Optical spectroscopy

Nanotechnology and Material Science
Lecture XI.
Department of Physics, BME
2024.

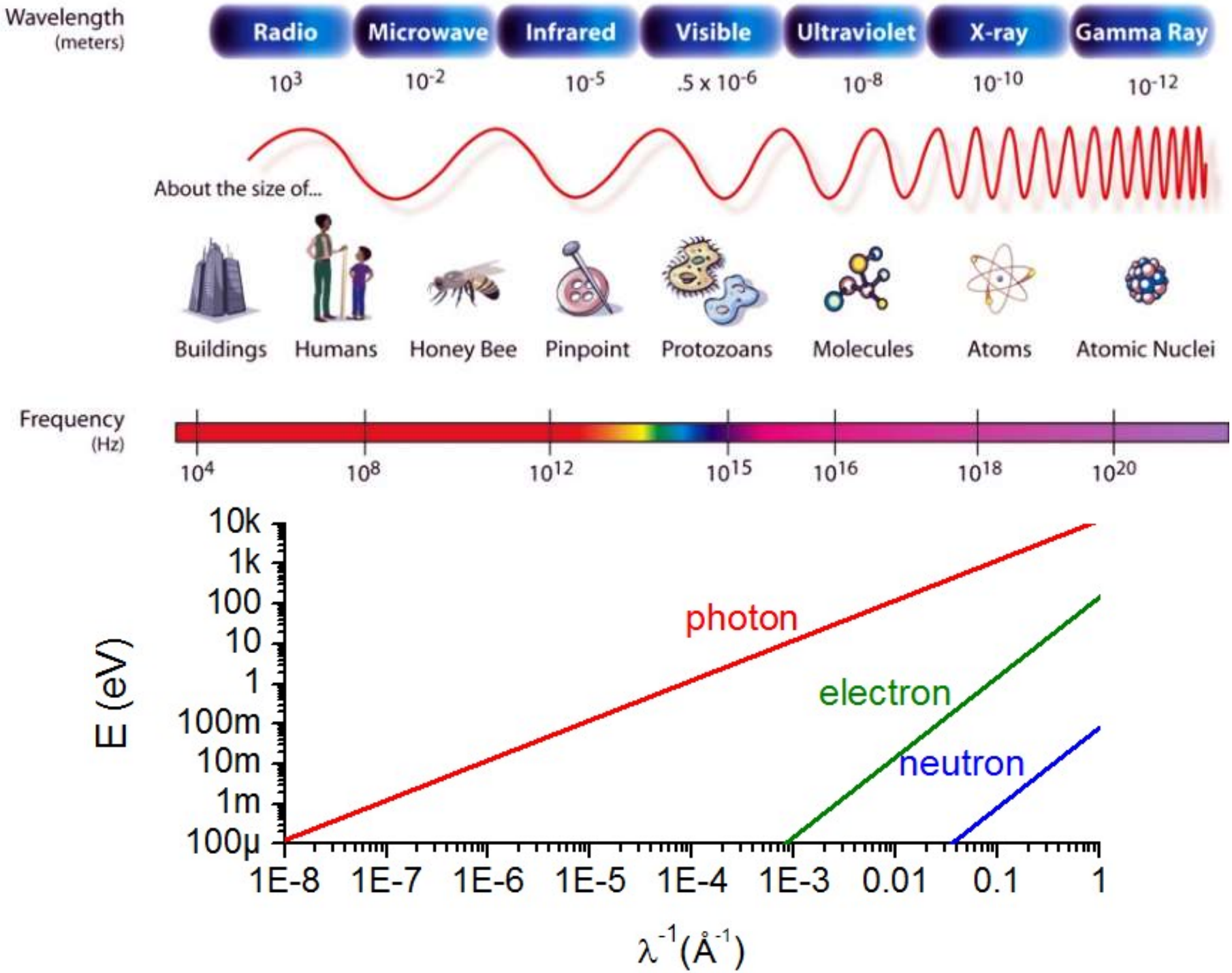
BMETE11MF58

Sándor Bordács

website: https://physics.bme.hu/BMETE11MF58_kov?language=en

Email: bordacs.sandor@ttk.bme.hu

Optical spectroscopy



Optical spectroscopy

Recommended literature

Tanner: Optical effects in solids (Library of the Physics Institute)

Dressel: Electrodynamics of solids

Atkins: Molecular quantum mechanics

Struve: Fundamentals of molecular spectroscopy

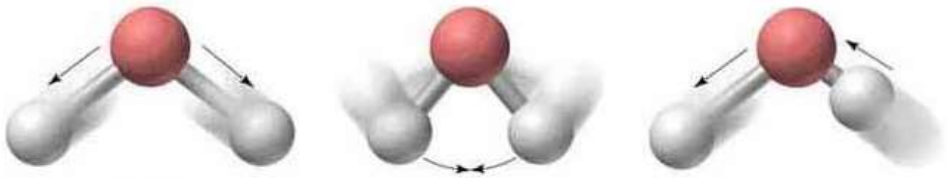
Kamarás: Bevezetés a modern optikába V. 11. fejezet

Sólyom: A modern szilárdtest-fizika alapjai I. 13. fejezet

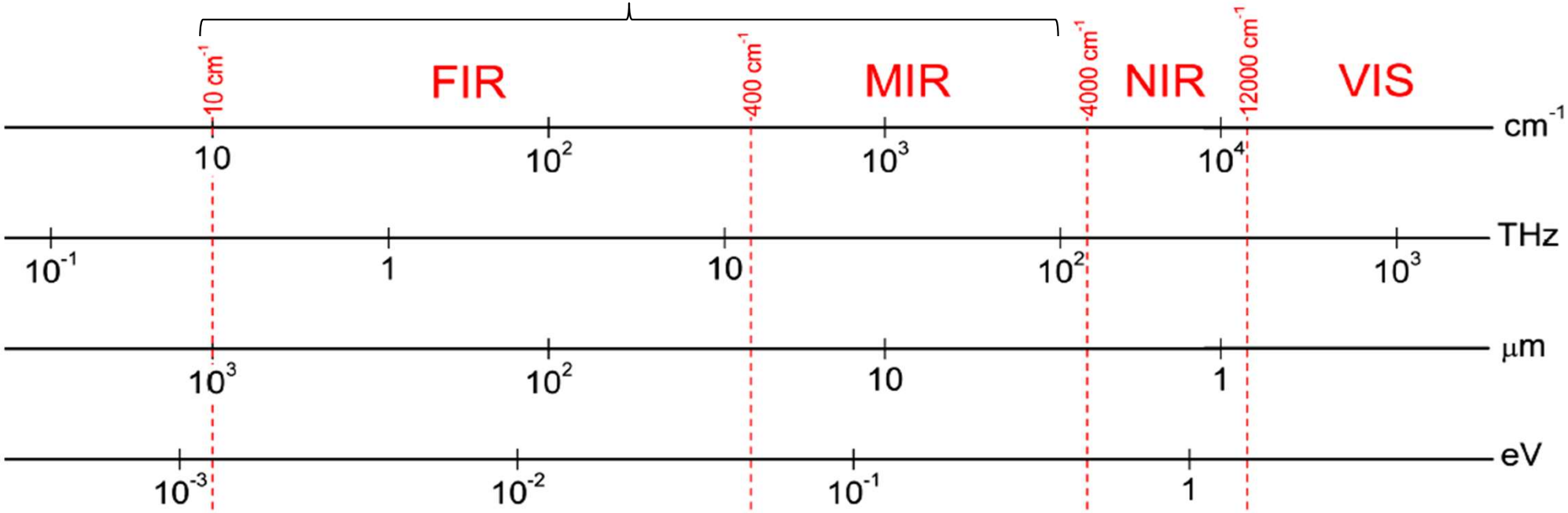
More details in the spring semester

Optikai spektroszkópia az anyagtudományban (BMETE11MF39)
(Optical Spectroscopy in Materials Science)

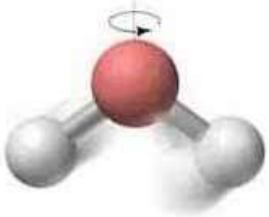
Optical spectroscopy



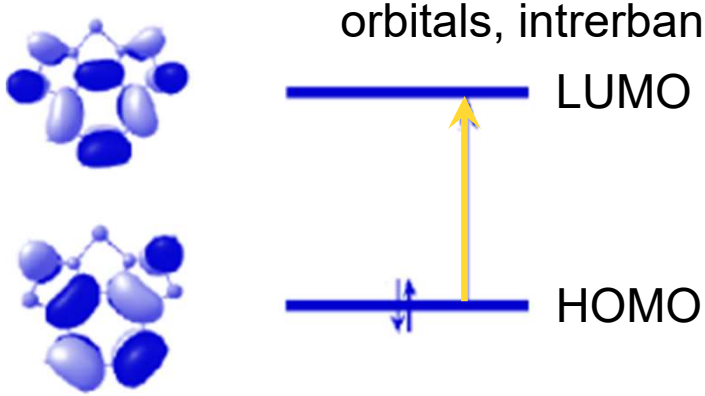
Vibrations of molecules and solids



Rotation of molecules



Electronic excitations between atomic and molecular orbitals, intrerband excitations in solids

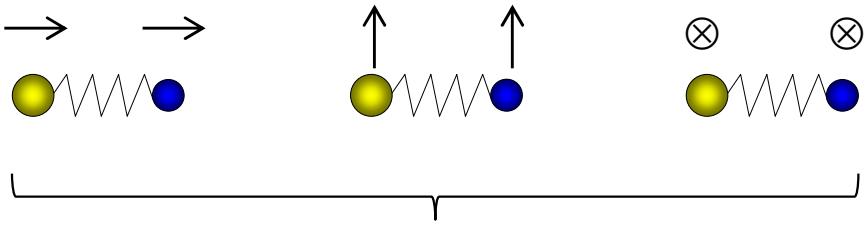


Optical spectroscopy: vibrational spectroscopy

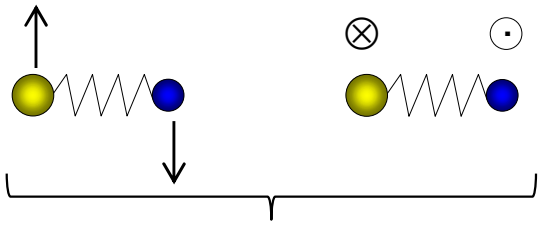
A diatomic molecule: (eg. HCl)

m_1, +e m_2, -e

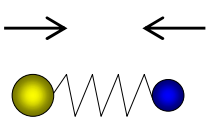
2×3 dimensinal displacement field: {x_1, y_1, z_1, x_2, y_2, z_2}



translational modes



rotational modes



vibrational mode

Equation of motions:

$$m_1\frac{d^2u_1}{dt^2}=-D(u_1-u_2)-\gamma m_1\frac{du_1}{dt}+eE(t)$$

$$m_2\frac{d^2u_2}{dt^2}=-D(u_2-u_1)-\gamma m_2\frac{du_2}{dt}-eE(t)$$

Long wavelength approximation:

$$E(t)=E_\omega e^{i\omega t}$$

trial function:

$$u_2(t)-u_1(t)=\Delta u_\omega e^{i\omega t}$$

$$-\omega^2\Delta u_\omega=-D\frac{m_1+m_2}{m_1m_2}\Delta u_\omega+i\gamma\omega\Delta u_\omega+\frac{m_1+m_2}{m_1m_2}eE_\omega$$

$$\mu=\frac{m_1m_2}{m_1+m_2}$$

$$\omega_0^2=\frac{D}{\mu}$$

$$P_\omega=en\Delta u_\omega=\frac{ne^2}{\mu}\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}E_\omega$$

$$\Omega_{pl}^2=\frac{ne^2}{\varepsilon_0\mu}$$

$$\varepsilon(\omega)=1+\chi(\omega)=1+\frac{\Omega_{pl}^2}{\omega_0^2-\omega^2-i\gamma\omega}$$

Optical spectroscopy: vibrational spectroscopy

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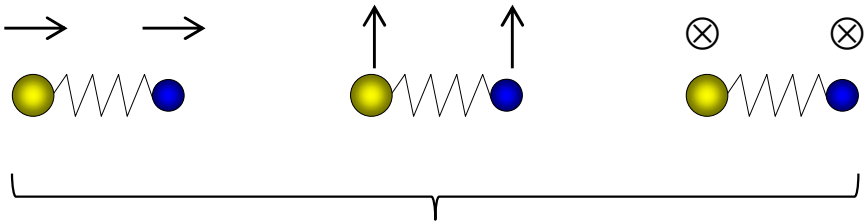
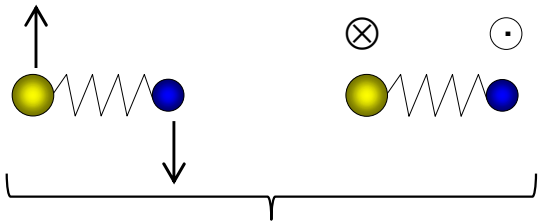
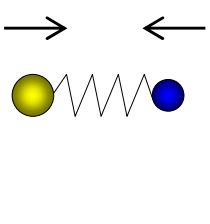


translational modes

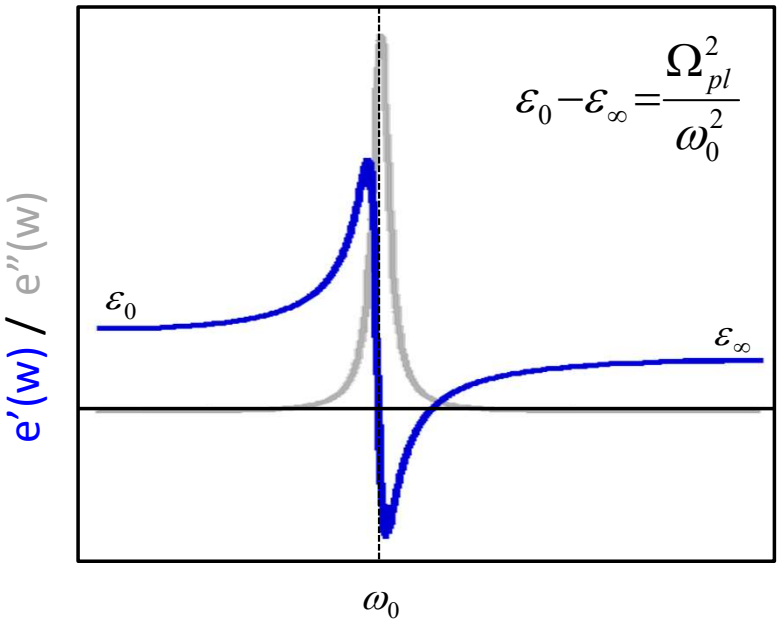


rotational modes



vibrational mode

$$\varepsilon(\omega)=\varepsilon_\infty+\chi(\omega)=\varepsilon_\infty+\frac{\Omega_{pl}^2}{\omega_0^2-\omega^2-i\gamma\omega}$$



Absorption coefficient:

$$E(r,t)=E_{q,\omega}e^{i(qr-\omega t)}=E_{q,\omega}e^{i\left[\frac{\omega}{c}\sqrt{\varepsilon}r-\omega t\right]}=E_{q,\omega}e^{i\left[\frac{\omega}{c}(n+ik)r-\omega t\right]}$$

$$\sqrt{\varepsilon}=n+ik\Leftrightarrow\begin{cases}n^2-k^2=\varepsilon'\\2nk=\varepsilon''\end{cases}$$

$$\overline{I(r)}=\left|E_{q,\omega}\right|^2e^{-2k\frac{\omega}{c_v}r}\equiv I_0e^{-\alpha r}\approx I_0e^{-\sqrt{2\varepsilon''}\frac{\omega}{c_v}r}$$

Close to the resonance

Reflectivity

$$R=\left|\frac{\sqrt{\varepsilon}-1}{\sqrt{\varepsilon}+1}\right|^2\qquad\varepsilon'=0\Rightarrow R=1$$

Optical spectroscopy: vibrational spectroscopy

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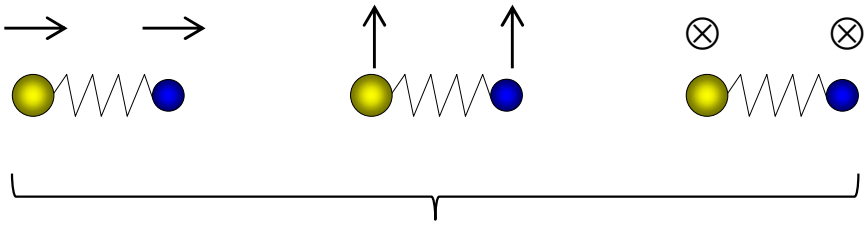
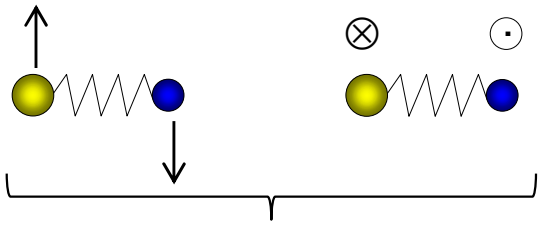
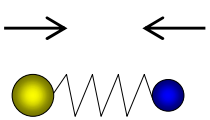
2×3 dimensinal displacement field: {x_1, y_1, z_1, x_2, y_2, z_2}



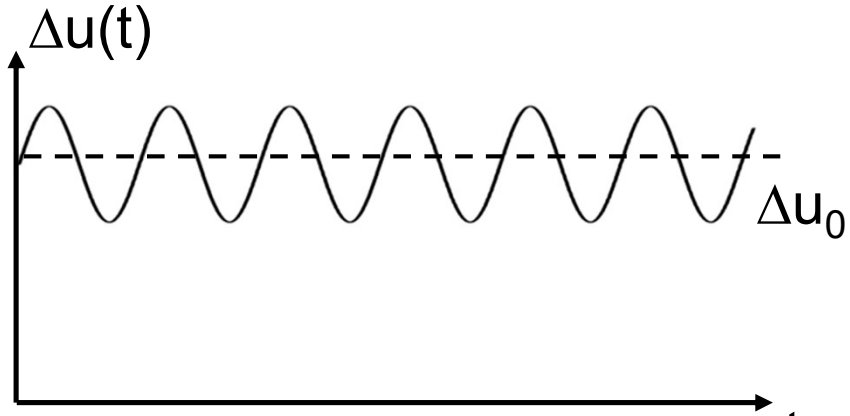
translational modes

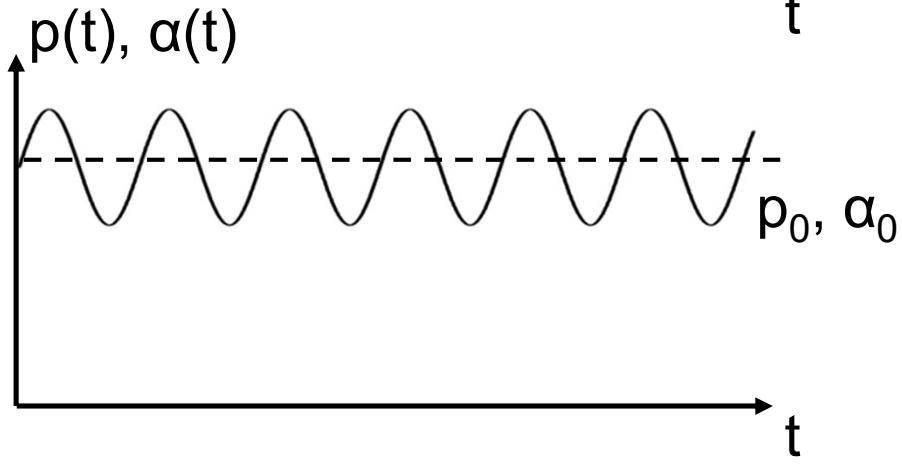


rotational modes



vibrational mode





Oscillations of the polarizability (Raman scattering):

$$p(t)=(\alpha_0+\frac{\partial\alpha}{\partial q}q+\ldots)E_\omega\cos(\omega t)$$

$$p(t)\approx(\alpha_0+\frac{\partial\alpha}{\partial\Delta u}\Delta u\cos(\omega_0 t))E_\omega\cos(\omega t)$$

$$p(t)\approx\alpha_0 E_\omega\cos(\omega t)+\frac{\Delta\alpha E_\omega}{2}[\cos((\omega_0+\omega)t)+\cos((\omega_0-\omega)t)]$$

anti-Stokes Stokes

Optical spectroscopy: vibrational spectroscopy

A diatomic molecule: (eg. HCl)

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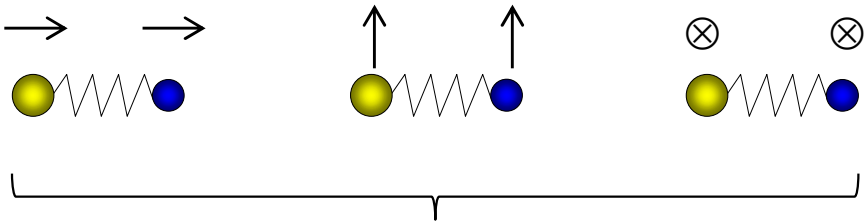
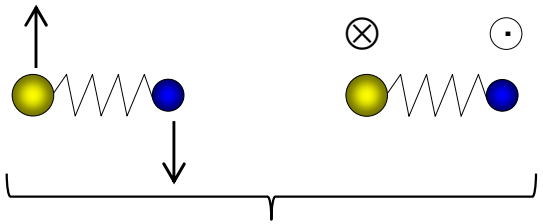
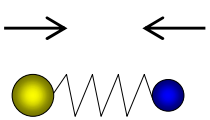


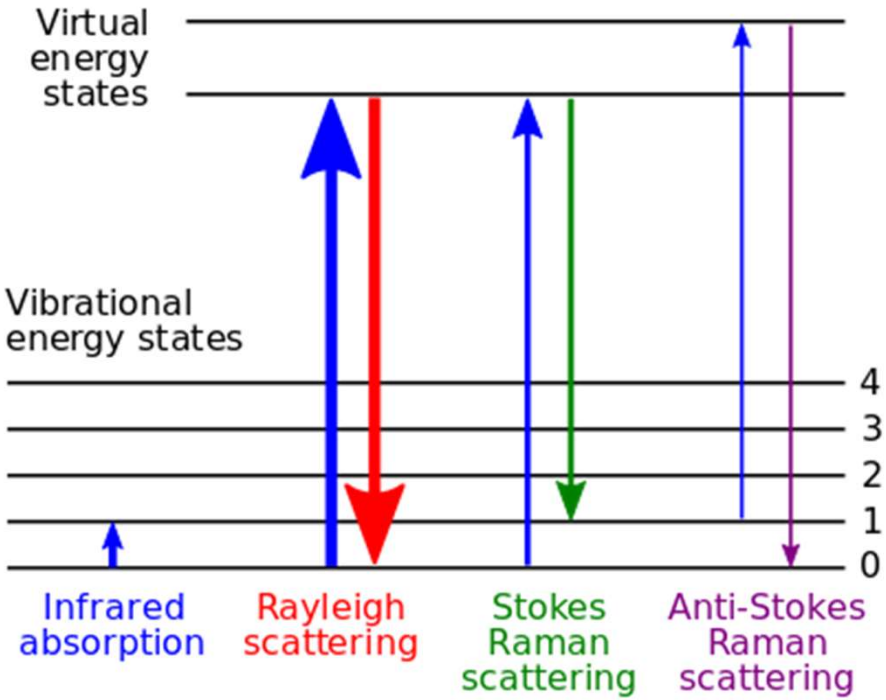
translational modes



rotational modes



vibrational mode



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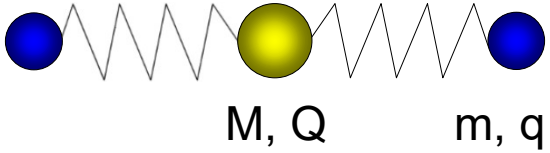
anti-Stokes Stokes

Vibrational spectroscopy

3 atomic linear molecule, 1d displacement: (eg. CO2)

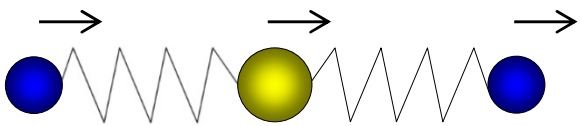


$$m\frac{d^2x_{O1}}{dt^2}=-D(x_{O1}-x_C)$$

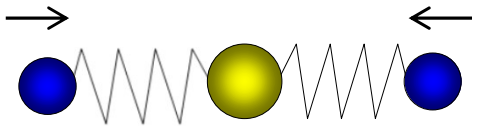
$$M\frac{d^2x_C}{dt^2}=-D(x_C-x_{O1})-D(x_C-x_{O2})$$

$$m\frac{d^2x_{O2}}{dt^2}=-D(x_{O2}-x_C)$$

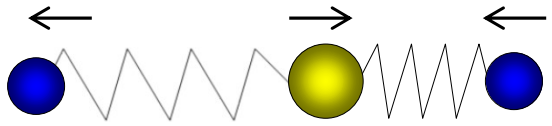
$$-\omega^2\begin{bmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{bmatrix}\begin{bmatrix} x_{O1} \\ x_C \\ x_{O2} \end{bmatrix}=\begin{bmatrix} -D & D & 0 \\ D & -D & D \\ 0 & D & -D \end{bmatrix}\begin{bmatrix} x_{O1} \\ x_C \\ x_{O2} \end{bmatrix}$$



$$\omega=0 \quad \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$



$$\omega^2=\frac{D}{m}\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$



$$\omega^2=\frac{D}{m}+\frac{2D}{M}\begin{bmatrix} 1 \\ -\frac{2m}{M} \\ 1 \end{bmatrix}$$

Vibrational spectroscopy

Polarization/polarizability:

m_1, +e m_2, -e

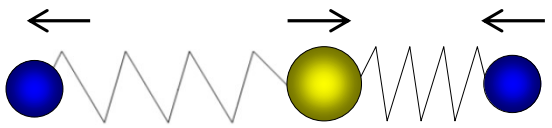
$P_0 \neq 0$

m_1, +e m_2, -e

$P_0 = 0$

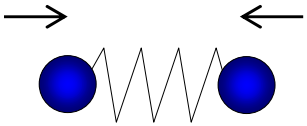
$P_\omega \neq 0, \alpha_\omega \neq 0$

IR, Raman



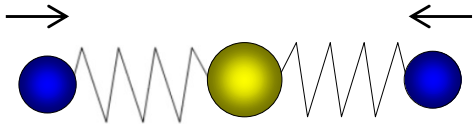
$P_\omega \neq 0, \alpha_\omega = 0$

IR



$P_\omega = 0, \alpha_\omega \neq 0$

Raman



$P_\omega = 0, \alpha_\omega \neq 0$

Raman

If the molecule has inversion symmetry, i.e. $\left[\hat{H}, i\right] = 0$, then the eigenfunctions of $\hat{H}$ are either even or odd → Vibrations are either Raman or IR active, respectively.

Vibrational spectroscopy

webbook.nist.gov/chemistry/

National Institute of Standards and Technology
U.S. Department of Commerce

NIST Chemistry WebBook, SRD 69

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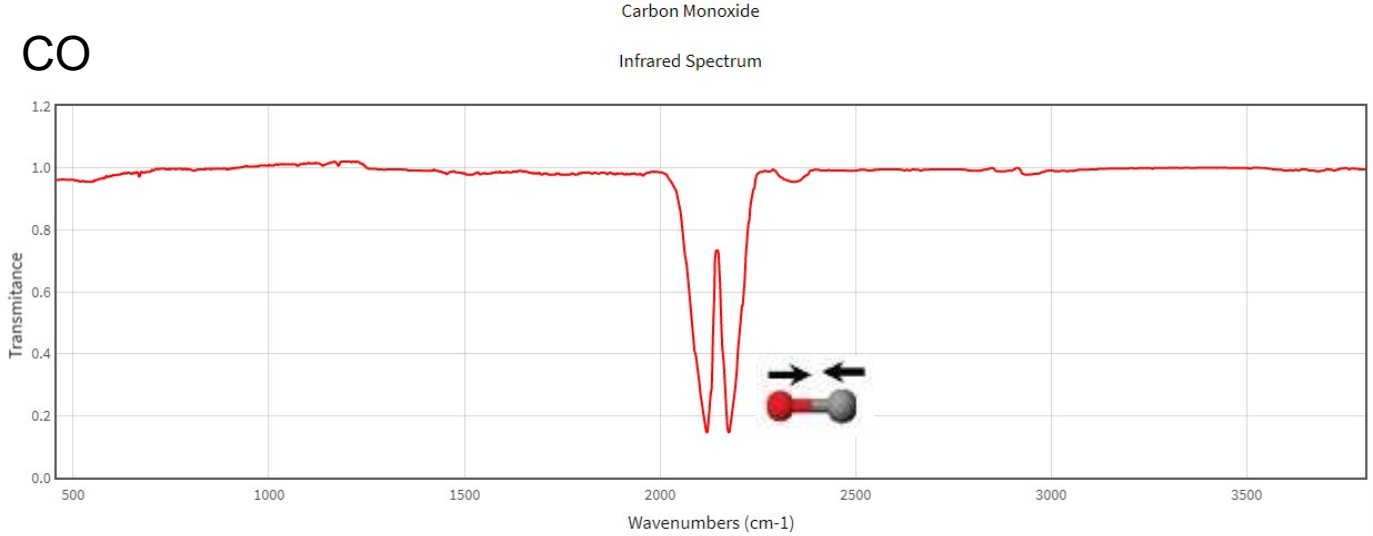
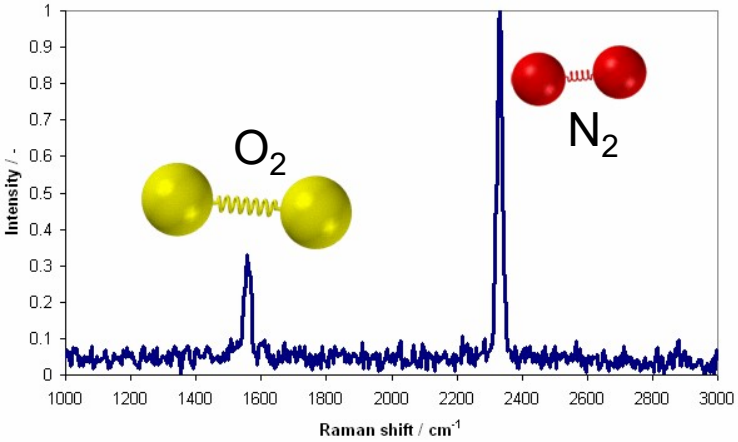
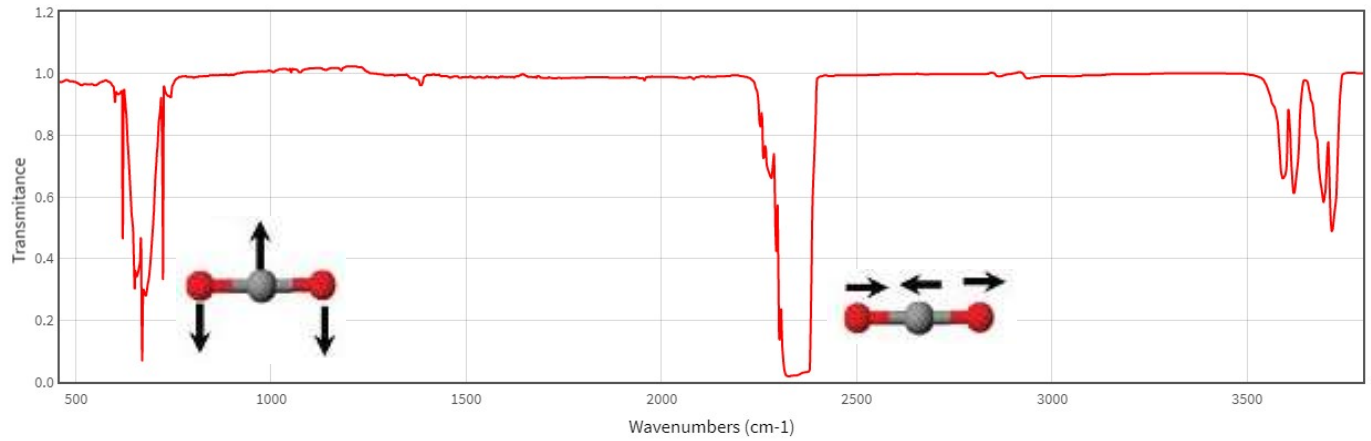
NIST Chemistry WebBook

CO

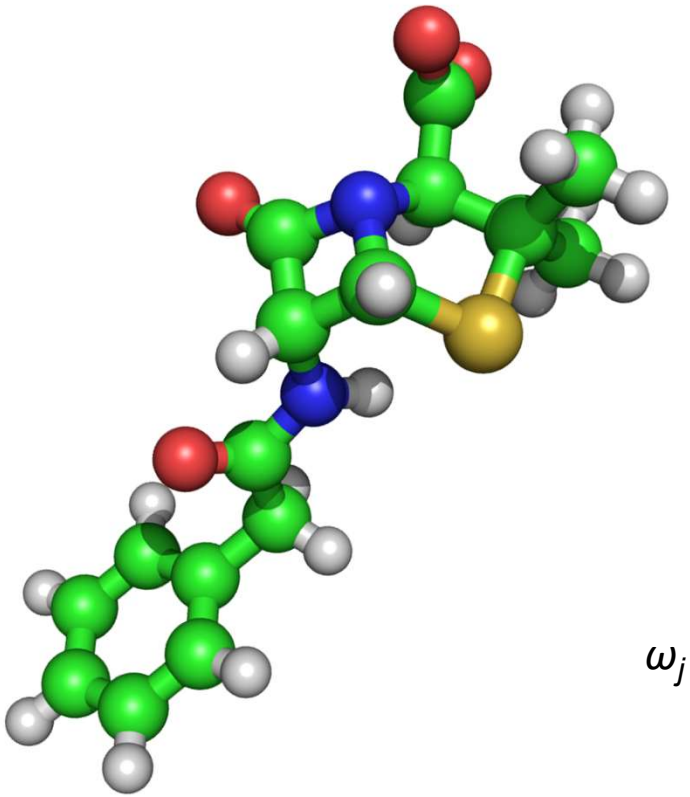




CO_2



Vibrational spectroscopy



N×3 dimensional displacement field: $\{x_1, y_1, z_1, \ldots, x_N, y_N, z_N\}$

Classical: $$m_j \frac{d^2 u_j(t)}{dt^2} = -\frac{\partial E_{harm}}{\partial u_j} = -\sum_{k \neq j} D_{j,k} u_k(t) \qquad u_j(t) = u_j e^{i\omega t}$$

$$\Downarrow$$

$$m_j \omega_j^2 u_j = \sum_{k \neq j} D_{j,k} u_k$$

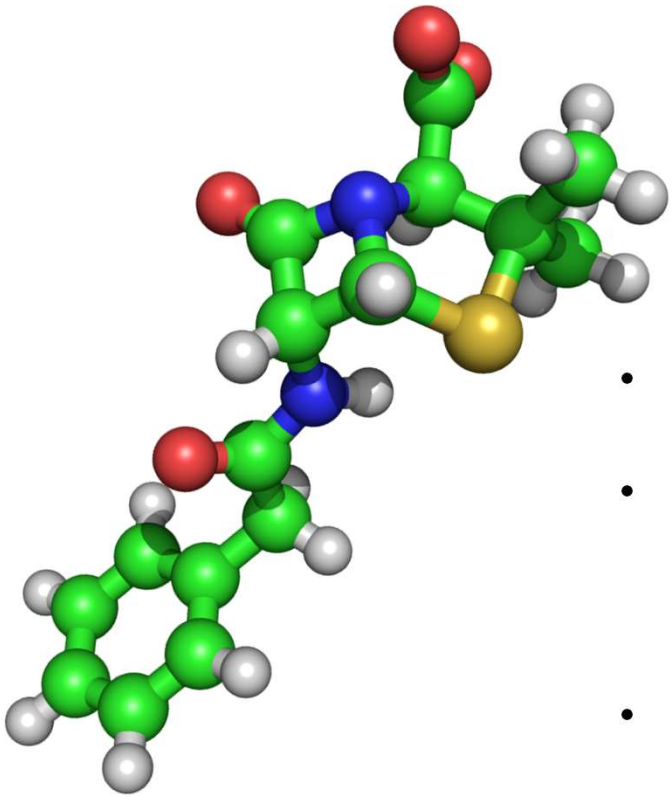
ω_j eigenfrequencies and u_j eigenmodes → diagonalise $D_{j,k}$

Quantum: $$\hat{H} = \sum_{j=1}^{3N} \frac{p_j^2}{2m_j} + \frac{1}{2} \sum_{j \neq k} u_j D_{j,k} u_k = \frac{1}{2} \sum_{j=1}^{3N} \left(\tilde{p}_j^2 + \omega_j^2 \tilde{u}_j^2 \right) = \sum_{j=1}^{3N} \hbar \omega_j \left(\hat{a}_j^+ \hat{a}_j + \frac{1}{2} \right)$$

ω_j eigenfrequencies and u_j eigenmodes (polarization) → diagonalise $D_{j,k}$

3N harmonic oscillators

Vibrational spectroscopy



N×3 dimensional displacement field: $\{x_1, y_1, z_1, ..., x_N, y_N, z_N\}$

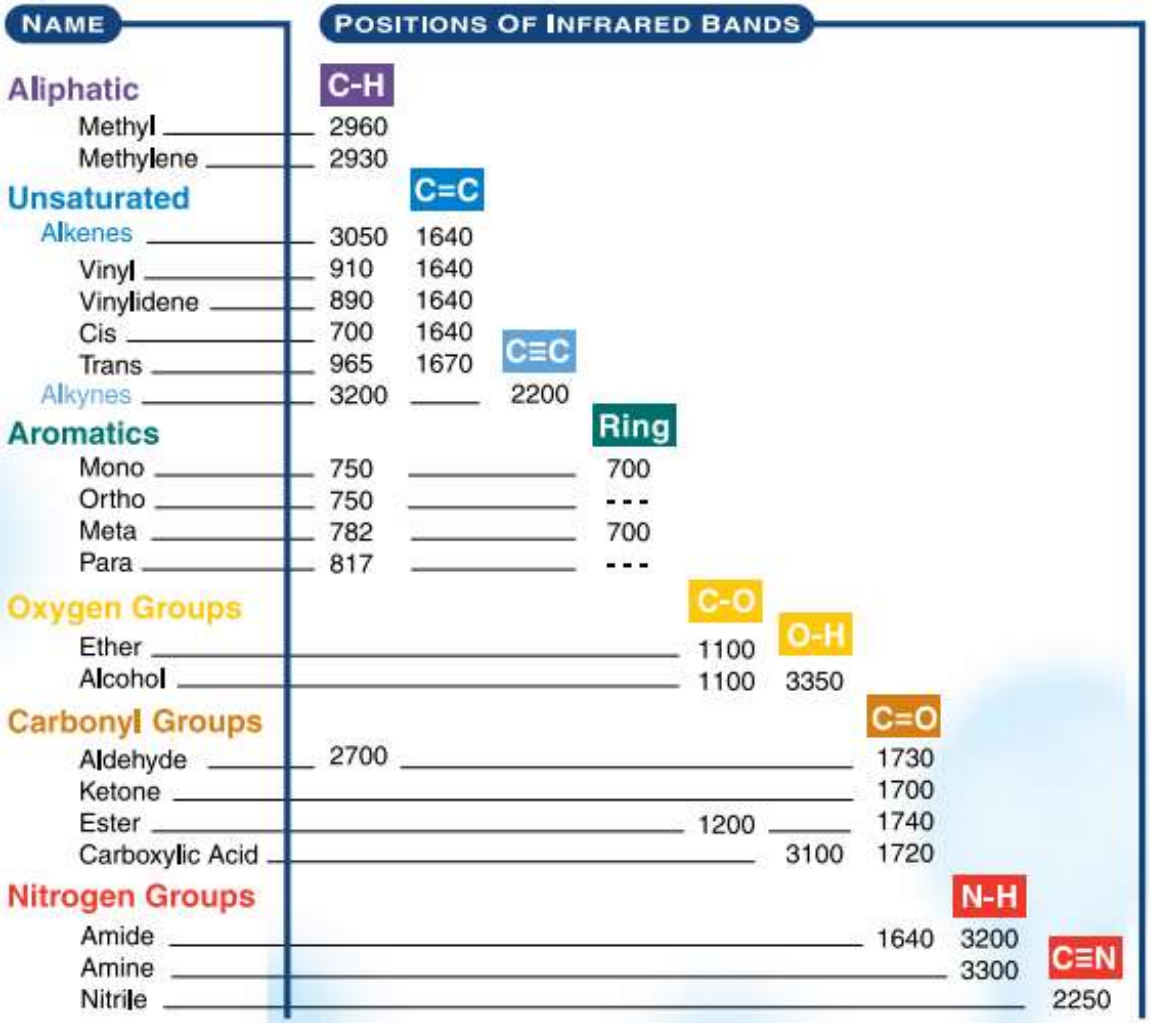
3N harmonic oscillators

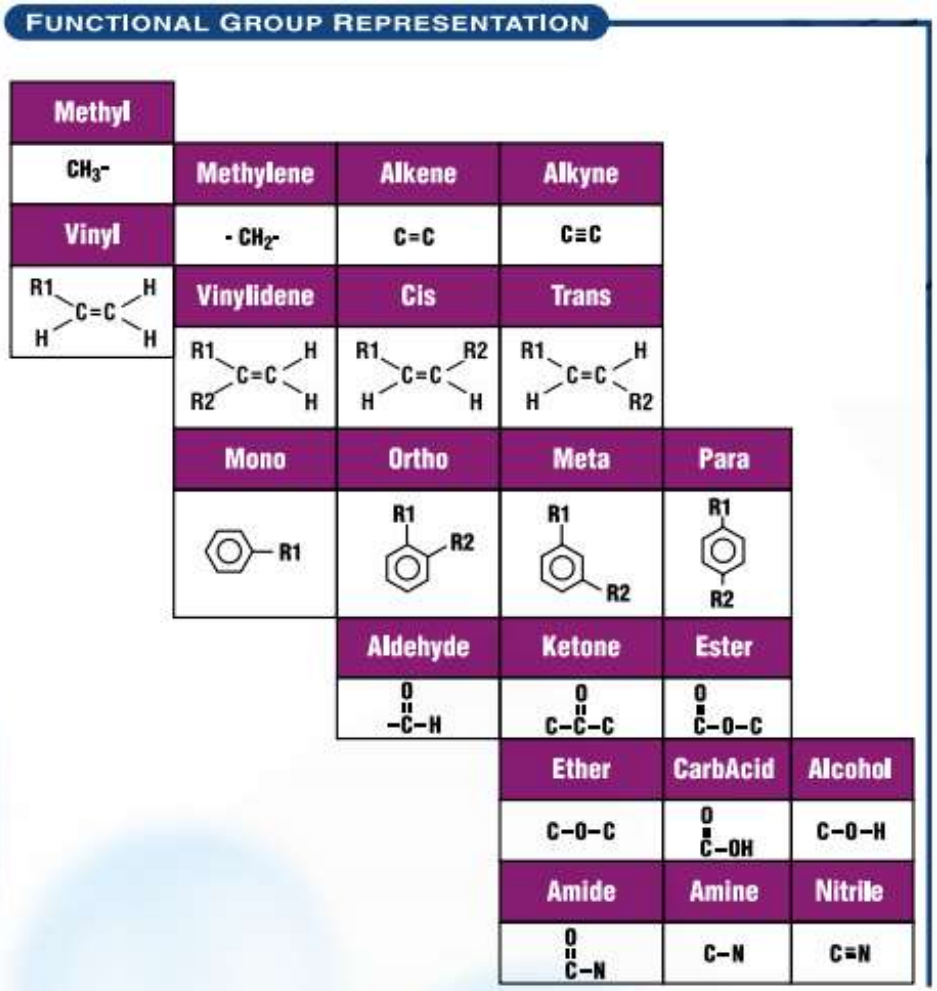
- 3 translational modes: only the center of mass moves
- 3 rotational modes: rigid rotations around the center of mass,
  2 in case of linear molecules,
  may be IR active, MHz - GHz
- 3N-3-3 vibrational modes, ω_i eigenfrequencies

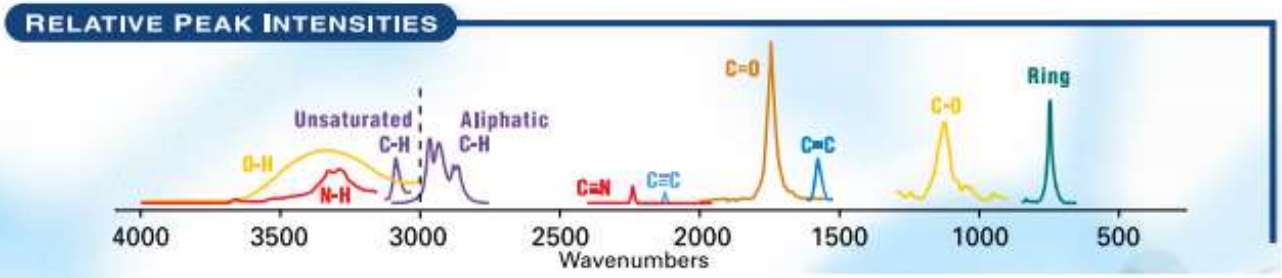
$$\varepsilon(\omega)=\varepsilon_\infty+\sum_j \frac{e^2}{K_j}\frac{\omega_j^2}{\omega_j^2-\omega^2-2i\gamma_j\omega}$$

- IR active modes: posses oscillating electric dipole moments (thus not all modes are IR active)
- Raman active modes: polarizability of the molecule changes
- Silent modes: neither IR nor Raman active modes

Vibrational spectroscopy







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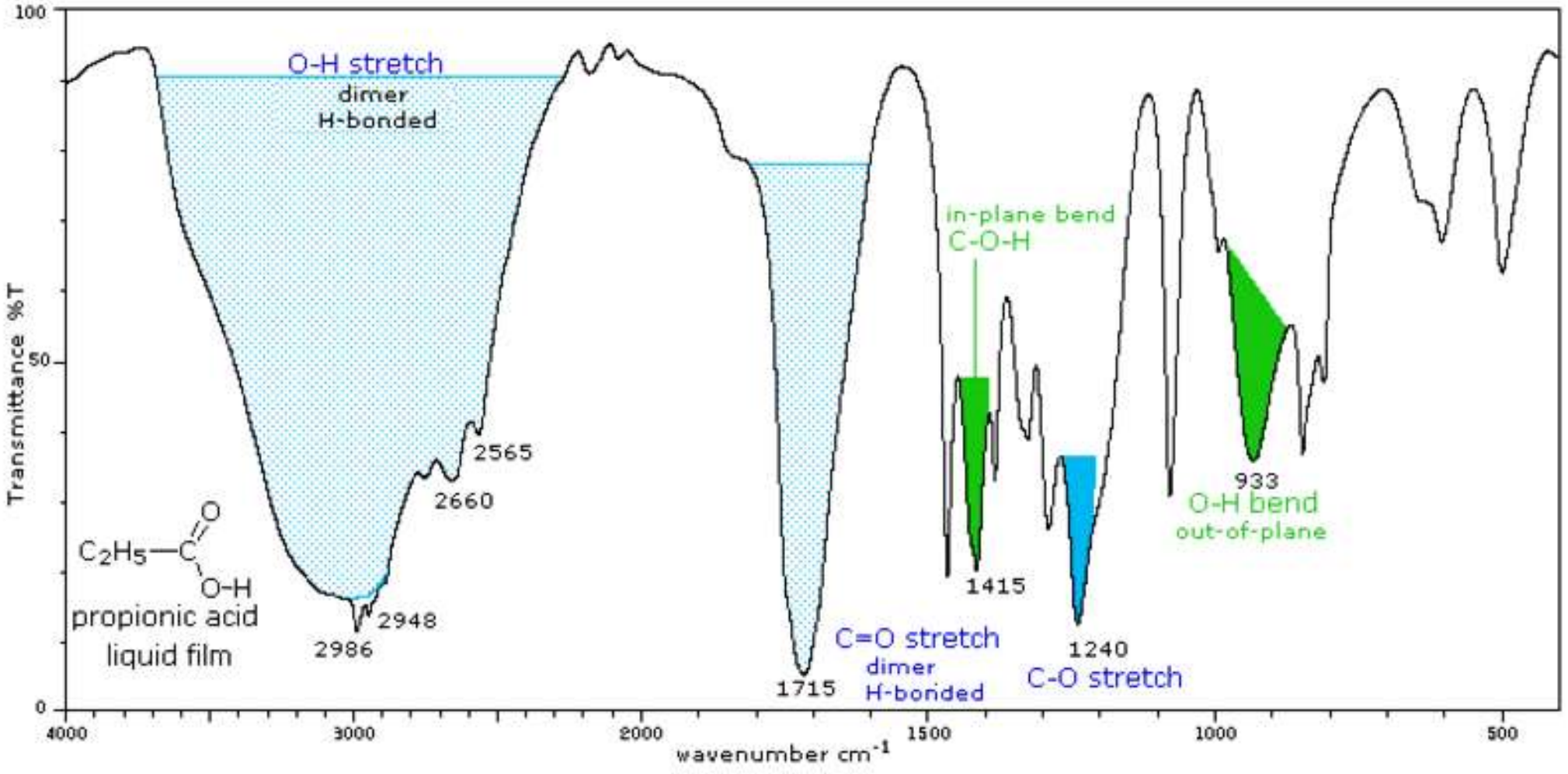
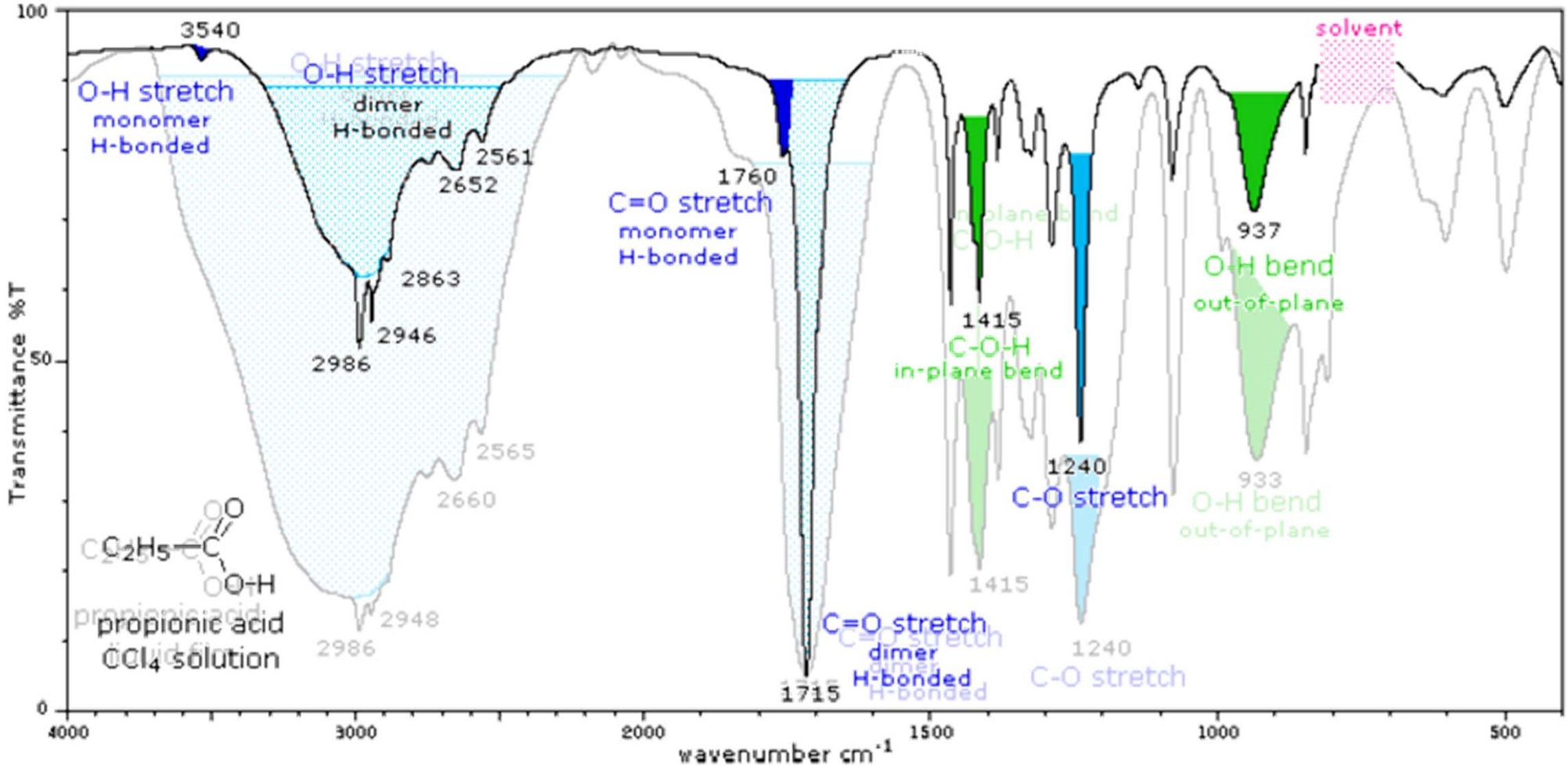
Vibrational spectroscopy



- IR and Raman spectra of known molecules are accessible in databases → composition, concentration of a molecule can be determined from spectroscopy
- Units of the molecules (O-H, C=O, ...) have characteristic frequencies (group frequencies), which do not change much → spectroscopy can be used to determine the structure of new molecules
- In case of smaller molecules it is possible to calculate the structure and the vibrational modes from first principels

Vibrational spectroscopy



- IR and Raman spectra of known molecules are accessible in databases → composition, concentration of a molecule can be determined from spectroscopy
- Units of the molecules (O-H, C=O, ...) have characteristic frequencies (group frequencies), which do not change much → spectroscopy can be used to determine the structure of new molecules
- In case of smaller molecules it is possible to calculate the structure and the vibrational modes from first principels
- Solvent: frequency shift, different damping

Vibrational spectroscopy

C_{60} fullerén:

The Nobel Prize in Chemistry 1996

Robert F. Curl Jr., Sir Harold Kroto, Richard E. Smalley

The discovery of carbon atoms bound in the form of a ball is rewarded

Robert F. Curl, Richard E. Smalley: *Probing C_{60}*
Science **242**, 1017 (1988)

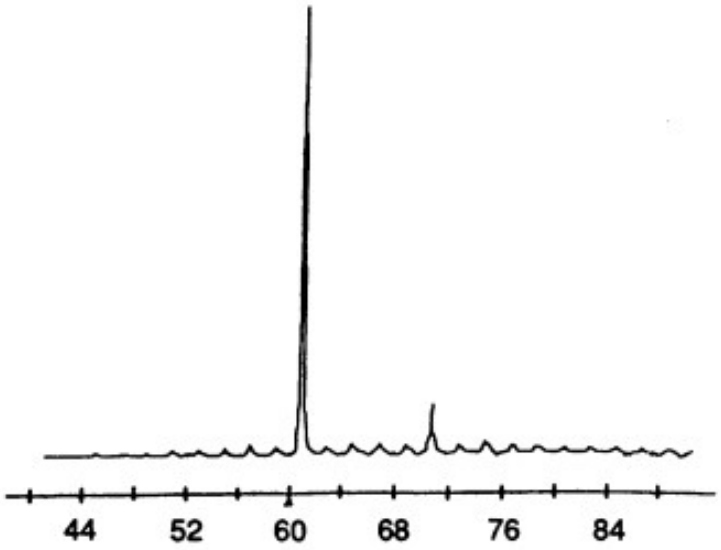
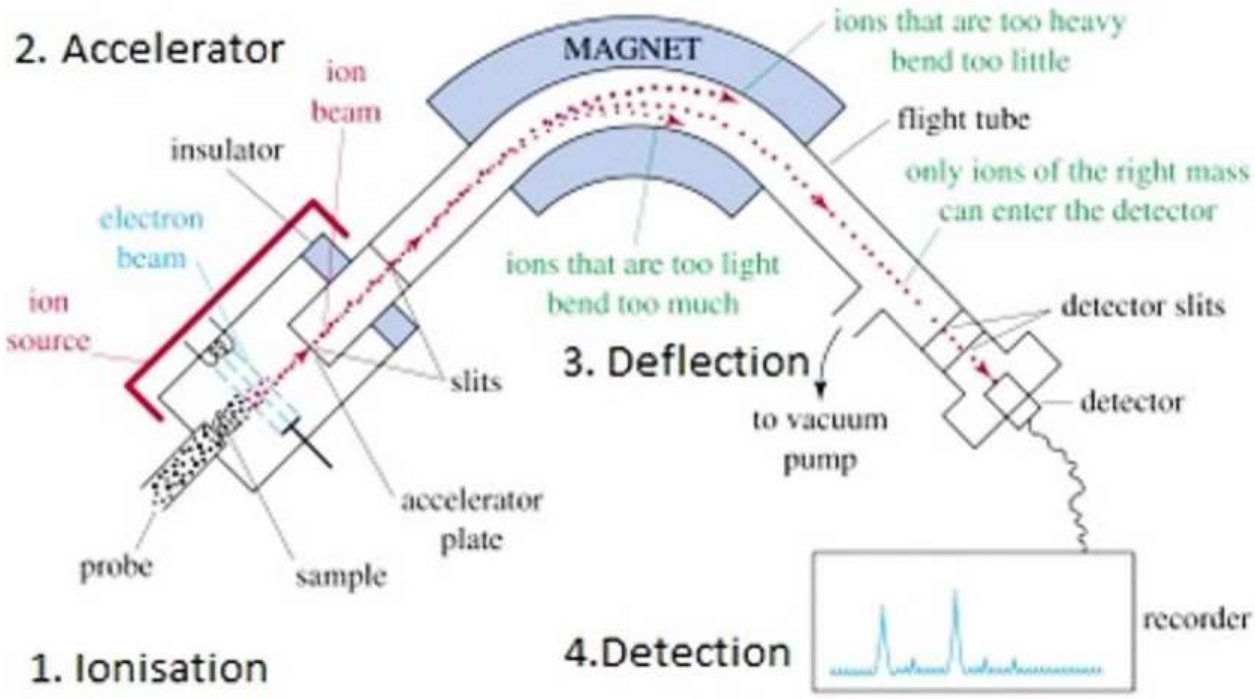


Fig. 1. Mass spectra of carbon cluster distributions in a supersonic beam produced by laser vaporization



Vibrational spectroscopy

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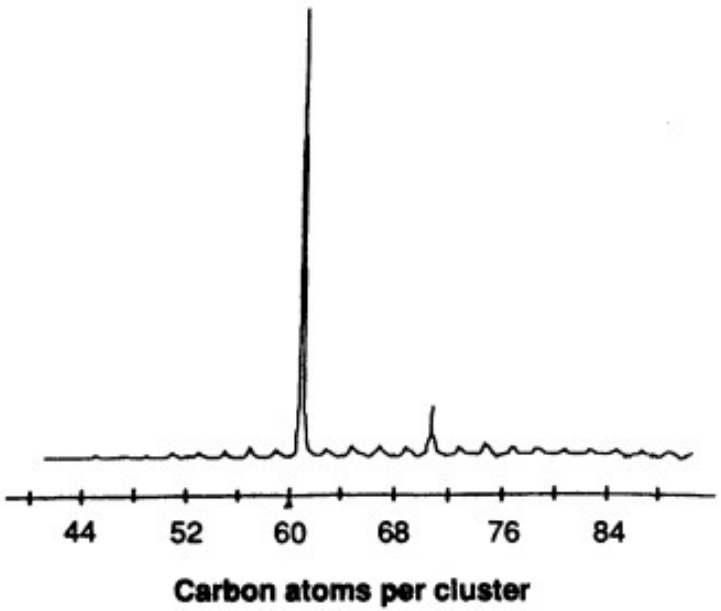

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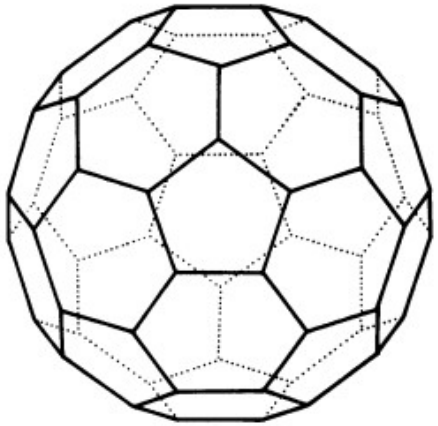


Fig. 2. Truncated icosahedral structure proposed for C_{60}.

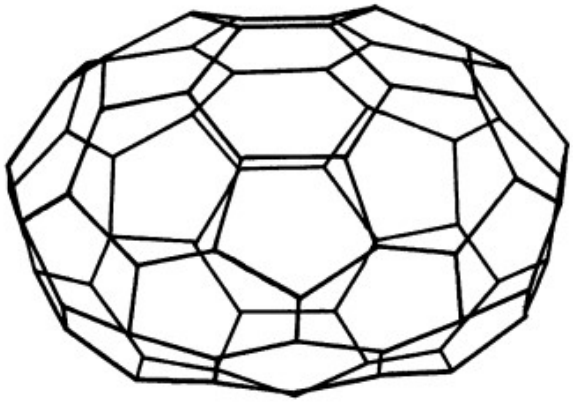


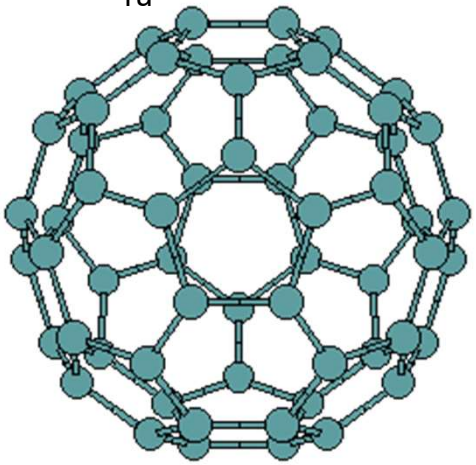
Fig. 3. A possible fullerene structure for the cluster C_{72}.

Vibrational spectroscopy

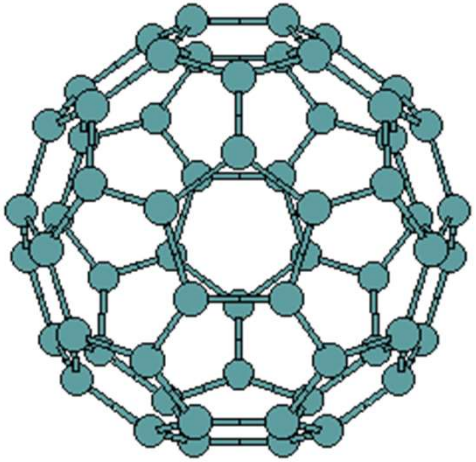
Vibrations of C_{60} fulleren

- Vibrational modes: N×3-6=174 harmonic oscillatros
- Icosahedral symmetry → 46 normal modes: 4 IR active, 10 Raman active, 32 silent modes

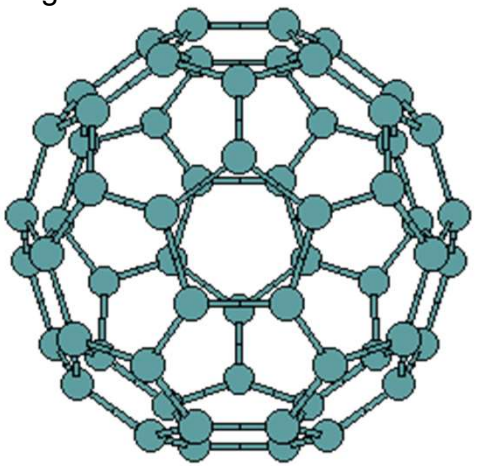
T_{1u} IR 526 cm^{-1}



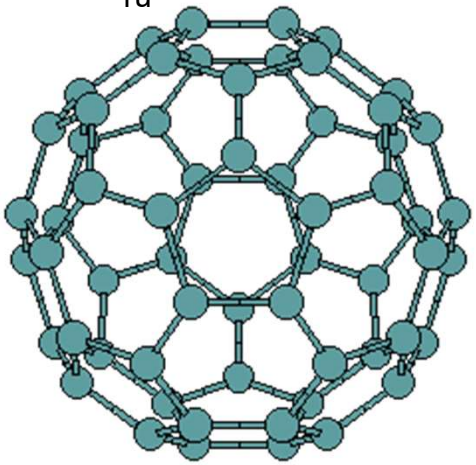
T_{1u} IR 575 cm^{-1}



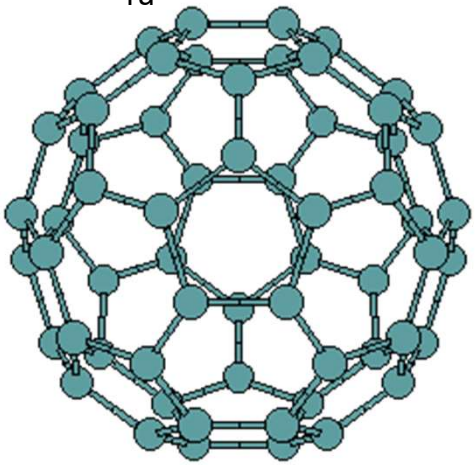
A_{1g} Raman breathing mode



T_{1u} IR 1182 cm^{-1}



T_{1u} IR 1429 cm^{-1}

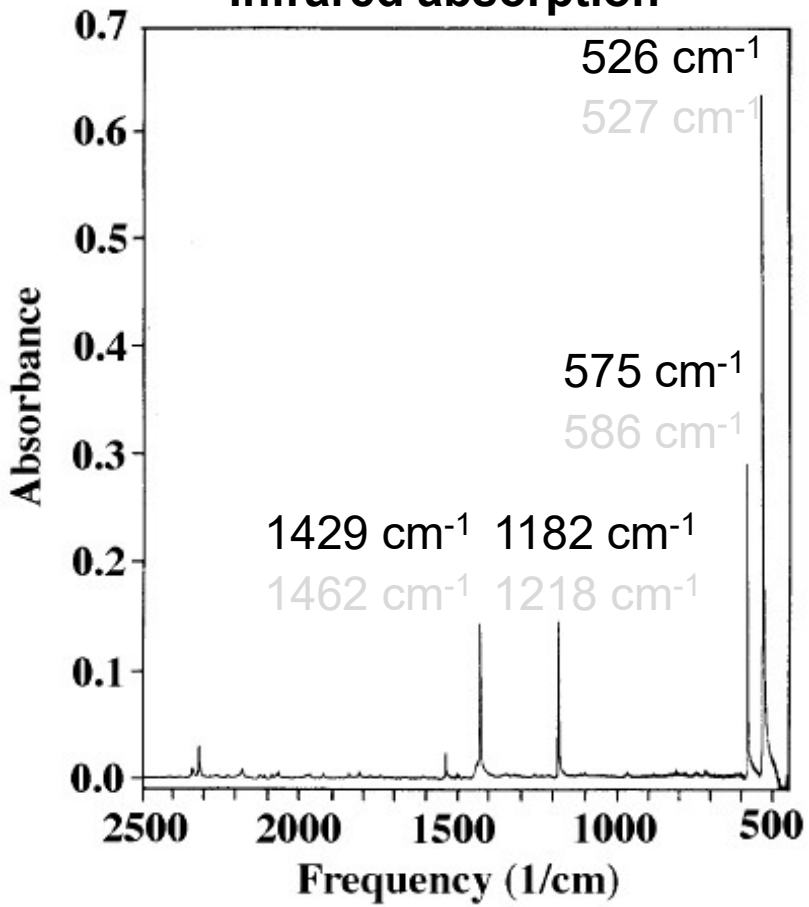


Vibrational spectroscopy

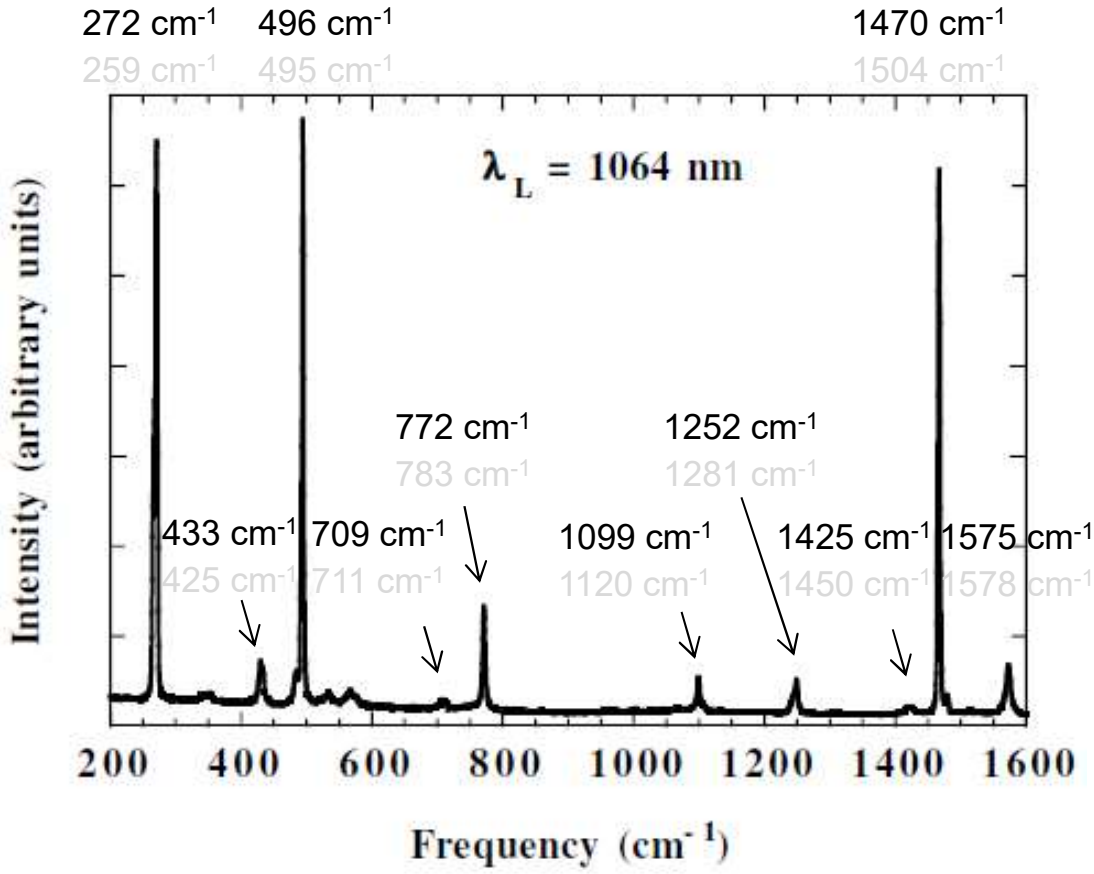
Vibrations of C_{60} fulleren

- Icosahedral symmetry → 46 normal modes: 4 IR active, 10 Raman active, 32 silent modes
- First principles calculations: C_{60} icosahedral ground state, vibrational frequencies with ~1-2% error

Infrared absorption



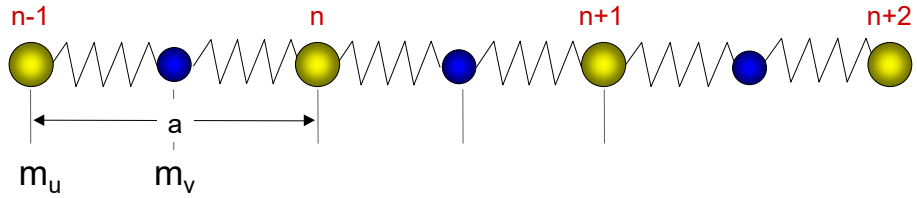
Raman scattering



Measurement in 1.4 mm thick films: B. Chase, N. Herron, E. Holler: J. Phys. Chem. **96**, 4262 (1992)

Vibrational spectroscopy

Vibrations in crystals (Phonon modes)



$$m_u \frac{d^2 u_n}{dt^2} = -D(u_n - v_{n-1}) - D(u_n - v_n)$$

$$m_v \frac{d^2 v_n}{dt^2} = -D(v_n - u_n) - D(v_n - u_{n+1})$$

$$\begin{bmatrix} -2D & D & & & 0 \\ D & -2D & D & & \\ & D & -2D & D & \\ & & D & -2D & D \\ 0 & & & D & -2D \end{bmatrix} \begin{bmatrix} u_{n-1} \\ v_{n-1} \\ u_n \\ v_n \\ u_{n+1} \end{bmatrix}$$

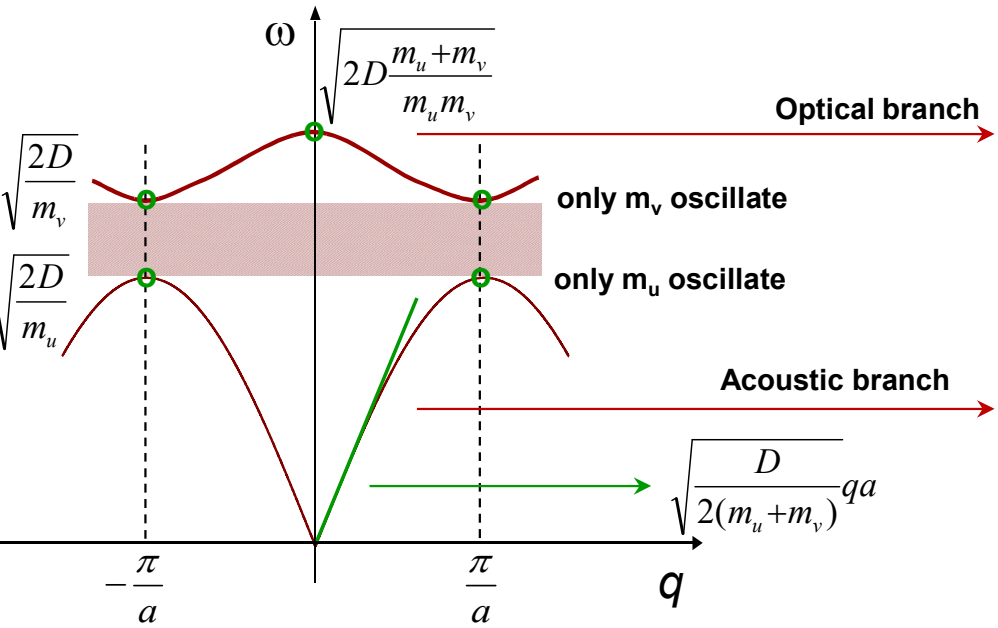
$$-\omega^2 u m_u = 2D\left(v\cos\frac{qa}{2} - u\right)$$

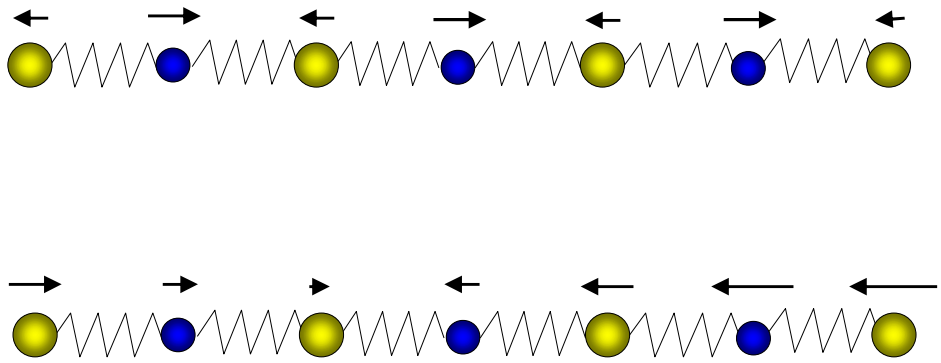
$$-\omega^2 v m_v = 2D\left(u\cos\frac{qa}{2} - v\right)$$

v_{n-1} u_n v_n u_{n+1}

$$u_n = u e^{i(qna - \omega t)} \qquad v_n = v e^{i(q\{n+\frac{1}{2}a\} - \omega t)}$$

Dispersion relation: $\omega(q)^2 = D\frac{m_u + m_v}{m_u m_v} \pm D\sqrt{\left(\frac{m_u + m_v}{m_u m_v}\right)^2 - \frac{4\sin^2(qa/2)}{m_u m_v}}$

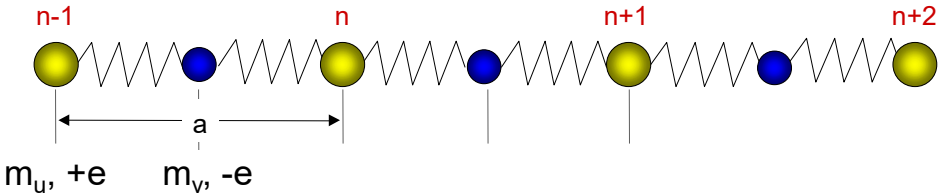




Vibrational spectroscopy

$$m_u \frac{d^2u_n}{dt^2} = D(v_n + v_{n-1} - 2u_n) - \gamma m_u \frac{du_n}{dt} + eE(t)$$

$$m_v \frac{d^2v_n}{dt^2} = D(u_n + u_{n-1} - 2v_n) - \gamma m_v \frac{dv_n}{dt} - eE(t)$$



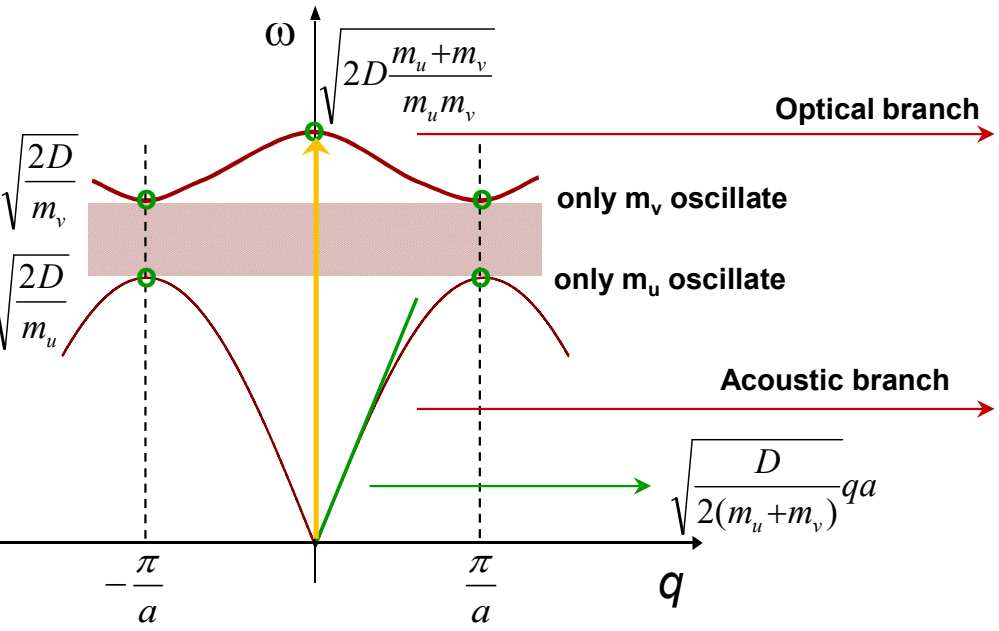
$$\lambda >> a \Rightarrow q << \frac{\pi}{a} \Rightarrow \begin{cases} E(r,t) \approx E_\omega e^{i\omega t} \\ u_n(t) \approx u e^{-i\omega t} \\ v_n(t) \approx v e^{-i\omega t} \end{cases}$$

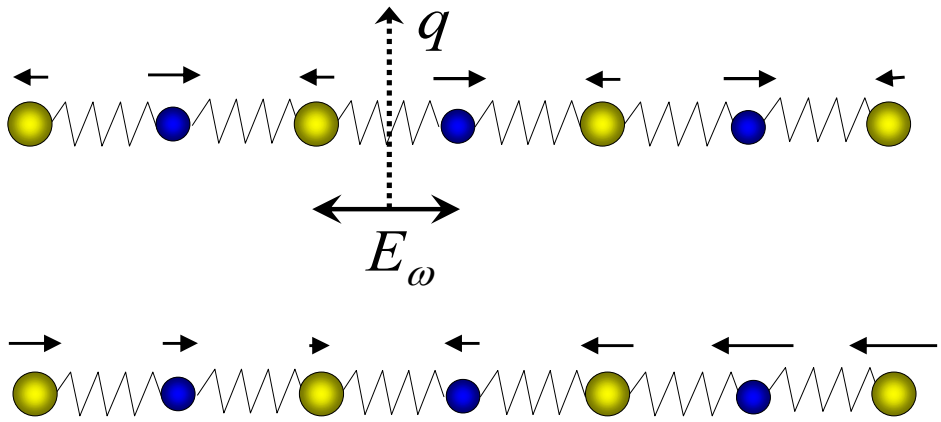
$$\omega_{TO} = \sqrt{2D\frac{m_u + m_v}{m_u m_v}}$$

$$P_\omega = en(u_\omega - v_\omega) = \frac{ne^2}{\mu}\frac{1}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}E_\omega$$

$$\varepsilon(\omega) = 1 + \frac{\Omega_{pl}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}$$

The q=0 case is equivalent to a diatomic molecule, atoms move respect to the center of mass





Vibrational spectroscopy

Wave equation for Fourier components: $0=\mathbf{q}\times(\mathbf{q}\times\mathbf{E}_{\mathbf{q},\omega})+\frac{\omega^2}{c^2}\varepsilon(\omega)\mathbf{E}_{\mathbf{q},\omega}$

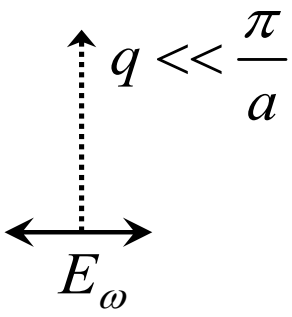
Longitudinal solution: $0=\mathbf{q}\times\mathbf{E}_{\mathbf{q},\omega}\Leftrightarrow\varepsilon(\omega)=0\Rightarrow\omega^2=\omega_{TO}^2+\frac{\Omega_{pl}^2}{\varepsilon_\infty}\equiv\omega_{LO}^2$

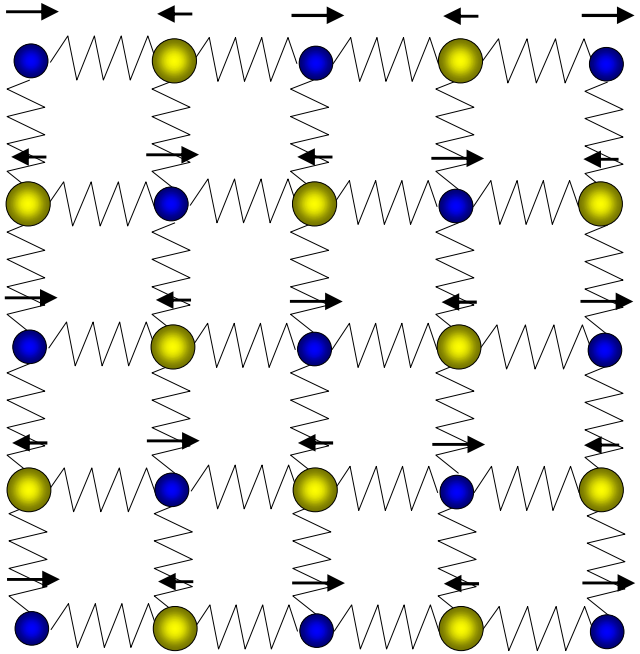
$$\omega_{TO}=\sqrt{2D\frac{m_u+m_v}{m_u m_v}}$$

$$\varepsilon(\omega)=\varepsilon_\infty+\frac{\Omega_{pl}^2}{\omega_{TO}^2-\omega^2}=\varepsilon_\infty\frac{\omega_{TO}^2+\frac{\Omega_{pl}^2}{\varepsilon_\infty}-\omega^2}{\omega_{TO}^2-\omega^2},\qquad 1\to\varepsilon_\infty$$ to take into account the high frequency electronic excitations, $\gamma=0$

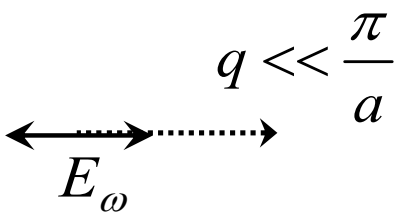
$$\varepsilon(\omega)=\varepsilon_\infty\frac{\omega_{LO}^2-\omega^2}{\omega_{TO}^2-\omega^2}$$

Transverse





Longitudinal



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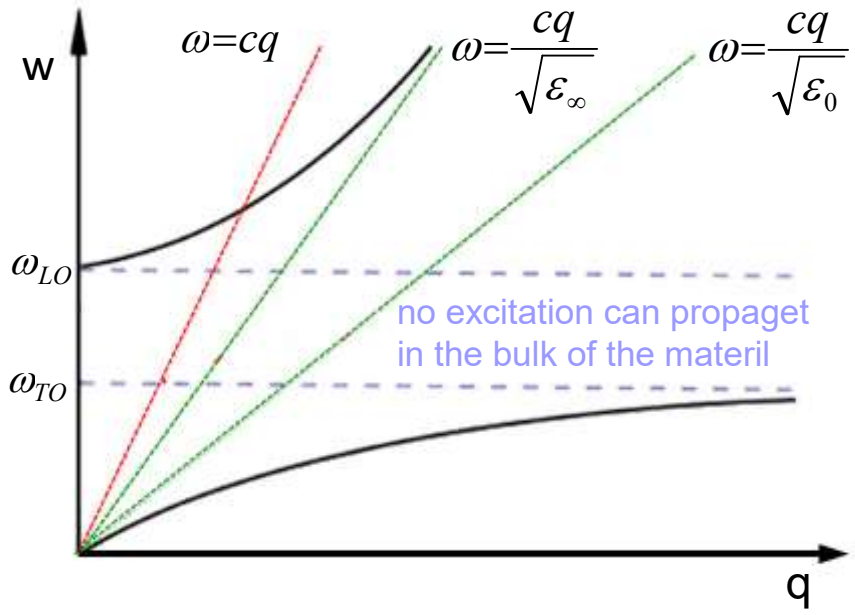
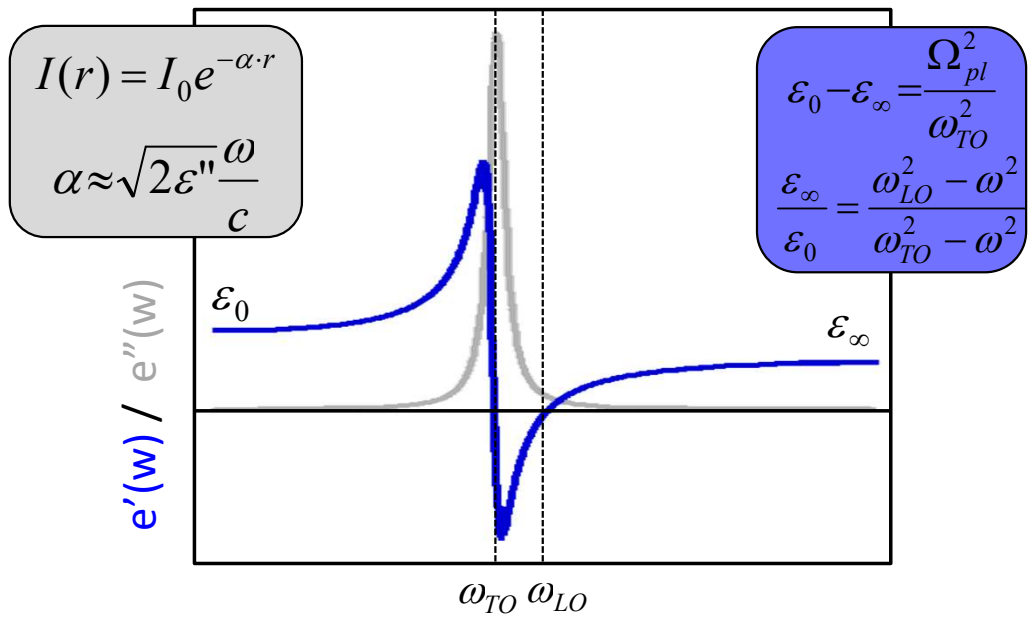
Dispersion relation: $q^2=\frac{\omega^2}{c^2}\varepsilon(\omega)=\frac{\omega^2}{c^2}\varepsilon_\infty\frac{\omega_{LO}^2-\omega^2}{\omega_{TO}^2-\omega^2}\Rightarrow\omega(q)=\frac{1}{2}\left(\frac{c^2q^2}{\varepsilon_\infty}+\omega_{LO}^2\pm\sqrt{\left(\frac{c^2q^2}{\varepsilon_\infty}+\omega_{LO}^2\right)^2-4\frac{c^2q^2}{\varepsilon_\infty}\omega_{TO}^2}\right)$





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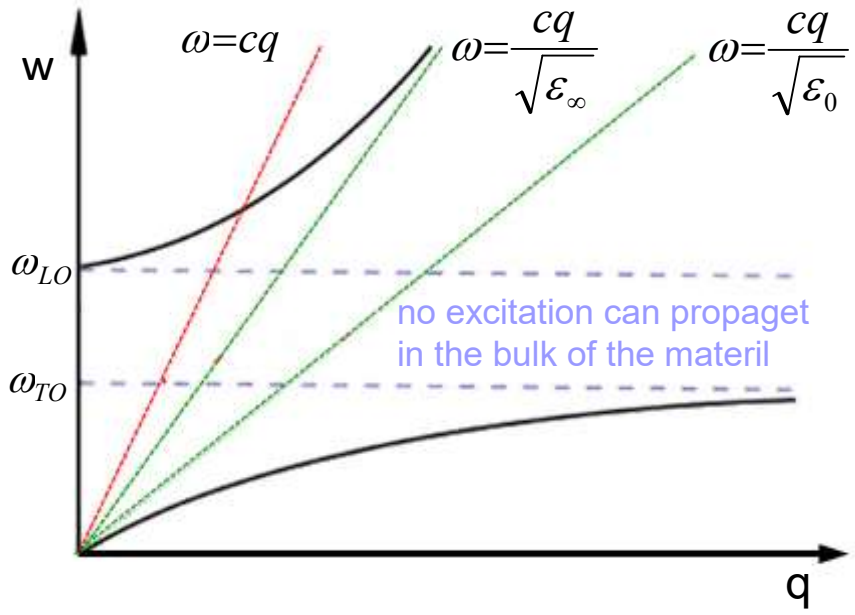
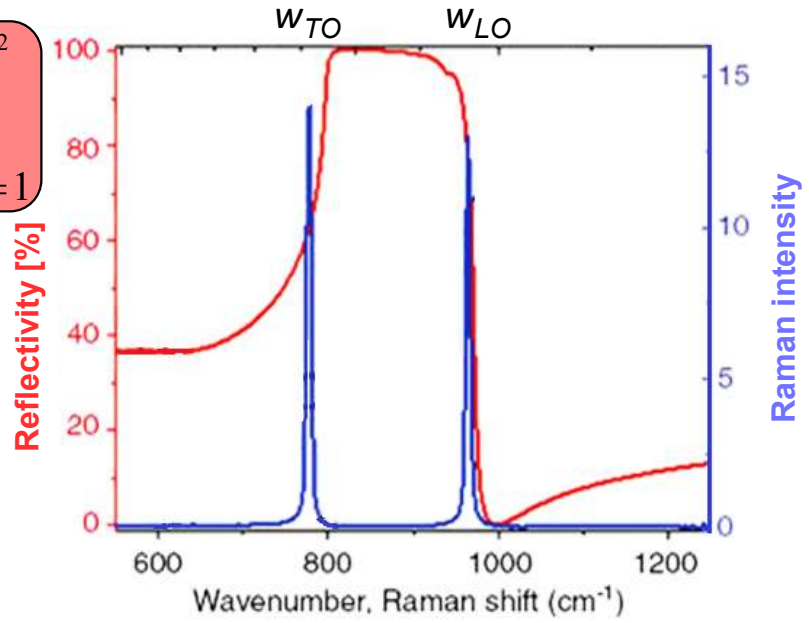


$R=\left|\frac{\sqrt{\varepsilon}-1}{\sqrt{\varepsilon}+1}\right|^2$

$\varepsilon'=0\Rightarrow R=1$



Vibrational spectroscopy

Phonon modes as determined by inelastic neutron scattering

$$\hat{H} = \frac{1}{2M}\sum_{\mathbf{q}}\left|\hat{\mathbf{p}}(\mathbf{q})\right|^2 + \frac{1}{2}\sum_{\mathbf{q}}\lambda_s(\mathbf{q})\left|\hat{\mathbf{u}}(\mathbf{q})\right|^2$$

$$\hat{H} = \sum_{\mathbf{q},s}\hbar\omega_s(\mathbf{q})\left(\hat{\mathbf{a}}^{+}_{\mathbf{q},s}\hat{\mathbf{a}}_{\mathbf{q},s} + \frac{1}{2}\right)$$

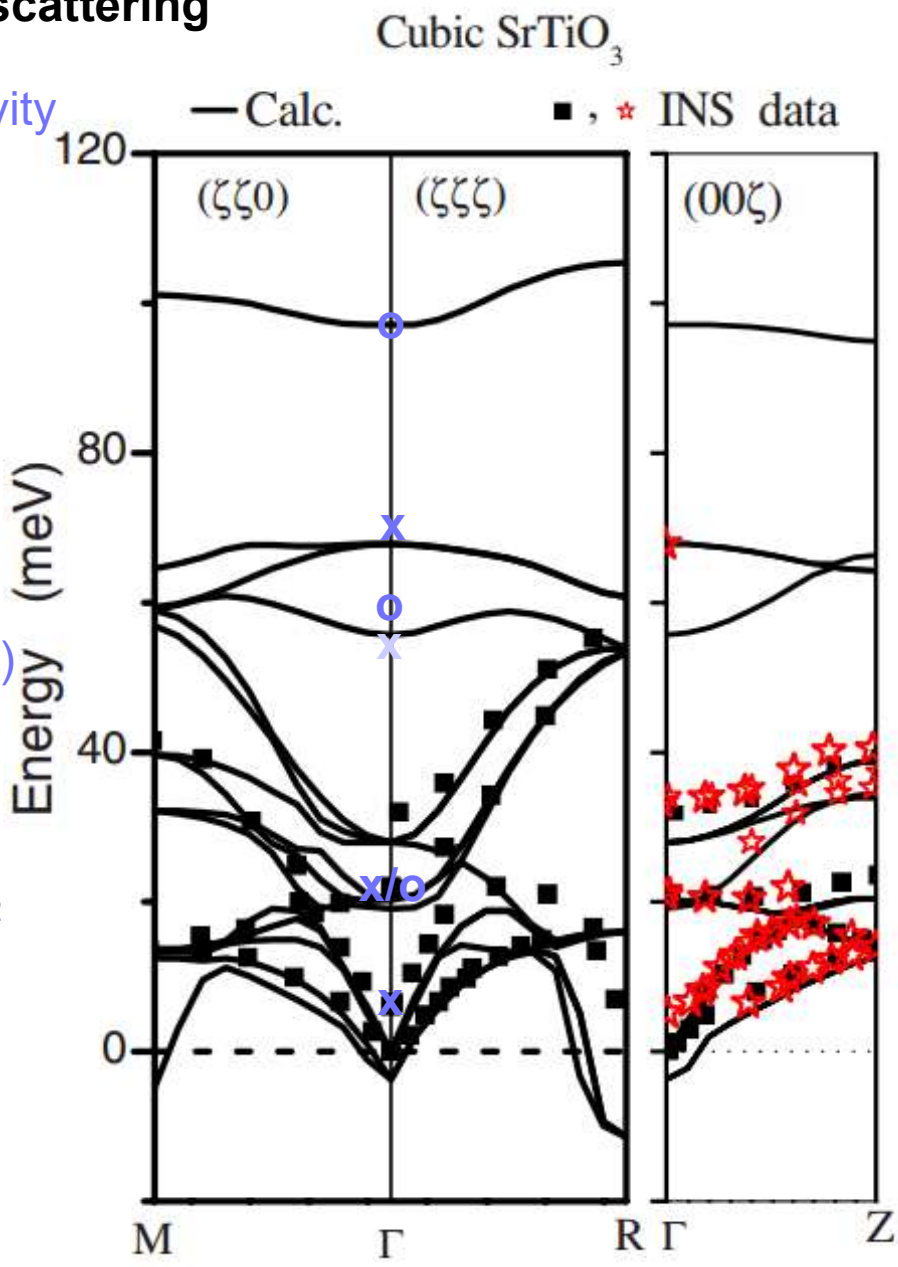
3×N×M harmonic oscillator:

- 3×M phonon branches
- N k points in each branches

Conservation laws in case of neutron-cristal interaction

$$\begin{cases} \dfrac{p'^2}{2M_n} = \dfrac{p^2}{2M_n} \pm \hbar\omega(\mathbf{q}) \\ \hbar\mathbf{q} = \mp\,\mathbf{p}' - \mathbf{p} - \hbar\mathbf{G} \end{cases}$$

IR reflectivity

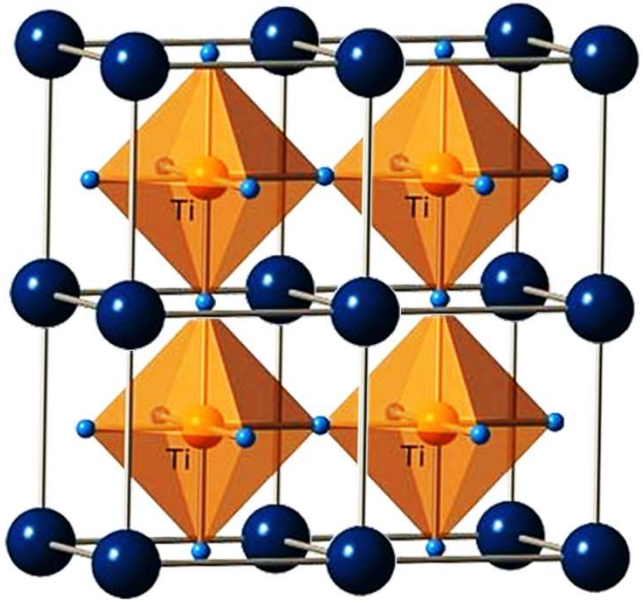


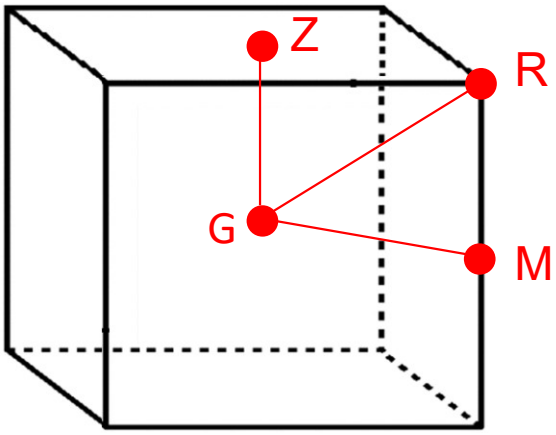
Choudhury et al., Phys. Rev. B **77**, 134111 (2008)

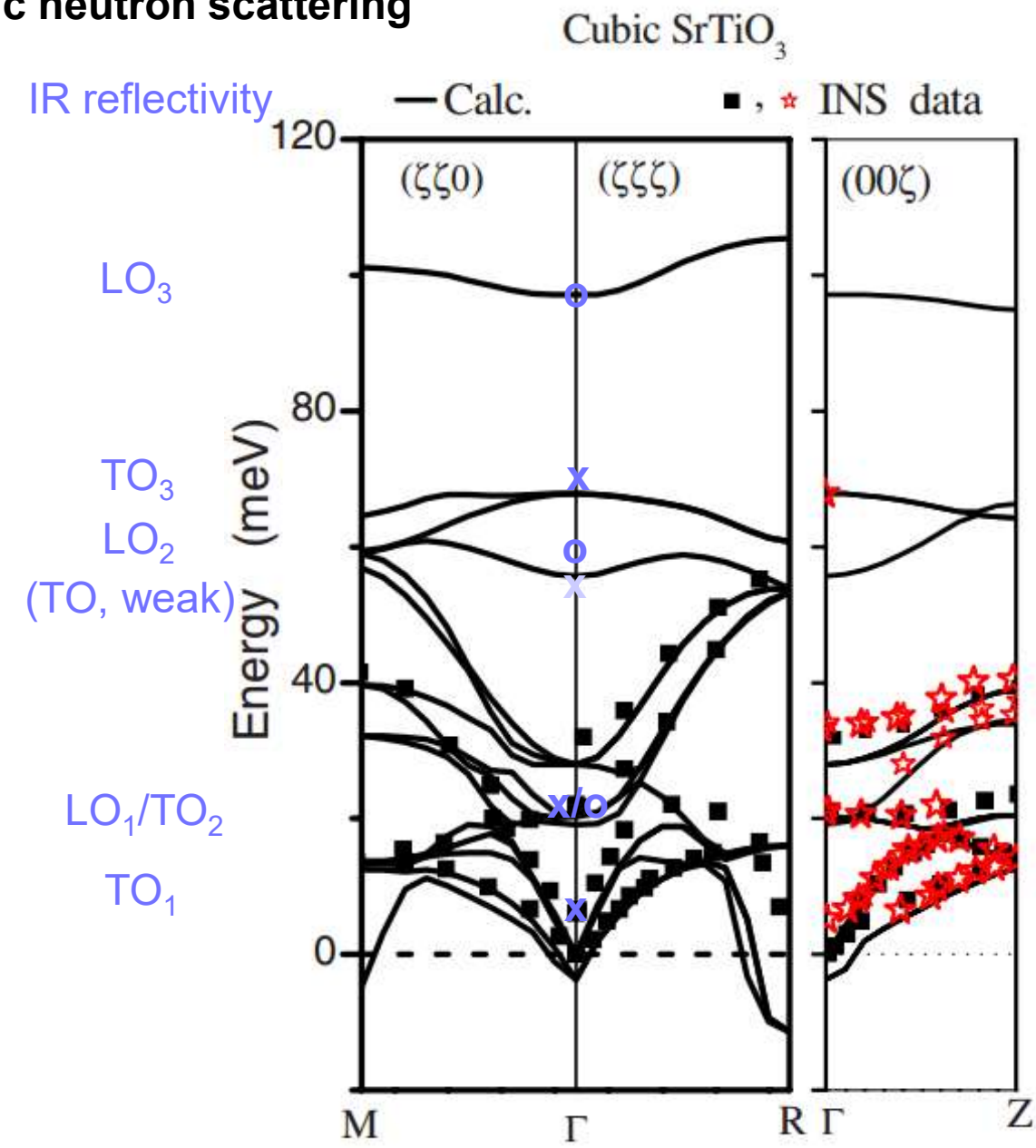
Vibrational spectroscopy

Phonon modes as determined by inelastic neutron scattering

$SrTiO_3$







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Vibrational spectroscopy

Phonon modes as determined by inelastic neutron scattering

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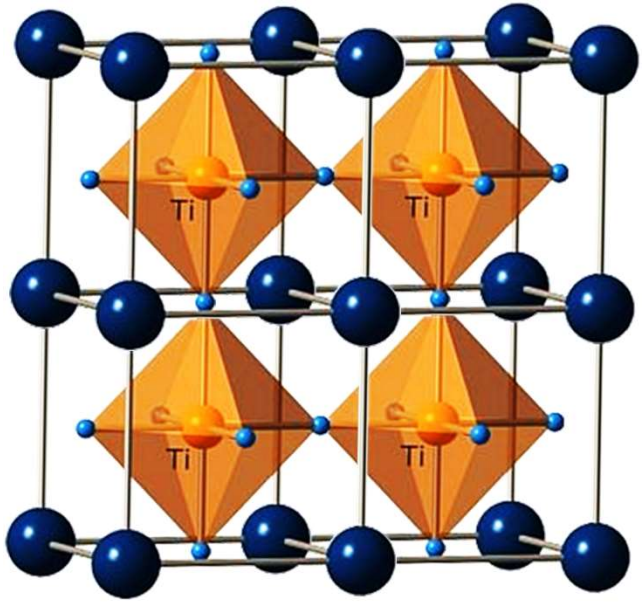
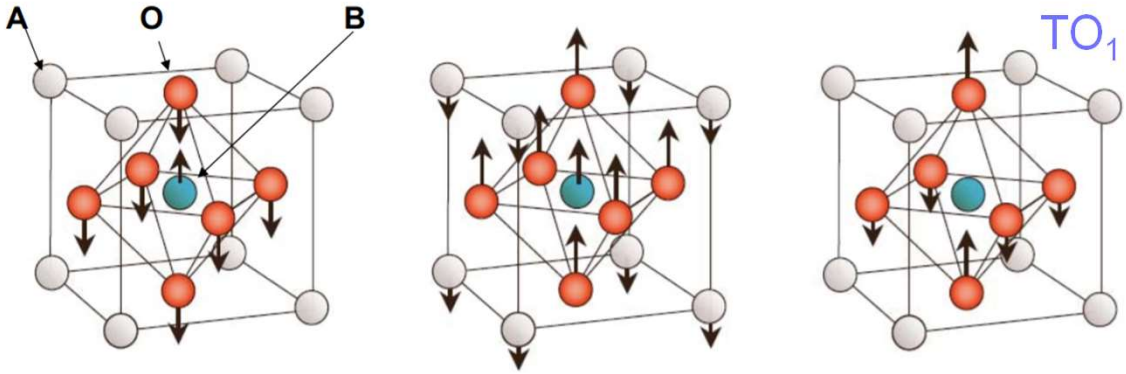


3 IR active modes of the cubic phase:



IR reflectivity

LO_3

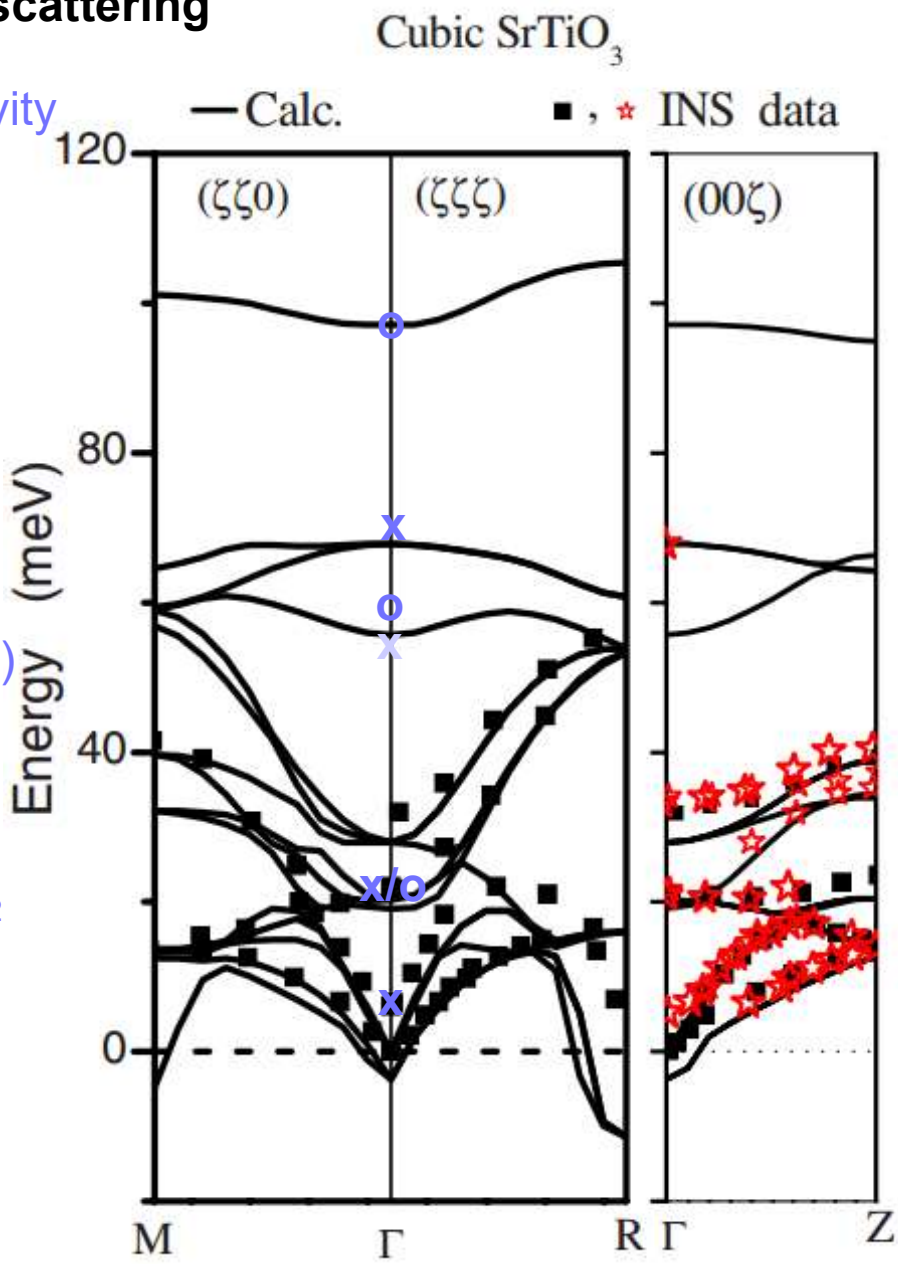
TO_3

LO_2

(TO, weak)

LO_1/TO_2

TO_1



Choudhury et al., Phys. Rev. B **77**, 134111 (2008)

Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes

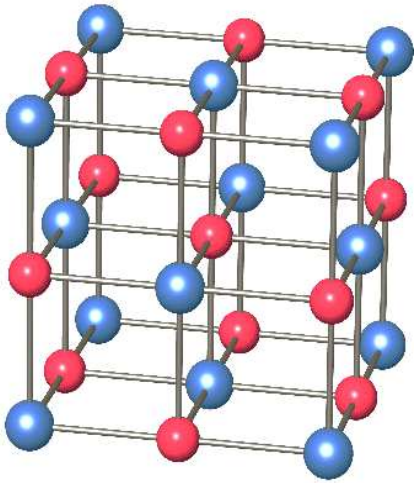
The Nobel Prize in Physics 1994

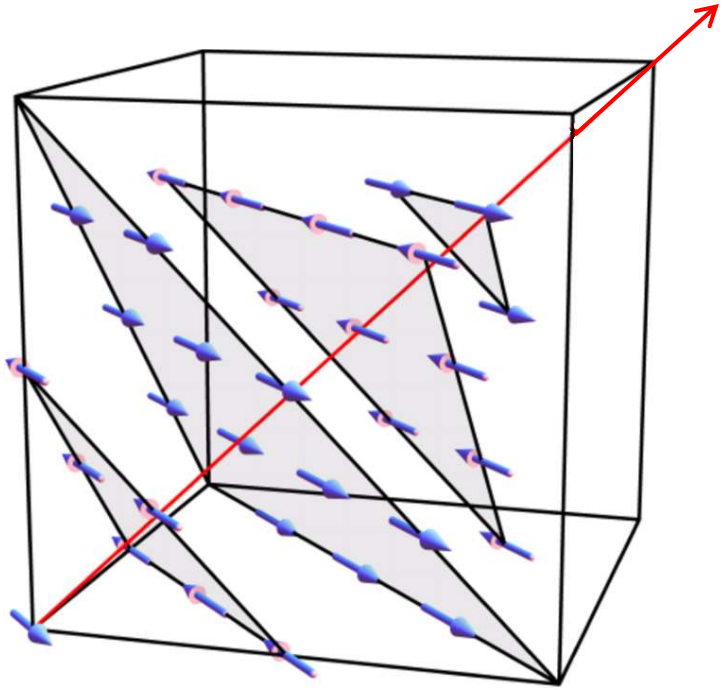
Bertram N. Brockhouse, Clifford G. Shull

The Nobel Prize in Physics 1994 was awarded *"for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter"*

MnO

- FCC lattice with 2 atoms in the unit cell, NaCl structure
- Antiferromagnetic order below T_N=118K (Nobel prize, magnetic neutron scattering)
- The crystal symmetry changes from cubic to rhombic due to the magnetic order

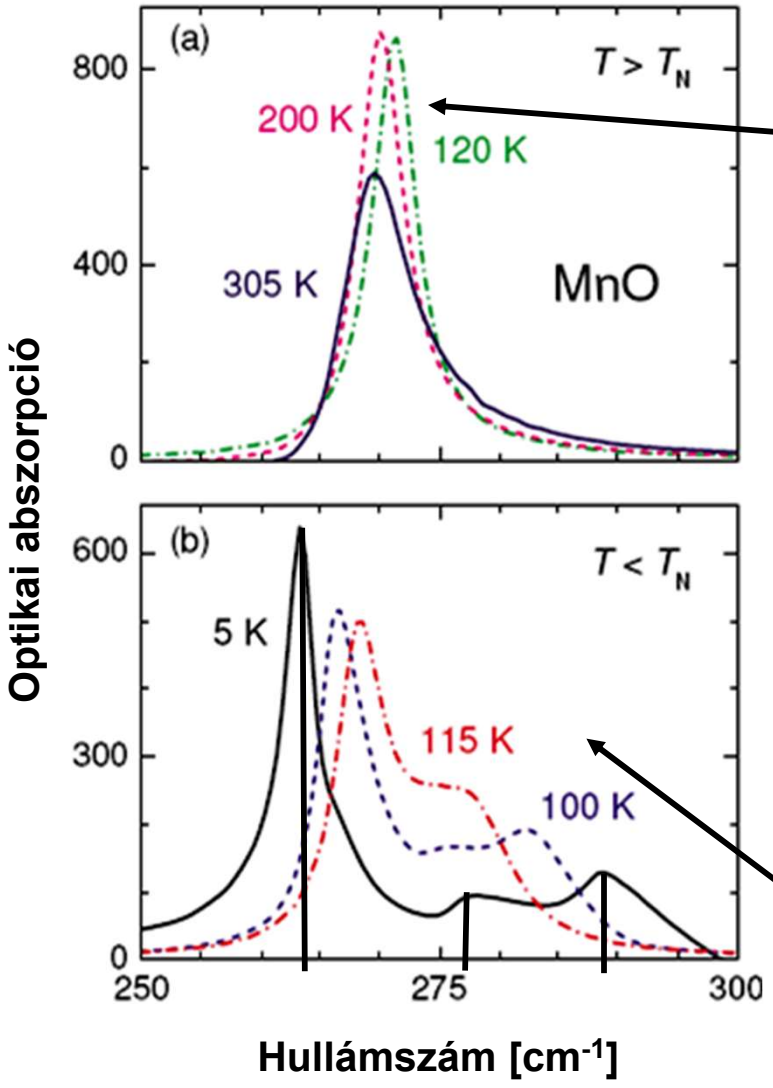




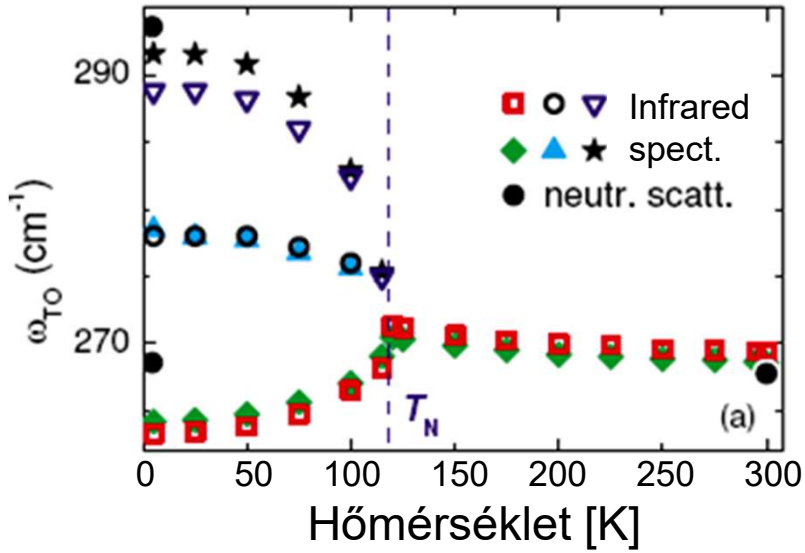
Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes

The crystal symmetry of MnO changes from cubic to rhombic lower than rhombic due to the magnetic order!



As the temperature is lowered phonon modes become:
- harder as the lattice shrinks
- sharper as the phonon-phonon scattering freeze out



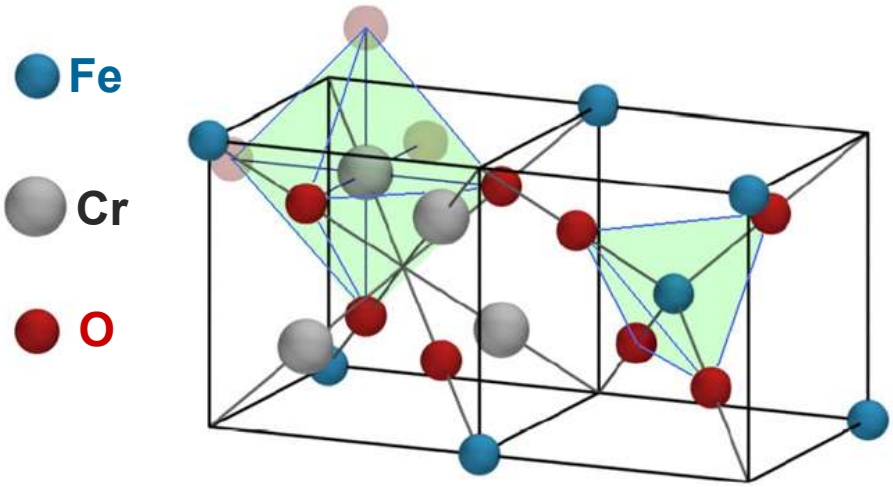
- 2 atoms in the unit cell: 3 acoustic + 3 optical branches
- $T>T_N$ 3× degeneracy, cubic phase
- $T<T_N$ no degeneracy, orthorhombic phase

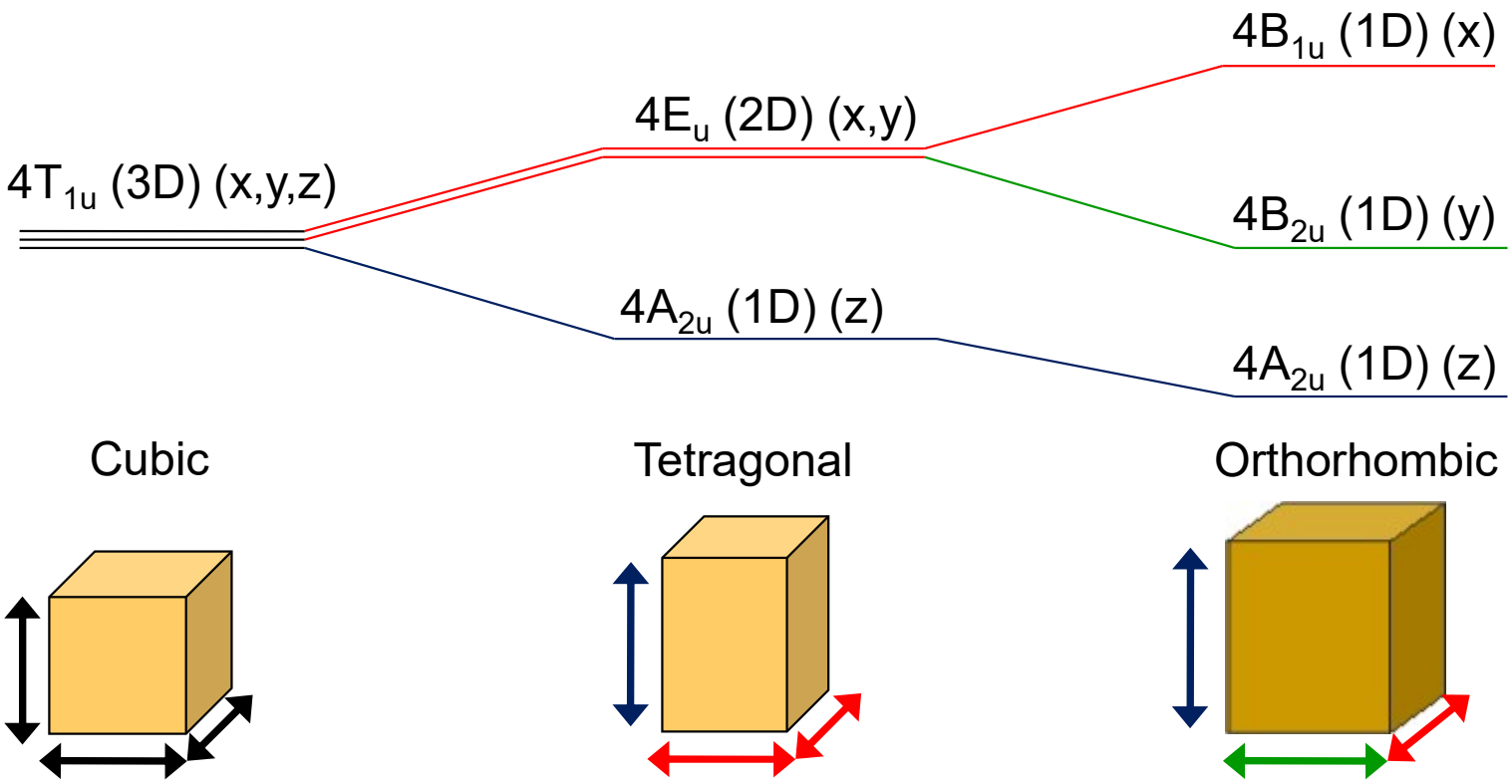
Physical Review B 77, 024421 (2008)

Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes

- Spinel structure: AB_2X_4
- FCC unit cell contains 2 formula units
- Symmetry analysis of the IR active modes



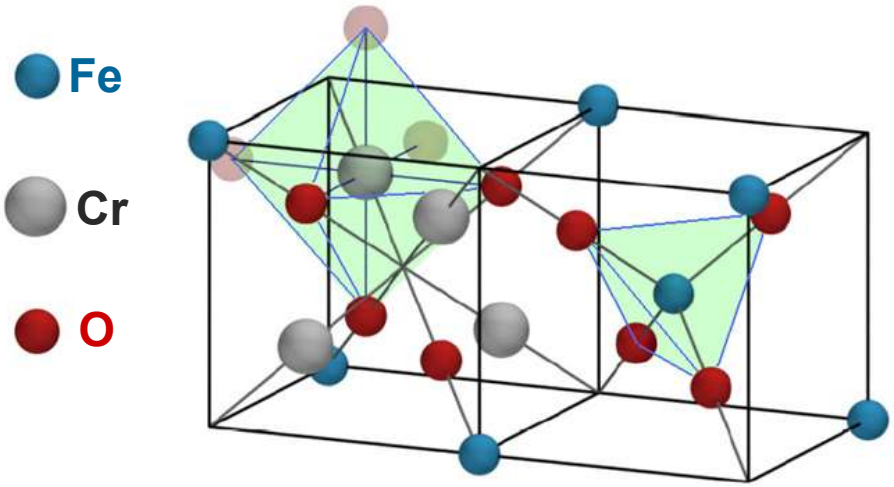


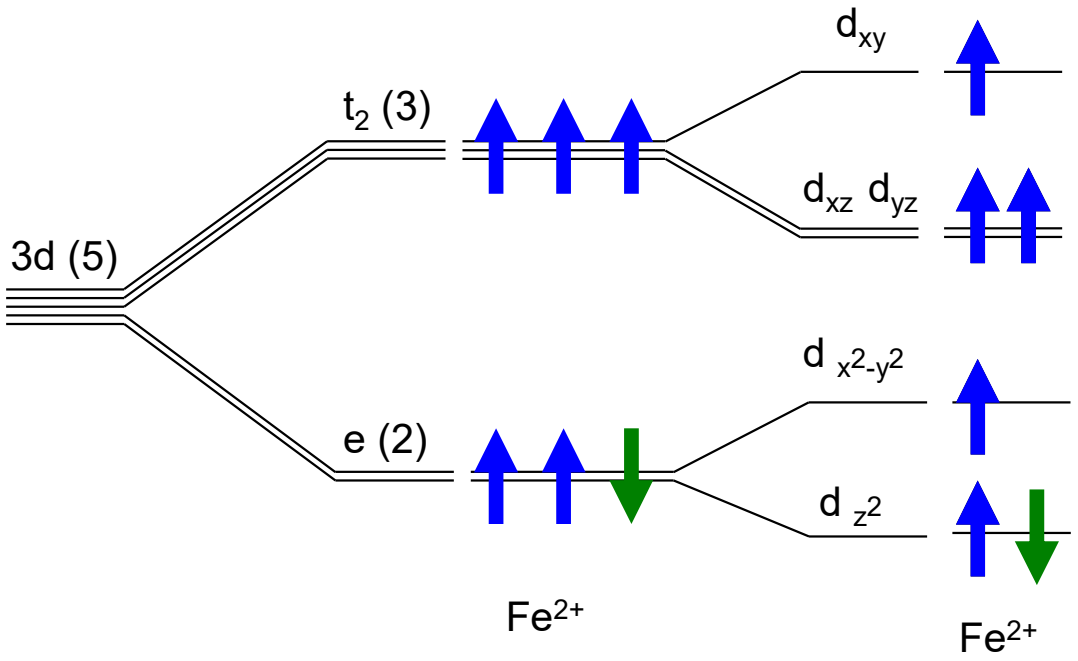
Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes

Fe^{2+} ions d shell is partially filled:

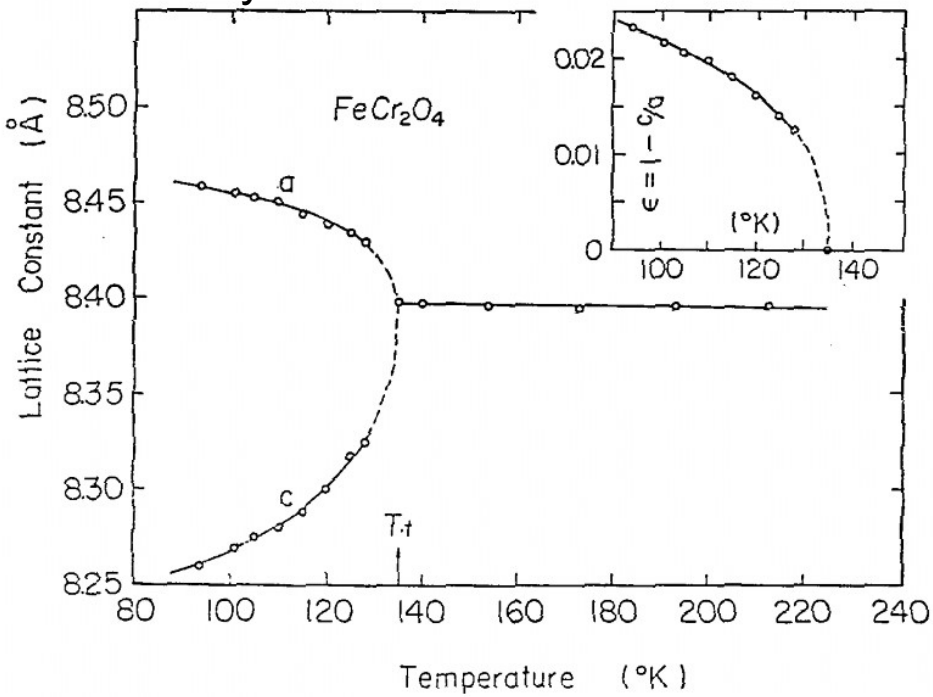
- Orbital degeneracy → Jahn-Teller distortion, T_{JT}
- Magnetic ordering, T_C





Free ion Cubic crystal field Tetragonal crystal field

X-ray diffraction



Tanaka et al., J. Phys. Soc. Japan **21**, 262 (1966)

Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes

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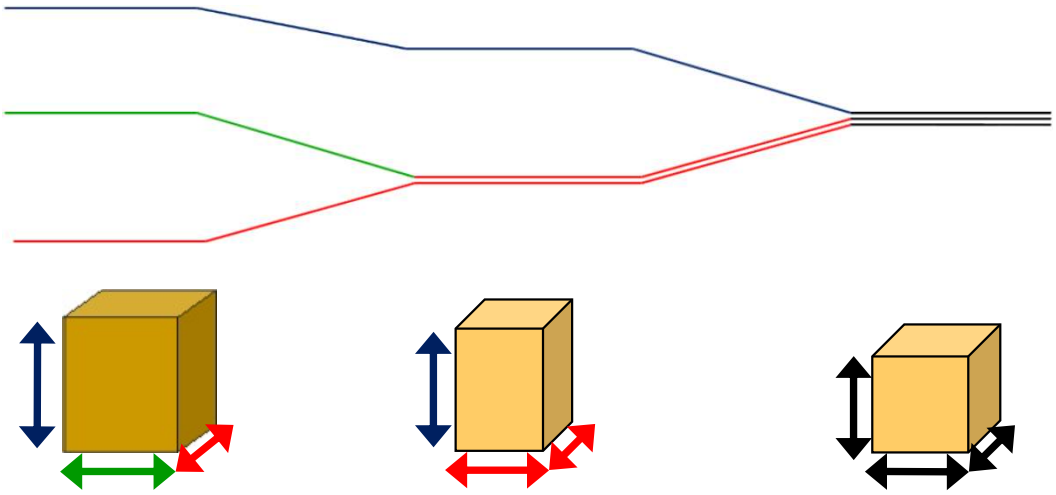
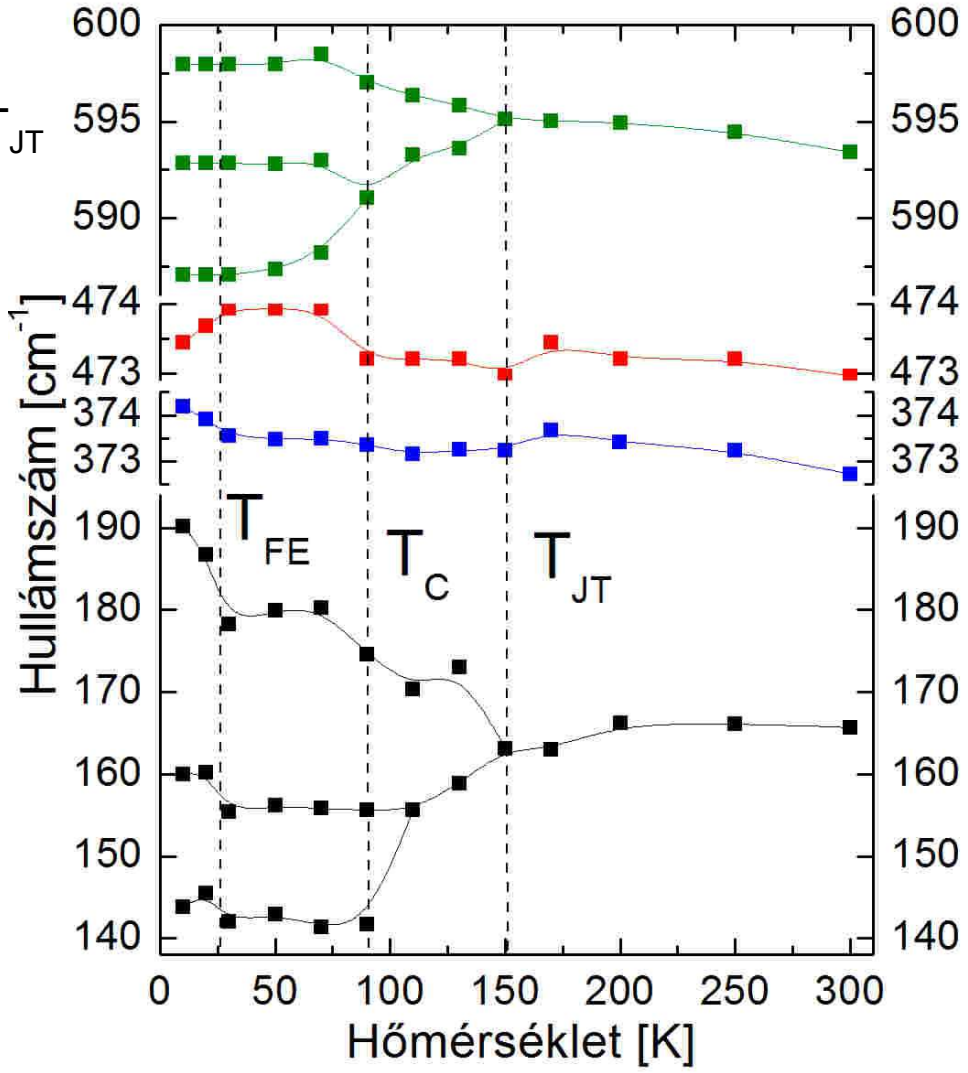


Orthorhombic Tetragonal Cubic



Bordács et al., Phys. Rev. Lett. **103**, 077205 (2009)

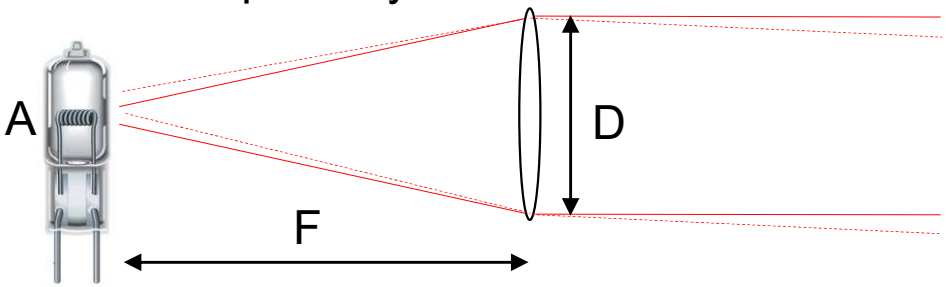
Grating spectroscopy

Grating spectrometer

Radiant flux: (Total emitted power) $\Phi = \iint_A \mathbf{S} d\mathbf{A}$

Brightness: (Radiance) $B = \frac{\delta^2 \Phi}{\delta\Omega \delta A \cos\theta}$

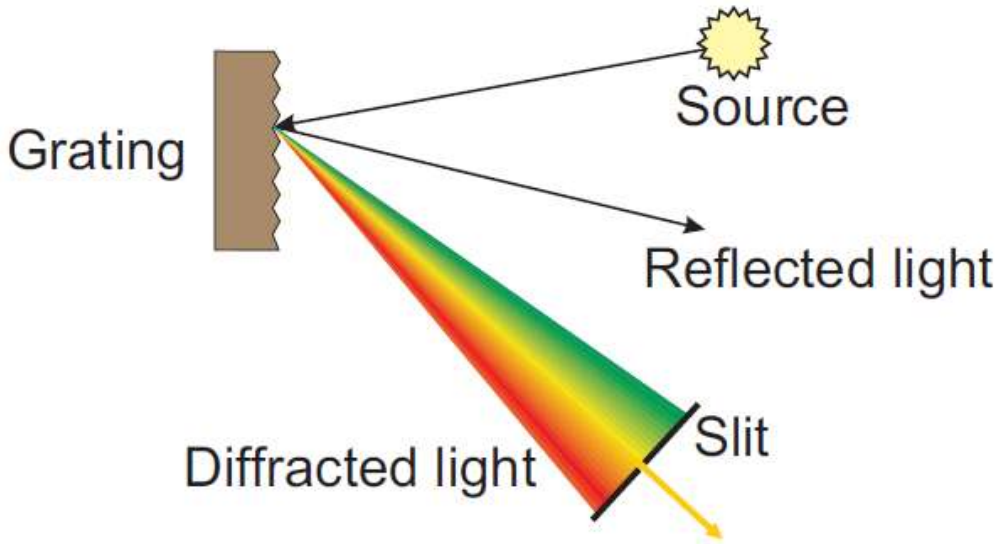
Brightness is conserved in an ideal loss-less optical system



$$B = \frac{\Phi}{A * \frac{\pi (D/2)^2}{F^2}} = B' = \frac{\Phi}{\pi \left(\frac{D}{2}\right)^2 * \frac{A}{F^2}}$$ ✓

Etendue (throughput): E=A*Ω

f-number = F/D
notation: f/# , e.g. f/2 = 100 mm / 50 mm = 2
Numerical aperture: NA = nsinθ=nsin(arctg(D/2F))
small f-number or large NA is better



Reciprocal dispersion [nm/mm] $\frac{\delta\lambda}{\delta L}$

$2\,a \sin\vartheta = m\lambda$ Bragg's law

$$\frac{\delta\vartheta}{\delta\lambda} = \frac{m}{a\cos\vartheta}$$ grating equation

$$\Delta\lambda = \frac{\delta\lambda}{\delta L} W = \frac{\delta\lambda}{F\delta\vartheta} W$$

$$E_G \propto WH\left(\frac{D}{F}\right)^2 \propto \frac{H}{F} D^2 \frac{\Delta\lambda}{\lambda}$$

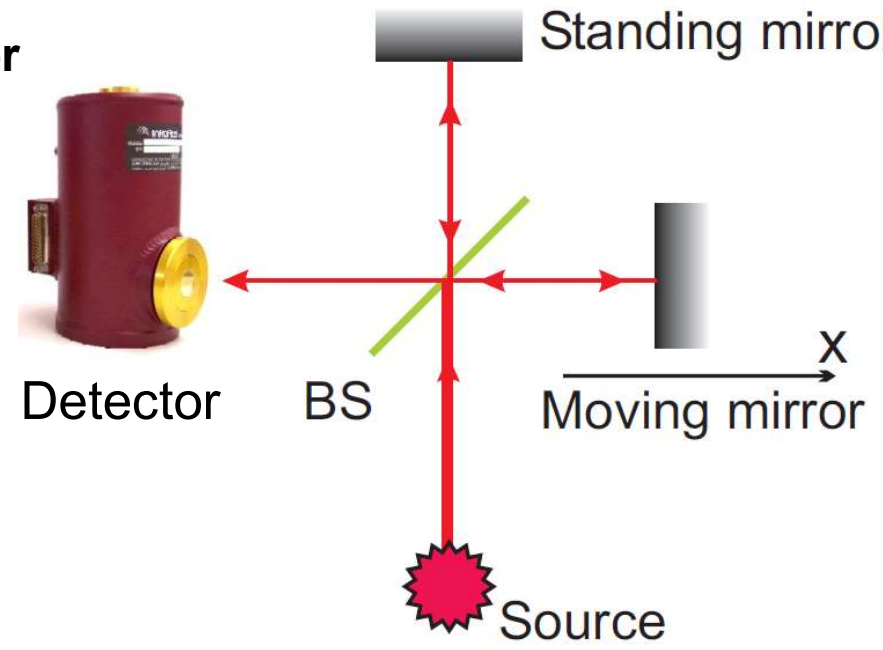
Fourier transform spectroscopy

Fourier transform infrared (FT-IR) spectrometer

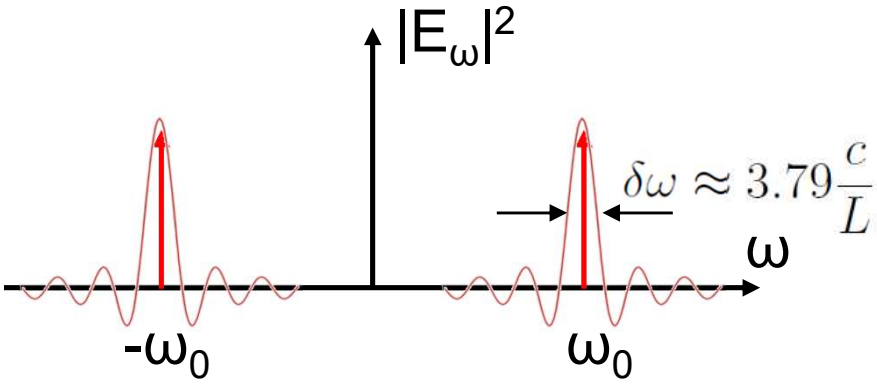
$$E_D = \int \left(\frac{E_\omega}{2} + \frac{E_\omega}{2} e^{i\frac{\omega}{c}2x}\right) e^{-i\omega t} \frac{d\omega}{2\pi}$$

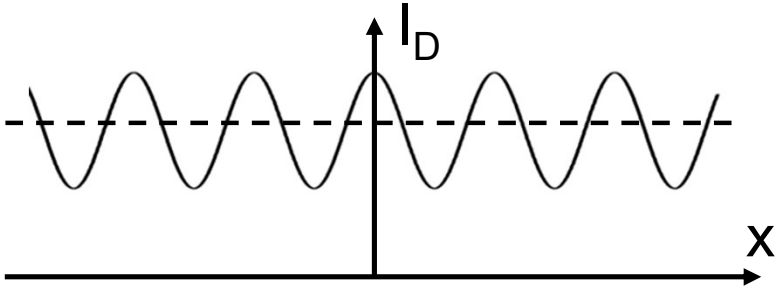
$$I_D = \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}}\langle E_D^* E_D \rangle$$

$$I_D(x) \simeq \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}}\frac{1}{2}\int |E_\omega|^2 \cos\left(\frac{\omega}{c}2x\right)\frac{d\omega}{2\pi}$$



$$E(t) = E_o \cos(\omega_o t)$$





$$I_D(K) = \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}}\int_{-L/2}^{L/2}\frac{1}{2}\int\frac{1}{4}(\delta(\omega-\omega_o)+\delta(\omega+\omega_o))\cos\left(\frac{\omega}{c}2x\right)e^{iKx}\frac{d\omega}{2\pi}dx =$$

$$= \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}}\frac{L}{32\pi}\left(\frac{\sin[(2\omega_o - Kc)\frac{L}{2c}]}{(2\omega_o - Kc)\frac{L}{2c}} + \frac{\sin[(2\omega_o + Kc)\frac{L}{2c}]}{(2\omega_o + Kc)\frac{L}{2c}}\right)$$

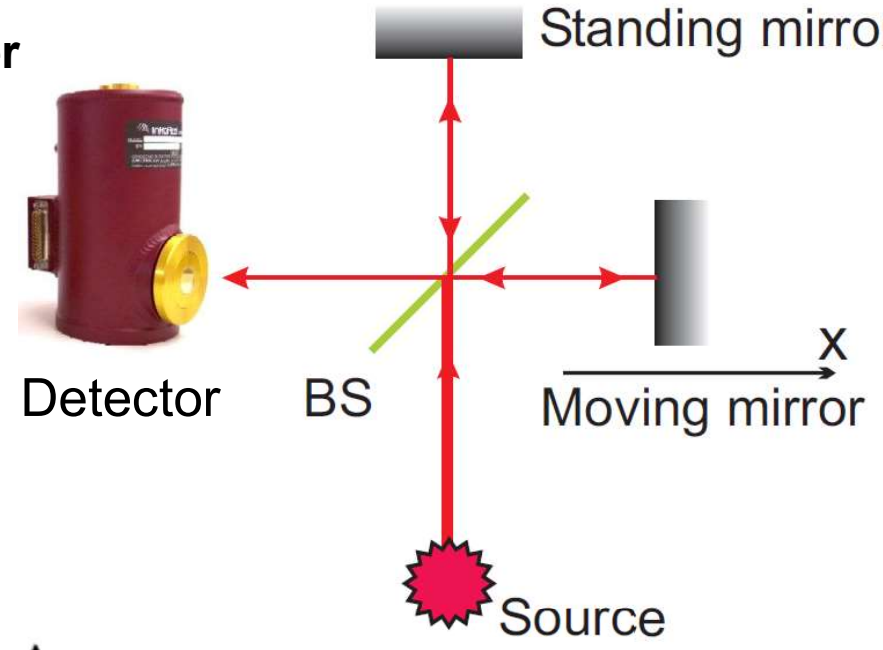
Fourier transform spectroscopy

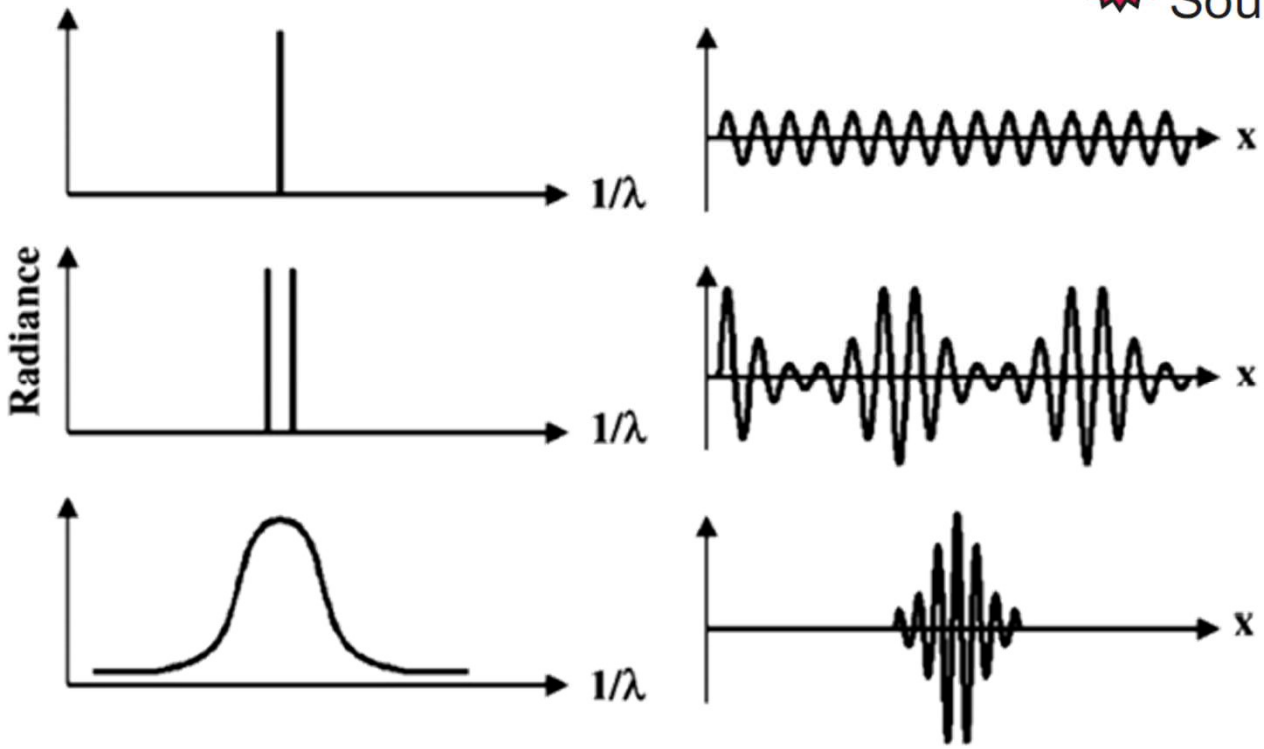
Fourier transform infrared (FT-IR) spectrometer

$$E_D = \int (\frac{E_\omega}{2} + \frac{E_\omega}{2} e^{i\frac{\omega}{c}2x}) e^{-i\omega t} \frac{d\omega}{2\pi}$$

$$I_D = \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}} \langle E_D^* E_D \rangle$$

$$I_D(x) \simeq \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}} \frac{1}{2} \int |E_\omega|^2 \cos(\frac{\omega}{c} 2x) \frac{d\omega}{2\pi}$$



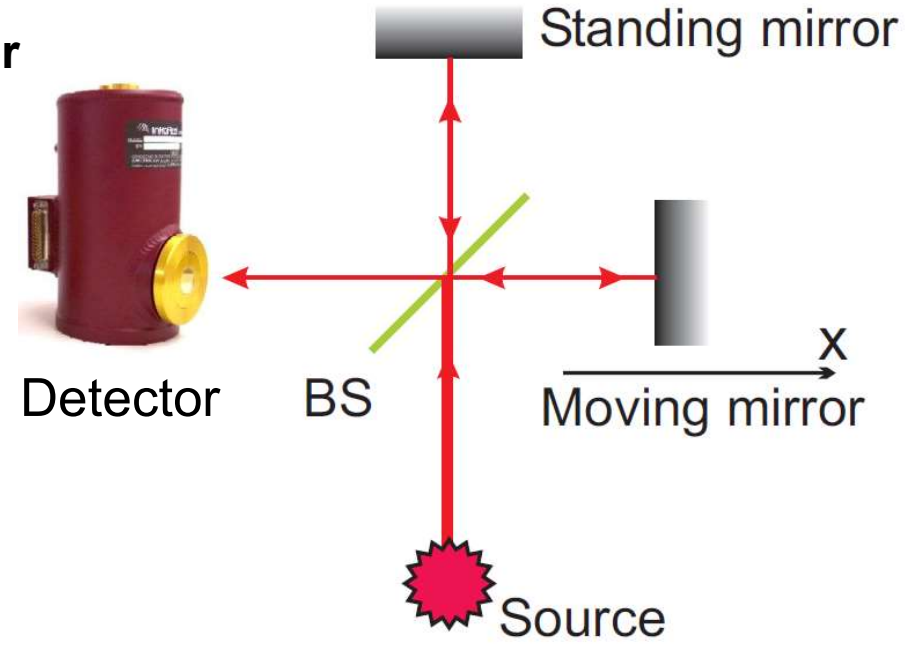


K-P. Mollmann and M. Vollmer Eur. J. Phys. 34 S123 (2013).

Fourier transform spectroscopy

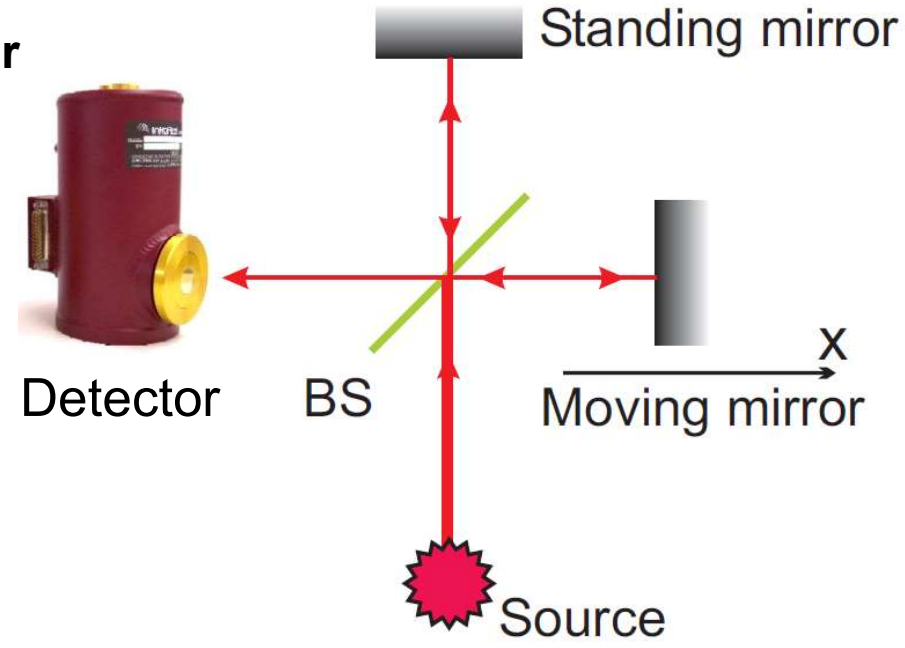
Fourier transform infrared (FT-IR) spectrometer

Discrete Fourier Transform (DFT)
finite sampling interval, Δx
finite high frequency cut-off $\omega_M = \frac{\pi c}{2\Delta x}$



Fourier transform spectroscopy

Fourier transform infrared (FT-IR) spectrometer



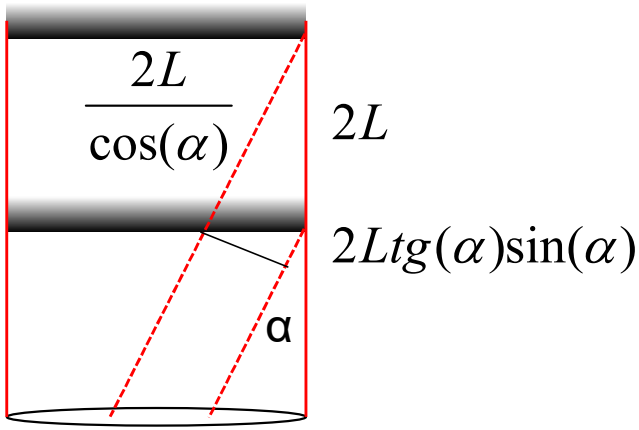
Discrete Fourier Transform (DFT)
finite sampling interval, Δx
finite high frequency cut-off $\omega_M = \frac{\pi c}{2\Delta x}$

multiplex advantage

throughput advantage

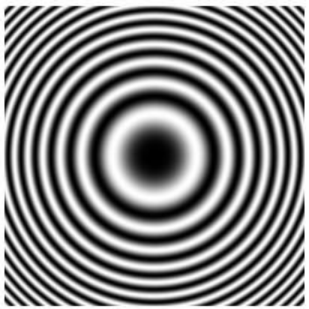
$$\xi = \left[\frac{2L}{\cos(\alpha)} - 2Ltg(\alpha)\sin(\alpha) \right] - 2L$$

path difference = [deflected beam] - centered beam
when ξ~λ cancellation on the detector,
no point to further move the mirror



$$\lambda \approx L\alpha^2$$
$$\frac{\Delta\lambda}{\lambda} \approx \alpha^2$$

$$E_{FT} \propto \left(\frac{D}{2}\right)^2 \pi \left(\frac{D}{F}\right)^2 \propto \alpha^2 D^2 = D^2 \frac{\Delta\lambda}{\lambda}$$



$$\frac{E_{FT}}{E_G} \propto \frac{F}{H} >> 1$$

Raman spectroscopy

Raman spectrometer