Vibrational Spectroscopy via Computer Simulations: Raman, Infra-Red and Related Methods

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MASTANI Summer School, July 11th 2014

Vibrational spectroscopies

Introduction

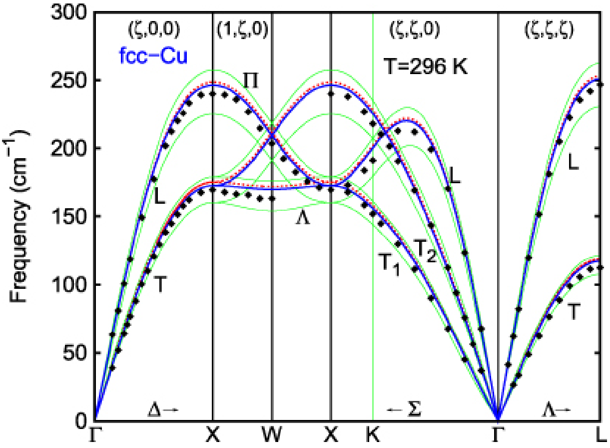
- Characterisation of the system via its vibrations
- Different vibrational spectroscopies
  - Neutron scattering spectroscopy
  - Infra-red spectroscopy
  - Raman spectroscopy

Neutron scattering

- Strong scattering at low-Z elements
- No charge
- Nuclear interaction simple
- Magnetic dipole moment, studies of magnetic structures
- Low energy, non-distructive

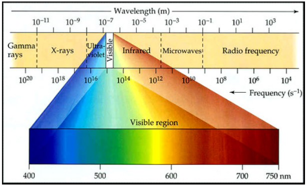
- Expensive to produce
- Interact weakly with matter, large samples needed

Neutron scattering spectroscopy: Example

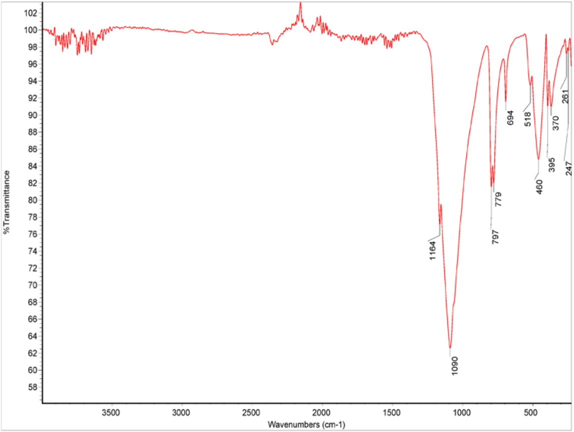


Infra-red spectroscopy

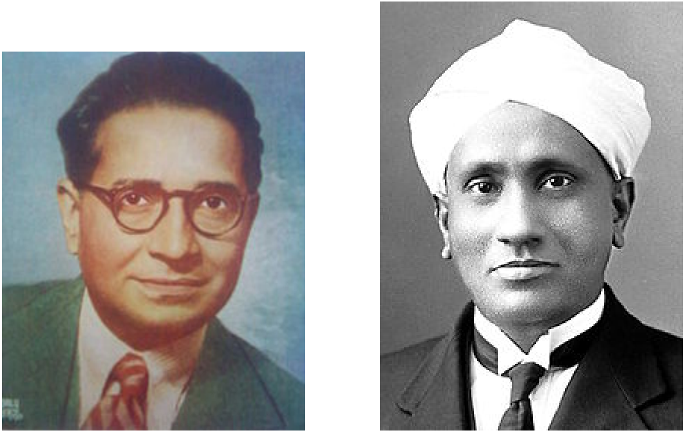
- Dispersion of light at frequencies comparable with those of vibrational modes
- Wave lengths are macroscopic compared to the size of the interatomic distance or units cells $\Rightarrow$ only $\mathbf{q} = 0$
- Linear spectroscopy here; non-linear methods like multi-dimensional (several photons) like 2D-IR beyond the scope



Infra-red spectroscopy: Example



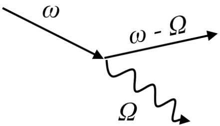
Raman effect

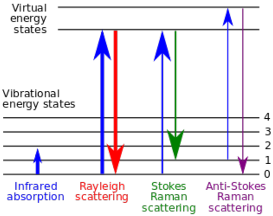


Raman scattering spectroscopy

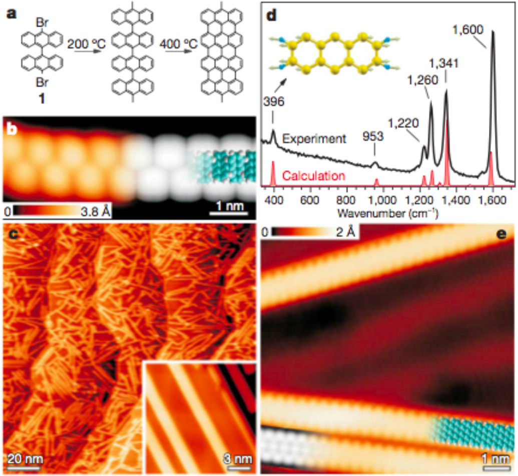
- Based on inelastic scattering of light; $\mathbf{q} \approx 0$
- Only non-resonant processes possible nowadays
- Central quantity: polarisability tensor $\overline{\overline{\alpha}}$
- Cross section of mode ν:

$$\frac{d\sigma^{\nu}}{d\Omega} = \frac{{\omega_{\nu}}^{4}}{(4\pi\varepsilon_0)^2 c^4} \left| \mathbf{e}_i \cdot \overline{\overline{A}}^{\nu} \cdot \mathbf{e}_s \right|^2$$





Raman spectroscopy: Example



Static approach

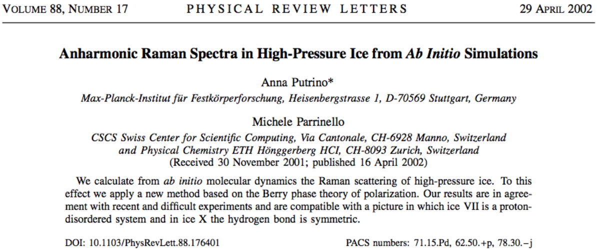
- Harmonic theory
- Eigenfrequencies and eigenmodes calculated using DFPT/linear response, intensity needed

Dynamic approach

- Molecular dynamics/time evolution of dipole M (IR) or polarisability α (Raman):

$$I_{\mathrm{IR}}(\omega) \propto FT\left\{\int_{t=0}^{\infty} M(t)M(t=0)\,dt\right\}$$

$$I_{\mathrm{Raman}}(\omega) \propto FT\left\{\int_{t=0}^{\infty} \alpha(t)\alpha(t=0)\,dt\right\}$$



VOLUME 88, NUMBER 17 PHYSICAL REVIEW LETTERS 29 APRIL 2002

Anharmonic Raman Spectra in High-Pressure Ice from *Ab Initio* Simulations

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(Received 30 November 2001; published 16 April 2002)

We calculate from *ab initio* molecular dynamics the Raman scattering of high-pressure ice. To this effect we apply a new method based on the Berry phase theory of polarization. Our results are in agreement with recent and difficult experiments and are compatible with a picture in which ice VII is a proton-disordered system and in ice X the hydrogen bond is symmetric.

DOI: 10.1103/PhysRevLett.88.176401 PACS numbers: 71.15.Pd, 62.50.+p, 78.30.–j

Selection rules

- IR: Active modes produce dipole, symmetry operations transforming like x, y, z
- Raman: Active modes produce polarisability, symmetry operations transforming like xy, yz, zx

Vibrational spectroscopies

1. Introduction
2. Infra-red spectroscopy
3. Raman spectroscopy
4. Using Quantum ESPRESSO

Infra-red spectroscopy

- Dispersion of light at frequencies comparable with those of vibrational modes
- Coupling of vibrational with electromagnetic modes
- Central quantities:
    - Dielectric function $\varepsilon(\omega)$,
    - $\varepsilon_1 = \Re\{\varepsilon(\omega)\}$,
    - $\varepsilon_2 = \Im\{\varepsilon(\omega)\}$,
    - Energy-loss $-\Im\left\{\frac{1}{\varepsilon(\omega)}\right\}$

IR: System in an electric field

- Displacement from equilibrium position $u_{I\mu}$
- Equation of motion:

$$M_I \ddot{u}_{I\mu} = -\sum_{J\lambda} \sqrt{M_I M_J}\, D_{I\mu,J\lambda} u_{J\lambda} + \mathbf{Z}^*_{I\mu} \cdot \mathbf{E}\ ,$$

where

  - dynamical matrix $D_{I\mu,J\lambda} = \frac{1}{\sqrt{M_I M_J}} \left.\frac{\partial^2 E_{\mathrm{tot}}}{\partial u_{I\mu} \partial u_{J\lambda}}\right|_{u_{I\mu}=0, u_{J\lambda}=0}$ with eigenfrequencies ω_n and normalised eigenmodes $e^n_{I\mu}$
  - Born effective charges $\mathbf{Z}^*_{I\mu\lambda} = -\left.\frac{\partial^2 E_{\mathrm{tot}}}{\partial u_{I\mu} \partial \mathbf{E}_\lambda}\right|_{u_{I\mu}=0, \mathbf{E}_\lambda=0}$

IR: Oscillating electric field

- Oscillating field $\mathbf{E} = \mathbf{E}^0 e^{(i\omega+\eta)t}$
- Linear order: $u_{I\mu}(t) = u^0_{I\mu} e^{(i\omega+\eta)t}$

$$\Rightarrow \quad u^0_{I\mu} = \sum_{nJ\lambda} \frac{1}{(\eta - i\omega)^2 - \omega_n} \frac{e^n_{I\mu}}{\sqrt{M_I}} \frac{e^n_{J\lambda}}{\sqrt{M_J}} \mathbf{Z}^*_{J\lambda} \cdot \mathbf{E}^0$$

- Thus absorption occurs at eigenfrequencies of the system, with amplitudes $\propto \mathbf{Z}^*$

IR: Intensity from the dipole

- The effective dipole $= \mathbf{Z}^*_I \cdot u_I$, and the intensity

$$I^{\nu}_{\mathrm{IR}} = \sum_{\mu} \left| \sum_{I} \mathbf{Z}^*_{I\mu} \cdot u^{\nu}_I \right|^2$$

$$\mathbf{Z}^*_{I\mu\lambda} = - \left. \frac{\partial^2 E_{\mathrm{tot}}}{\partial u_{I\mu} \partial \mathbf{E}_\lambda} \right|_{u_{I\mu}=0, \mathbf{E}_\lambda=0} = \Omega \left. \frac{\partial P}{\partial u_{I\mu}} \right|_{u_{I\mu}=0} = \left. \frac{\partial F_I}{\partial \mathbf{E}_\lambda} \right|_{\mathbf{E}_\lambda=0}$$

(Could be used with finite differences)

IR: $\mathbf{Z}^*$ from DFT

- Born-Oppenheimer approximation
- (Kohn-Sham) Hamiltonian with a static electric field:

$$\hat{\mathcal{H}}(\mathbf{E}) = \hat{\mathcal{H}}(\mathbf{E}=0) + \hat{\mathcal{V}}^{\mathrm{el}}(\mathbf{E}) + \hat{\mathcal{V}}^{\mathrm{ion}}(\mathbf{E}) \ ,$$

  where
  - $\hat{\mathcal{V}}^{\mathrm{el}}(\mathbf{E}) = -e\,\mathbf{E}\cdot\hat{\mathbf{r}}$
  - $\hat{\mathcal{V}}^{\mathrm{ion}}(\mathbf{E}) = e\sum_I Z_I\,\mathbf{E}\cdot\mathbf{R}_I$
- Isolated system:
  - $\mathbf{P}^{\mathrm{el}}(\mathbf{E}) = \frac{e}{\Omega}\int n(\mathbf{r})\,\hat{\mathbf{r}}\,d\mathbf{r}$
  - $\mathbf{P}^{\mathrm{ion}}(\mathbf{E}) = -e\sum_I Z_I\,\mathbf{R}_I$

$$\Rightarrow \quad \mathbf{Z}^*_{I\mu,\lambda} = -e\sum_v \frac{\partial}{\partial u_{I\mu}}\langle\psi_v \mid \hat{\mathbf{r}}_\lambda \mid \psi_v\rangle + e\sum_I Z_I\,\delta_{\mu\lambda}$$

IR: $\mathbf{Z}^*$ from DFT

- Using DFPT in linear response regime

$$\mathbf{Z}^*_{I\mu,\lambda} = -e \sum_v \left(\left\langle \frac{\partial \psi_v}{\partial u_{I\mu}} \mid \hat{\mathbf{r}}_\lambda \mid \psi_v \right\rangle + \mathrm{c.c.} \right) + e \sum_I Z_I \, \delta_{\mu\lambda}$$

IR: Position operator in extended system

- $\langle \psi_m \mid \mathbf{r} \mid \psi_v \rangle$ not well defined
- Recasting

$$\langle \psi_m \mid \mathbf{r} \mid \psi_v \rangle = \frac{\langle \psi_m \mid [H_{\mathrm{KS}}, \mathbf{r}] \mid \psi_v \rangle}{\varepsilon_m - \varepsilon_v} \quad \forall m \neq n \, ,$$

where $[H_{\mathrm{KS}}, \mathbf{r}] = -\frac{\hbar^2}{m_e}\frac{\partial}{\partial \mathbf{r}} + [V_{\mathrm{NL}}, \mathbf{r}]$

- Using Green's functions

$$(H_{\mathrm{KS}} - \varepsilon_v) \left| \overline{\psi}_v^{\lambda} \right\rangle = P_m \, [H_{\mathrm{KS}}, \mathbf{r}] \mid \psi_v \rangle \ \ ,$$

where $\left| \overline{\psi}_v^{\lambda} \right\rangle = P_m \, \mathbf{r}_\lambda \, |\psi_v\rangle$ `solve_e.f90`

IR: Born effective charges

$$\mathbf{Z}^{*}_{I\mu,\lambda} = 2e \sum_{v} \left(\left\langle \frac{\partial \psi_v}{\partial u_{I\mu}} \mid \overline{\psi}_v^{\lambda} \right\rangle + \mathrm{c.c.} \right) + e \sum_{I} Z_I \, \delta_{\mu\lambda}$$

`zstar_eu.f90`

IR: Dielectric matrix and polarisability

- As by-products we obtain

$$\varepsilon^{\infty}_{\mu\lambda} = \delta_{\mu\lambda} + 4\pi \frac{\partial P_\lambda}{\partial \mathbf{E}_\mu} = \delta_{\mu\lambda} - \frac{4\pi}{\Omega} \frac{\partial^2 E_{\text{tot}}}{\partial \mathbf{E}_\lambda \partial \mathbf{E}_\mu} \; ,$$

where $P_\lambda = -\frac{1}{\Omega}\frac{\partial E_{\text{tot}}}{\partial \mathbf{E}_\lambda}$, and $\alpha_{\mu\lambda}$

`dielec.f90`

IR: Dielectric response

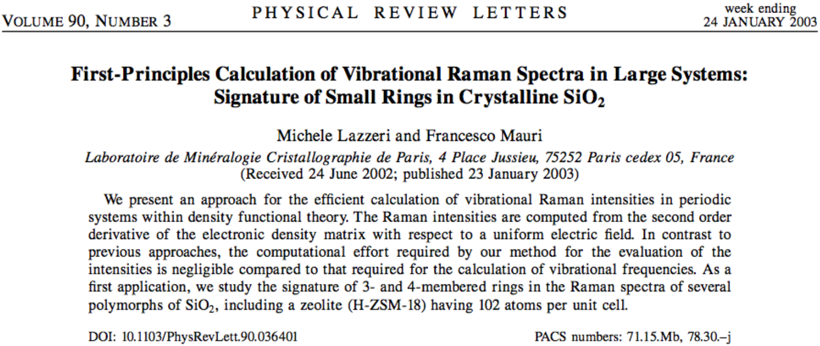
- Also

$$\begin{aligned} \varepsilon^1_{\mu\lambda} &= \varepsilon^\infty_{\mu\lambda} - \frac{4\pi}{\Omega}\sum_\nu \frac{F^\nu_\mu F^\nu_\lambda}{\omega^2 - \omega^2_\nu} \\ \varepsilon^2_{\mu\lambda} &= \frac{4\pi}{\Omega}\sum_\nu \frac{F^\nu_\mu F^\nu_\lambda}{2\omega^2_\nu}\delta(\omega - \omega_\nu) \end{aligned}$$

where $F^\nu_\mu = \sum_{I\lambda} \mathbf{Z}^*_{I\mu,\lambda} \frac{u_{I\lambda}}{\sqrt{M_I}}$

Vibrational spectroscopies

Raman spectroscopy in QE: Implementation



VOLUME 90, NUMBER 3 PHYSICAL REVIEW LETTERS week ending 24 JANUARY 2003

First-Principles Calculation of Vibrational Raman Spectra in Large Systems: Signature of Small Rings in Crystalline SiO_2

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(Received 24 June 2002; published 23 January 2003)

We present an approach for the efficient calculation of vibrational Raman intensities in periodic systems within density functional theory. The Raman intensities are computed from the second order derivative of the electronic density matrix with respect to a uniform electric field. In contrast to previous approaches, the computational effort required by our method for the evaluation of the intensities is negligible compared to that required for the calculation of vibrational frequencies. As a first application, we study the signature of 3- and 4-membered rings in the Raman spectra of several polymorphs of SiO_2, including a zeolite (H-ZSM-18) having 102 atoms per unit cell.

DOI: 10.1103/PhysRevLett.90.036401 PACS numbers: 71.15.Mb, 78.30.–j

Raman spectroscopy: Intensity

- Intensity of eigenmode μ:

$$I^{\nu} \propto \frac{(\omega_i - \omega_{\nu})^4}{\omega_{\nu}} \left| \mathbf{e}_i \cdot \overline{\overline{A}}^{\nu} \cdot \mathbf{e}_s \right|^2 (n_{\nu} + 1) \; ,$$

  where

  - $\mathbf{e}_i$, $\mathbf{e}_s$ = polarisation of incident, scattered photon, n_{ν} = Bose-Einstein occupation factor and

$$\overline{\overline{A}}^{\nu} = \sum_{I\mu} \frac{\partial^3 E^{\mathrm{el}}}{\partial \mathbf{E}\, \partial \mathbf{E}\, \partial u_{I\mu}} \frac{e_{I\mu}}{\sqrt{M_I}} \; ,$$

    or

$$\overline{\overline{A}}^{\nu} = \sum_{I\mu} \frac{\partial \overline{\overline{\alpha}}}{\partial u_{I\mu}} \frac{e_{I\mu}}{\sqrt{M_I}} \; ,$$

    the change in polarisability along a displacement along the normal mode

Raman spectroscopy: Implementation

- An alternative formulation, using the Kohn-Sham density matrix

$$n(\mathbf{r},\mathbf{r}') = \sum_{v} |\psi_v\rangle \langle\psi_v| \ ,$$

$$\frac{\partial E^{\mathrm{el}}}{\partial u_{I\mu}} = 2\mathrm{Tr}\left[n(\mathbf{r},\mathbf{r}') \frac{\partial V^{\mathrm{ext}}}{\partial u_{I\mu}} \right] \ , \ (\mathrm{H-F\ theorem})$$

$$\frac{\partial^3 E^{\mathrm{el}}}{\partial \mathbf{E}\, \partial \mathbf{E}\, \partial u_{I\mu}} = 2\mathrm{Tr}\left[\frac{\partial^2 n(\mathbf{r},\mathbf{r}')}{\partial \mathbf{E}\, \partial \mathbf{E}} \frac{\partial V^{\mathrm{ext}}}{\partial u_{I\mu}} \right]$$

- Evaluation of $\frac{\partial^2 n(\mathbf{r},\mathbf{r}')}{\partial \mathbf{E}\, \partial \mathbf{E}}$ requires six second-order calculations, independent of number of atoms

Raman spectroscopy: Implementation

- Perturbation theory:

$$\frac{\partial^2 n(\mathbf{r},\mathbf{r}')}{\partial\lambda\,\partial\mu} = \sum_v \Bigg[\left| P\eta_v^{(\lambda,\mu)} \right\rangle \langle\psi_v| + \left| P\frac{\partial\psi_v}{\partial\lambda} \right\rangle \left\langle \frac{\partial\psi_v}{\partial\mu} P \right| \\ + \sum_{v'} |\psi_{v'}\rangle \left\langle \frac{\partial\psi_{v'}}{\partial\lambda} P \,\middle|\, P\frac{\partial\psi_v}{\partial\mu} \right\rangle \langle\psi_v| \Bigg] + \text{c.c.}$$

- Terms $\left| P\frac{\partial\psi_v}{\partial\lambda} \right\rangle$, $\left| P\eta_v^{(\lambda,\mu)} \right\rangle$ calculated using Green's functions
- Involve $\partial V^{\mathrm{KS}}/\partial\lambda$, $\partial^2 V^{\mathrm{KS}}/(\partial\lambda\partial\mu)$, self-consistency needed

`solve_e2.f90`

Vibrational spectroscopies

Usage: IR, input

```
Normal modes for CO2
 &inputph
  tr2_ph    = 1e-14
  prefix    = 'CO2'
  amass(1)  = 12.010
  amass(2)  = 15.999
  outdir    = './scratch/'
  epsil     = .true.
  trans     = .true.
  asr       = .true.
  fildyn    = 'dmat.co2'
 /
 0.0 0.0 0.0
```

Usage: IR, output

```
     Electric Fields Calculation

      iter #   1 total cpu time :    81.9 secs   av.it.:   6.7
      thresh= 1.000E-02 alpha_mix =  0.700 |ddv_scf|^2 =  2.125E-08

      iter #   2 total cpu time :   113.7 secs   av.it.:  14.0
      thresh= 1.458E-05 alpha_mix =  0.700 |ddv_scf|^2 =  7.433E-08

...

      iter #   7 total cpu time :   261.3 secs   av.it.:  13.7
      thresh= 1.306E-08 alpha_mix =  0.700 |ddv_scf|^2 =  1.010E-14

      iter #   8 total cpu time :   291.5 secs   av.it.:  14.0
      thresh= 1.005E-08 alpha_mix =  0.700 |ddv_scf|^2 =  4.752E-17

     End of electric fields calculation
```

Usage: IR, output

```
     Dielectric constant in cartesian axis

     (       1.097029260       0.034059205       0.000000675 )
     (       0.034059205       1.097029260       0.000000675 )
     (       0.000003118       0.000003118       1.063644537 )

Polarizability (a.u.)^3                    Polarizability (A^3)
20.52      7.44      0.00             3.0413        1.1021        0.0001
 7.44     20.52      0.00             1.1021        3.0413        0.0001
 0.00      0.00     13.61             0.0000        0.0000        2.0166

     Effective charges (d Force / dE) in cartesian axis

      atom      1 C
 Ex  (       1.36251       0.91927       0.00000 )
 Ey  (       0.91927       1.36251       0.00000 )
 Ez  (      -0.00015      -0.00015       0.44133 )
      atom      2 O
 Ex  (      -0.67618      -0.46117      -0.00021 )
 Ey  (      -0.46117      -0.67618      -0.00021 )
 Ez  (      -0.00032      -0.00032      -0.22308 )
      atom      3 O
 Ex  (      -0.67538      -0.46058      -0.00009 )
 Ey  (      -0.46058      -0.67538      -0.00009 )
 Ez  (       0.00009       0.00009      -0.22323 )
```

Usage: Raman, input

```
&inputph
    tr2_ph               = 1e-14
    prefix               = 'gar-w_03-1H'
    amass(1)             =  12.0107
    amass(2)             =   1.0079
    outdir               = './scratch/'
    fildyn               = 'gar-w_03-1H-ph.dyn'
    recover              = .false.
    epsil                = .true.
    lraman               = .true.
    trans                = .true.
    fildrho              = "gar-w_03-1H-ph.fildrho"
    max_seconds          = 350000
/
0.0 0.0 0.0
```

Usage: Raman, output

```
Raman tensor (au^-1) in cartesian axis

 atom      1
(      0.664735398      -0.007862947       0.000000000 )
(     -0.007862947       0.011455170       0.000000000 )
(      0.000000000       0.000000000       0.000420683 )

(      0.109910490       0.045691031       0.000000000 )
(      0.045691031      -0.053438482       0.000000000 )
(      0.000000000       0.000000000      -0.003141788 )

(     -0.000000000       0.000000000      -0.031312700 )
(      0.000000000      -0.000000000      -0.001689833 )
(     -0.031312700      -0.001689833      -0.000000000 )

 atom      2
```

...

Usage: Raman, output

```
     Raman tensor (A^2)

     atom #    1    pol.  1
      0.408888389268E+02     -0.483661299120E+00      0.000000000000E+00
     -0.483661299120E+00      0.704624143907E+00      0.000000000000E+00
      0.000000000000E+00      0.000000000000E+00      0.258768276476E-01
     atom #    1    pol.  2
      0.676075372141E+01      0.281052160573E+01      0.000000000000E+00
      0.281052160573E+01     -0.328707859334E+01      0.000000000000E+00
      0.000000000000E+00      0.000000000000E+00     -0.193255963525E+00
     atom #    1    pol.  3
     -0.277499384006E-19      0.000000000000E+00     -0.192608963659E+01
      0.000000000000E+00     -0.170828783391E-22     -0.103944090539E+00
     -0.192608963659E+01     -0.103944090539E+00     -0.192182381315E-23
     atom #    2    pol.  1
     -0.408888389268E+02     -0.483661299120E+00      0.000000000000E+00
     -0.483661299120E+00     -0.704624143907E+00      0.000000000000E+00
      0.000000000000E+00      0.000000000000E+00     -0.258768276476E-01

...
```

Usage: Symmetries

```
     Mode symmetry, D_2h (mmm)  point group:

     freq (  1 -  1) =        -43.9  [cm-1]   --> B_1u            I
     freq (  2 -  2) =         24.8  [cm-1]   --> B_3g            R
     freq (  3 -  3) =         47.4  [cm-1]   --> B_3u            I
     freq (  4 -  4) =         73.1  [cm-1]   --> B_2u            I
     freq (  5 -  5) =        173.8  [cm-1]   --> B_1u            I
     freq (  6 -  6) =        342.2  [cm-1]   --> A_u
     freq (  7 -  7) =        350.7  [cm-1]   --> B_1g            R
     freq (  8 -  8) =        353.0  [cm-1]   --> B_3g            R
     freq (  9 -  9) =        386.3  [cm-1]   --> B_2g            R
     freq ( 10 - 10) =        530.4  [cm-1]   --> B_1u            I
     freq ( 11 - 11) =        536.8  [cm-1]   --> A_g             R
     freq ( 12 - 12) =        540.1  [cm-1]   --> B_1g            R
     freq ( 13 - 13) =        560.0  [cm-1]   --> B_2g            R
     freq ( 14 - 14) =        651.0  [cm-1]   --> B_3u            I
     freq ( 15 - 15) =        730.4  [cm-1]   --> B_1u            I
     freq ( 16 - 16) =        732.3  [cm-1]   --> A_u
     freq ( 17 - 17) =        740.5  [cm-1]   --> B_3g            R
     freq ( 18 - 18) =        762.7  [cm-1]   --> B_3u            I
     freq ( 19 - 19) =        826.2  [cm-1]   --> B_2u            I
     freq ( 20 - 20) =        846.5  [cm-1]   --> B_2g            R
     freq ( 21 - 21) =        912.0  [cm-1]   --> B_2g            R
     freq ( 22 - 22) =        912.4  [cm-1]   --> A_u
...
```

Usage

Character table for point group D_{2h}

D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ(xy)	σ(xz)	σ(yz)	linear functions, rotations	quadratic functions	cubic functions
A_g	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	-	x^2, y^2, z^2	-
B_{1g}	$+1$	$+1$	-1	-1	$+1$	$+1$	-1	-1	R_z	xy	-
B_{2g}	$+1$	-1	$+1$	-1	$+1$	-1	$+1$	-1	R_y	xz	-
B_{3g}	$+1$	-1	-1	$+1$	$+1$	-1	-1	$+1$	R_x	yz	-
A_u	$+1$	$+1$	$+1$	$+1$	-1	-1	-1	-1	-	-	xyz
B_{1u}	$+1$	$+1$	-1	-1	-1	-1	$+1$	$+1$	z	-	z^3, y^2z, xz^2
B_{2u}	$+1$	-1	$+1$	-1	-1	$+1$	-1	$+1$	y	-	yz^2, x^2y, y^3
B_{3u}	$+1$	-1	-1	$+1$	-1	$+1$	$+1$	-1	x	-	xz^2, xy^2, x^3

Usage: Symmetries

```
     Mode symmetry, D_2h (mmm)  point group:

     freq (  1 -   1) =        -43.9  [cm-1]   --> B_1u            I
     freq (  2 -   2) =         24.8  [cm-1]   --> B_3g            R
     freq (  3 -   3) =         47.4  [cm-1]   --> B_3u            I
     freq (  4 -   4) =         73.1  [cm-1]   --> B_2u            I
     freq (  5 -   5) =        173.8  [cm-1]   --> B_1u            I
     freq (  6 -   6) =        342.2  [cm-1]   --> A_u
     freq (  7 -   7) =        350.7  [cm-1]   --> B_1g            R
     freq (  8 -   8) =        353.0  [cm-1]   --> B_3g            R
     freq (  9 -   9) =        386.3  [cm-1]   --> B_2g            R
     freq ( 10 -  10) =        530.4  [cm-1]   --> B_1u            I
     freq ( 11 -  11) =        536.8  [cm-1]   --> A_g             R
     freq ( 12 -  12) =        540.1  [cm-1]   --> B_1g            R
     freq ( 13 -  13) =        560.0  [cm-1]   --> B_2g            R
     freq ( 14 -  14) =        651.0  [cm-1]   --> B_3u            I
     freq ( 15 -  15) =        730.4  [cm-1]   --> B_1u            I
     freq ( 16 -  16) =        732.3  [cm-1]   --> A_u
     freq ( 17 -  17) =        740.5  [cm-1]   --> B_3g            R
     freq ( 18 -  18) =        762.7  [cm-1]   --> B_3u            I
     freq ( 19 -  19) =        826.2  [cm-1]   --> B_2u            I
     freq ( 20 -  20) =        846.5  [cm-1]   --> B_2g            R
     freq ( 21 -  21) =        912.0  [cm-1]   --> B_2g            R
     freq ( 22 -  22) =        912.4  [cm-1]   --> A_u
...
```

Usage: Extracting intensities, plotting spectra

- Here we use `dynmat.x`, a simplified version of analysis
- Limitations: Beyond LDA *only* with shortcuts
- No ultra-soft PP, PAW with electric field