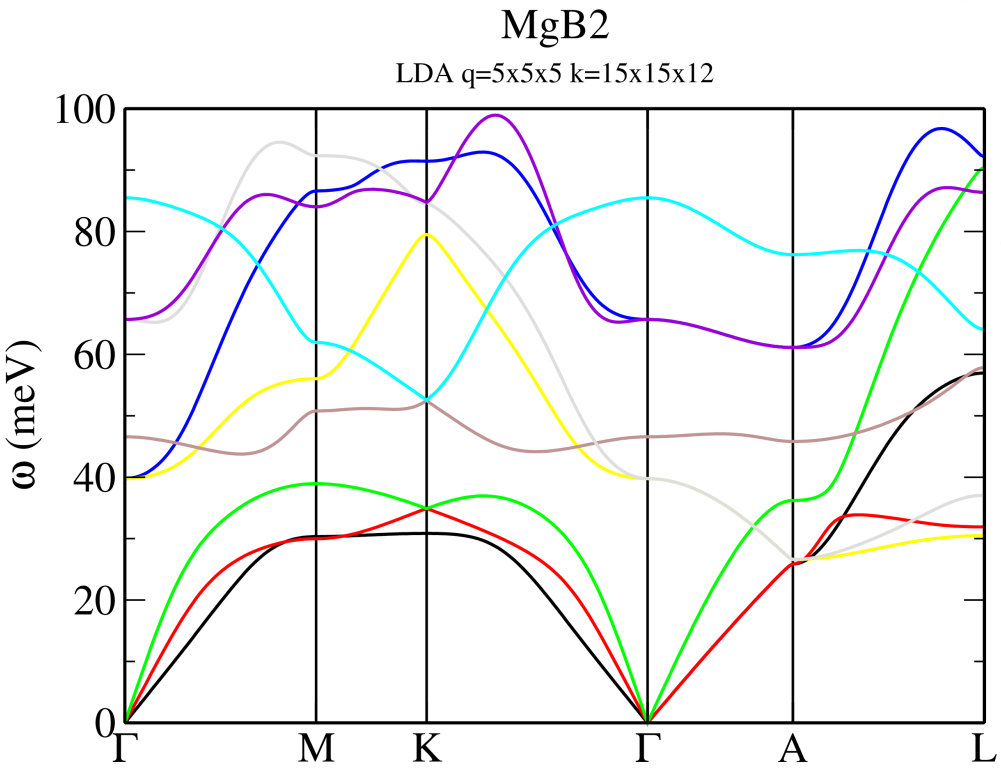
DFPT Phonons for Metals





- Metallic phonon DFPT
- Fourier interpolation for full DOS
- and dispersion calculations.

Under Development

Much faster Raman activities using DFPT

DFPT for magnetic systems

Non-collinear magnetism

GW for many-body perturbation theory
Treatment of excitations

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Acknowledgements

Stewart Parker, Timmy Ramirez Cuesta & Mark Adams, Daniel Bowron, Alan Soper, Jon Taylor, Steve Bennington (ISIS)

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