

Advanced School on  
**QUANTUM MODELLING**  
of Materials with CRYSTAL

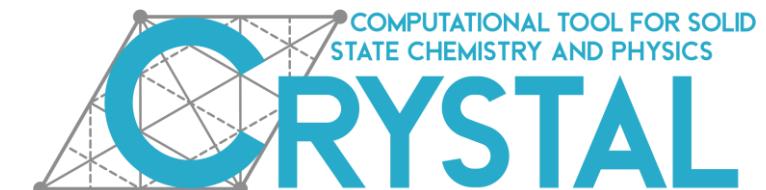
# Harmonic Frequencies and Spectra

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Hands-On Session



UNIVERSITÀ  
DI TORINO



# Tutorial Outline

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- ✓ Computing harmonic vibrational frequencies with CRYSTAL
  - ✓ The theoretical minimum
  - ✓ Input/Output tour
- ✓ IR and Raman intensities
  - ✓ Berry-Phase (numerical)
  - ✓ CPHF/KS (analytical)
- ✓ Plotting Vibrational Spectra:
  - ✓ Optional keywords
  - ✓ Tools (CRYSPLOT, CRYSTALClear,...)

# Vibrational Frequencies in CRYSTAL (II)

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- ✓ The mass-weighted Hessian is calculated:

$$W_{\alpha i, \beta j}(\mathbf{k} = \mathbf{0}) = \frac{H_{ij}}{\sqrt{M_\alpha M_\beta}}$$

Where  $M_\alpha$  and  $M_\beta$  are the masses of the atoms  $\alpha$  and  $\beta$  associated with the  $i$ -th and  $j$ -th coordinates, respectively.

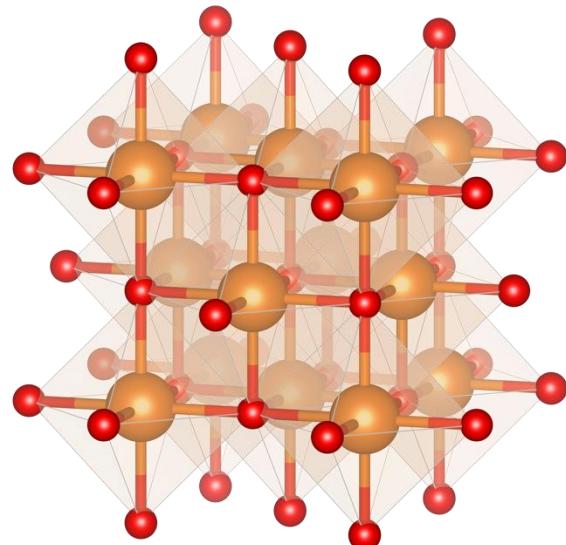
- ✓ The mass-weighted Hessian is diagonalized:
  - Eigenvalues → frequencies
  - Eigenvectors → normal modes

# Vibrational Frequencies in CRYSTAL (III)

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- ✓ Special properties of the  $\Gamma$  point ( $\mathbf{k}=0$ ):
  - The Hessian is simple to calculate
  - 3 modes have zero frequency (i.e., acoustic modes that correspond to translations in  $\Gamma$ )
  - The Hessian possesses the point symmetry of the crystal
  - $\Gamma$ -point vibrational modes give rise to IR and Raman spectra
- ✓ A supercell approach can be adopted to include more points of the first Brillouin zone
  - Phonon dispersion (`SCELPHONO` keyword)
  - Relevant for accurate thermodynamic properties
- ✓ The point group symmetry of the system is fully exploited to reduce the number of calculations (SCF+gradient) to be considered. On each numerical step, the residual symmetry is preserved during the SCF process and the gradients calculation.

# Input for Frequency Calculation



```
MgO - PBE/pob-DVZVP-rev2
CRYSTAL
0 0 0
225
4.26844350
2
12 0. 0. 0.
8 0.5 0.5 0.5
FREQCALC
END
BASISSET
POB-DZVP-REV2
DFT
PBE
END
SHRINK
8 8
END
```

Geometry Block

Basis set

DFT functional

Shrinking factor

# Infrared Intensities in CRYSTAL

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- ✓ The (harmonic) IR intensity  $I_i^{\text{IR}}$  of the  $i$ -th mode is defined as

$$I_i^{\text{IR}} \propto d_i \left( \frac{\partial \mu}{\partial Q_i} \right)^2 \quad \text{Born tensor in the basis of normal modes}$$

i.e., it is proportional to the first-derivative of the electric dipole moment  $\mu$  with respect to the normal mode  $Q_i$  times the degeneracy  $d_i$  of the  $i$ -th mode.

- ✓ Elements of the Born tensor can be computed in 3 different ways:
  - ✓ Berry phase (default)
  - ✓ Wannier functions
  - ✓ Coupled-perturbed Hartree-Fock/Kohn-Sham

# Input for IR Intensities

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FREQCALC block

```
FREQCALC
  RESTART
  INTENS
  INTCPHF
  END
  IRSPEC
  DAMPFAC
  4.0
  RANGE
  1200 1500
END
```

} Restart from previous calculation  
} CPHF/KS analytical approach  
} Simulate IR spectrum and store it in IRSPEC.DAT  
} Full width at half maximum (FWHM), default is 8.0  
} Frequency range, default is [0.0,  $\nu_{\max} \times 1.3$ ]

Keywords in *italic* are optional

# FREQCALC Output (I)

#### FORCE CONSTANT MATRIX - NUMERICAL ESTIMATE

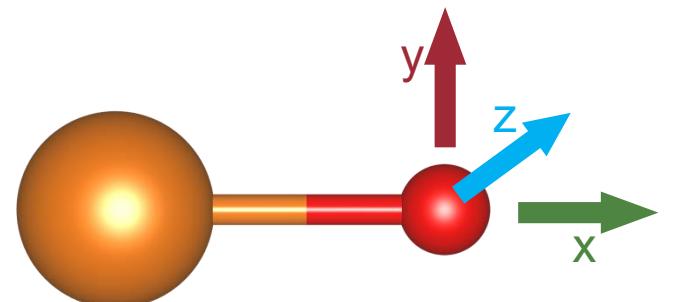
THE CENTRAL POINT

DE : ENERGY DIFFERENCE WITH RESPECT TO THE CENTRAL POINT  
(DE IS EXPECTED TO BE POSITIVE FOR ALL DISPLACEMENTS)

ATOM	MAX ABS (DGRAD)	TOTAL ENERGY (AU)	N.CYC	DE	SYM
CENTRAL POINT		-2.751735599829E+02	8	0.0000E+00	48
2 O DX	2.9289E-04	-2.751735591513E+02	4	8.3165E-07	8
2 O DY		GENERATED FROM A PREVIOUS LINE			
2 O DZ		GENERATED FROM A PREVIOUS LINE			

The mass-weighted Hessian  $H_{ij}$  is computed by numerical evaluation of first-derivatives of the analytical atomic gradients

$$H_{ij} = \left( \frac{\partial g_i}{\partial u_j} \right)_0 \approx \frac{g_i(0, \dots, u_j, 0, \dots)}{u_j}$$



# FREQCALC Output (II)

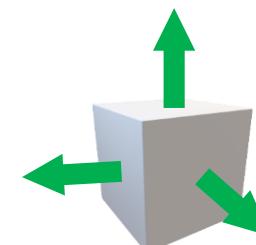
## Upon diagonalization of the mass-weighted Hessian...

## CONVERSION FACTORS FOR FREQUENCIES:

1 CM\*\* (-1) = 0.4556335E-05 HARTREE

$$1 \text{ THZ} = 0.3335641 \text{E+02 CM}^{**} (-1)$$

MODES	EIGV	FREQUENCIES	IRREP	IR	INTENS	RAMAN
	(HARTREE**2)	(CM**-1)	(THZ)		(KM/MOL)	
1 - 3	0.4758E-21	0.0000	0.0000	(Fu )	A ( 0.00)	I
4 - 6	0.2954E-05	377.1845	11.3077	(Fu )	A ( 1202.18)	I



**rigid translations of  
the whole crystal**

### 3 degenerate vibrational modes

# FREQCALC Output (III)

## NORMAL MODES NORMALIZED TO CLASSICAL AMPLITUDES (IN BOHR)

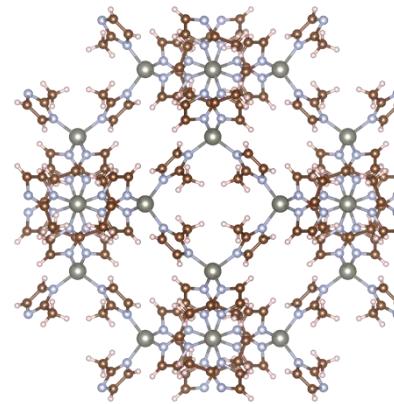
FREQ (CM\*\*-1)      0.00      0.00      0.00      377.18      377.18      377.18

AT.	1	MG	X	0.1582	0.0000	0.0000	0.0000	-0.0730	0.0000
			Y	0.0000	0.1582	0.0000	-0.0730	0.0000	0.0000
			Z	0.0000	0.0000	0.1582	0.0000	0.0000	-0.0730
AT.	2	O	X	0.1582	0.0000	0.0000	0.0000	0.1094	0.0000
			Y	0.0000	0.1582	0.0000	0.1094	0.0000	0.0000
			Z	0.0000	0.0000	0.1582	0.0000	0.0000	0.1094

# Exercise

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1. Perform a calculation of the IR spectrum of MgO. Make use of the Berry-phase approach.
2. Perform the same calculation by making use of the CPKS approach (slow).
3. Use **CRYSPLOT** to visualize lattice vibrations and IR spectrum of MgO (quite boring...).
4. Use **CRYSPLOT** to visualize lattice vibrations and IR spectrum of ZIF-8 (way more interesting!). Can you identify the frequencies corresponding to the “gate-opening” modes?



# Raman Intensities in CRYSTAL

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- ✓ The Raman intensity for an oriented single-crystal (let's consider the  $ij$  directions) associated to the mode with frequency  $\omega_k$  is:

$$I_{ij}^{\text{Raman}} \propto C(\alpha_{ij}^k)^2$$

where the  $\alpha_{ij}^k$  element of the Raman tensor is given by:

$$\alpha_{ij}^k = \frac{\partial^3 E}{\partial Q_k \partial \mathcal{E}_i \partial \mathcal{E}_j}$$

where  $\vec{\mathcal{E}}$  is the external electric field.

The pre-factor  $C$  depends on the laser frequency  $\omega_L$  and on temperature  $T$  as follows

$$C \propto \frac{1 + n(\omega_k)}{30\omega_k} (\omega_L - \omega_k)^4 \quad \text{with} \quad 1 + n(\omega_k) = \left[ 1 - \exp \left( -\frac{\hbar\omega_k}{K_B T} \right) \right]^{-1}$$

# Input for Raman Intensities

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FREQCALC block

```
FREQCALC
  RESTART
  INTENS
  INTCPHF
  END
  INTRAMAN
    RAMANEXP
    250 488
    RAMSPEC
    END
  END
```

} Restart from previous calculation

} CPHF/KS analytical approach (mandatory)

} Experimental conditions  
(temperature, frequency of incoming laser)

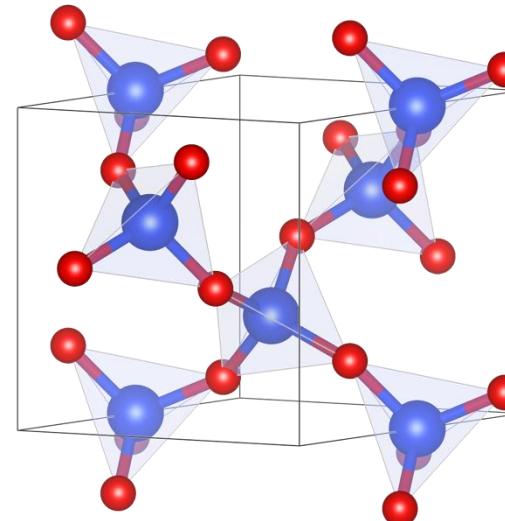
} Simulate Raman spectrum and store it in RAMSPEC.DAT

Keywords in *italic* are optional

# Exercise

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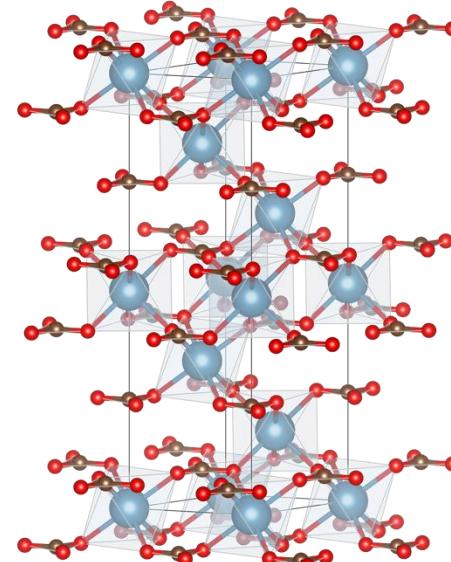
1. Starting from the  $\alpha$ -quartz input *qua\_hf\_2d\_f-raman\_295K\_488nm.d12*, insert the appropriate keywords to calculate the RAMAN intensities at 10 K and 400 K, using an incident radiation wavelength of 550 nm (use the **RAMANREA** keyword).
2. Simulate the corresponding Raman spectra (set the FWHM to 3).
3. Compare the two spectra using **CRYSPLOT**.



# Exercise

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1. Calculate the harmonic frequencies and IR intensities of calcite (RESTART).
2. Which are the irreducible representations? Which modes are IR active? And Raman active?
3. Analyse the normal modes by using **CRYSPLOT**. Which modes correspond to rigid shifts of the Ca lattice?



# Isotopic Substitution

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Isotopic substitution is a well-known technique adopted by experimentalists as a tool to help the assignment of an observed band in the vibrational spectrum. The same strategy can easily be implemented once the dynamical matrix is available.

This input allows to change the mass of the Si atoms of  $\alpha$ -quartz to 29 amu.

**FREQCALC**

*RESTART*

**ISOTOPES**

**3**                    number of atomic masses to be changed

**1 29**

**2 29**                label of atoms and isotopic mass (amu)

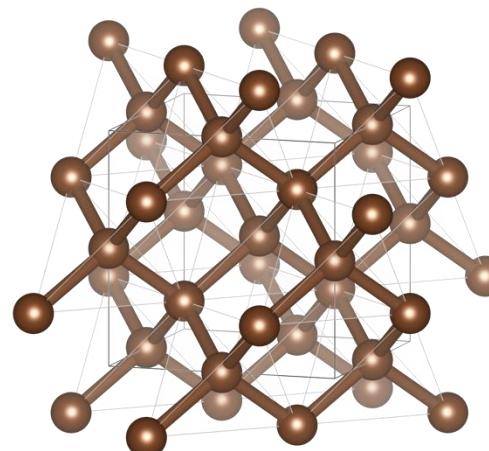
**3 29**

**END**

# Exercise

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1. Run a FREQCALC calculation on diamond.
2. Substitute natural carbon with  $^{13}\text{C}$  and recompute the harmonic frequencies (don't forget the RESTART keyword!)
3. Compute the ratio  $\frac{\omega_{13}}{\omega_{12}} = \sqrt{\frac{12}{13}}$  and compare with CRYSTAL output



# Exercise

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1. Run a FREQCALC calculation on the CO<sub>2</sub> molecule (D<sub>4h</sub> point group).
2. Recompute vibrational frequencies for the following substitutions:
  - $^{12}\text{C} \rightarrow ^{13}\text{C}$
  - $^{16}\text{O} \rightarrow ^{18}\text{O}$

Which isotope produces the largest frequency shift? Which mode is most sensitive to carbon mass?

3. Compute the ZPE for  $^{13}\text{C}^{16}\text{O}_2$  and  $^{12}\text{C}^{18}\text{O}_2$  : which structure is the most stable at low temperature?