

Materials Studio 5.0: Spectroscopy Methods in CASTEP

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Webinar Series: Materials Studio 5.0
December 2nd, 2009

Spectroscopic Modelling with CASTEP

Keith Refson
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December 2, 2009



First-principles modelling

The Ingredients

CASTEP

Molecular and Crystal
Boundary Conditions

The SCF Equations

Optical Spectroscopy

Lattice Dynamics

Lattice Dynamics in
CASTEP

LO/TO Splitting

Modelling of spectra



The Nobel Prize in Chemistry 1998

"for his development of the
density-functional theory"

"for his development of
computational methods in quantum
chemistry"



Walter Kohn

🏆 1/2 of the prize
USA

University of California
Santa Barbara, CA, USA
b. 1923
(in Vienna, Austria)



John A. Pople

🏆 1/2 of the prize
United Kingdom

Northwestern University
Evanston, IL, USA
b. 1925
d. 2004

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble."

P.A.M. Dirac, Proceedings of the Royal Society A123, 714 1929



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Modelling of spectra

- Complete description of materials chemistry and physics given in principle by quantum mechanics of electrons and nuclei.
- Covalent, ionic, metallic, van der Waals bonding are all the result of QM behaviour of electrons.
- **The Born-Oppenheimer Approximation** - Treat nuclei classically and assume electrons move adiabatically in field of fixed ions.
Then QM electrons give *interaction forces* between nuclei – or “atoms”.
- Primary computed quantity is ground state energy, E_0 .
- All observables related to *change* in E_0 when system perturbed.

Crystal Structure Ion positions and lattice parameters which minimize E_0 .

Phase stability Phase with lowest E_0 is most stable at $T=0$.

Forces on ions given by $\nabla_{r_i} E_0$.

Elastic Constants e.g. $K = V d^2 E / dV^2$.

Vibrational Frequencies given by $\frac{\partial^2 E_0}{\partial x_{\kappa, \alpha} \partial x_{\kappa', \beta}}$



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Modelling of spectra

- Comprehensive *ab-initio* simulation code.
S. J. Clark *et al.* Z. Kristall, **220**, 567-570 (2005)
- Uses plane-wave basis set with pseudopotentials
- XC-functionals LDA, PW91, PBE/RPBE, WC, HF, PBE0, B3LYP
- Vanderbilt Ultrasoft pseudopotentials (also supports norm-conserving)
- **Geometry Optimization** BFGS, cell optimisation, delocalised internals
- **Ab initio Lattice Dynamics**
 - Both supercell and DFPT with interpolation methods supported.
 - Phonon Spectra and Dispersion Curves.
 - IR intensities and raman activities
 - Dielectric Permittivity (electronic and ionic contributions)
 - Born Effective Charges
 - NMR Chemical Shifts
- GUI - Accelrys Materials Studio, (or file driven control)



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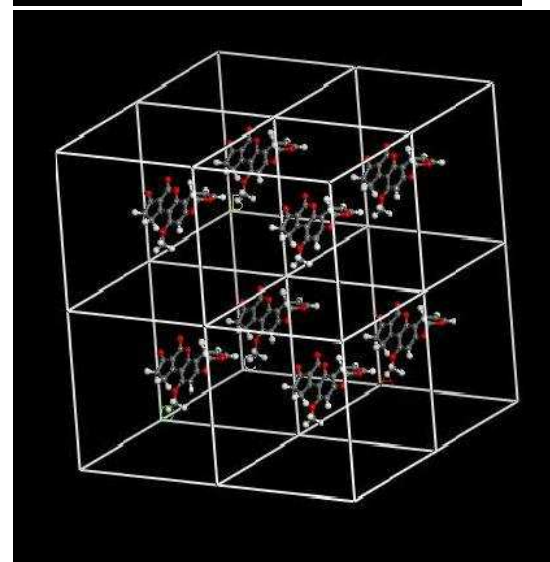
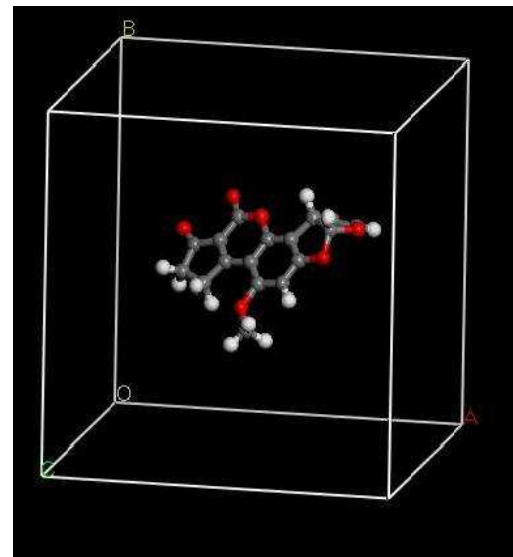
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Modelling of spectra

- For *molecules* usually model molecule in empty space. Most quantum chemistry codes (eg Gaussian, GAMESS) do this
- For *extended systems* (ie solids, liquids) this is a poor idea. Surface effects would dominate unless system very large.
- Most extended-system calculations use **periodic boundary conditions** e.g. CASTEP, CRYSTAL, DMOL, SIESTA,...
- Can model molecules or surfaces with periodic code using *supercell* or *slab* geometries.





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Density Functional Theory – Hohenberg Kohn and Sham

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{I-E}}(r) + V_{\text{H}}(r) + V_{\text{XC}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r)$$

- $\frac{-\hbar^2}{2m} \nabla^2 \psi_i(r)$ is kinetic energy of electrons.
- $V_{\text{H}}(r) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r}'$ the *Hartree potential*, is mean potential of other electrons. $n(\mathbf{r}) = 2 \sum_i |\psi_i|^2$ is the electron density.
- $V_{\text{I-E}}(r) = \frac{Z_I e}{|\mathbf{r}-\mathbf{R}_I|}$ is Coulomb interaction of electrons with nucleus
- $V_{\text{XC}}(r)$ is *exchange-correlation* potential. True form unknown but approximate by local density approximation (LDA), generalised gradient approximation (GGA) or hybrid functional.
- $\psi_i(\mathbf{r}_i)$ is wavefunction of single electron in effective potential of other electrons and nuclei.
- Hartree and XC potentials depend on $n(\mathbf{r})$ and in turn on $\psi_i(\mathbf{r}_i)$ Must be solved **self-consistently**.



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Infrared spectroscopy

Raman spectroscopy

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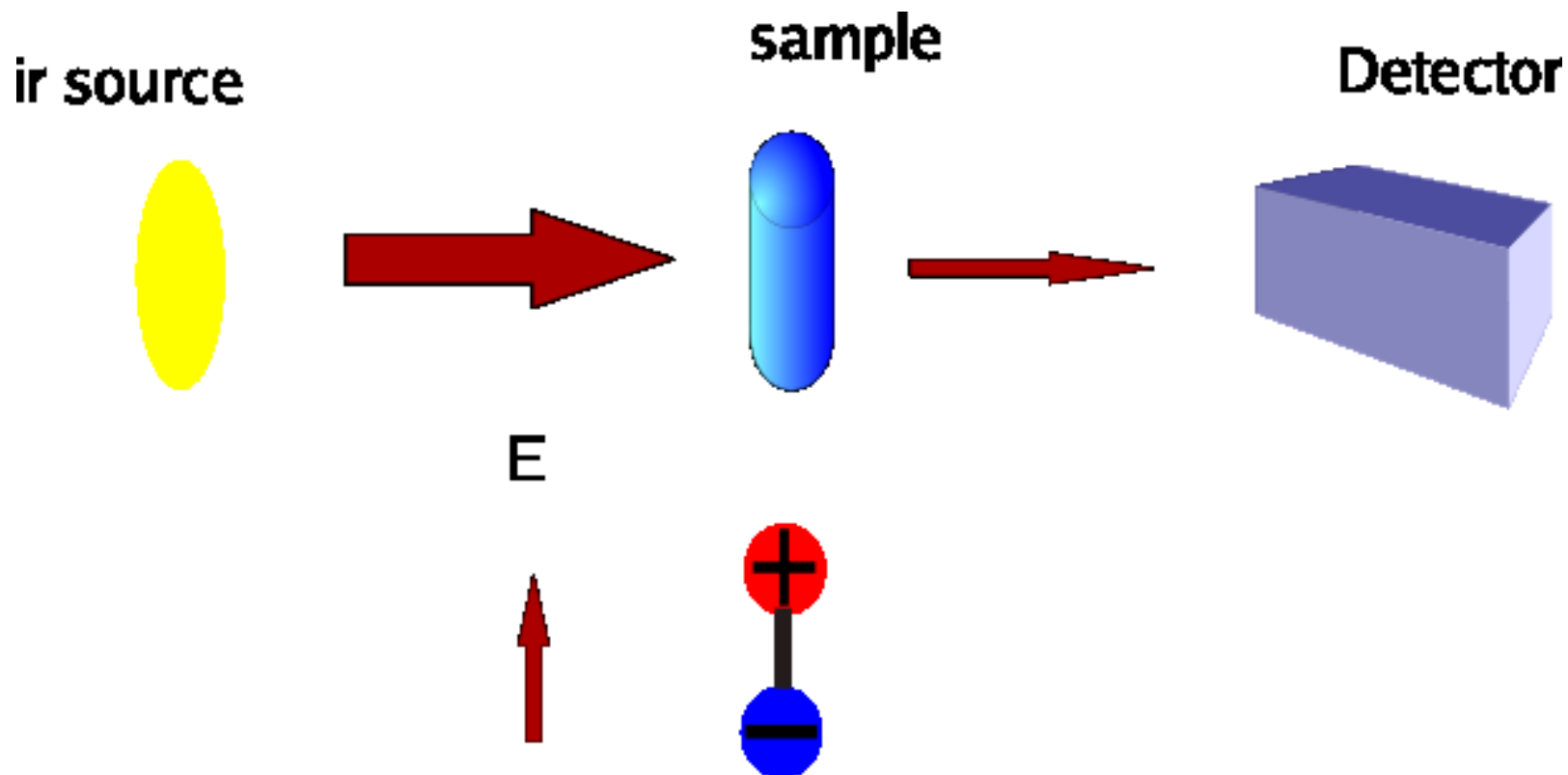
Raman spectroscopy

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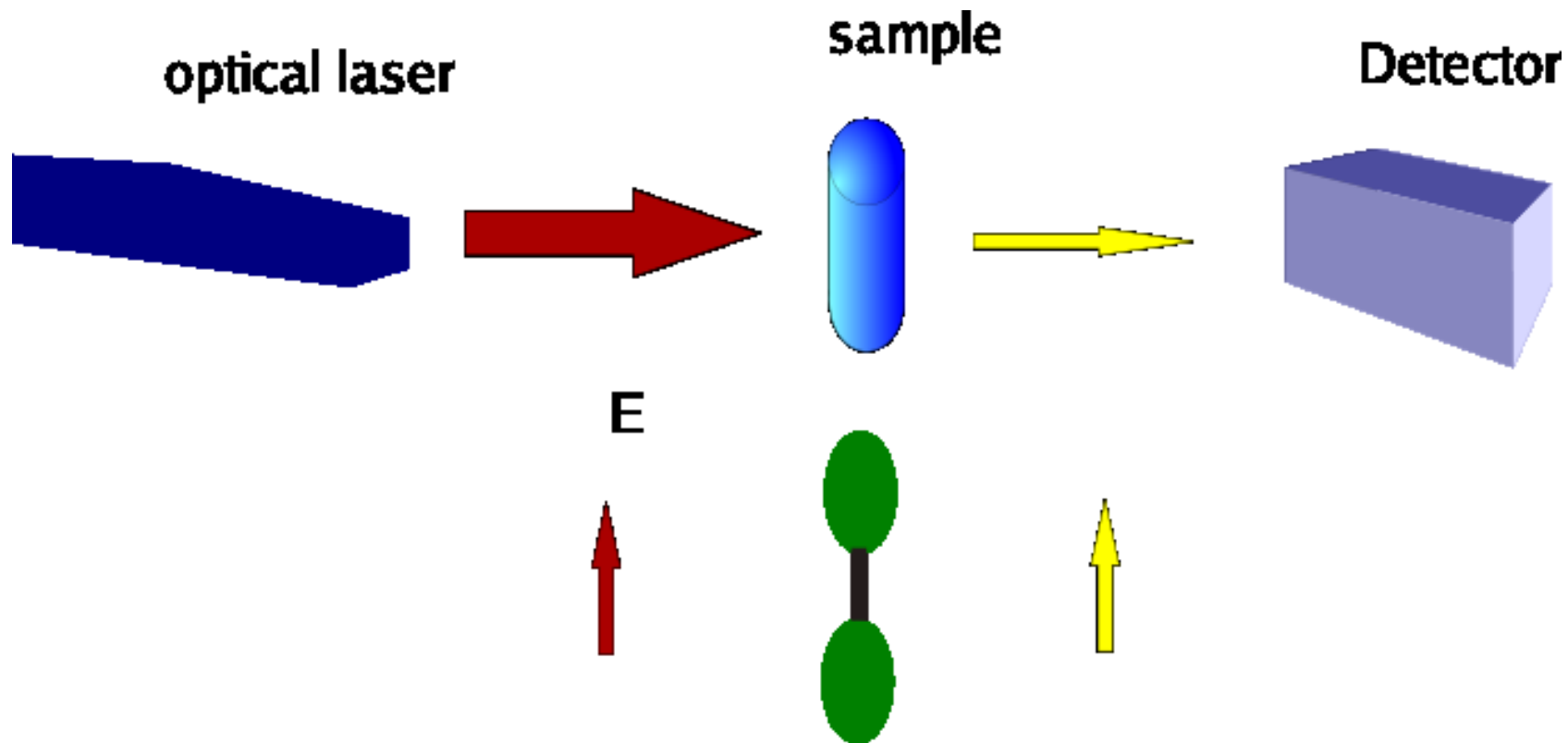


Ir spectroscopy measures *absorbance* or *transmittance* by excitation of *vibrational modes* of sample.

Light couples to modes with *electric dipole* character



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- Infrared spectroscopy
- Raman spectroscopy**
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Raman spectroscopy (inelastic light scattering) measures *frequency shift* of laser by excitation of *vibrational modes* of sample. Light couples to *polarisability of modes*.



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Modelling of spectra

- Based on expansion of total energy about structural equilibrium co-ordinates

$$E = E_0 + \sum_{\kappa,\alpha} \frac{\partial E}{\partial \mathbf{u}_{\kappa,\alpha}} \cdot \mathbf{u}_{\kappa,\alpha} + \frac{1}{2} \sum_{\kappa,\alpha,\kappa',\alpha'} \mathbf{u}_{\kappa,\alpha} \cdot \Phi_{\alpha,\alpha'}^{\kappa,\kappa'} \cdot \mathbf{u}_{\kappa',\alpha'} + \dots$$

where $\mathbf{u}_{\kappa,\alpha}$ is the vector of atomic displacements from equilibrium and $\Phi_{\alpha,\alpha'}^{\kappa,\kappa'}$ is the matrix of *force constants* $\Phi_{\alpha,\alpha'}^{\kappa,\kappa'} = \frac{\partial^2 E}{\partial \mathbf{u}_{\kappa,\alpha} \partial \mathbf{u}_{\kappa',\alpha'}}$

- At equilibrium the forces $F_{\kappa,\alpha} = -\frac{\partial E}{\partial \mathbf{u}_{\kappa,\alpha}}$ are all zero so 1st term vanishes.
- In the *Harmonic Approximation* the 3rd and higher order terms are assumed to be negligible.
- Plugging this into Newton's equation of motion yields matrix eigenvalue equation:

$$D\boldsymbol{\epsilon}_m = \omega_m^2 \boldsymbol{\epsilon}_m$$

where the **dynamical matrix** is $D_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \Phi_{\alpha,\alpha'}^{\kappa,\kappa'}$

- There are in general 3N (crystal) or 3N-6 (molecule) *normal modes* of frequency ω_m . Atomic displacements are given by *eigenvectors* $\boldsymbol{\epsilon}_{m\kappa,\alpha}$.



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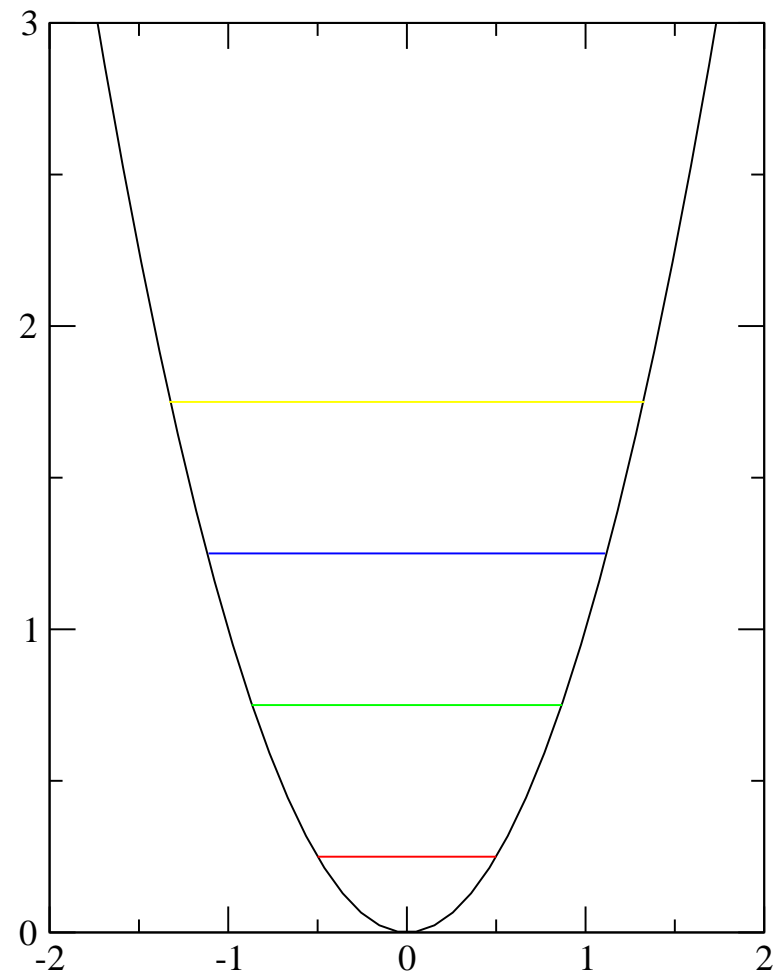
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- The energy expression can be transformed into a quantum-mechanical Hamiltonian with energy levels $E_{m,n} = (n + \frac{1}{2}) \hbar\omega_m$ for mode m .
- Quantum excitations of modes known as *phonons* in crystal
- Transitions between levels n_1 and n_2 interact with photons of energy $(n_2 - n_1) \hbar\omega_m$, ie multiples of *fundamental* frequency ω_m .
- In *anharmonic* case where 3rd-order term not negligible, *overtone* frequencies are not multiples of fundamental.





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Modelling of spectra

Compute force constants as second derivatives of energy *directly* from electronic structure formalism, ie compute *response* of electrons to atomic displacement.

$$E^{(2)} = \frac{1}{2} \frac{d^2 E}{d\tau_{\kappa,\alpha}^2} = \sum_m \left\langle \phi_m^{(0)} \left| \frac{dV}{d\tau_{\kappa,\alpha}} \right| \phi_m^{(1)} \right\rangle + \frac{1}{2} \sum_m \left\langle \phi_m^{(0)} \left| \frac{d^2 V}{d\tau_{\kappa,\alpha}^2} \right| \phi_m^{(0)} \right\rangle$$

DFPT formalism gives $D_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q})$ directly from primitive-cell calculation. (a.k.a. linear response)

Need to compute *first-order* KS orbitals $\phi^{(1)}$, the linear response to λ . V is *self-consistent* potential.

DFPT can also calculate

- Born Effective Charges (a.k.a. atomic polar tensors)
- polarisability/dielectric permittivity
- LO/TO splitting
- infra-red reflectivity/absorption coefficients
- Raman tensor

Similar schemes in quantum chemistry known as *analytic second derivatives* or *coupled Hartree Fock*.



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In DFPT need *first-order* KS orbitals $\phi^{(1)}$, the *linear response* to the perturbation
First-order response orbitals are solutions of **Sternheimer equation**

$$\left(H^{(0)} - \epsilon_m^{(0)} \right) \left| \phi_m^{(1)} \right\rangle = -P_c V^{(1)} \left| \phi_m^{(0)} \right\rangle$$

P_c is projection operator onto unoccupied states. First-order potential $v^{(1)}$ includes response terms of Hartree and XC potentials and therefore depends on first-order *density* $n^{(1)}(\mathbf{r})$ which depends on $\phi^{(1)}$.

Finding $\phi^{(1)}$ is therefore a *self-consistent* problem just like solving the Kohn-Sham equations for the ground state.

Two major approaches to finding $\phi^{(1)}$ are suited to plane-wave basis sets:

- Green's function (S. Baroni *et al* (2001), Rev. Mod. Phys **73**, 515-561).
- Variational DFPT (X. Gonze (1997) PRB **55** 10377-10354).

CASTEP uses Gonze's variational DFPT method.

DFPT has huge advantage - can calculate response to *incommensurate* q from a calculation on primitive cell. Disadvantage of DFPT - more programming required.



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The finite displacement method:

- Displace ion κ' in direction α' by small distance $\pm u$.
- Use single point energy calculations and evaluate *forces* on *every* ion in system $F_{\kappa,\alpha}^+$ and $F_{\kappa,\alpha}^-$ for +ve and -ve displacements.
- Compute numerical derivative using central-difference formula

$$\frac{dF_{\kappa,\alpha}}{du} \approx \frac{F_{\kappa,\alpha}^+ - F_{\kappa,\alpha}^-}{2u} = \frac{d^2 E_0}{du_{\kappa,\alpha} du_{\kappa',\alpha'}}$$

- Have calculated entire *row* k', α' of $D_{\alpha,\alpha'}^{\kappa,\kappa'}(\mathbf{q} = 0)$
- Only need $6N_{\text{at}}$ SPE calculations to compute entire dynamical matrix.
- This is a *general* method, applicable to any system.
- Can take advantage of space-group symmetry to avoid computing symmetry-equivalent perturbations.
- Works only at $\mathbf{q} = 0$.



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CASTEP can perform *ab-initio* lattice dynamics using

- Primitive cell finite-displacement at $\mathbf{q} = 0$
- Supercell finite-displacement for any \mathbf{q}
- DFPT at arbitrary \mathbf{q} .
- DFPT on M-P grid of \mathbf{q} with Fourier interpolation to arbitrary fine set of \mathbf{q} .

Full use is made of space-group symmetry to only compute only

- symmetry-independent elements of $D_{\alpha, \alpha'}^{\kappa, \kappa'}(\mathbf{q})$
- \mathbf{q} -points in the irreducible Brillouin-Zone for interpolation
- electronic k -points adapted to symmetry of perturbation.

Limitations: DFPT currently implemented only for norm-conserving pseudopotentials and insulators.



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- DFT usually gives frequencies within a few percent of experiment. Exceptions are usually strongly-correlated systems, e.g. some transition-metal Oxides where DFT description of bonding is poor.
- Discrepancies can also be due to anharmonicity. A frozen-phonon calculation can test this.
- In case of OH-bonds, DFT errors and anharmonic shift cancel each other!
- In solid frequencies may be strongly pressure-dependent. DFT error can resemble *effective pressure*. In that case, best comparison with expt. may not be at experimental pressure.
- Hartree-Fock approximation *systematically* overestimates vibrational frequencies by 5-15%. Common practice is to multiply by “scaling factor” ≈ 0.9 .
- Scaling not recommended for DFT where error is not systematic. Over- and under-estimation equally common.
- For purposes of mode assignment, or modelling experimental spectra to compare intensity it can sometimes be useful to apply a small empirical shift on a per-peak basis. This does not generate an “ab-initio frequency”.
- When comparing with experiment remember that disagreement may be due to *anharmonicity*.
- Less obviously *agreement* may also be due to anharmonicity. There is a “lucky” cancellation of anharmonic shift by PBE GGA error in OH stretch!



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LO/TO Splitting

Two similar structures
Zincblende and diamond
dispersion

LO/TO splitting

DFPT with LO/TO
splitting in NaCl

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Two similar structures

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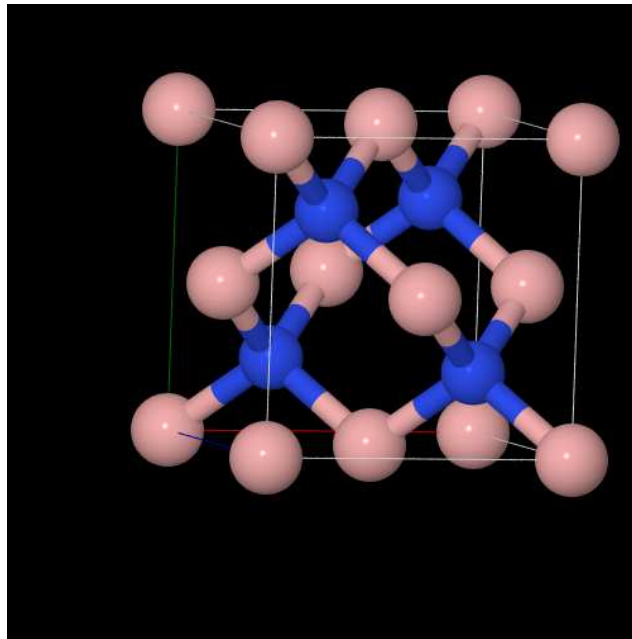
Two similar structures

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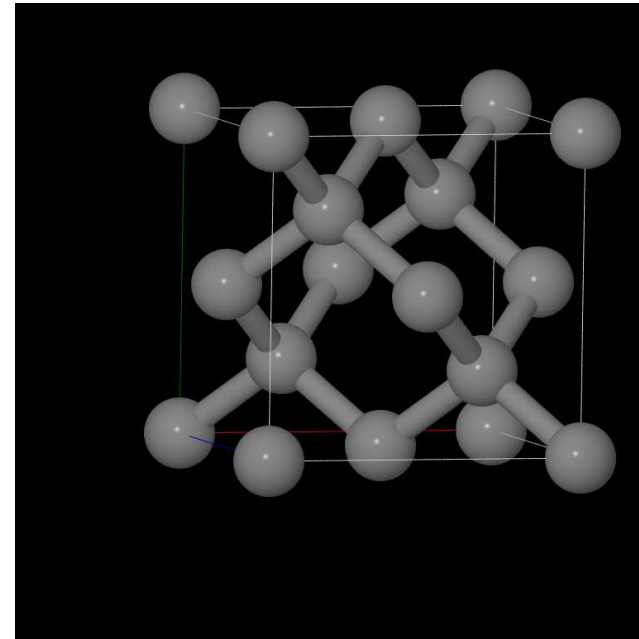
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Zincblende BN



Diamond



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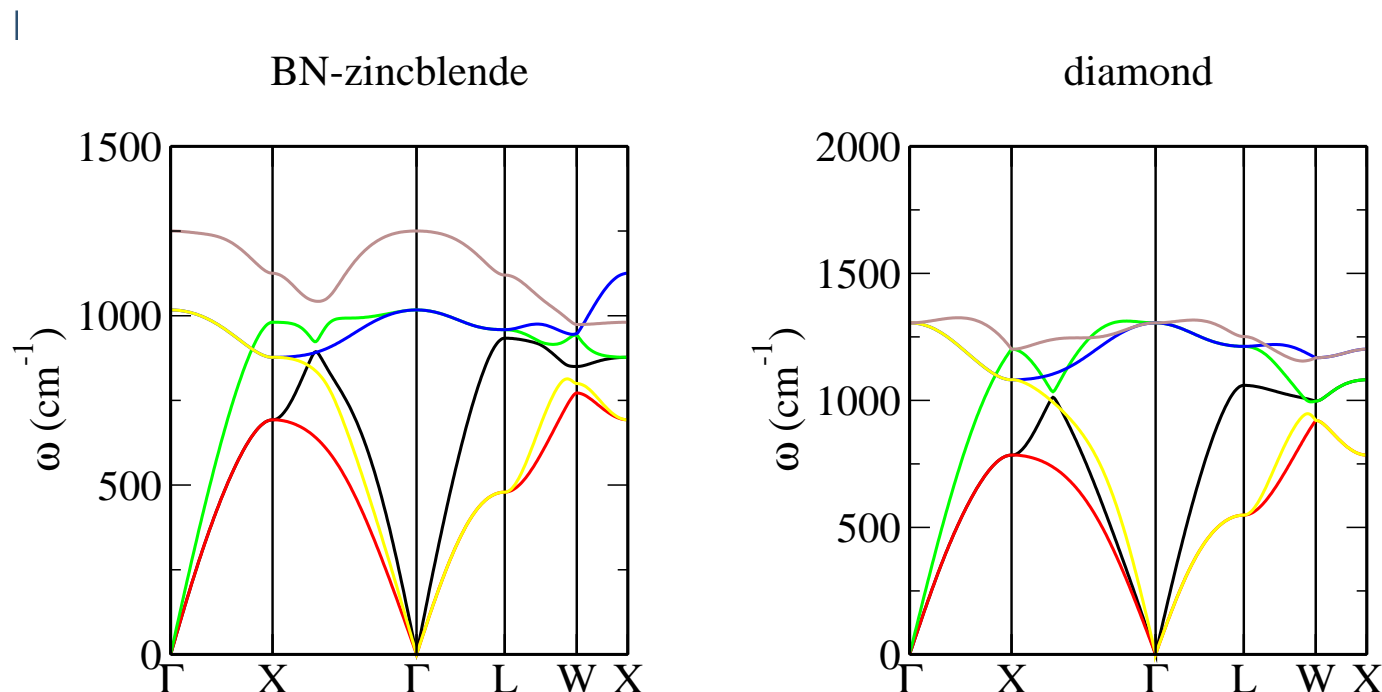
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Cubic symmetry of Hamiltonian predicts *triply degenerate* optic mode at Γ in both cases.

2+1 optic mode structure of BN violates group theoretical prediction.
Phenomenon known as **LO/TO splitting**.

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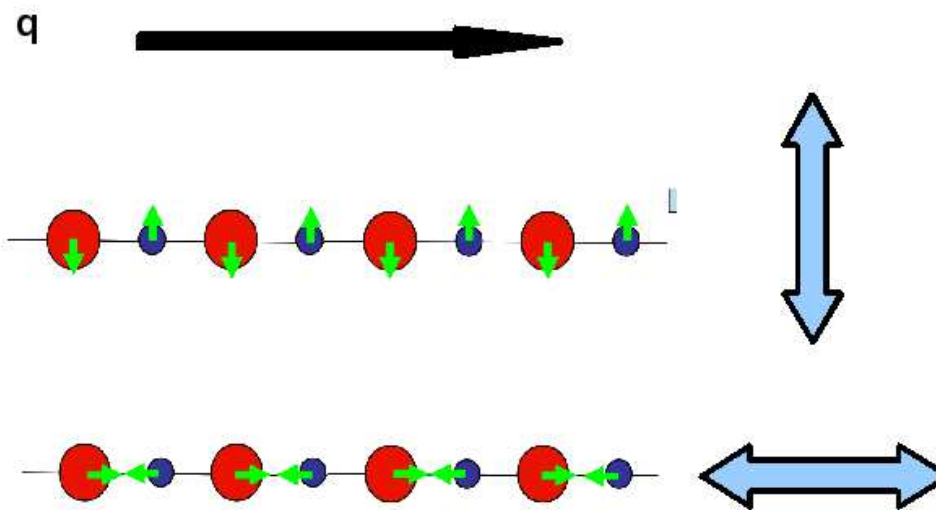
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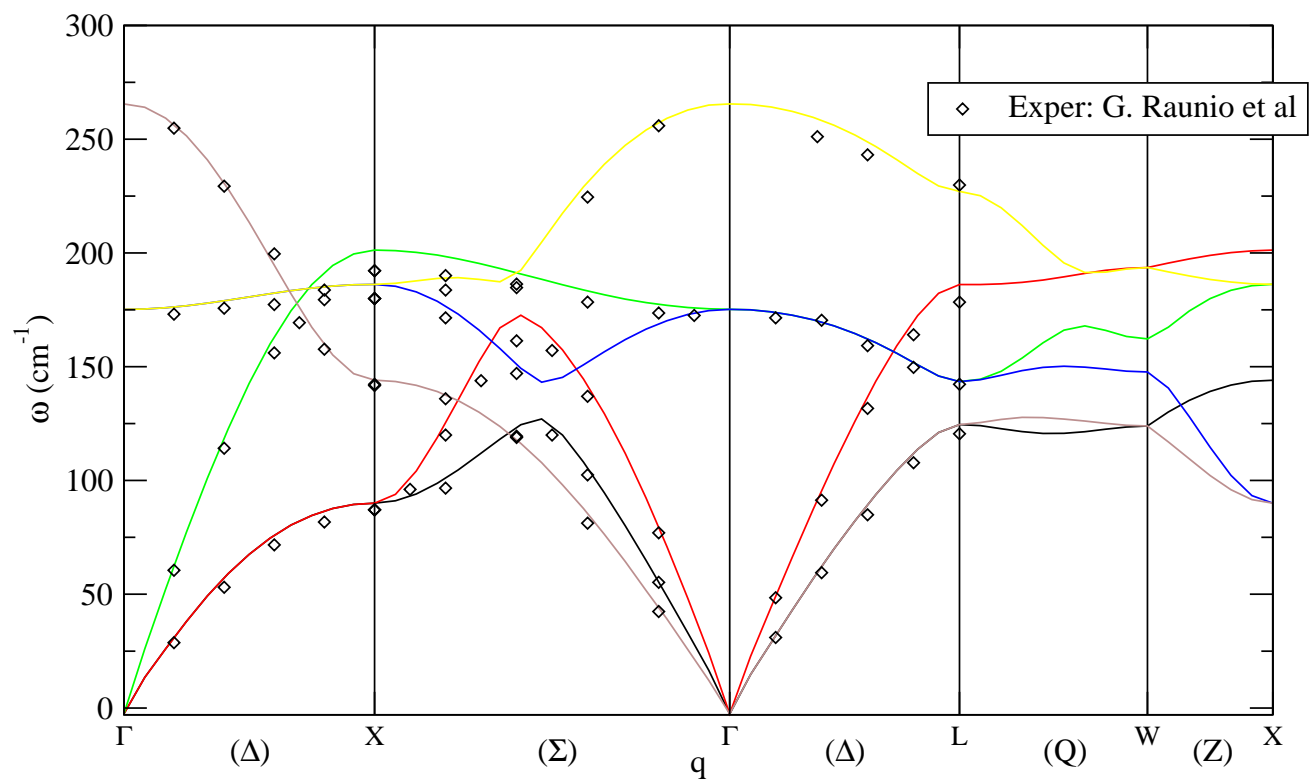
Modelling of spectra



- Dipole created by displacement of charges of long-wavelength LO mode creates induced electric field.
- For TO motion $\mathbf{E} \perp \mathbf{q} \Rightarrow \mathbf{E} \cdot \mathbf{q} = 0$
- For LO mode $\mathbf{E} \cdot \mathbf{q} \neq 0$ and E-field adds additional restoring force.
- Frequency of LO mode is upshifted.
- Lyndane-Sachs-Teller relation for cubic case: $\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_0}{\epsilon_\infty}$
- LO frequencies at $\mathbf{q} = 0$ depend on *dielectric permittivity*



LO modes can be seen in infrared, INS, IXS experiments, but not raman.
NaCl phonon dispersion



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Powder infrared

Modelling of powder IR

Non-resonant raman

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To model spectra need to treat scattering dynamics of incident and emergent radiation.

In case of INS interaction is between point neutron and nucleus - scalar quantity b depends only on nucleus – specific properties.

$$\frac{d^2\sigma}{dEd\Omega} = \frac{k_f}{k_i} b^2 S(\mathbf{Q}, \omega)$$

\mathbf{Q} is scattering vector and ω is frequency - interact with phonons at same wavevector and frequency.

Full measured spectrum includes overtones and combinations and instrumental geometry and BZ sampling factors.

Need specific spectral modelling software to incorporate effects as postprocessing step following CASTEP phonon DOS calculation.

A-Climax : A. J. Ramirez-Cuesta Comput. Phys. Comm. **157** 226 (2004))



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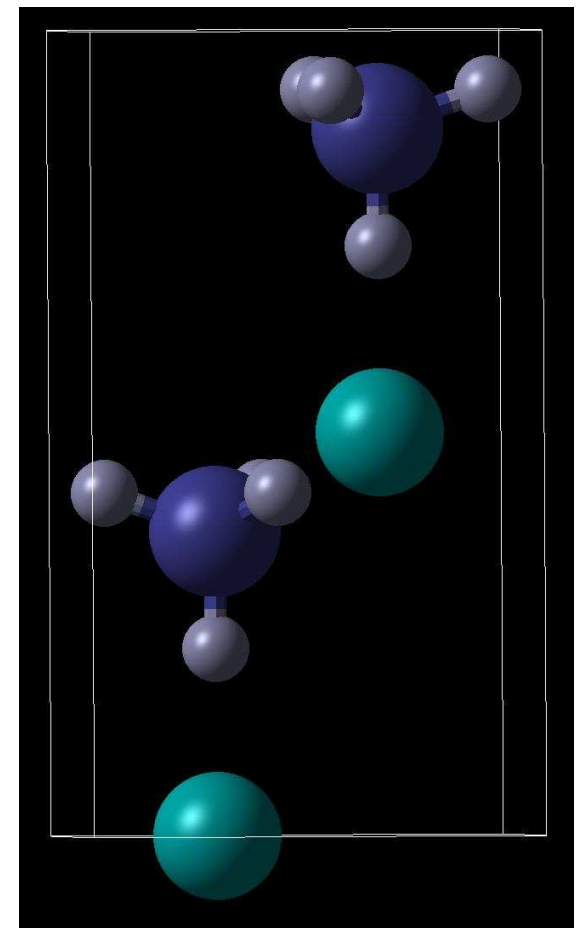
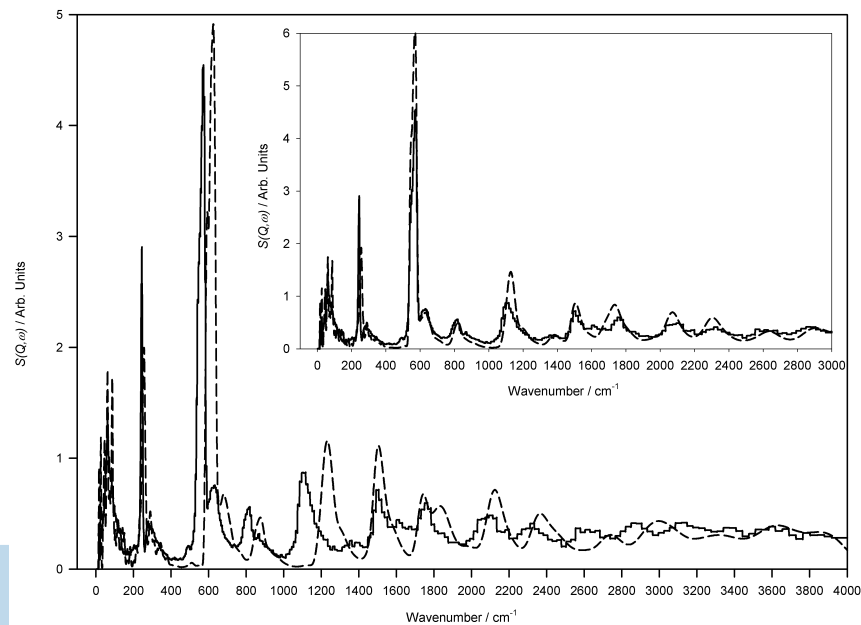
Single-crystal infrared

Powder infrared

Modelling of powder IR

Non-resonant raman

- NH_4F is one of a series of ammonium halides studied in the TOSCA spectrometer. Collab. Mark Adams (ISIS)
- Structurally isomorphic with ice Ih
- INS spectrum modelled using A-CLIMAX software (A. J. Ramirez Cuesta, ISIS)
- Predicted INS spectrum in mostly excellent agreement with experiment
- NH_4 libration modes in error by $\approx 5\%$.
- Complete mode assignment achieved.





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Prediction of reflectivity of optically flat single crystal surface given as function of q - projected permittivity $\epsilon_q(\omega)$

$$R(\omega) = \left| \frac{\epsilon_q^{1/2}(\omega) - 1}{\epsilon_q^{1/2}(\omega) + 1} \right|^2$$

with ϵ_q defined in terms of ϵ^∞ and mode oscillator strength $S_{m,\alpha\beta}$

$$\epsilon_q(\omega) = \mathbf{q} \cdot \epsilon^\infty \cdot \mathbf{q} + \frac{4\pi}{\Omega_0} \sum_m \frac{\mathbf{q} \cdot \mathbf{S} \cdot \mathbf{q}}{\omega_m^2 - \omega^2} = \mathbf{q} \cdot \epsilon(\omega) \cdot \mathbf{q}$$

$\epsilon(\omega)$ is tabulated in the `seend-name.efield` file written from a CASTEP efield response calculation.

Example BiFeO₃ (Hermet et al, Phys. Rev B 75, 220102 (2007))

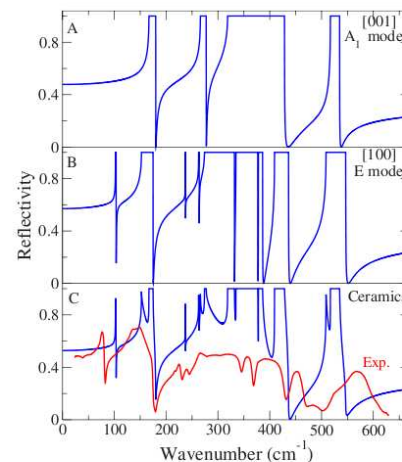


FIG. 1. (Color online) Calculated IR reflectivity spectra (blue) of a BiFeO₃ monocystal (A), (B) and ceramics (C). Experimental data (20 K) from Ref. 12 (red).



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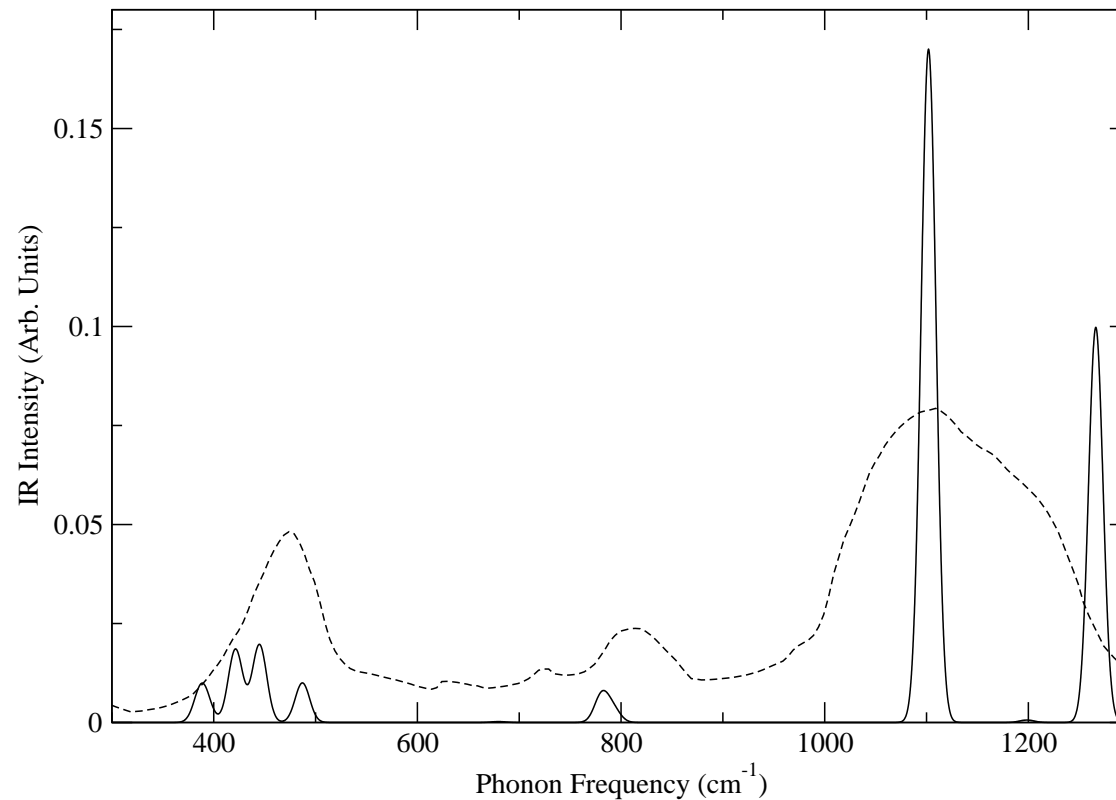
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α -quartz



- Straightforward to compute peak *areas*.
- Peak shape modelling depends on sample and experimental variables.
- Multiphonon and overtone terms less straightforward.



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Non-resonant raman

See E. Balan, A. M. Saitta, F. Mauri, G. Calas. *First-principles modeling of the infrared spectrum of kaolinite*. *American Mineralogist*, 2001, 86, 1321-1330.
Spectral shape determined by optical effects and shifted LO modes in specific size/shape of crystallites.

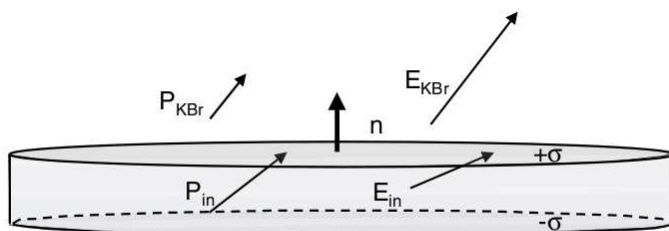


FIGURE 1. Schematic view of a dielectric plate showing the electric field and polarization vectors used to calculate the IR absorption spectrum. The surface charges $+\sigma$ and $-\sigma$ produce the depolarization field, E_{KBr} .

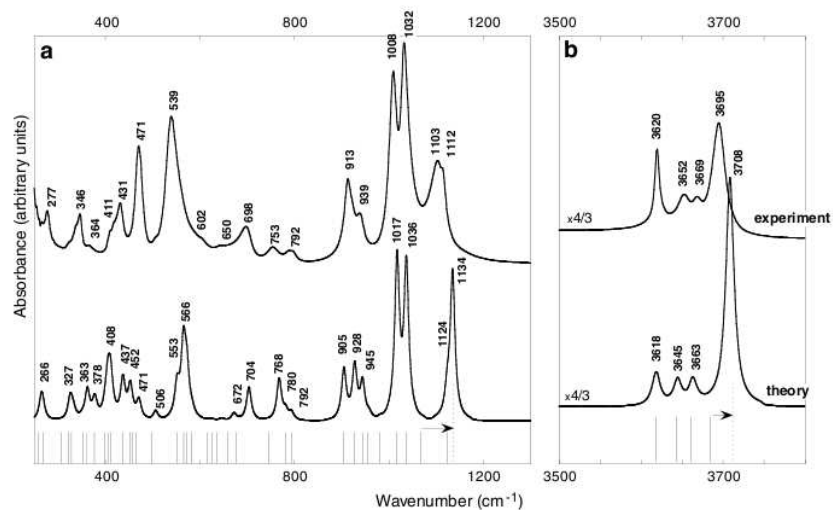


FIGURE 5. Experimental (top) and theoretical (bottom) IR absorption spectra of kaolinite: (a) mid-IR range, (b) OH-stretching region. Positions of the major features are indicated by their wavenumbers. The vertical bars at the bottom correspond to the theoretical TO phonon frequencies (see Table 4), i.e., to the resonances of the imaginary part of the dielectric function. Note the shift between the absorption bands (dotted vertical bars) and the corresponding TO frequencies observed for the Si-O and OH stretching modes polarized along c.



First-principles modelling

The Ingredients

CASTEP

Molecular and Crystal
Boundary Conditions

The SCF Equations

Optical Spectroscopy

Lattice Dynamics

Lattice Dynamics in
CASTEP

LO/TO Splitting

Modelling of spectra

Inelastic Neutron
Scattering

INS of Ammonium
Fluoride

Single-crystal infrared

Powder infrared

Modelling of powder IR

Non-resonant raman

Raman scattering depends on raman activity tensor

$$I_{\alpha\beta}^{\text{raman}} = \frac{d^3 E}{d\varepsilon_\alpha d\varepsilon_\beta dQ_m} = \frac{d\varepsilon_{\alpha\beta}}{dQ_m}$$

i.e. the activity of a mode is the derivative of the dielectric permittivity with respect to the displacement along the mode eigenvector.

CASTEP evaluates the raman tensors using hybrid DFPT/finite displacement approach.

Raman calculation is fairly expensive \Rightarrow and is not activated by default (though group theory prediction of active modes is still performed)

Parameter `calculate_raman = true` in a `task=phonon` calculation.

Spectral modelling of IR spectrum is relatively simple function of activity.

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi\nu)^4}{c^4} |\mathbf{e}_S \cdot \mathbf{I} \cdot \mathbf{e}_L|^2 \frac{h(n_m + 1)}{4\pi\omega_m}$$

with the thermal population factor

$$n_m = \left[\exp\left(\frac{\hbar\omega_m}{k_B T}\right) - 1 \right]^{-1}$$

which is implemented in `dos.pl` using the `-raman` flag.

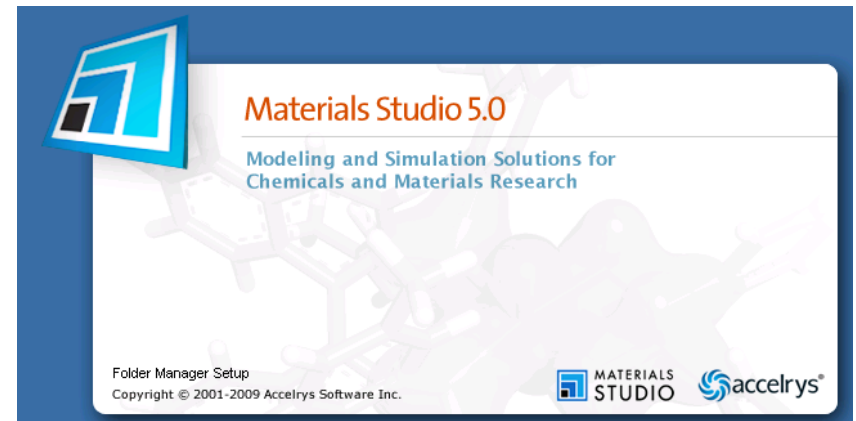
Spectroscopy in CasteP: Applications

Stewart Clark

Department of Physics
University of Durham, UK
<http://cmt.dur.ac.uk/sjc/>

Spectroscopic Methods

- In this talk:
 - Infra-red Spectroscopy (phonons)
 - Raman Spectroscopy (phonons)
- In Castep, but not discussed here
 - NMR (Magnetic Resonance)
 - Core Level Spectroscopy
- Castep v5.0



Convergence Criteria

Check you have a well
CONVERGED
calculation!

- Require accurate electronic ground state
- Require an accurate geometry

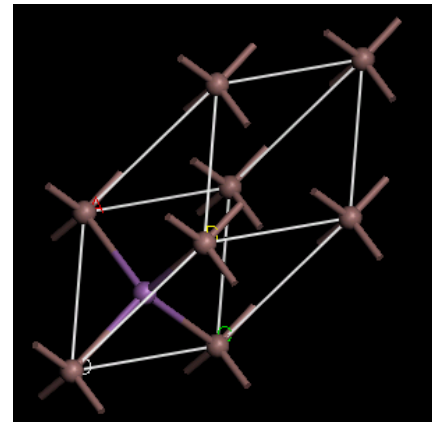
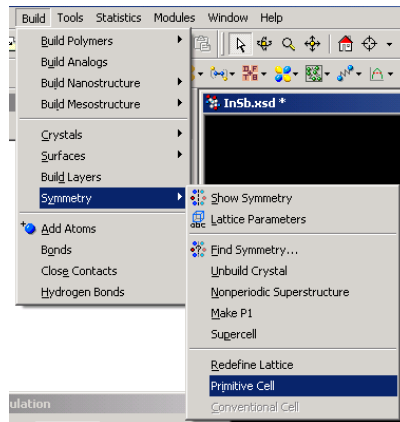
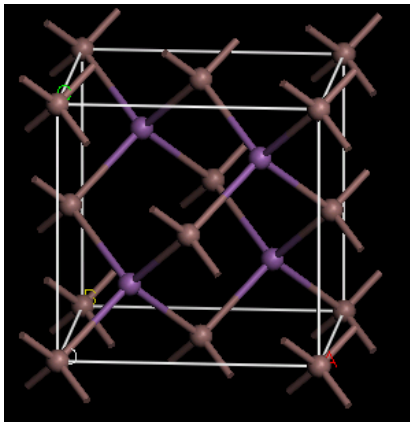
The COARSE setting in MS-Castep is for testing only: proceed with caution!

Convergence

- Vibrational frequencies and spectroscopic intensities are derivatives of total energy
- Derivatives converge more slowly with respect to
 - Plane wave cut-off energy
 - K-point sampling
- Ensure to test your results are reliable with respect to these convergence criteria

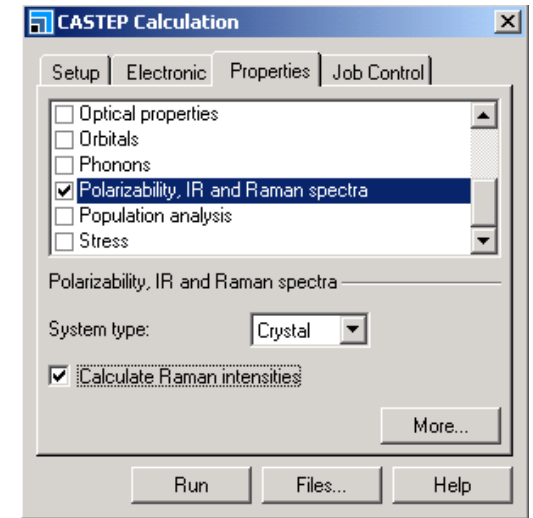
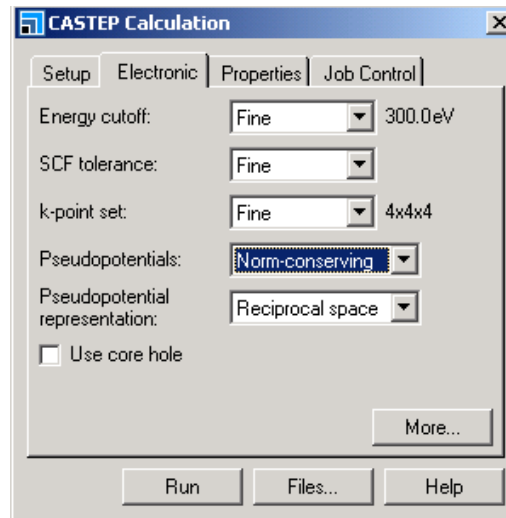
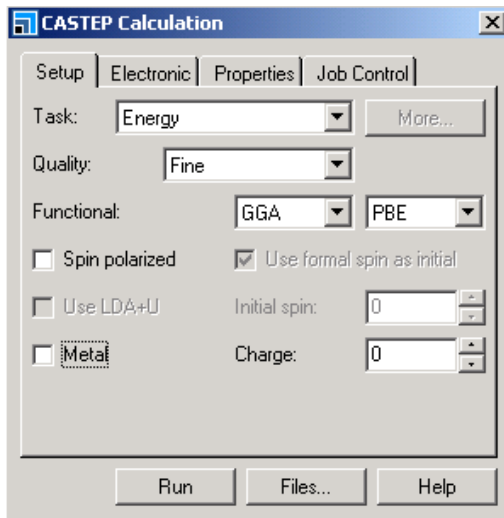
Example of IR and Raman (InSb)

- InSb has the zincblende structure (spacegroup F-43m)
- Model in Materials Studio (File/Import/Structures/Semiconductors)
- Use the primitive unit cell
- The atomic positions are fixed by symmetry, so (in this case) there's no need to optimise geometry



Set up the calculation

- Under Castep/Calculation
- Set the task to Energy and click off the 'Metal' switch
- In the 'Electronic' tab, set Pseudopotentials to Norm-conserving
- Under the 'Properties' tab, select IR and Raman Spectra. Also click on the 'Calculate Raman intensities' if you want them too



- Click on 'Run'!

Examine the output

- After a short time the run will finish and the output can be examined
- As with all Castep calculations, a very important set is to examine the output (*.castep) file
- This will be the main source of checking for any problems
- In particular look for any WARNING markers

DFPT Header

- When doing density functional perturbation calculations you'll see the header:

```
+-----+
| D D D D   F F F F F   P P P P   T T T T T |
| D         D F         P         P   T |
| D         D F F F F   P P P P   T |
| D         D F         P         T |
| D D D D   F         P         T |
+-----+
| welcome to Castep Linear Response (DFPT) |
| copyright (c) 2006 - 2009 |
| Please cite the following publications in all |
| work arising from your use of CASTEP LR. |
| K. Refson, S. J. Clark and P. R. Tulip |
| Variational density functional perturbation |
| theory for dielectrics and lattice dynamics |
| Phys. Rev. B 73(15), 155114 (2006) |
+-----+
```

The SCF

- Since we require higher order wavefunctions (derivative of wavefunction with respect to perturbation) then we need a good SCF calculation

SCF loop	Energy	Energy gain per atom	Timer (sec)	<-- SCF
Initial	-2.07111789E+002		6.86	<-- SCF
1	-2.07112142E+002	1.76993074E-004	7.31	<-- SCF
2	-2.07112142E+002	1.37736650E-010	7.91	<-- SCF
3	-2.07112142E+002	-1.29159226E-008	8.64	<-- SCF
4	-2.07112142E+002	-2.25124137E-009	9.17	<-- SCF
5	-2.07112142E+002	1.48527914E-010	9.53	<-- SCF
6	-2.07112142E+002	1.67608995E-011	9.91	<-- SCF

Perturbation Calculations

- Next follows the perturbation calculations
 - There will be $3N$ phonon perturbations
 - There will be 3 electric field perturbations
 - This number will be reduced by use of symmetry

```
writing model to InSb_Efield.check
Phonon perturbation 1 (of 2): In ion 1 x at q-point ( 0.000 0.000 0.000) : 10.72 s
+----- MEMORY AND SCRATCH DISK ESTIMATES PER NODE -----+
|                                     Memory          Disk          |
| Model and support data              17.9 MB          0.0 MB          |
| DFPT phonon calculation requirements  1.6 MB          19.9 MB          |
|                                     -----          -----          |
| Approx. total storage required per node 19.5 MB          19.9 MB          |
| Requirements will fluctuate during execution and may exceed these estimates |
+-----+-----+-----+-----+
Phonon perturbation 2 (of 2): Sb ion 1 x at q-point ( 0.000 0.000 0.000) : 75.08 s
Efield perturbation 1: x 118.81 s
Phonon calculation: q-point 1 (of 1) ( 0.000 0.000 0.000) : 178.30 s
-----
```

Raman Calculations

- If Raman intensities are requested, Castepp will now evaluate them (3rd order perturbation) for each Raman active phonon mode

```
=====
+                               vibrational Frequencies                               +
+                               -----                               +
+                               +                               +
+ Performing frequency calculation at 1 wavevector (q-pt )                       +
+ =====+
+                               +                               +
+-----+
+                               Raman Intensity Progress Report                   +
+-----+
+ RAMAN: Not a continuation; generating Raman intensities from beginning         +
+-----+
+ Mode    1: not Raman active; calculation not required                          +
+ Mode    2: not Raman active; calculation not required                          +
+ Mode    3: not Raman active; calculation not required                          +
+ Mode    4: performing Raman intensity calculation                              +
+ Mode number: 4 completed;                time taken: 643.88 seconds +
+ Mode    5: performing Raman intensity calculation                              +
+ Mode number: 5 completed;                time taken: 560.34 seconds +
+ Checkpointing.....+
writing model to Insb_Efield.check
+ Mode    6: performing Raman intensity calculation                              +
+ Mode number: 6 completed;                time taken: 549.95 seconds +
+-----+
+   E N D   O F   R A M A N   I N T E N S I T Y   C A L C U L A T I O N   +
+   Raman intensity calculation completed in 1754.30 seconds +
+-----+
.
```

Frequencies and Intensities

- Frequencies, IR and Raman intensities are reported and also symmetry information

```

+ -----+
+ q-pt=   1 ( 0.000000 0.000000 0.000000)   1.000000+
+ -----+
+ Acoustic sum rule correction < 4.298639 cm-1 applied+
+   N      Frequency irrep.      ir intensity active  raman intensity active+
+           (cm-1)                ((D/A)**2/amu)                (A**4)+
+-----+-----+-----+-----+-----+-----+
+   1      -0.013003   a           0.0000000   N           0.0000000   N+
+   2      -0.013003   a           0.0000000   N           0.0000000   N+
+   3      -0.013003   a           0.0000000   N           0.0000000   N+
+   4      175.820857   a           1.7214877   Y           189.3929243  Y+
+   5      175.820857   a           1.7214877   Y           189.3460292  Y+
+   6      175.820857   a           1.7214877   Y           189.3893314  Y+
+-----+-----+-----+-----+-----+-----+
+ .....+
+           character table from group theory analysis of eigenvectors+
+           Point Group = 30, Td+
+ .....+
+ Rep  Mu1 |   E   2   3 m_v  -4+
+ .....+
+ a T2   2 |   3  -1   0   1  -1+
+ =====+

```

Raman Tensors

- Raman intensities are tensor quantities: the full tensor is also reported for each mode

```
=====
+                               Raman Intensity Tensors                               +
+-----+-----+-----+-----+
+ Mode number:   1 Raman tensor   +
+   0.0000   0.0000   0.0000   +
+   0.0000   0.0000   0.0000   +
+   0.0000   0.0000   0.0000   +
+-----+-----+-----+-----+
+ Mode number:   2 Raman tensor   +
+   0.0000   0.0000   0.0000   +
+   0.0000   0.0000   0.0000   +
+   0.0000   0.0000   0.0000   +
+-----+-----+-----+-----+
+ Mode number:   3 Raman tensor   +
+   0.0000   0.0000   0.0000   +
+   0.0000   0.0000   0.0000   +
+   0.0000   0.0000   0.0000   +
+-----+-----+-----+-----+
+ Mode number:   4 Raman tensor   +
+  -0.0015   0.0000  -1.5892   +
+   0.0000  -0.0039   0.0000   +
+  -1.5892   0.0000  -0.0015   +
+-----+-----+-----+-----+
+ Mode number:   5 Raman tensor   +
+  -0.0002   1.5890   0.0000   +
+   1.5890  -0.0002   0.0000   +
+   0.0000   0.0000   0.0030   +
+-----+-----+-----+-----+
+ Mode number:   6 Raman tensor   +
+   0.0007   0.0000   0.0000   +
+   0.0000  -0.0011   1.5892   +
+   0.0000   1.5892  -0.0011   +
+-----+-----+-----+-----+
```

Other DFPT quantities

- Finally a range of other quantities that are calculated as part of the phonon/Raman/IR calculation are reported

- Dielectric permittivity:

- Polarisability:

- Born effective charges:

$$\epsilon_{\alpha,\beta}^{\infty} = \delta_{\alpha,\beta} - \frac{4\pi}{\Omega} \frac{\partial^2 E}{\partial F_{\alpha} \partial \epsilon_{\beta}}$$

$$\alpha_{\alpha,\beta}^{\infty} = -\frac{1}{\Omega} \frac{\partial^2 E}{\partial \epsilon_{\alpha} \partial \epsilon_{\beta}}$$

$$Z_{\alpha,\beta}^* = \Omega \frac{\partial P_{\beta}}{\partial u_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial \epsilon_{\beta}} = \frac{\partial^2 E}{\partial u_{\kappa,\alpha} \partial \epsilon_{\beta}}$$

```

=====
optical Permittivity (f->infinity)                DC Permittivity (f=0)
-----
10.45394    0.00000    0.00000    12.20099    0.00000    0.00000
0.00000    10.45394    0.00000    0.00000    12.20099    0.00000
0.00000    0.00000    10.45394    0.00000    0.00000    12.20099
=====

```

```

=====
Polarisabilities (A**3)
-----
optical (f->infinity)                Static (f=0)
-----
51.14708    0.00000    0.00000    60.59885    0.00000    0.00000
0.00000    51.14708    0.00000    0.00000    60.59885    0.00000
0.00000    0.00000    51.14708    0.00000    0.00000    60.59885
=====

```

```

=====
Born Effective Charges
-----
In      1      2.09983    0.00000    0.00000
          0.00000    2.09983    0.00000
          0.00000    0.00000    2.09983
Sb      1      -2.09983   0.00000    0.00000
          0.00000   -2.09983   0.00000
          0.00000   0.00000   -2.09983
=====

```

Plots of spectroscopic data

- IR intensities are given by the change in electric dipole moment (μ) of the system with respect to the atomic motion under excitation of a phonon mode (R):

$$\frac{\partial \mu_i}{\partial R_k} = - \frac{\partial^2 E}{\partial G_i \partial R_k} = \frac{\partial F_k}{\partial G_i}$$

- Raman intensities are the change in polarisability (α) of the material under excitation of a phonon mode (R):

$$\frac{\partial \tilde{\alpha}_{ij}}{\partial R_k} = - \frac{\partial^3 E}{\partial G_i \partial G_j \partial R_k} = \frac{\partial^2 F_k}{\partial G_i \partial G_j}$$

- Where G represents the external electric field perturbation (photon)

Materials Studio Analysis

CASTEP Analysis

- Electron density difference
- Electron localization function
- Energy evolution
- IR spectrum**
- NMR
- Optical properties

IR spectrum

Results file: InSb_Efield.castep

Import Hessian from CASTEP output

Help

Tools Statistics Modules Window Help

- Atom Volumes & Surfaces
- Find Equivalent Atoms
- Reaction Preview
- Superpose Structures
- Miller Planes
- Brillouin Zone Path
- Vibrational Analysis**
- Scripting
- Settings Organizer
- File Transfer
- Server Console
- Options...

Vibrational Analysis

Analysis Options

Calculate modes:

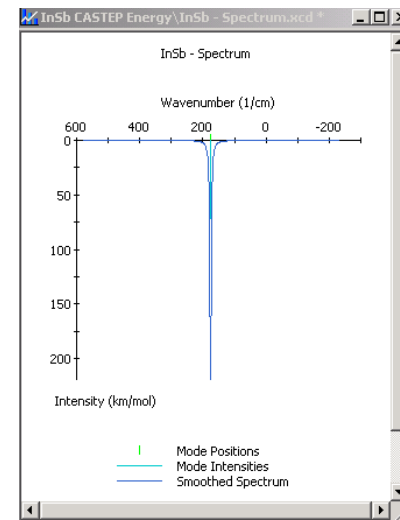
Frequency (1/cm)	Intensity (km/mol)
175.82	73.10
175.82	73.10
175.82	73.10

Output:

Animation Grid Spectrum

From: InSb CASTEP Energy\InSb.xsd

Help



CASTEP Analysis

- Population analysis
- Potentials
- Raman spectrum**
- STM profile
- Structure
- Thermodynamic properties

Raman spectrum

Results file: InSb_Efield.castep

Function: Activity

Temperature: 10.0 K

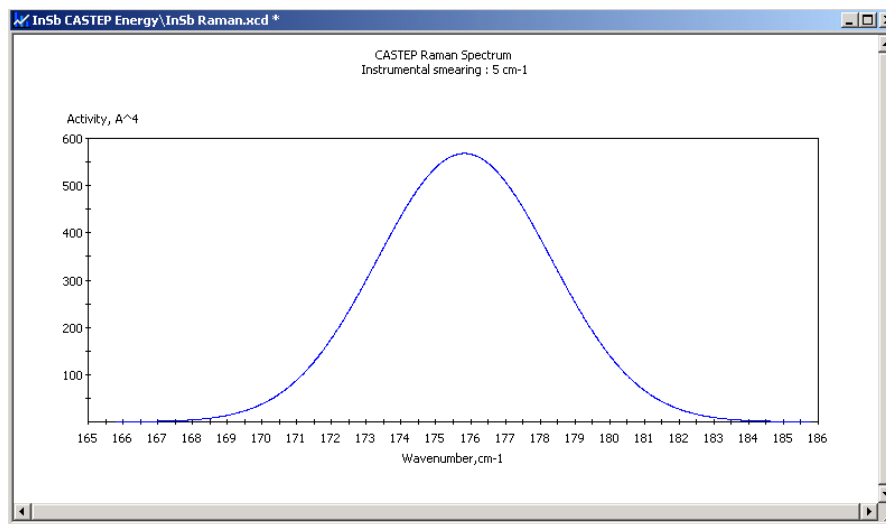
Smearing: 10.0 cm⁻¹

Units: cm⁻¹

Reverse wavenumber axis

Reverse intensity axis

View Help



Computational Speed

- In ground state electronic structure calculations, the number of k-points are reduced by symmetry
 - e.g. For silicon (diamond) a $8 \times 8 \times 8$ k-point set (512 k-points) are symmetry reduced to 60
- However, perturbations break symmetries
 - K-points are not reduced as much
 - Each perturbation takes longer
- Raman intensity calculations require 2 E-field calculations (polarisability) per Raman active mode

Larger Systems

- We will now present Castep phonon IR and Raman calculations that have been performed for larger systems
 - MgCO_3 (Magnesite)
 - THz (far IR) modes of molecular crystals
 - Ab initio characterisation of $[\text{ReH}_9]^{2-}$ ion
 - Spectroscopy of ZrO_2

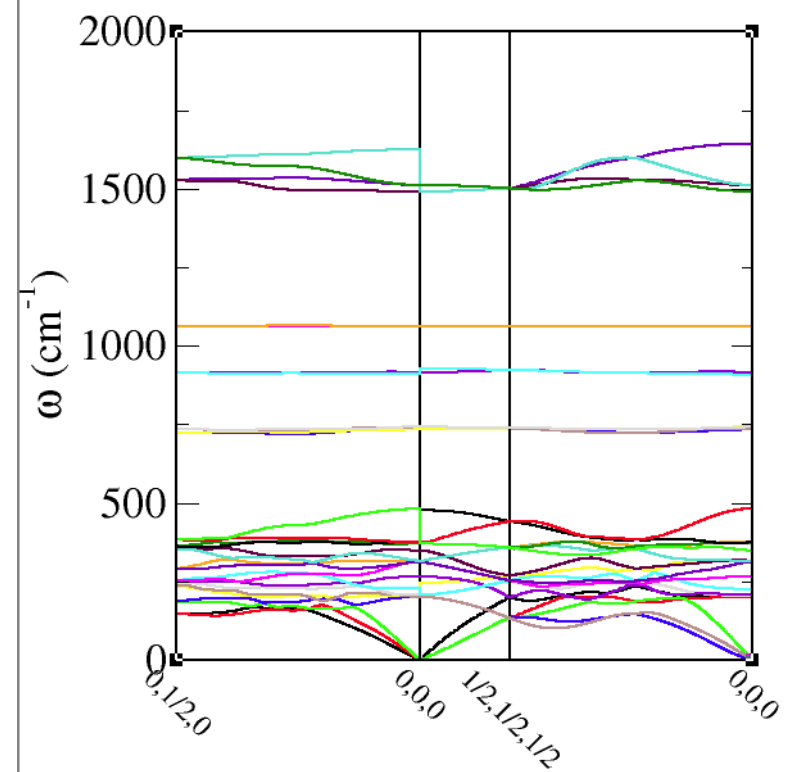
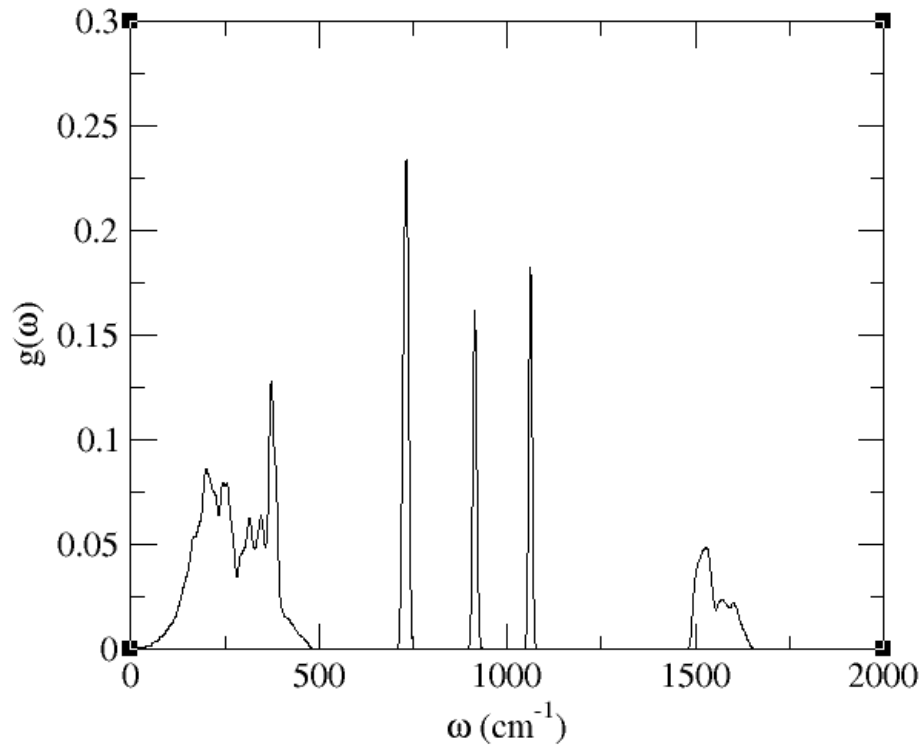
MgCO₃ (Magnesite) under pressure

- Predicting complete vibrational, IR and Raman spectra under pressure is important for understanding processes in Earth Minerals
- MgCO₃ structure: space group R-3c

Hexagonal

Rhombohedral

MgCO₃ Dispersion and DoS



IR and Raman (0 GPa and 50 GPa)

```

=====
+                               Vibrational Frequencies                               +
+                               -----                               +
+ Performing frequency calculation at 1 wavevector (q-pt)                          +
+=====+
+ q-pt= 1 ( 0.000000 0.000000 0.000000) 1.000000                               +
+-----+
+ N      Frequency irrep.   ir intensity active  raman intensity active +
+      (cm-1)              ((D/A)**2/amu)      (A**4)                  +
+-----+-----+-----+-----+
+ 1      6.815679   a      0.0000000 N      0.0000000 N      +
+ 2      8.896826   b      0.0000000 N      0.0000000 N      +
+ 3      8.896826   b      0.0000000 N      0.0000000 N      +
+ 4      204.207533 c      0.0000000 N      98.6264818 Y      +
+ 5      204.207533 c      0.0000000 N      99.6249552 Y      +
+ 6      221.604663 a      4.8373110 Y      0.0000000 N      +
+ 7      228.119564 b      1.9804546 Y      0.0000000 N      +
+ 8      228.119564 b      1.9804546 Y      0.0000000 N      +
+ 9      293.529027 d      0.0000000 N      0.0000000 N      +
+ 10     299.013346 b      1.3791215 Y      0.0000000 N      +
+ 11     299.013346 b      1.3791215 Y      0.0000000 N      +
+ 12     320.923109 c      0.0000000 N      2036.6623897 Y    +
+ 13     320.923109 c      0.0000000 N      396.6478890 Y      +
+ 14     350.978302 b      13.5875127 Y      0.0000000 N      +
+ 15     350.978302 b      13.5875127 Y      0.0000000 N      +
+ 16     352.914341 d      0.0000000 N      0.0000000 N      +
+ 17     357.843506 a      6.2908806 Y      0.0000000 N      +
+ 18     367.262579 e      0.0000000 N      0.0000000 N      +
+ 19     750.789322 c      0.0000000 N      2740.7726644 Y    +
+ 20     750.789322 c      0.0000000 N      1578.4651217 Y    +
+ 21     759.074753 b      0.1020993 Y      0.0000000 N      +
+ 22     759.074753 b      0.1020993 Y      0.0000000 N      +
+ 23     934.212786 a      3.3810839 Y      0.0000000 N      +
+ 24     943.691776 d      0.0000000 N      0.0000000 N      +
+ 25     1063.623655 f      0.0000000 N      1084.5054801 Y    +
+ 26     1064.499192 e      0.0000000 N      0.0000000 N      +
+ 27     1477.394745 b      60.1305243 Y      0.0000000 N      +
+ 28     1477.394745 b      60.1305243 Y      0.0000000 N      +
+ 29     1497.569299 c      0.0000000 N      326.8876303 Y      +
+ 30     1497.569299 c      0.0000000 N      166.1035373 Y      +
+-----+-----+-----+-----+
+ Character table from group theory analysis of eigenvectors                      +
+ Point Group = 20, D3d                                                            +
+-----+-----+-----+-----+
+ Rep  Mul | E  3  2'  I  -3 m_v  +
+-----+-----+-----+-----+
+ a A2u  4 | 1  1  -1  -1  -1  1  +
+ b Eu   6 | 2  -1  0  -2  1  0  +
+ c Eg   4 | 2  -1  0  2  -1  0  +
+ d A2g  3 | 1  1  -1  1  1  -1  +
+ e A1u  2 | 1  1  1  -1  -1  -1  +
+ f A1g  1 | 1  1  1  1  1  1  +
=====

```

```

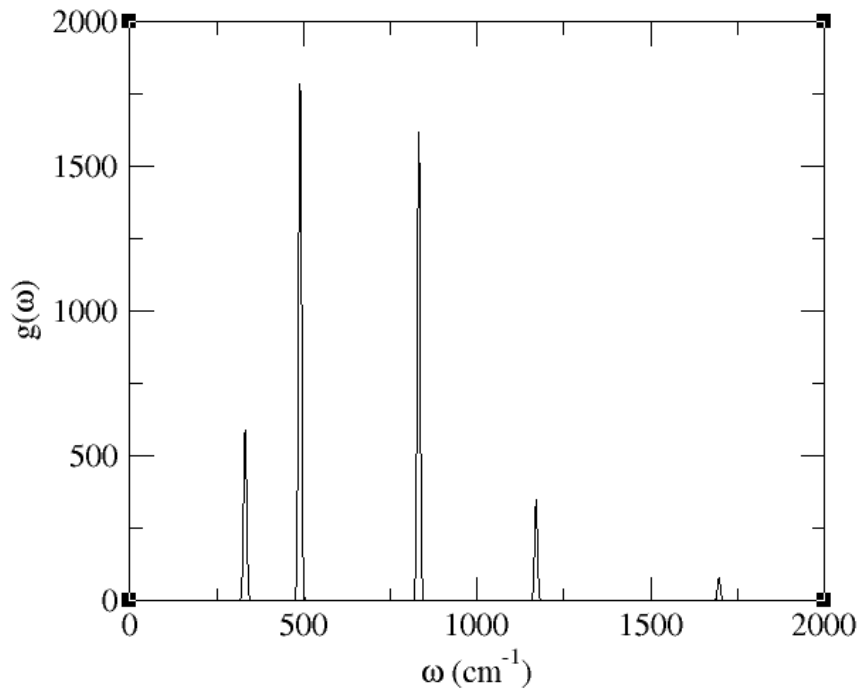
=====
+                               Vibrational Frequencies                               +
+                               -----                               +
+ Performing frequency calculation at 1 wavevector (q-pt)                          +
+=====+
+ q-pt= 1 ( 0.000000 0.000000 0.000000) 1.000000                               +
+-----+
+ N      Frequency irrep.   ir intensity active  raman intensity active +
+      (cm-1)              ((D/A)**2/amu)      (A**4)                  +
+-----+-----+-----+-----+
+ 1      39.749322   a      0.0000000 N      0.0000000 N      +
+ 2      39.749322   a      0.0000000 N      0.0000000 N      +
+ 3      52.778560   b      0.0000000 N      0.0000000 N      +
+ 4      199.161809 b      3.9290085 Y      0.0000000 N      +
+ 5      226.501587 a      1.8015706 Y      0.0000000 N      +
+ 6      226.501587 a      1.8015706 Y      0.0000000 N      +
+ 7      332.157239 c      0.0000000 N      146.2201274 Y      +
+ 8      332.157239 c      0.0000000 N      255.0960635 Y      +
+ 9      416.249989 d      0.0000000 N      0.0000000 N      +
+ 10     472.072821 a      1.4666606 Y      0.0000000 N      +
+ 11     472.072821 a      1.4666606 Y      0.0000000 N      +
+ 12     484.618753 e      0.0000000 N      0.0000000 N      +
+ 13     489.870460 c      0.0000000 N      1821.1632853 Y      +
+ 14     489.870460 c      0.0000000 N      212.5054495 Y      +
+ 15     552.345551 d      0.0000000 N      0.0000000 N      +
+ 16     605.708678 a      10.0867743 Y      0.0000000 N      +
+ 17     605.708678 a      10.0867743 Y      0.0000000 N      +
+ 18     635.503946 b      4.8697887 Y      0.0000000 N      +
+ 19     831.975435 c      0.0000000 N      1969.8312210 Y      +
+ 20     831.975435 c      0.0000000 N      1427.0347802 Y      +
+ 21     878.738103 a      1.4037034 Y      0.0000000 N      +
+ 22     878.738103 a      1.4037034 Y      0.0000000 N      +
+ 23     939.909301 b      6.1851687 Y      0.0000000 N      +
+ 24     950.038261 d      0.0000000 N      0.0000000 N      +
+ 25     1170.261937 f      0.0000000 N      1052.2920976 Y      +
+ 26     1178.980341 e      0.0000000 N      0.0000000 N      +
+ 27     1666.983123 a      60.5770370 Y      0.0000000 N      +
+ 28     1666.983123 a      60.5770370 Y      0.0000000 N      +
+ 29     1696.909816 c      0.0000000 N      96.6539168 Y      +
+ 30     1696.909816 c      0.0000000 N      258.2564498 Y      +
+-----+-----+-----+-----+
+ Character table from group theory analysis of eigenvectors                      +
+ Point Group = 20, D3d                                                            +
+-----+-----+-----+-----+
+ Rep  Mul | E  3  2'  I  -3 m_v  +
+-----+-----+-----+-----+
+ a Eu   6 | 2  -1  0  -2  1  0  +
+ b A2u  4 | 1  1  -1  -1  -1  1  +
+ c Eg   4 | 2  -1  0  2  -1  0  +
+ d A2g  3 | 1  1  -1  1  1  -1  +
+ e A1u  2 | 1  1  1  -1  -1  -1  +
+ f A1g  1 | 1  1  1  1  1  1  +
=====

```

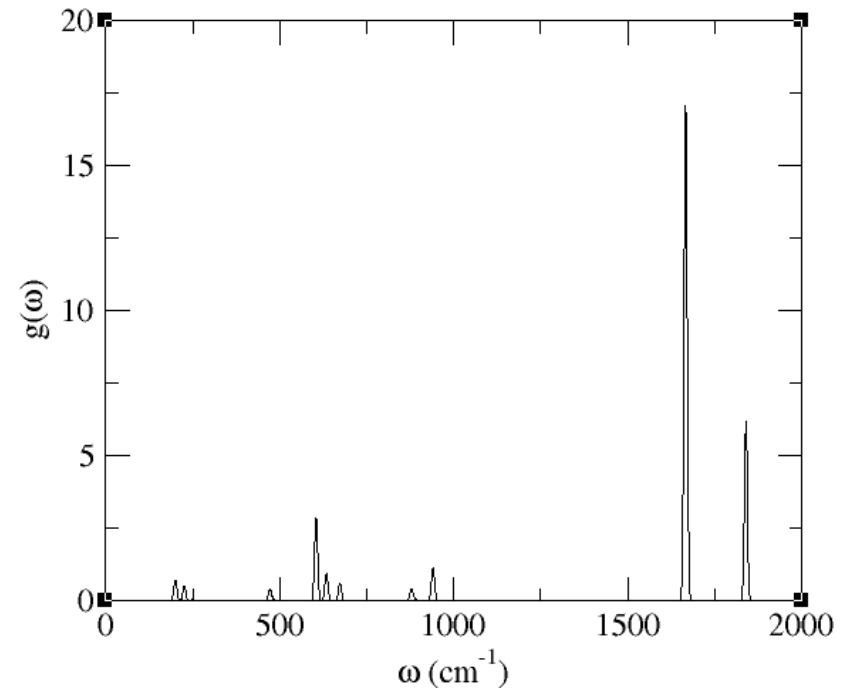
Mode frequencies, IR intensities and Raman intensities

Mode symmetry assignments

MgCO₃ Spectra (50 GPa)



Raman Spectrum



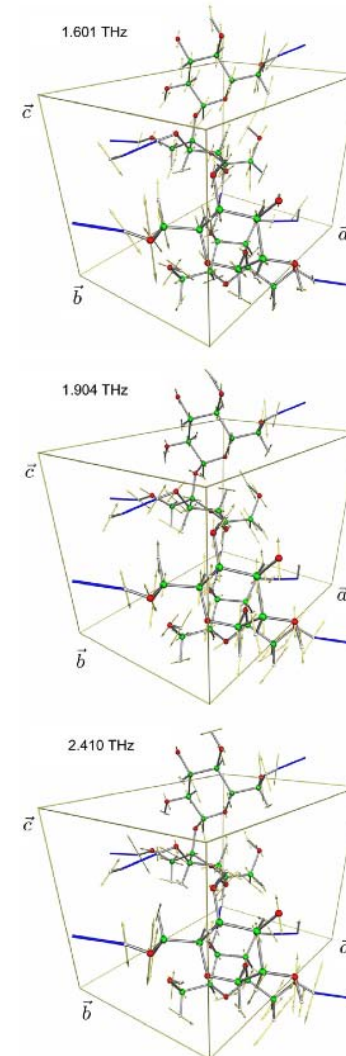
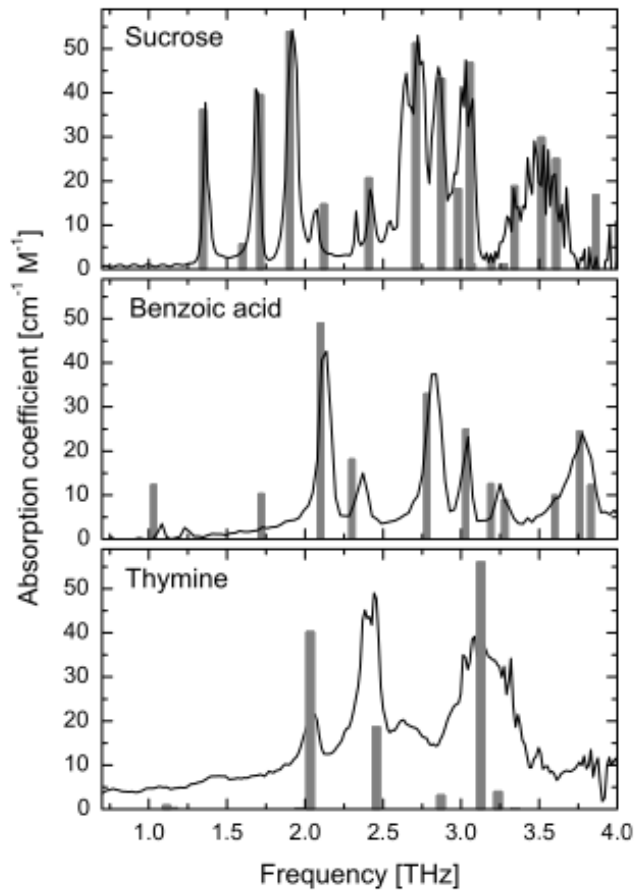
IR Spectrum

S. J. Clark, P. Jouanna, J. Haines and D. Mainprice, Phys. Rev. B (Submitted), 2009.

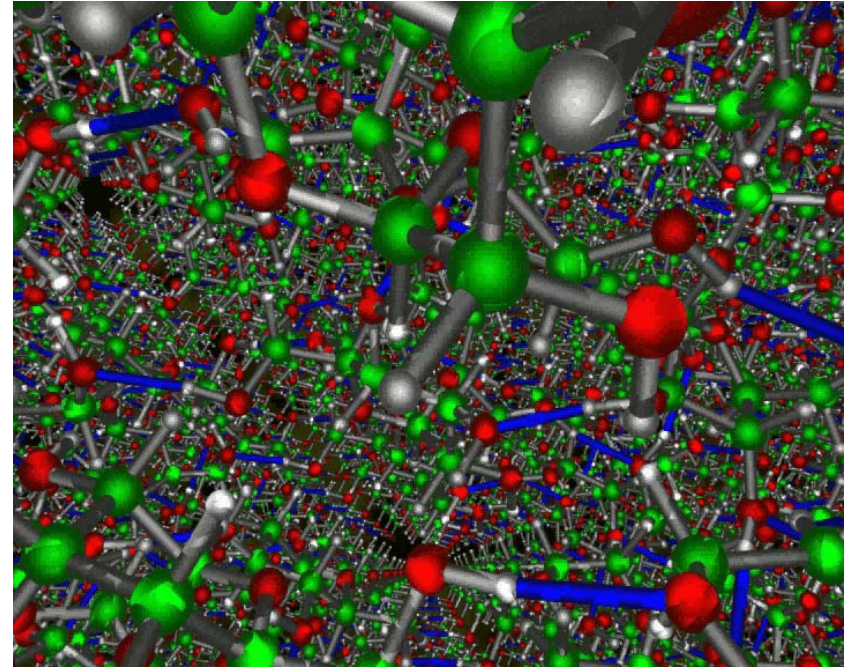
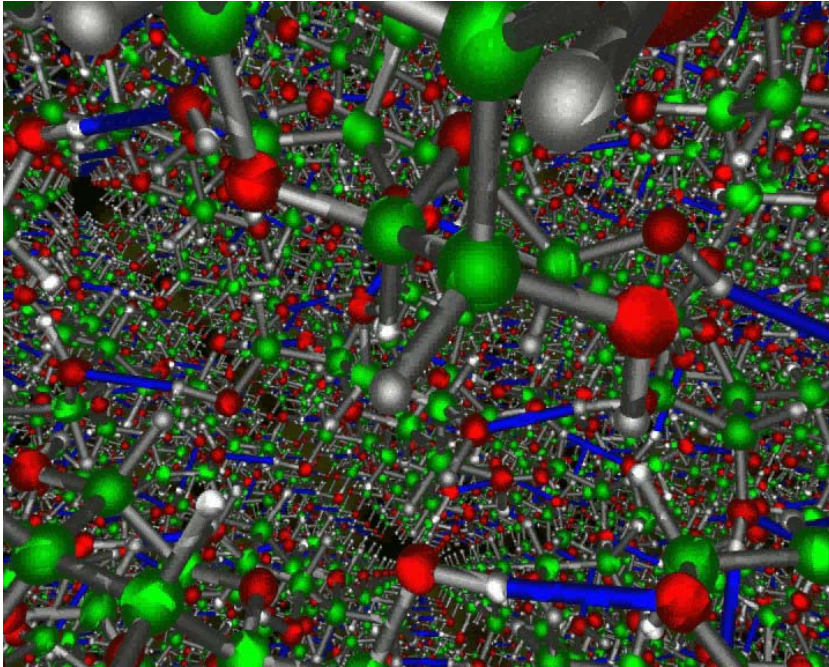
THz Measurements

- Now we make comparison between THz time-domain spectroscopy results and Castep's DFPT calculations
- Low frequency phonon modes have the highest computational noise (most sensitive to convergence issues)
 - Electronic SCF convergence to machine accuracy 10^{-13} eV
 - Residual forces on atoms better than 10^{-4} eV/Å
 - High k-point sampling
 - Computationally, a very demanding calculation

Spectrum and phonon eigenvectors



Phonon Eigenvectors

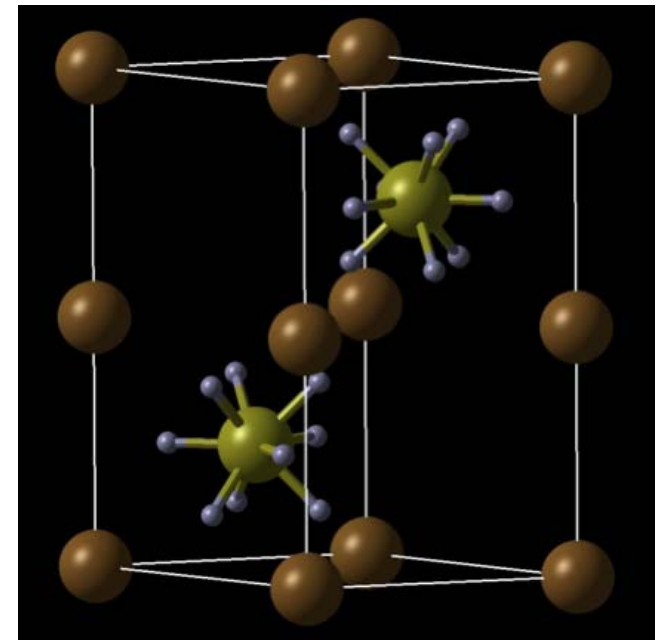
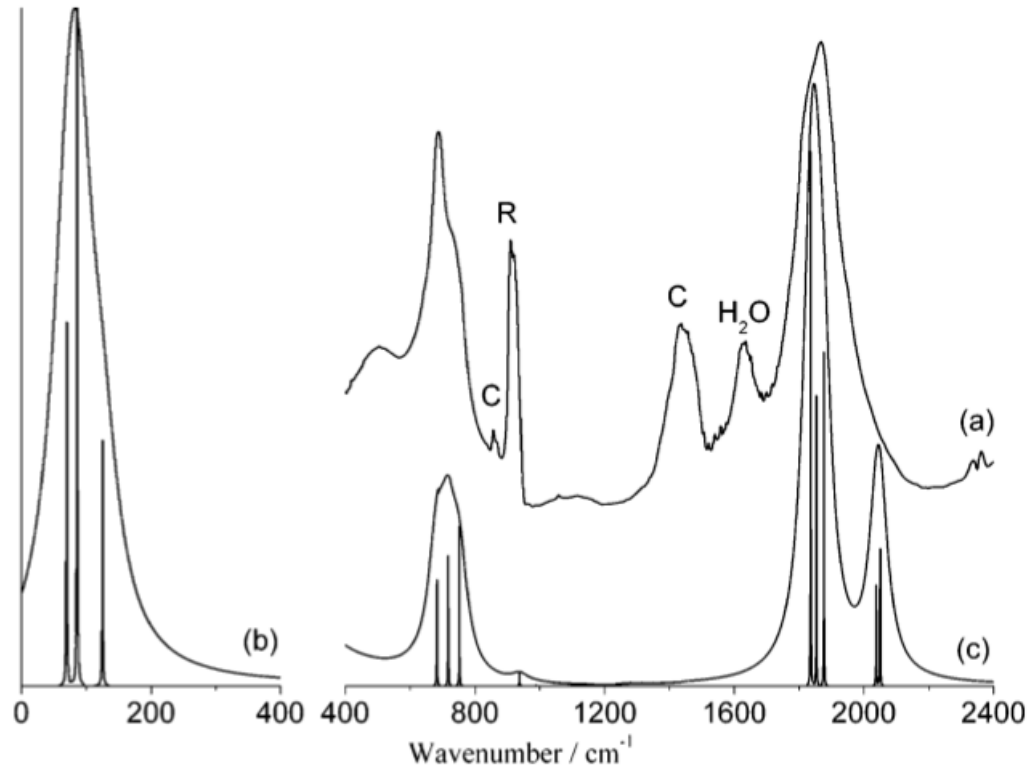


Phonon eigenvectors represent atomic motion: they describe the direction in which atoms move under excitation of a given phonon

Ab initio characterisation of $[\text{ReH}_9]^{2-}$

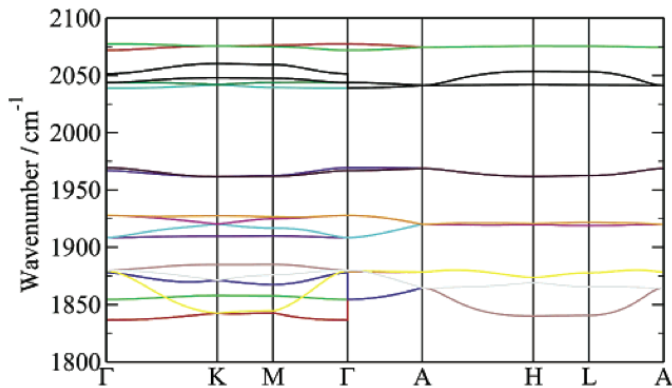
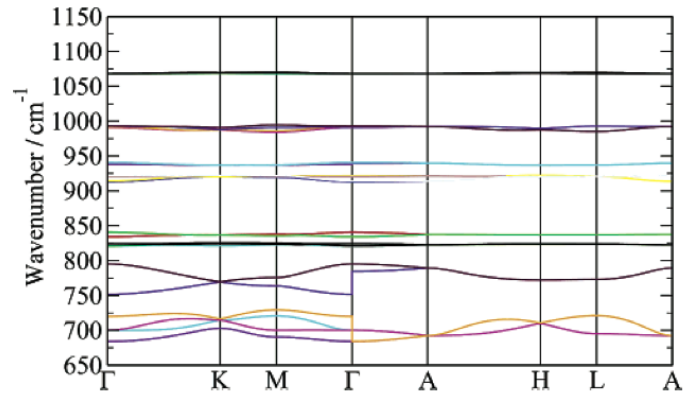
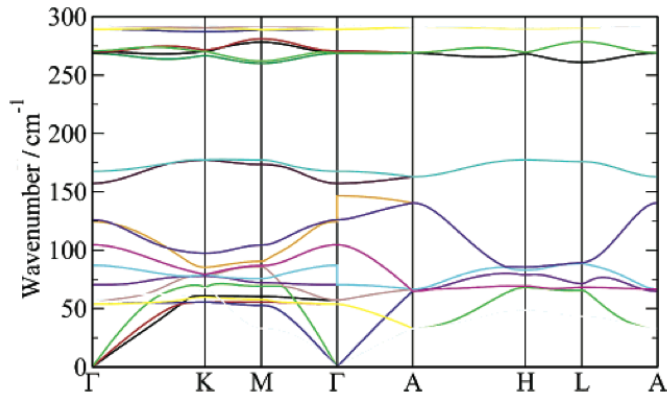
- Dynamics of the complex $\text{Ba}[\text{ReH}_9]$ investigated
- Contains the D_{3h} face capped trigonal $[\text{ReH}_9]^{2-}$ ion
- Investigated using Castep's DFPT, IR, Raman and inelastic neutron scattering
- Long range interactions important (must use periodic unit cell)

IR Spectrum



Crystal structure of BaReH₉

DFPT Dispersion Curves and Charges



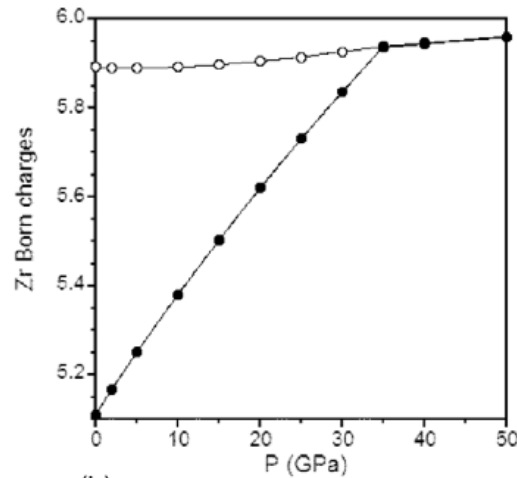
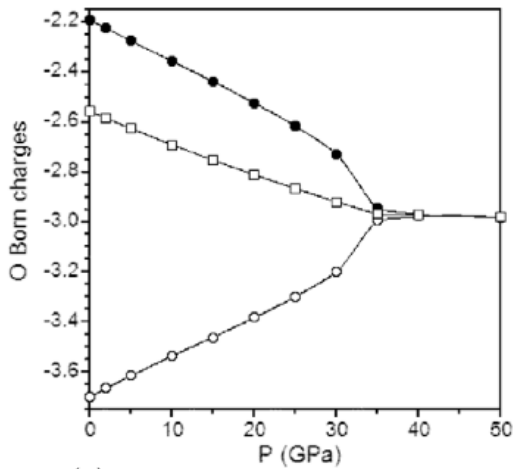
species	s	p	d	total	Mulliken charge	Born effective charges
H _{cap}	1.20			1.20	-0.20	xx = -0.647 yy = 0.260 zz = 0.156
H _{prism}	1.21			1.21	-0.21	xx = -0.736 yy = 0.122 zz = 0.230
Re	0.33	0.19	6.01	6.53	+0.47	xx = -1.769 yy = -1.772 zz = -1.757
Ba	2.03	6.00	0.60	8.63	+1.37	xx = 2.668 yy = 2.668 zz = 3.037

Vibrational Properties of ZrO_2 under pressure: a DFPT study

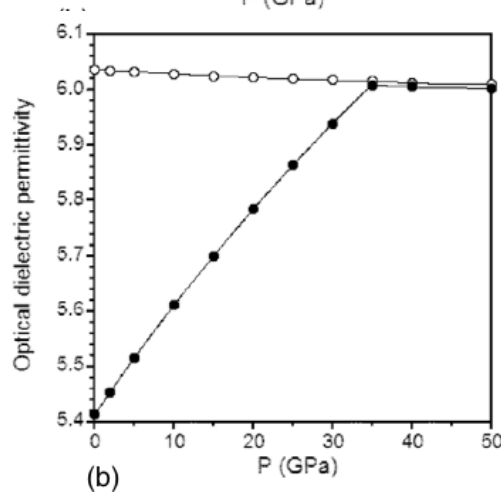
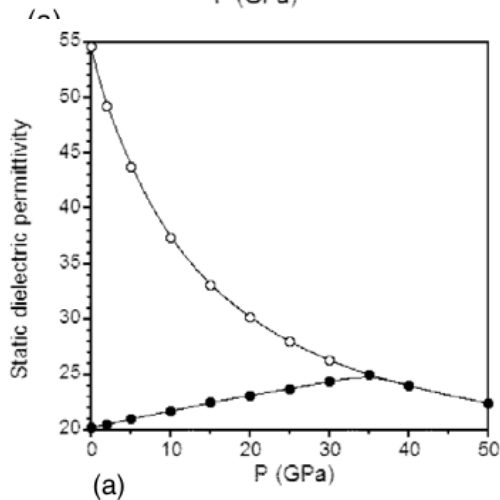
- ZrO_2 extremely important for modern technological applications
 - Useful mechanical properties for medical devices
 - Engineering applications
 - Electronic device applications
- Ambient pressure has three polymorphs
- Cubic, tetragonal and monoclinic
- Full phase diagram shows a rich variety of transformations are possible
- Assignment of vibrational modes was a long standing open issue

V. Milman, A. Perlov, K. Refson, S. J. Clark, J. Gavartin and B. Winkler,
J. Phys. Condens. Matter 21, 485404 (2009)

Pressure dependence on properties

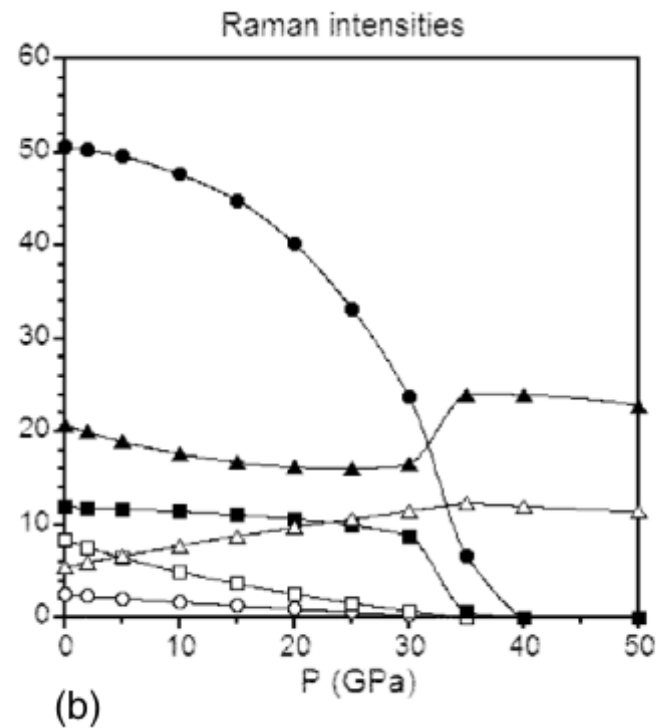
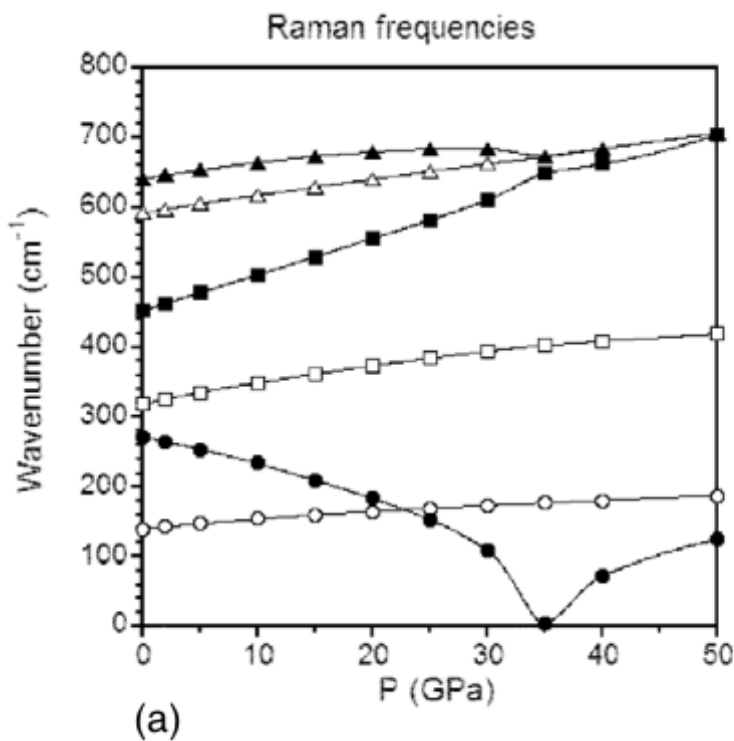


Pressure dependence on Born effective charges in tetragonal zirconia

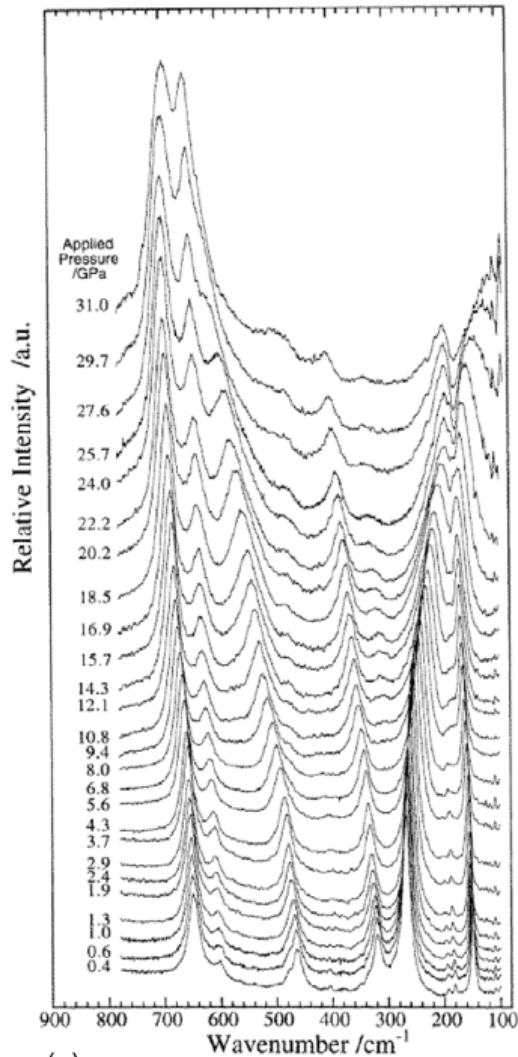


Pressure dependence on the (a) static and (b) optical dielectric permittivity (ϵ_{xx} and ϵ_{zz})

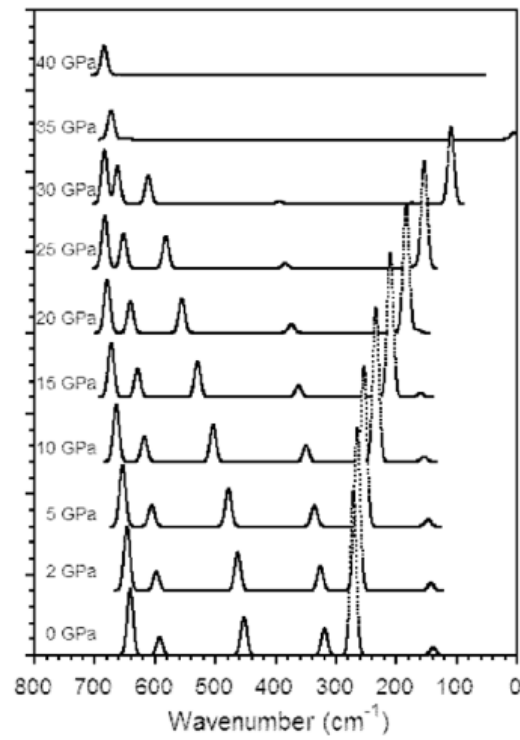
Pressure dependence on Raman frequencies



Raman Spectra



(a)



(b)

- Tetragonal distortions disappear at 37 GPa
- Structure is fluorite-like cubic modification at higher pressures
- Transition clear in vibrational frequencies, dielectric permittivity and Born charges
- Strongest Raman line (A_{1g}) softens under pressure
- Structure remains cubic until at least 50 GPa

Summary

- Wide range of spectroscopic calculations
 - Phonons (DoS and Dispersion)
 - Both Perturbation and finite displacement methods
 - IR intensities (spectrum)
 - Raman intensities (spectrum)
 - Polarisability
 - Permittivity
 - Born Charges
- Not mentioned today
 - NMR
 - core level spectroscopy

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