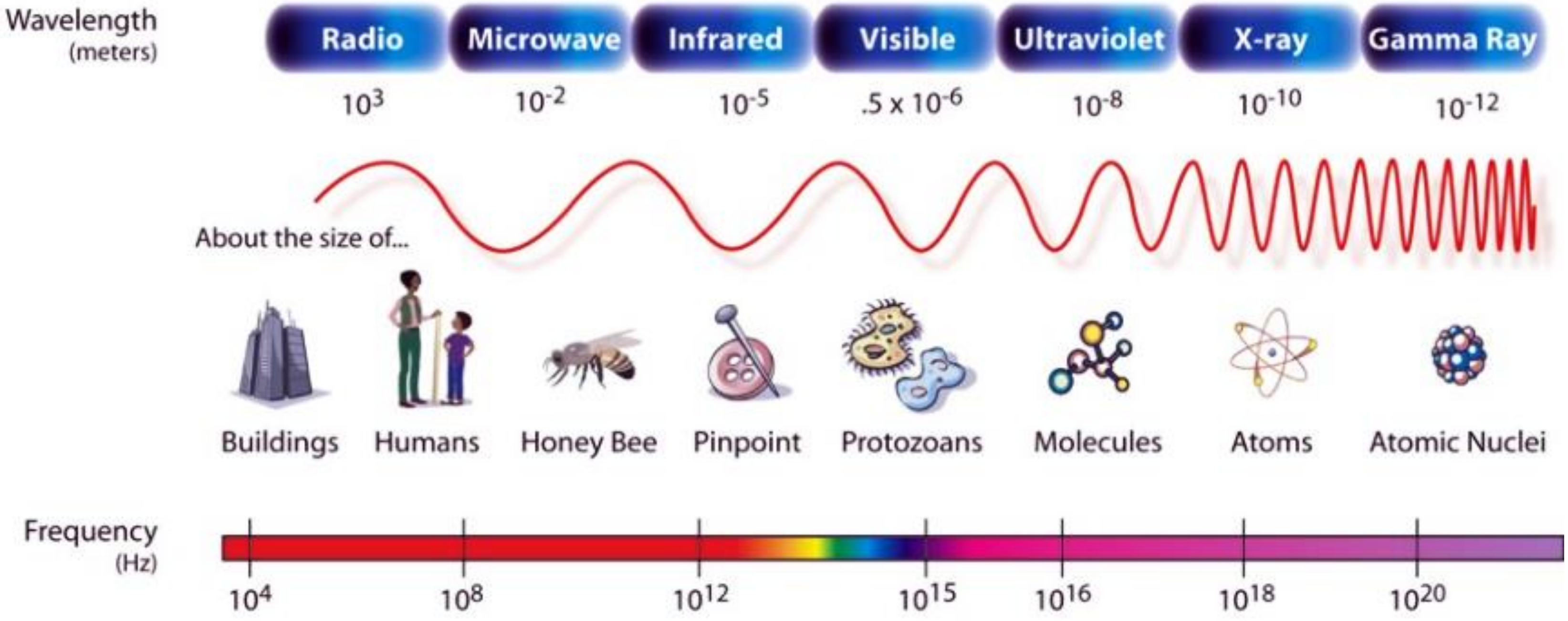
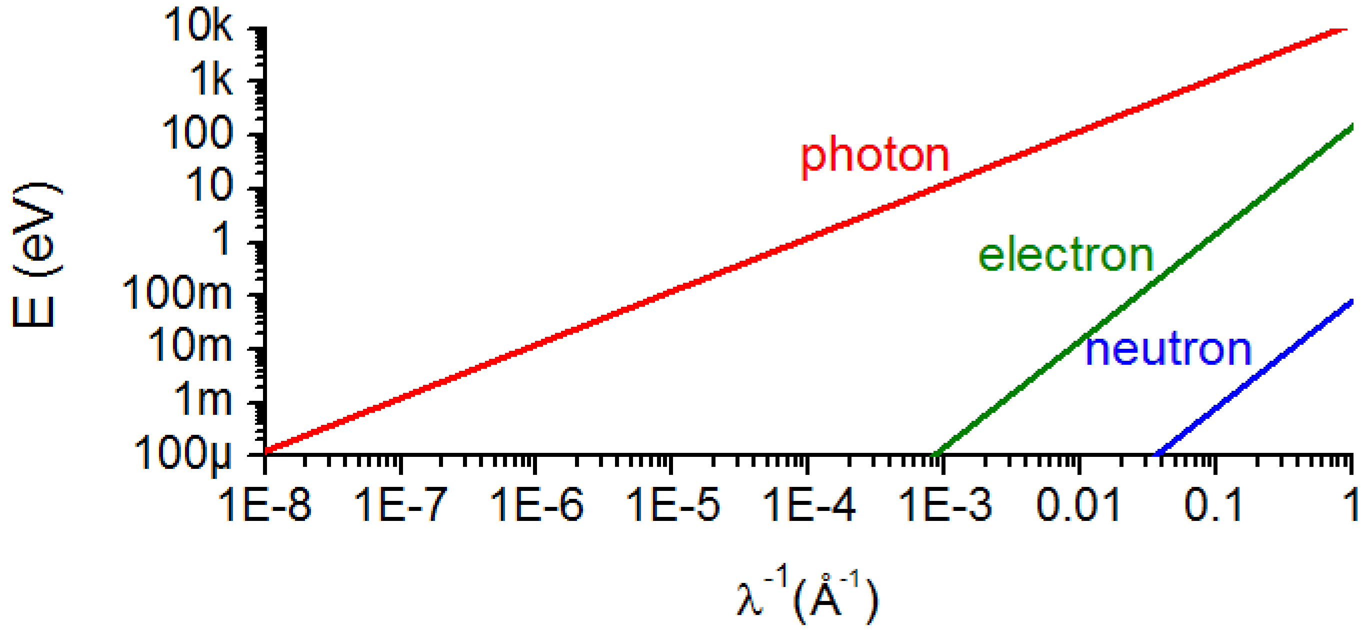
Optical spectroscopy





Optical spectroscopy

Recommended literature:

Atkins: Molecular quantum mechanics

Kamarás: Bevezetés a modern optikába V. 11. fejezet (FI könyvtár)

Sólyom: A modern szilárdtest-fizika alapjai I. 13. fejezet (FI könyvtár)

Struve: Fundamentals of molecular spectroscopy

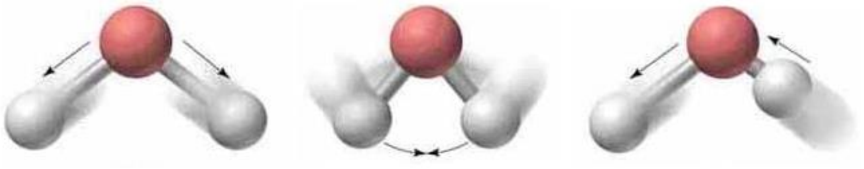
Tinkham: Group theory and quantum mechanics (FI könyvtár)

Dressel: Electrodynamics of solids (FI könyvtár)

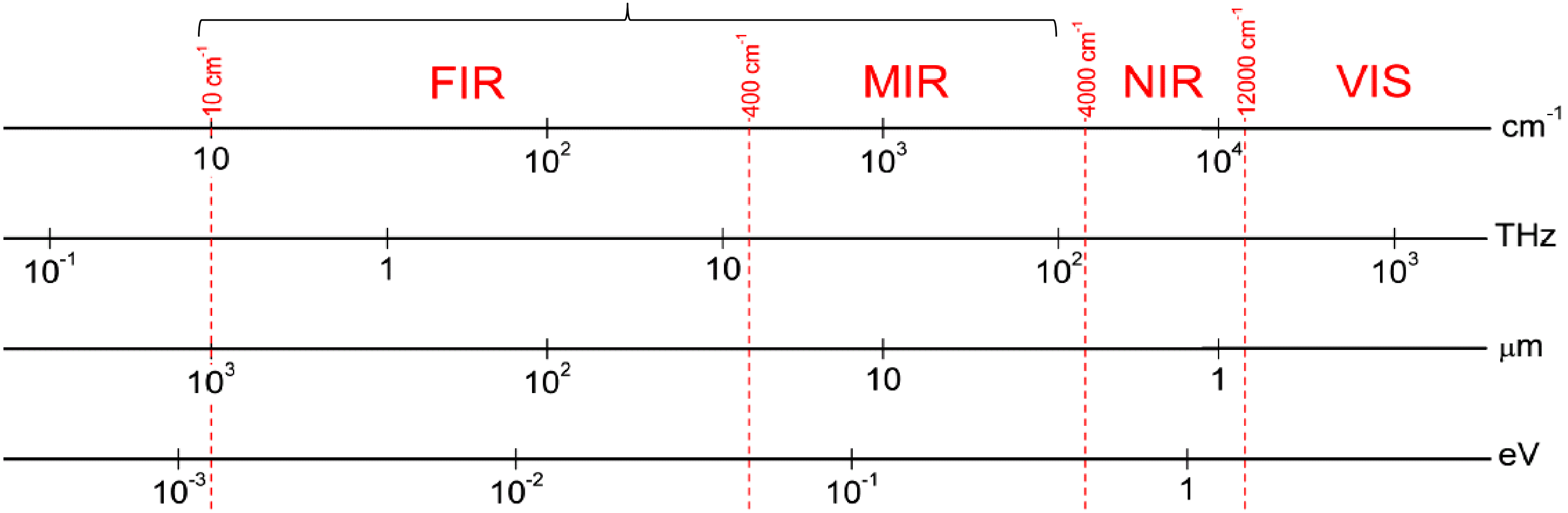
Details will come in the spring semester:

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

Optical spectroscopy

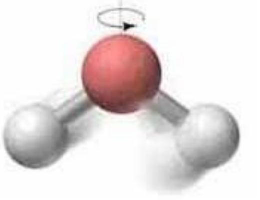


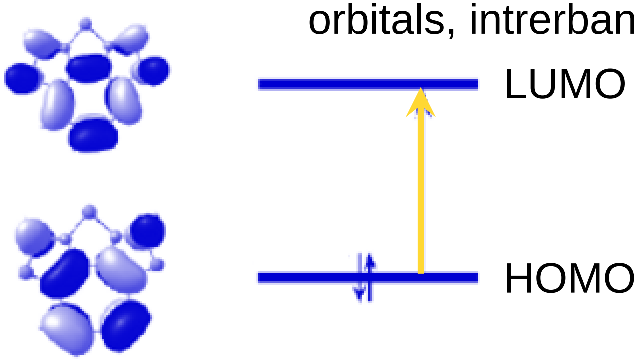
Vibrations of molecules and solids



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

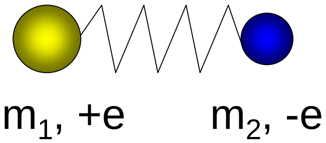
Rotation of molecules



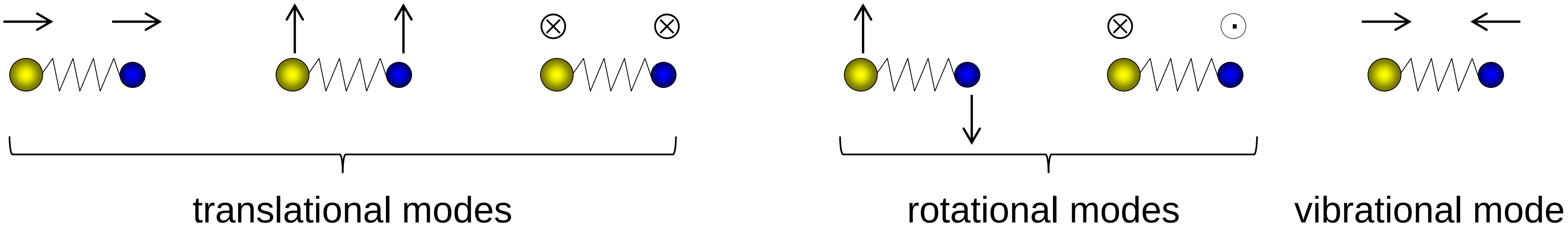


Optical spectroscopy: vibrational spectroscopy

A diatomic molecule:
(eg. HCl)



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



Equation of motions:

$$\left.\begin{aligned} m_1\frac{d^2u_1}{dt^2} &= -D(u_1-u_2)-\gamma m_1\frac{du_1}{dt}+eE(t) \\ m_2\frac{d^2u_2}{dt^2} &= -D(u_2-u_1)-\gamma m_2\frac{du_2}{dt}-eE(t) \end{aligned}\right\}$$

Long wavelength approximation:

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

trial function:

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

$$\Downarrow$$

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

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

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

$$\Downarrow$$

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

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

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

Optical spectroscopy: vibrational spectroscopy

A diatomic molecule:
(eg. HCl)

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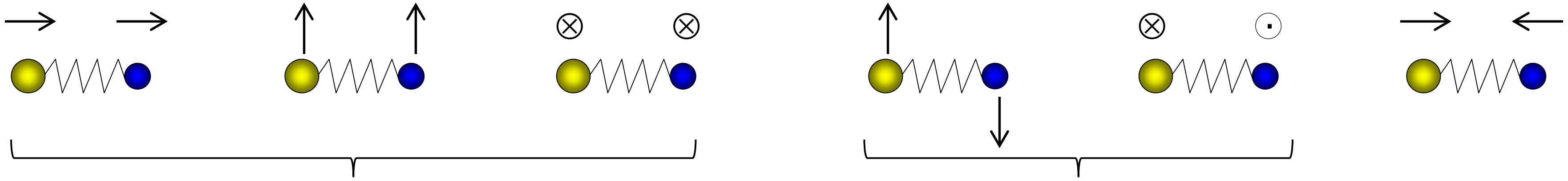
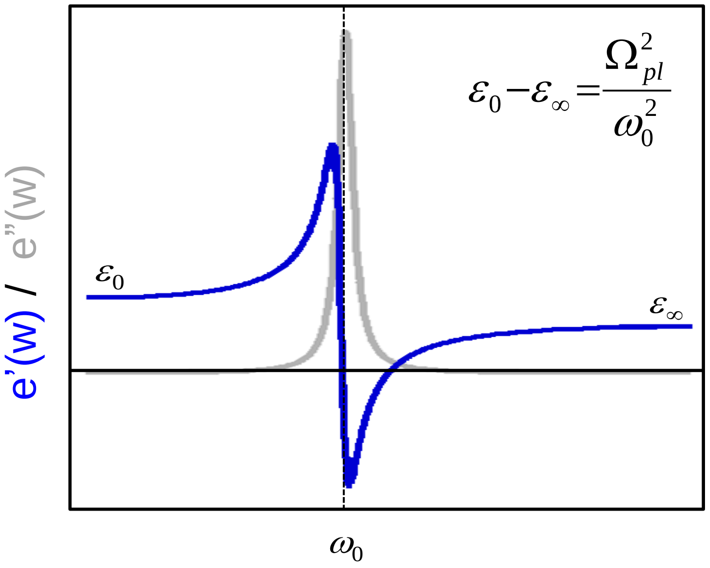


$$\varepsilon(\omega)=\varepsilon_\infty+\chi(\omega)=\varepsilon_\infty+\frac{\Omega_{pl}^2}{\omega_0^2-\omega^2-i\gamma\omega}$$



$$\varepsilon_0-\varepsilon_\infty=\frac{\Omega_{pl}^2}{\omega_0^2}$$

Absorption coefficient:

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

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

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

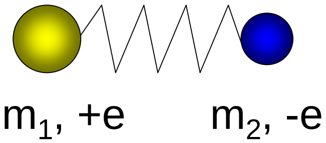
⇧ Close to the resonance

Reflectivity

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

Optical spectroscopy: vibrational spectroscopy

A diatomic molecule:
(eg. HCl)



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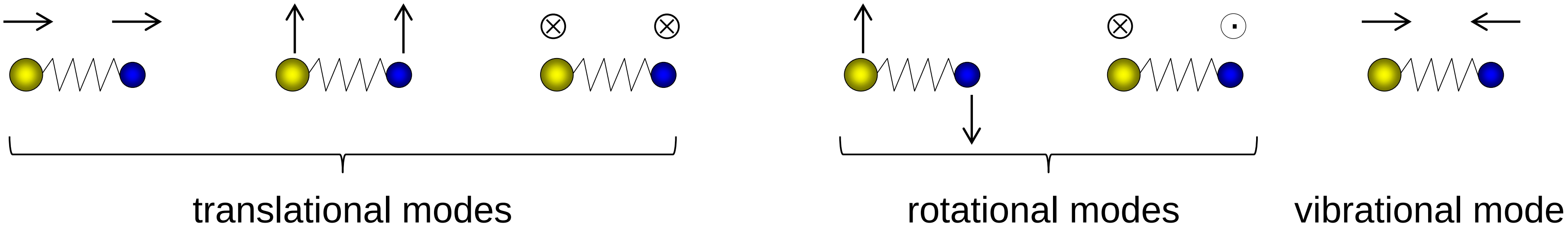
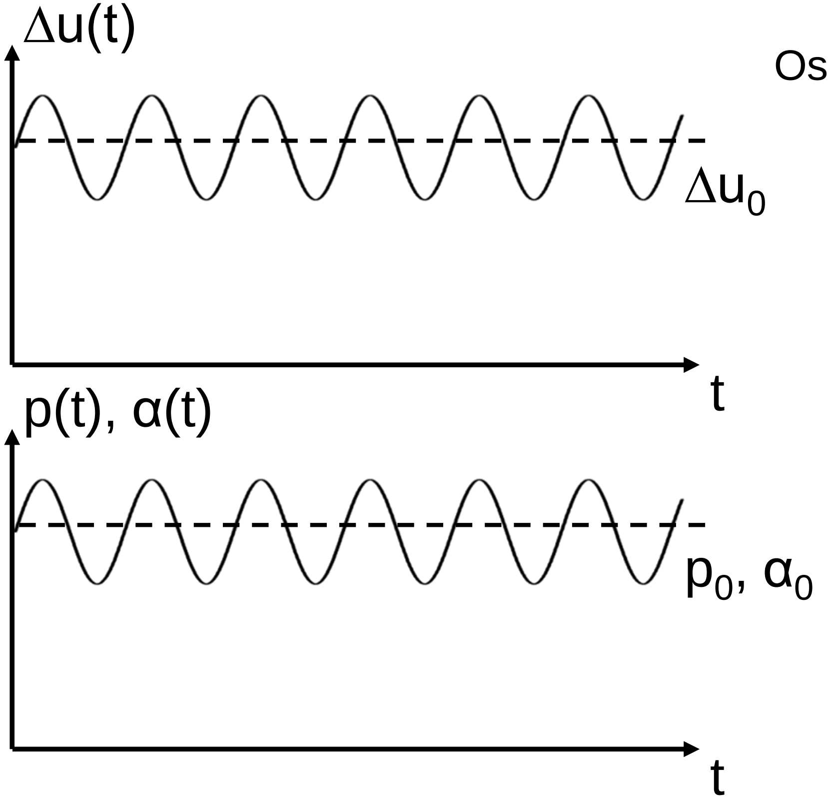




Oscillations of the polarizability (Raman scattering):

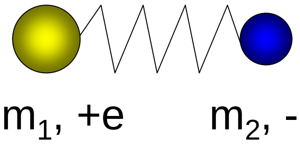
$$p(t)=\left(\alpha_0+\frac{\partial\alpha}{\partial q}q+\ldots\right)E_\omega\cos(\omega t)$$

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

$$p(t)\approx\alpha_0E_\omega\cos(\omega t)+\frac{\Delta\alpha E_\omega}{2}\left[\underbrace{\cos((\omega_0+\omega)t)}_{\text{anti-Stokes}}+\underbrace{\cos((\omega_0-\omega)t)}_{\text{Stokes}}\right]$$

Optical spectroscopy: vibrational spectroscopy

A diatomic molecule:
(eg. HCl)



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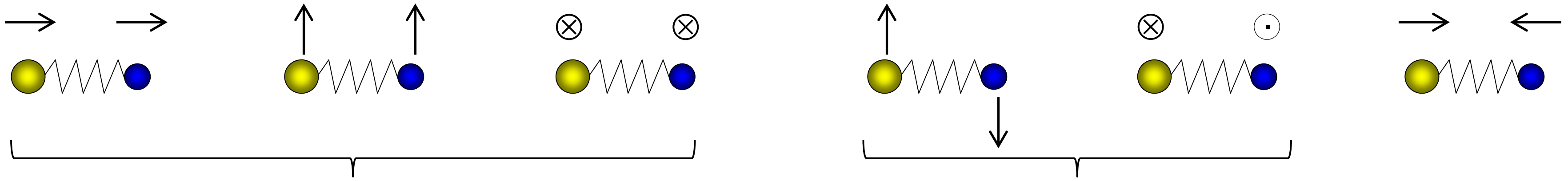


translational modes

rotational modes

vibrational mode

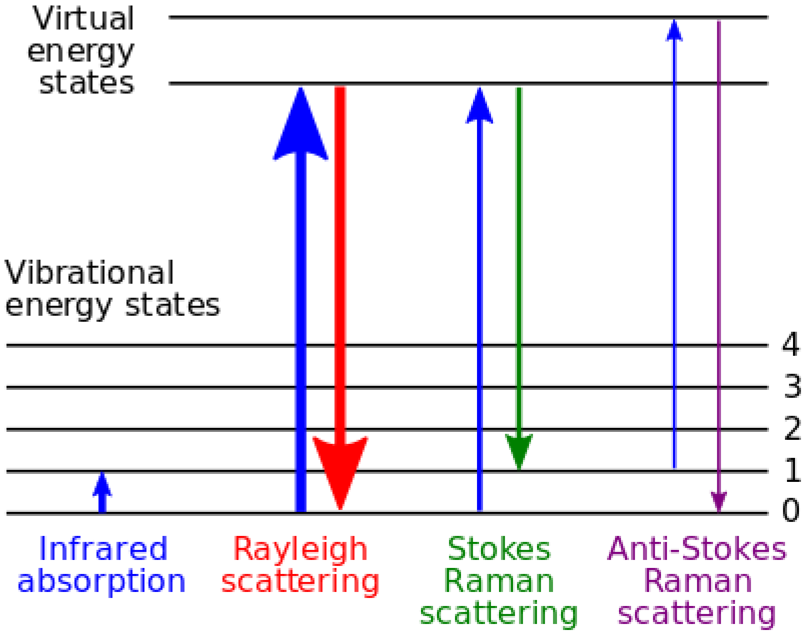
Oscillations of the polarizability (Raman scattering):

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

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

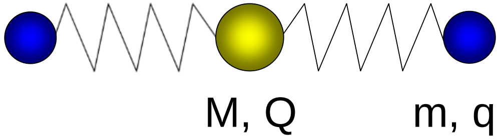
$$p(t)\approx\alpha_0 E_\omega\cos(\omega t)+\frac{\Delta\alpha E_\omega}{2}[\cos((\omega_0+\omega)t)+\cos((\omega_0-\omega)t)]$$

anti-Stokes Stokes



Vibrational spectroscopy

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

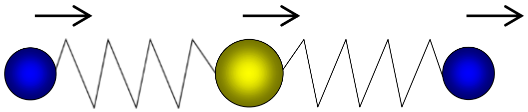


$$m\frac{d^2x_{O1}}{dt^2} = -D(x_{O1} - x_C)$$

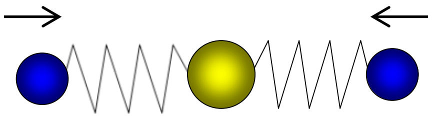
$$M\frac{d^2x_C}{dt^2} = -D(x_C - x_{O1}) - D(x_C - x_{O2})$$

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

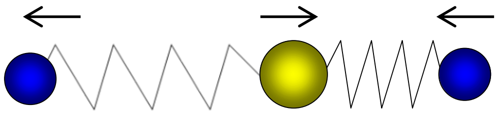
$$-\omega^2\begin{bmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{bmatrix}\begin{bmatrix} x_{O1} \\ x_C \\ x_{O2} \end{bmatrix} = \begin{bmatrix} -D & D & 0 \\ D & -D & D \\ 0 & D & -D \end{bmatrix}\begin{bmatrix} x_{O1} \\ x_C \\ x_{O2} \end{bmatrix}$$



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



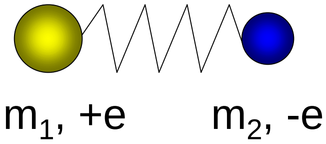
$$\omega = \frac{D}{m} \qquad \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$



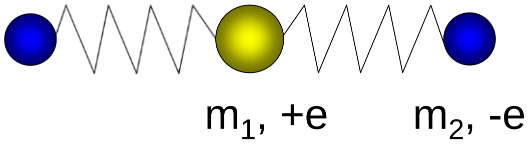
$$\omega = \frac{D}{m} + \frac{2D}{M} \qquad \begin{bmatrix} 1 \\ -\frac{2m}{M} \\ 1 \end{bmatrix}$$

Vibrational spectroscopy

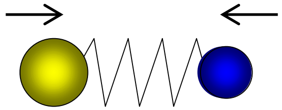
Polarization/polarizability:



$P_0 \neq 0$

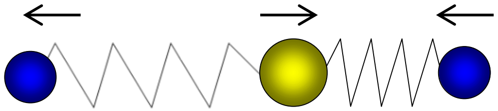


$P_0 = 0$



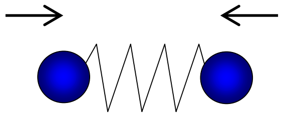
$P_\omega \neq 0, \alpha_\omega \neq 0$

IR, Raman



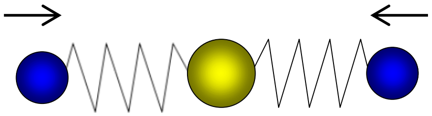
$P_\omega \neq 0, \alpha_\omega = 0$

IR



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

Raman



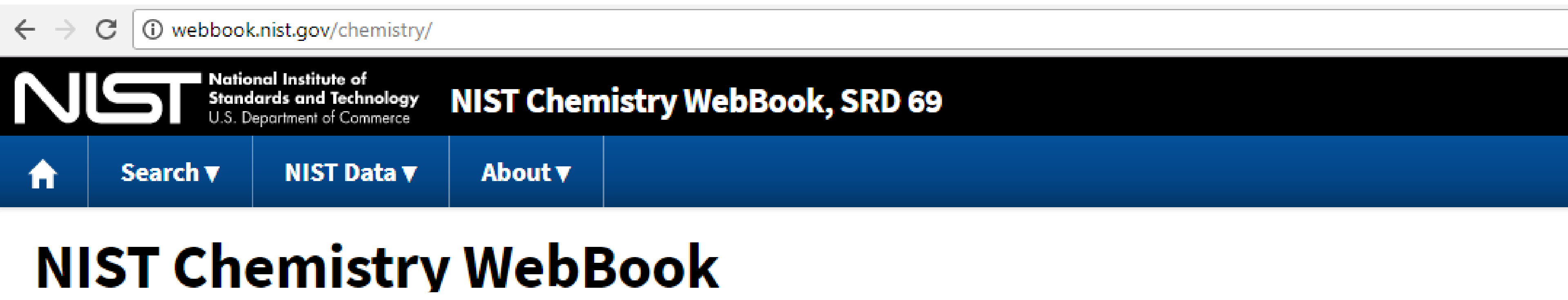
$P_\omega = 0, \alpha_\omega \neq 0$

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.

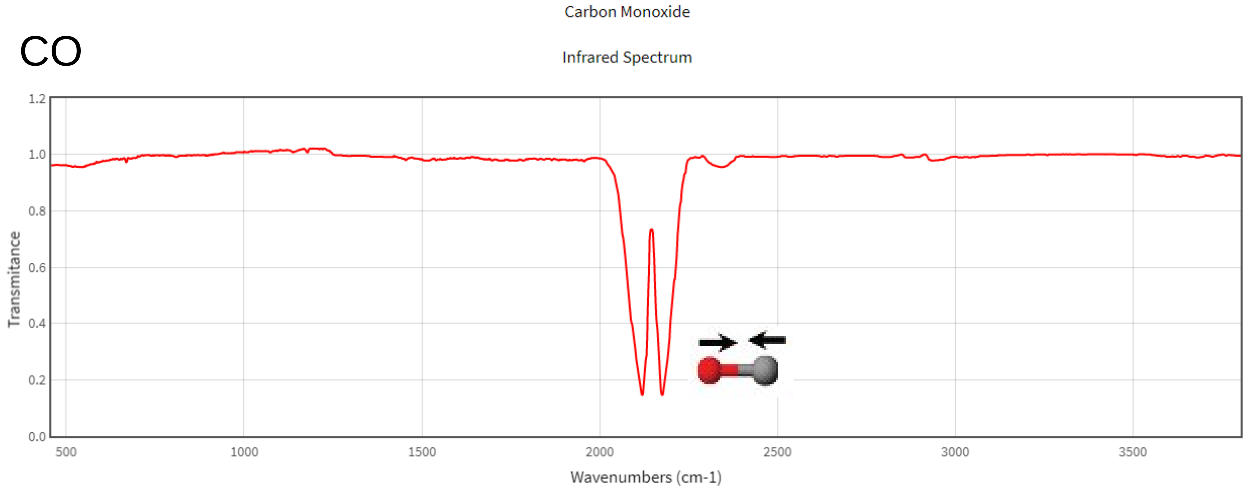
Vibrational spectroscopy

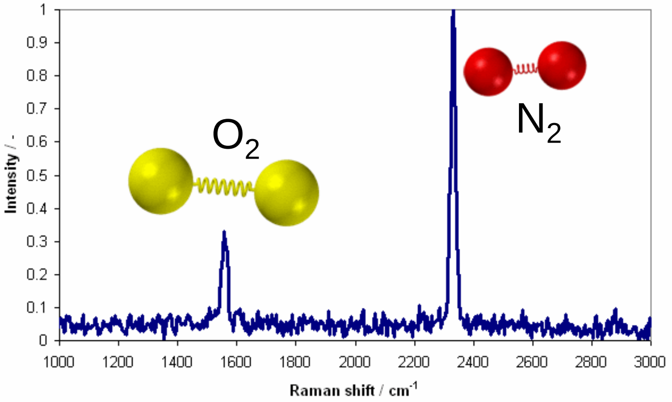


webbook.nist.gov/chemistry/

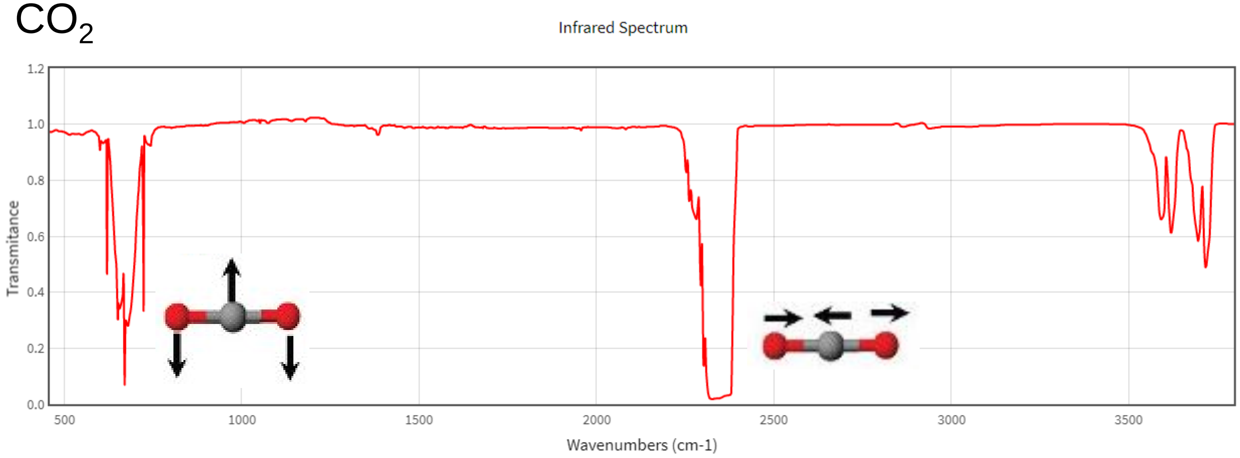
NIST Chemistry WebBook

CO

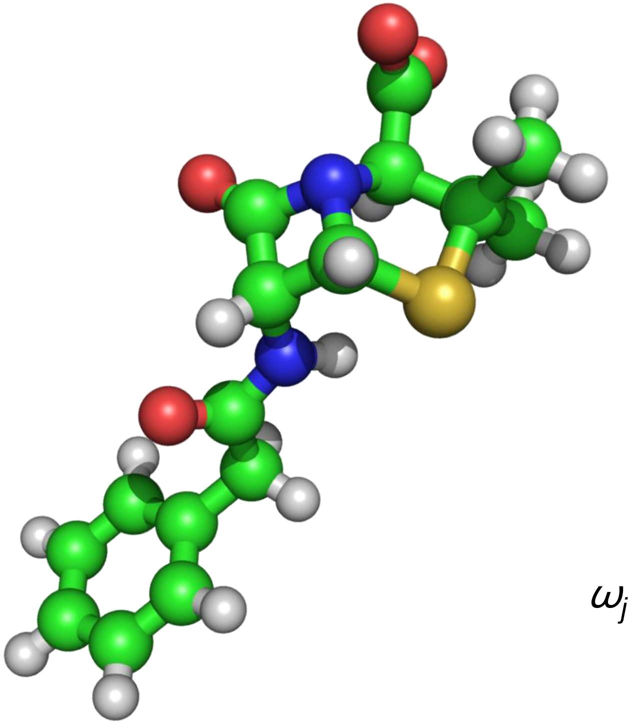




CO_2



Vibrational spectroscopy



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

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

$$\Downarrow$$

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

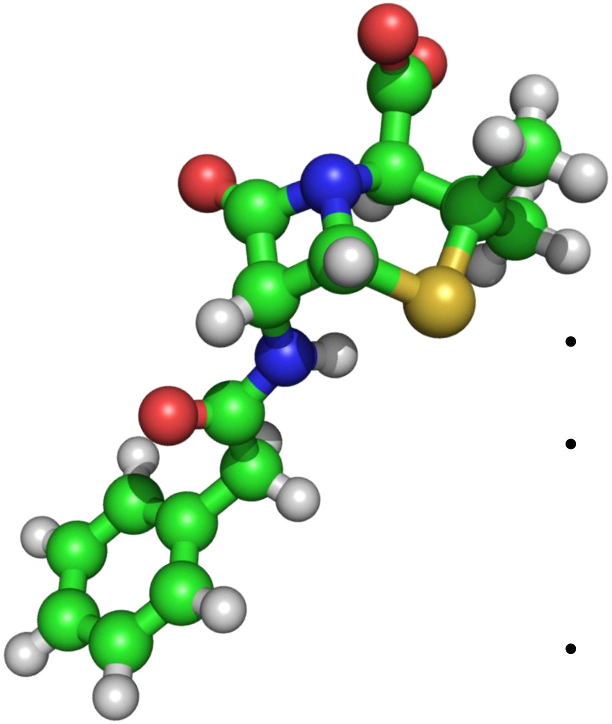
ω_j eigenfrequencies and u_j eigenmodes → diagonalise $D_{j,k}$

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

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

3N harmonic oscillators

Vibrational spectroscopy



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

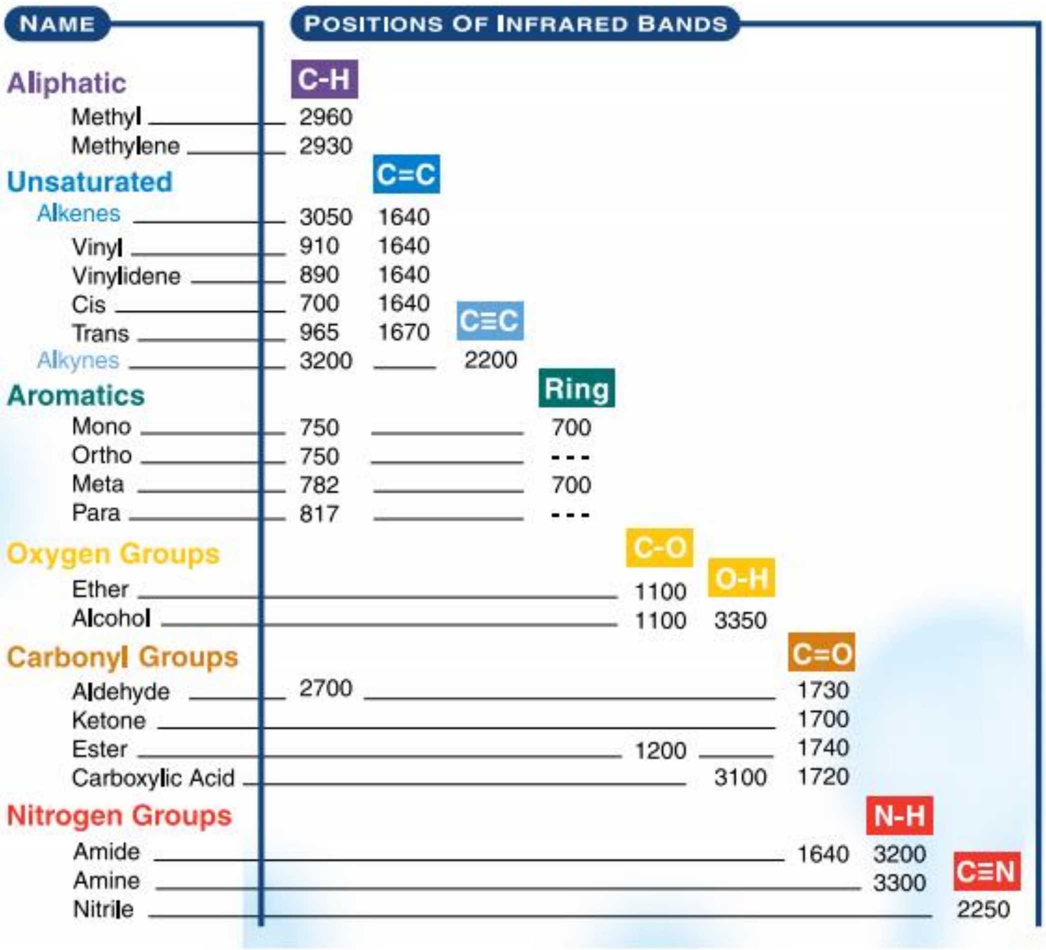
3N harmonic oscillators

- 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

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

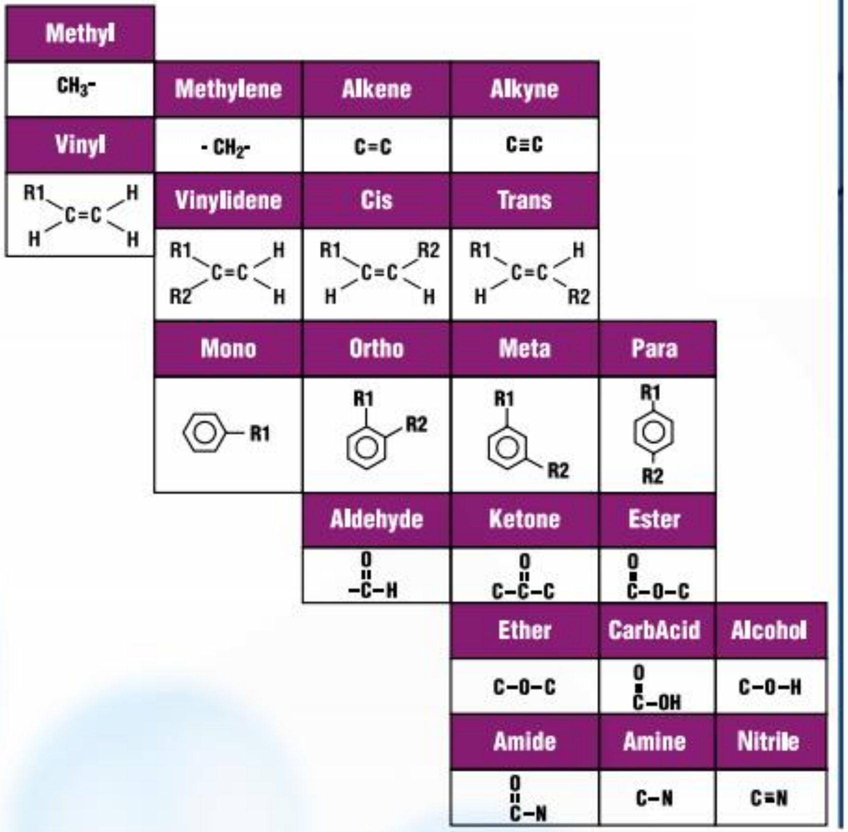
- IR active modes: posses oscillating electric dipole moments (thus not all modes are IR active)
- Raman active modes: polarizability of the molecule changes
- Silent modes: neither IR nor Raman active modes

Vibrational spectroscopy



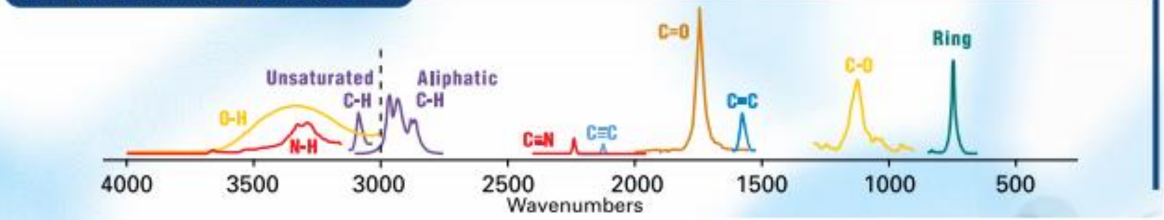
NAME	POSITIONS OF INFRARED BANDS: C-H	C=C	C≡C	Ring	C-O	O-H	C=O	N-H	C≡N
Aliphatic									
Methyl	2960								
Methylene	2930								
Unsaturated									
Alkenes	3050	1640							
Vinyl	910	1640							
Vinylidene	890	1640							
Cis	700	1640							
Trans	965	1670							
Alkynes	3200		2200						
Aromatics									
Mono	750			700					
Ortho	750			- - -					
Meta	782			700					
Para	817			- - -					
Oxygen Groups									
Ether					1100				
Alcohol					1100	3350			
Carbonyl Groups									
Aldehyde	2700						1730		
Ketone							1700		
Ester					1200		1740		
Carboxylic Acid						3100	1720		
Nitrogen Groups									
Amide							1640	3200	
Amine								3300	
Nitrile									2250

FUNCTIONAL GROUP REPRESENTATION



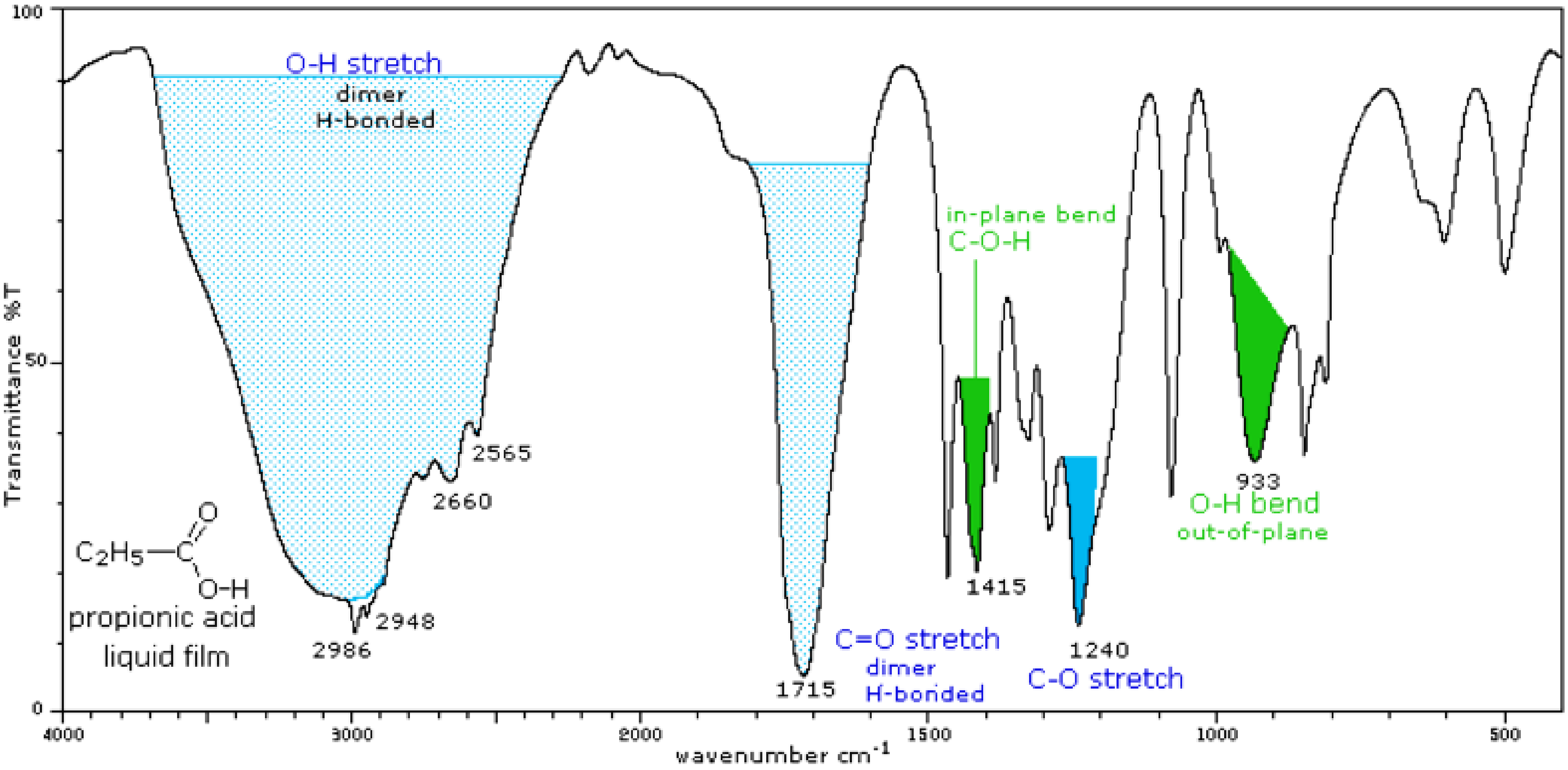
Name	Representation
Methyl	CH_3-
Methylene	$-CH_2-$
Alkene	C=C
Alkyne	C≡C
Vinyl	R1, H, C=C, H, H
Vinylidene	R1, R2, C=C, H, H
Cis	R1, R2, C=C, H, H
Trans	R1, H, C=C, H, R2
Mono	R1
Ortho	R1, R2
Meta	R1, R2
Para	R1, R2
Aldehyde	$-\overset{O}{\overset{\|}{C}}-H$
Ketone	$C-\overset{O}{\overset{\|}{C}}-C$
Ester	$\overset{O}{\overset{\|}{C}}-O-C$
Ether	C–O–C
CarbAcid	$\overset{O}{\overset{\|}{C}}-OH$
Alcohol	C–O–H
Amide	$\overset{O}{\overset{\|}{C}}-N$
Amine	C–N
Nitrile	C≡N

RELATIVE PEAK INTENSITIES



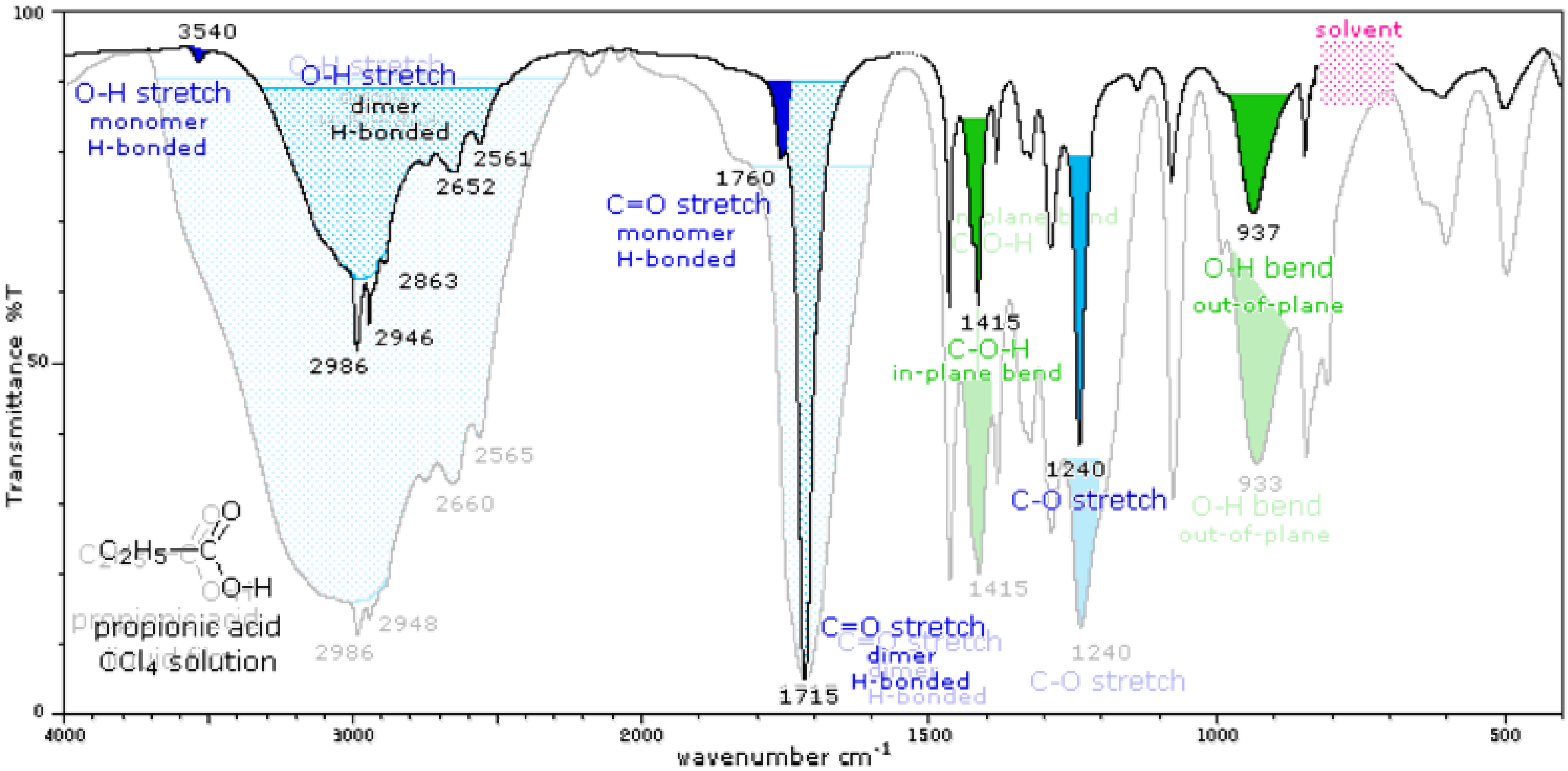
https://www.thermofisher.com

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



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- 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)

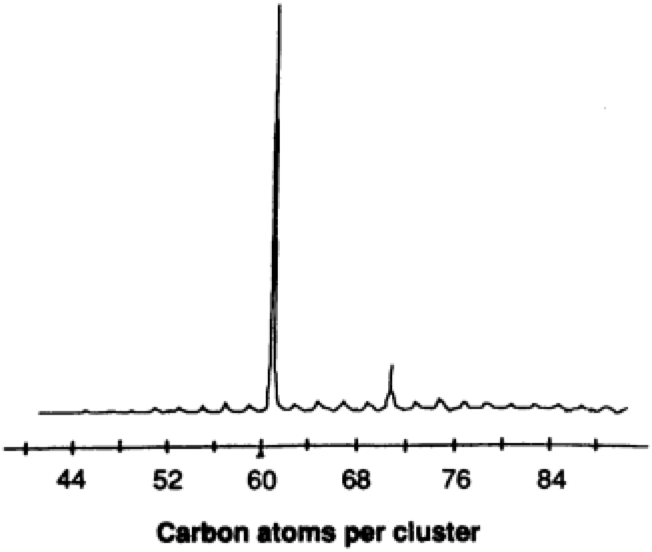
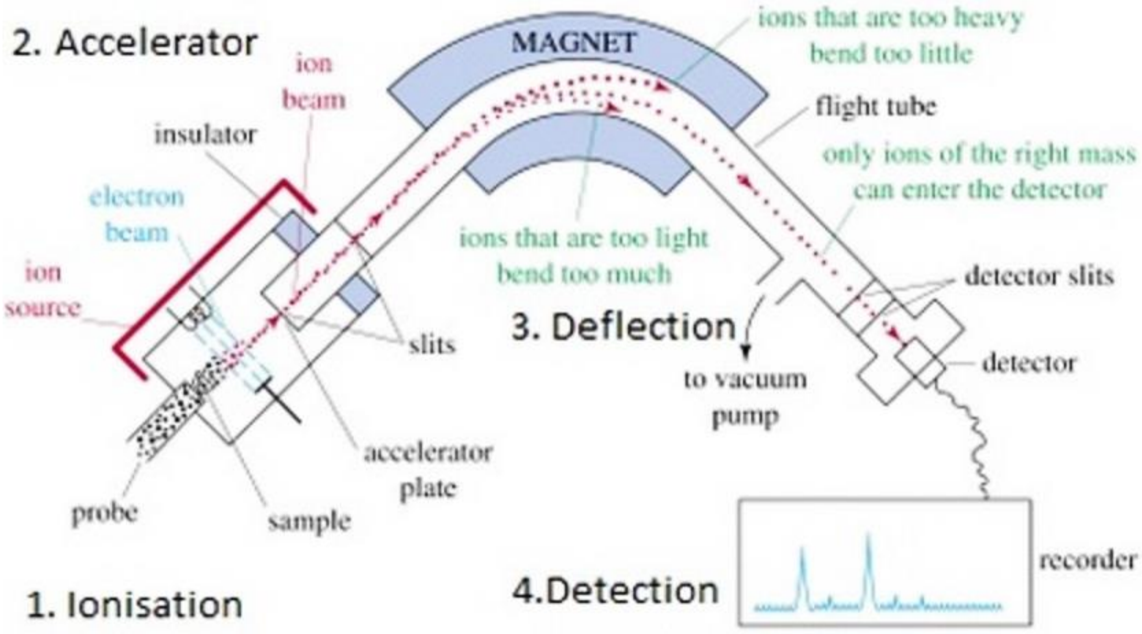


Fig. 1. Mass spectra of carbon cluster distributions in a supersonic beam produced by laser vaporization



Vibrational spectroscopy

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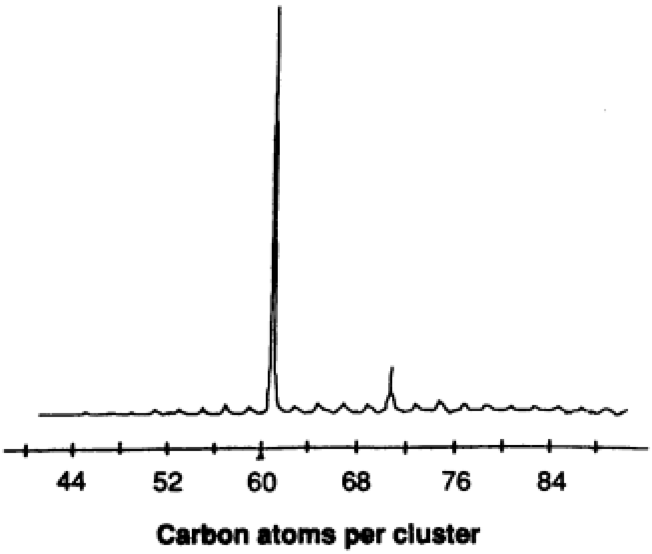

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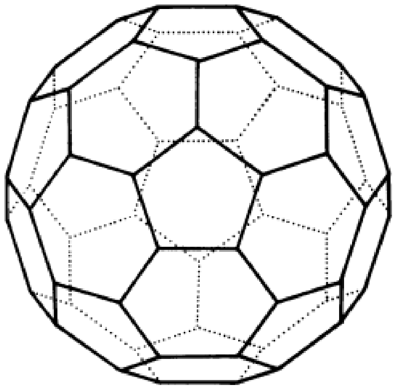


Fig. 2. Truncated icosahedral structure proposed for C_{60}.

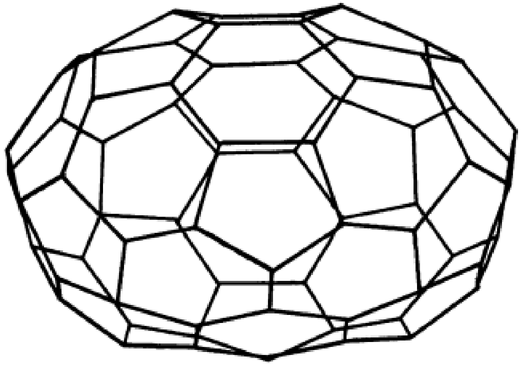


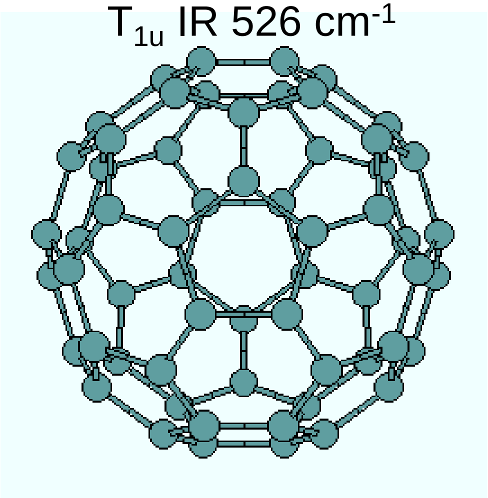
Fig. 3. A possible fullerene structure for the cluster C_{72}.

Vibrational spectroscopy

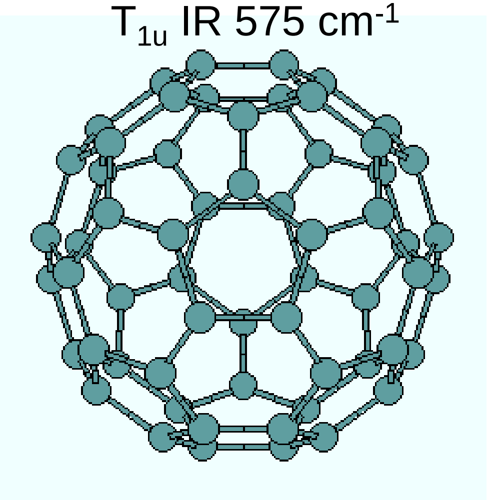
Vibrations of C_{60} fulleren

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

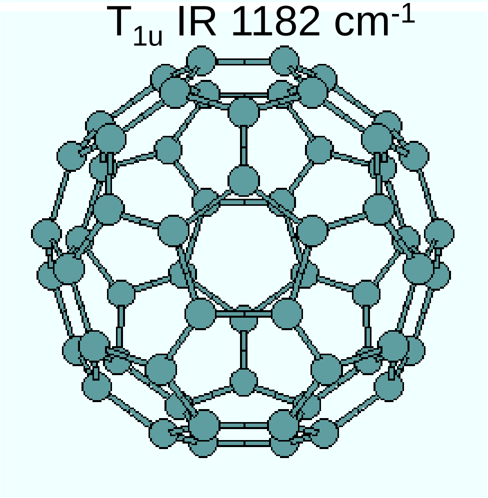
T_{1u} IR 526 cm^{-1}



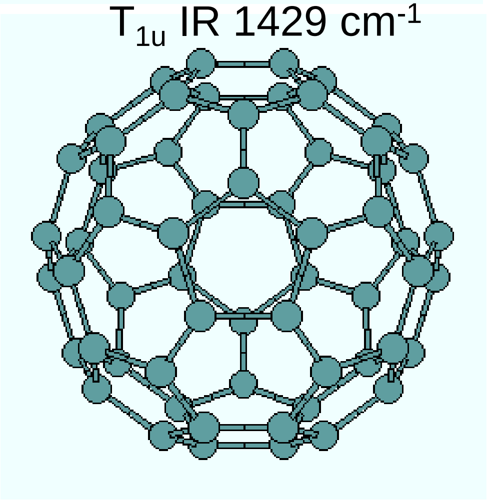
T_{1u} IR 575 cm^{-1}



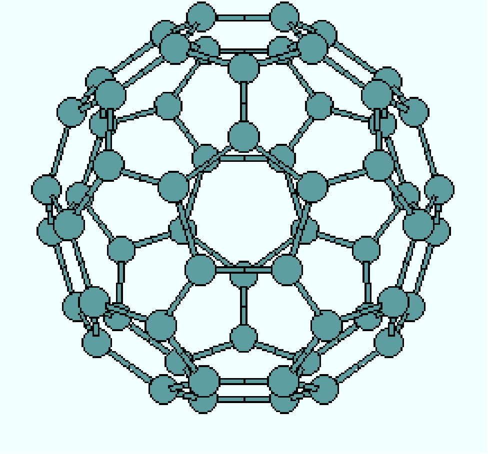
T_{1u} IR 1182 cm^{-1}



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



A_{1g} Raman breathing mode

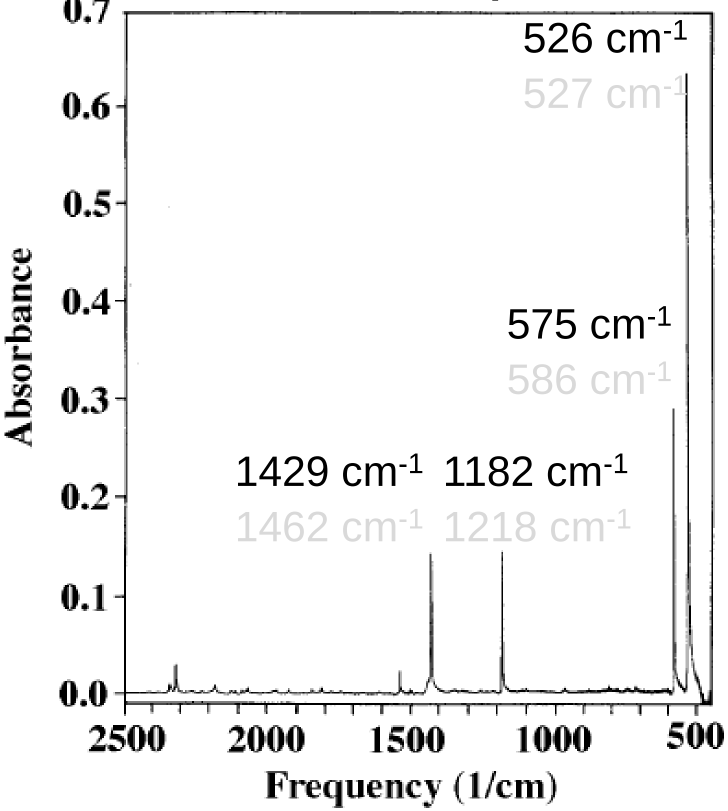


Rezgési spektroszkópia

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



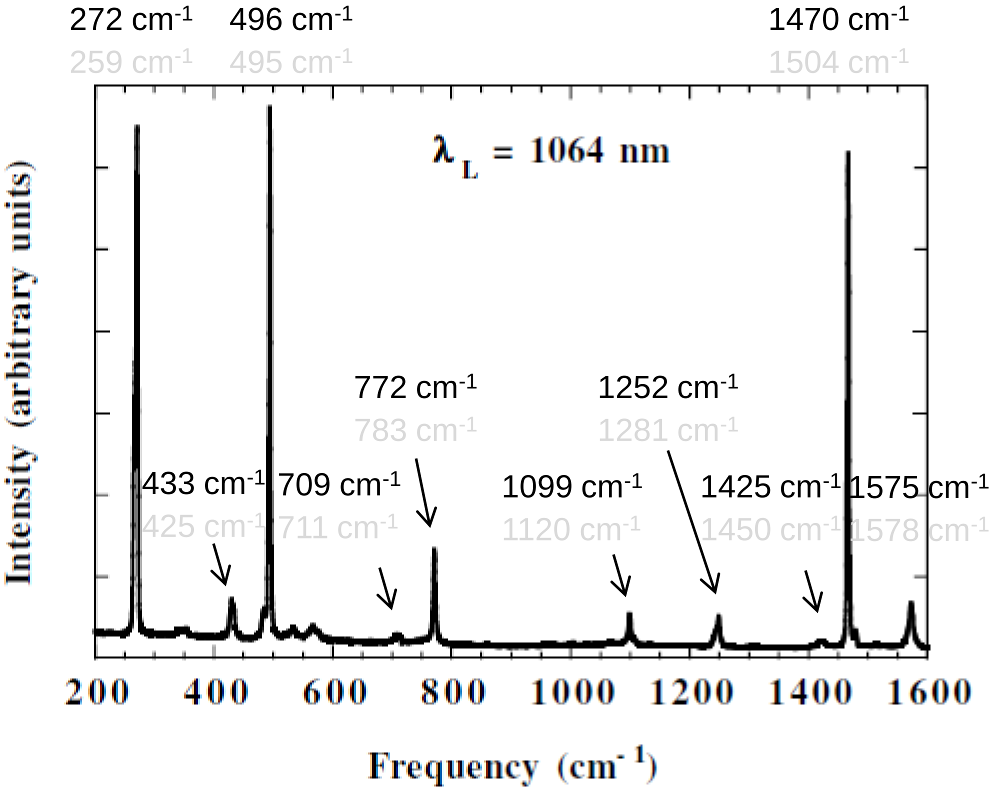
526 cm^{-1} 527 cm^{-1}

575 cm^{-1} 586 cm^{-1}

1429 cm^{-1} 1462 cm^{-1}

1182 cm^{-1} 1218 cm^{-1}

Raman scattering



272 cm^{-1} 259 cm^{-1}

496 cm^{-1} 495 cm^{-1}

1470 cm^{-1} 1504 cm^{-1}

772 cm^{-1} 783 cm^{-1}

1252 cm^{-1} 1281 cm^{-1}

433 cm^{-1} 425 cm^{-1}

709 cm^{-1} 711 cm^{-1}

1099 cm^{-1} 1120 cm^{-1}

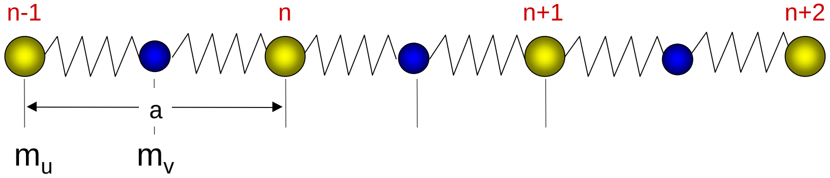
1425 cm^{-1} 1450 cm^{-1}

1575 cm^{-1} 1578 cm^{-1}

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)



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

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

$$\Downarrow$$

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

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

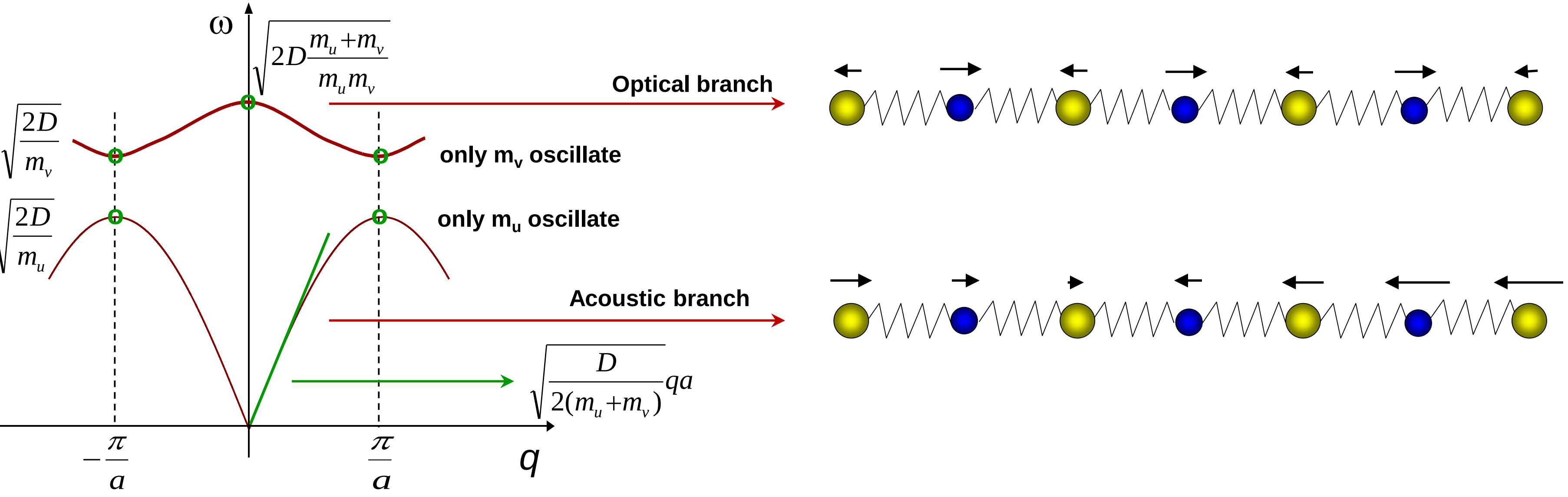
$$\begin{bmatrix} -2D & D & & & 0 \\ D & -2D & D & & \\ & D & -2D & D & \\ & & D & -2D & D \\ 0 & & & D & -2D \end{bmatrix} \begin{bmatrix} u_{n-1} \\ v_{n-1} \\ u_n \\ v_n \\ u_{n+1} \end{bmatrix}$$

$$v_{n-1} \quad u_n \quad v_n \quad u_{n+1}$$

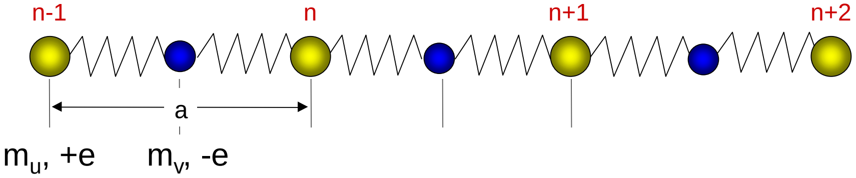
$$\swarrow \qquad \searrow$$

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

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



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

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

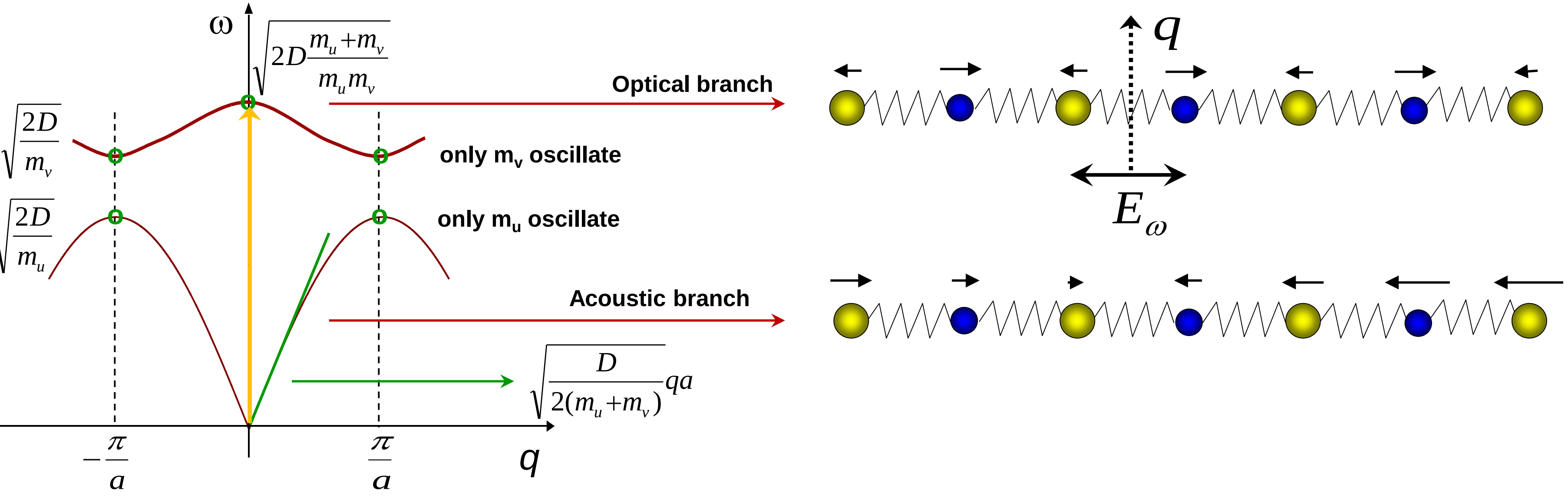
$$\lambda >> a \Rightarrow q << \frac{\pi}{a} \Rightarrow \begin{cases} E(r,t) \approx E_\omega e^{i\omega t} \\ u_n(t) \approx u e^{-i\omega t} \\ v_n(t) \approx v e^{-i\omega t} \end{cases}$$

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

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

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

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

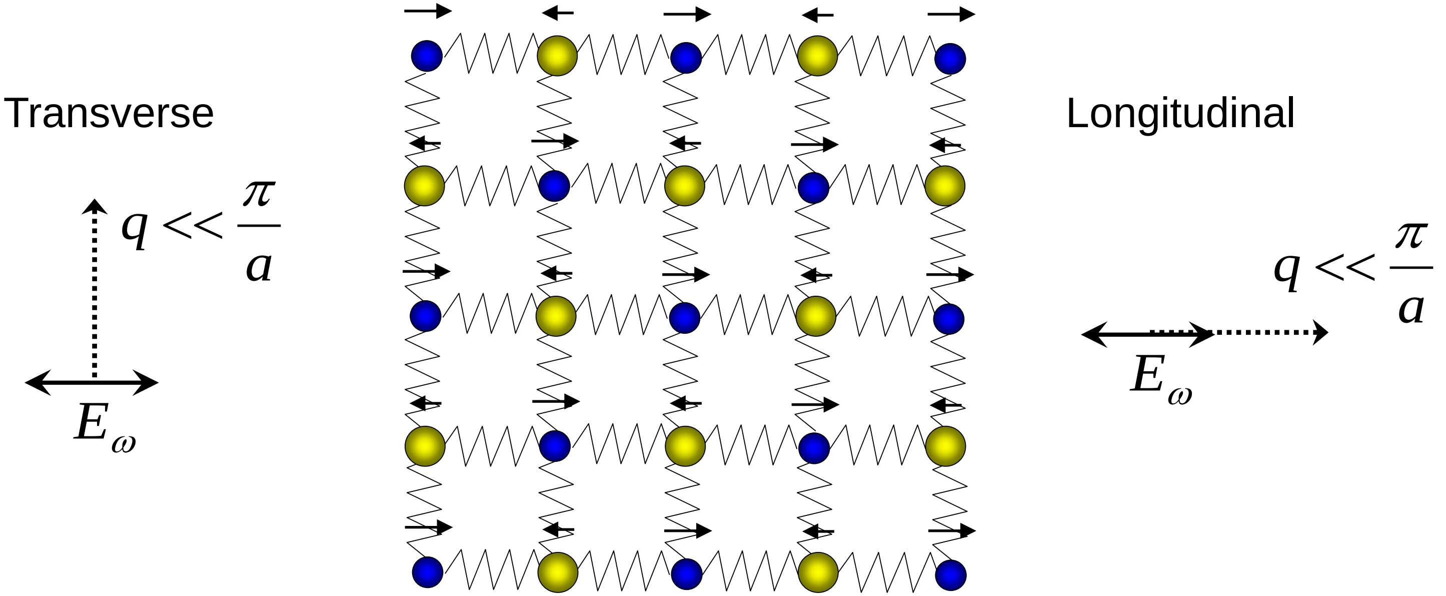
Longitudinal solution: $0=\mathbf{q}\times\mathbf{E}_{\mathbf{q},\omega}\Leftrightarrow\varepsilon(\omega)=0\Rightarrow\omega^2=\omega_{TO}^2+\frac{\Omega_{pl}^2}{\varepsilon_\infty}\equiv\omega_{LO}^2$

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

$$\varepsilon(\omega)=\varepsilon_\infty+\frac{\Omega_{pl}^2}{\omega_{TO}^2-\omega^2}=\varepsilon_\infty\frac{\omega_{TO}^2+\frac{\Omega_{pl}^2}{\varepsilon_\infty}-\omega^2}{\omega_{TO}^2-\omega^2},$$

$1\rightarrow\varepsilon_\infty$ to take into account the high frequency electronic excitations, $\gamma=0$

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

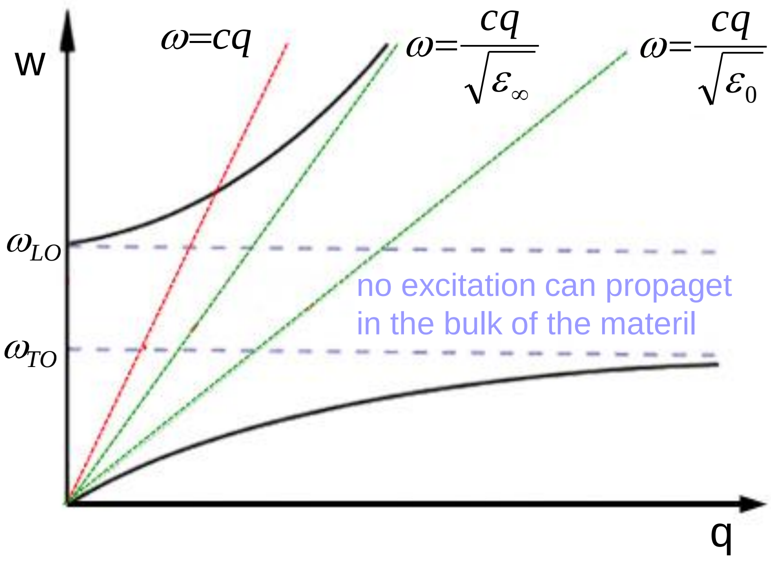


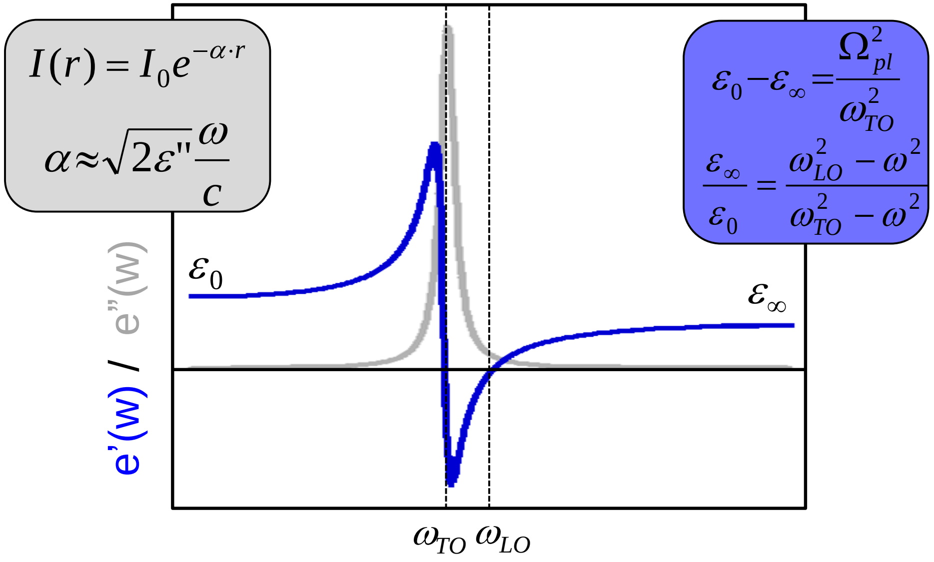
Vibrational spectroscopy

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

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





$$I(r)=I_0e^{-\alpha\cdot r}$$

$$\alpha\approx\sqrt{2\varepsilon''}\frac{\omega}{c}$$

$$\varepsilon_0-\varepsilon_\infty=\frac{\Omega_{pl}^2}{\omega_{TO}^2}$$

$$\frac{\varepsilon_\infty}{\varepsilon_0}=\frac{\omega_{LO}^2-\omega^2}{\omega_{TO}^2-\omega^2}$$

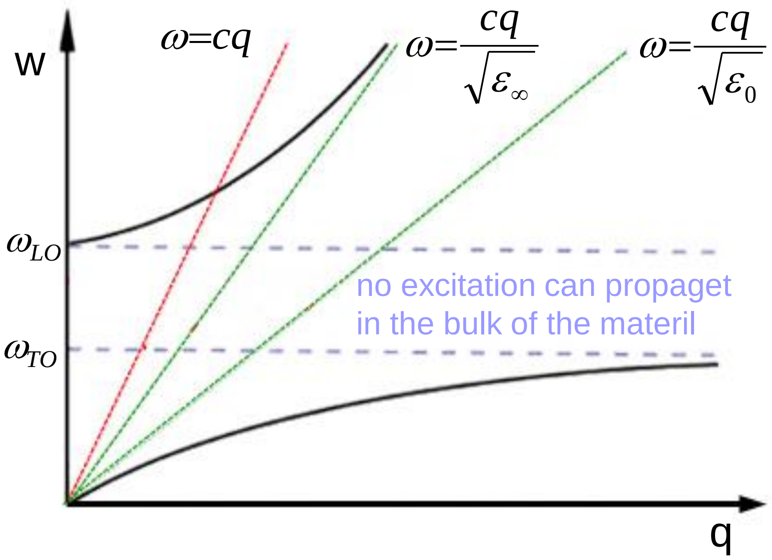
Vibrational spectroscopy

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

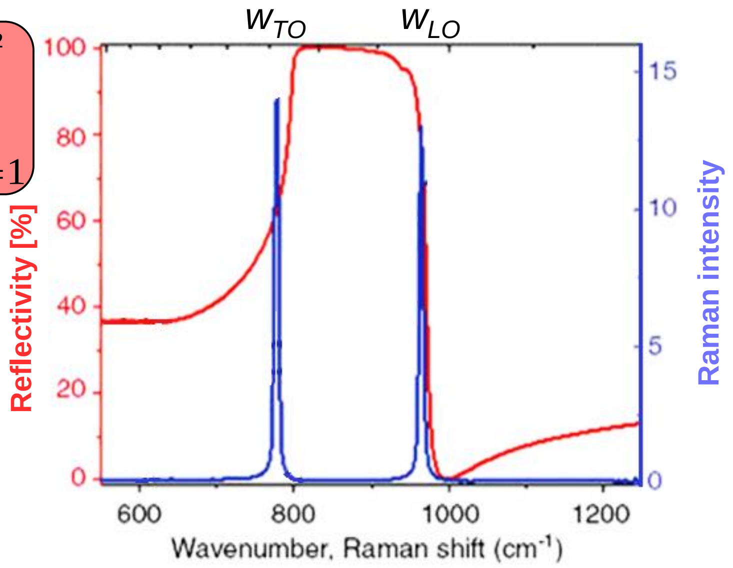
$$\omega_{TO}=\sqrt{2D\frac{m_u+m_v}{m_u m_v}}$$

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



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

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



Vibrational spectroscopy

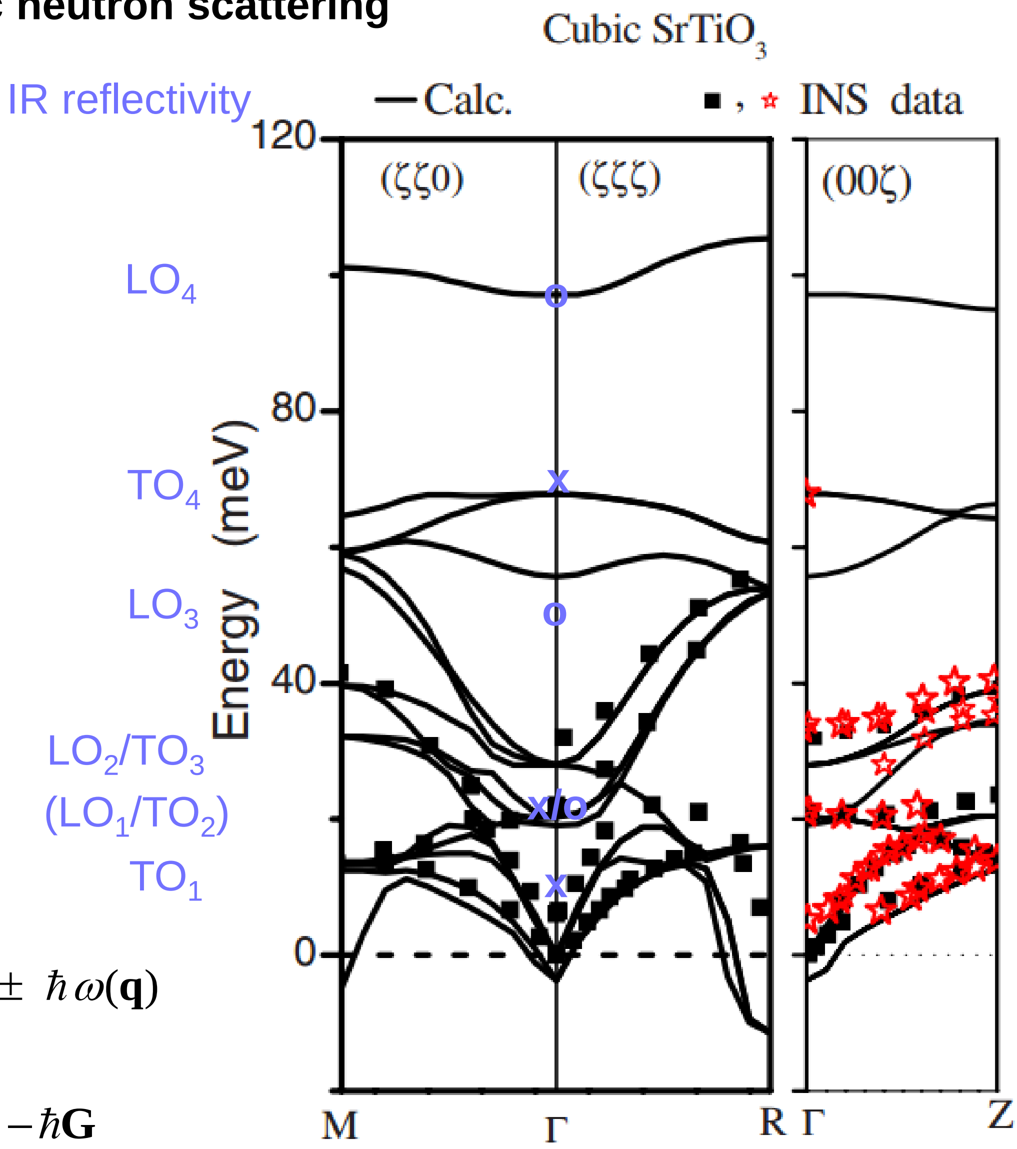
Phonon modes as determined by inelastic neutron scattering

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

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

3×N×M harmonic oscillator:

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



Conservation laws in case of neutron-cristal interaction

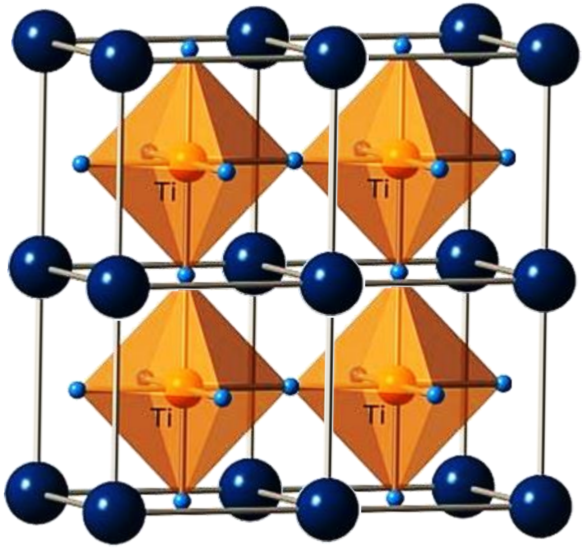
$$\begin{cases} \dfrac{p'^2}{2M_n} = \dfrac{p^2}{2M_n} \pm \hbar\omega(\mathbf{q}) \\ \hbar\mathbf{q} = \mp\,\mathbf{p}' - \mathbf{p} - \hbar\mathbf{G} \end{cases}$$

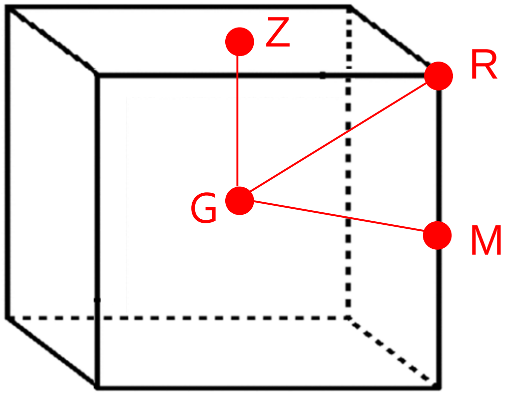
Choudhury et al., Phys. Rev. B **77**, 134111 (2008)

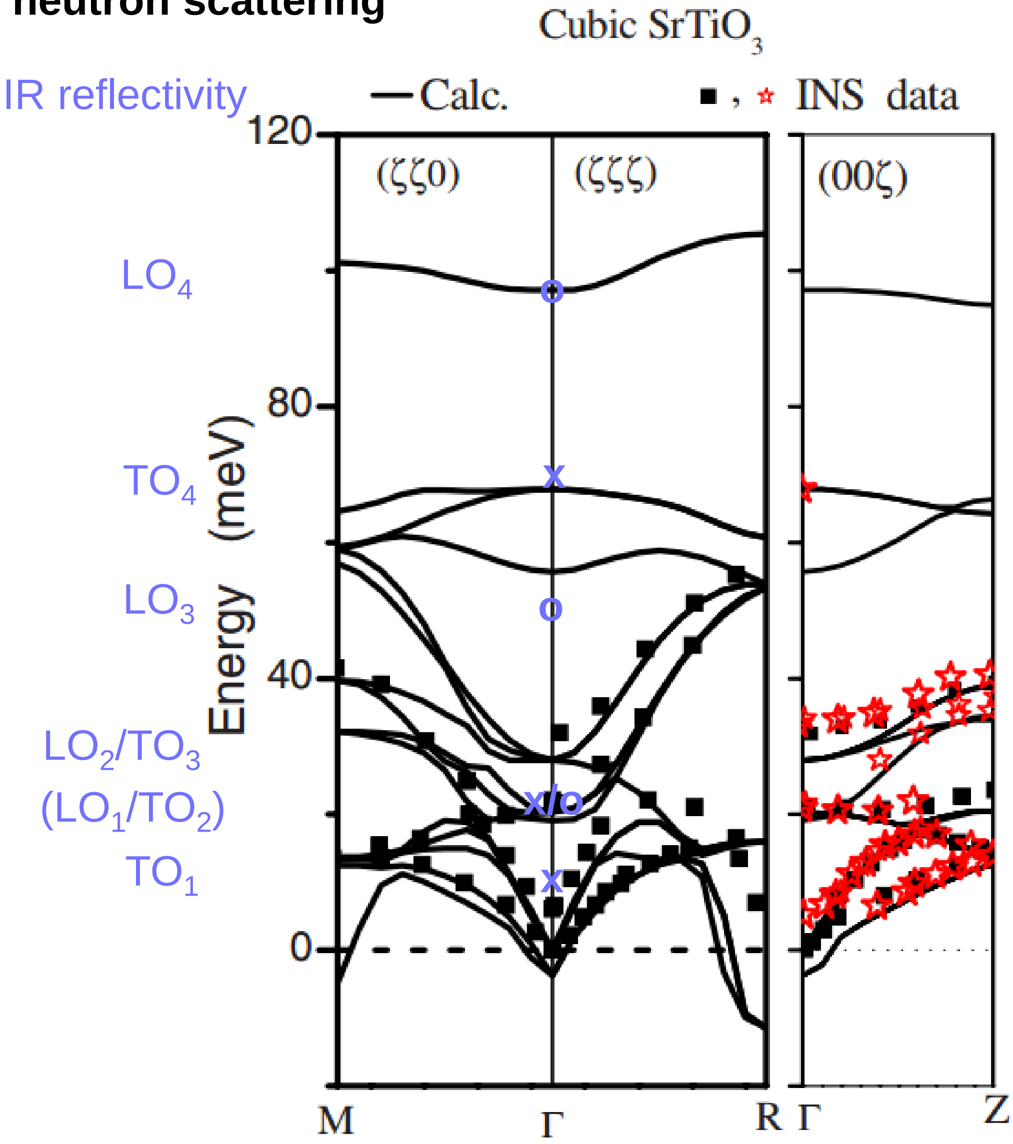
Vibrational spectroscopy

Phonon modes as determined by inelastic neutron scattering

$SrTiO_3$



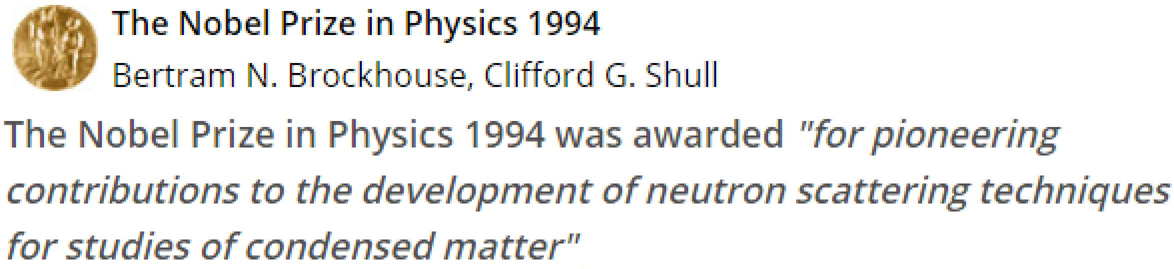




Choudhury et al., Phys. Rev. B **77**, 134111 (2008)

Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes



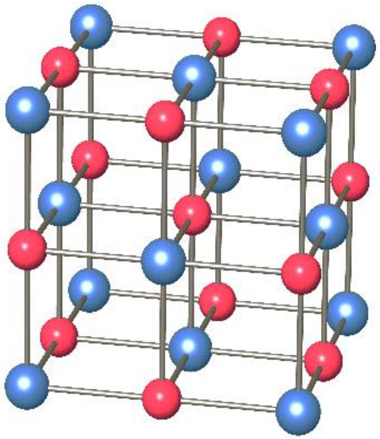
The Nobel Prize in Physics 1994

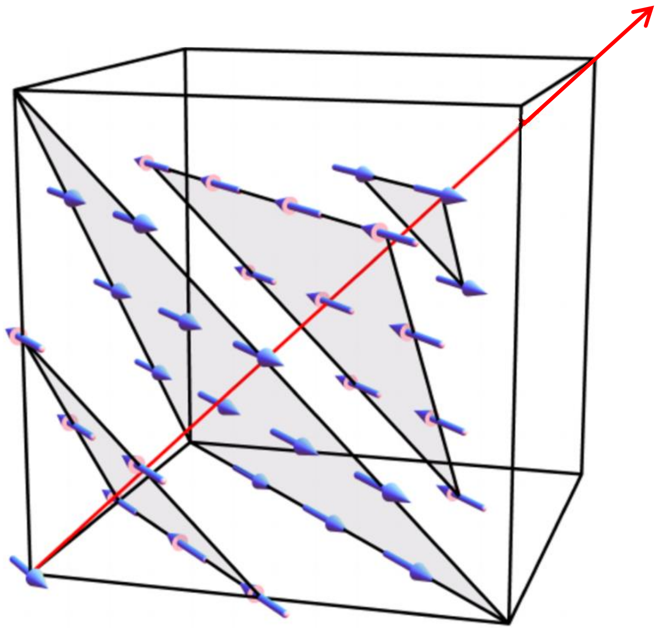
Bertram N. Brockhouse, Clifford G. Shull

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

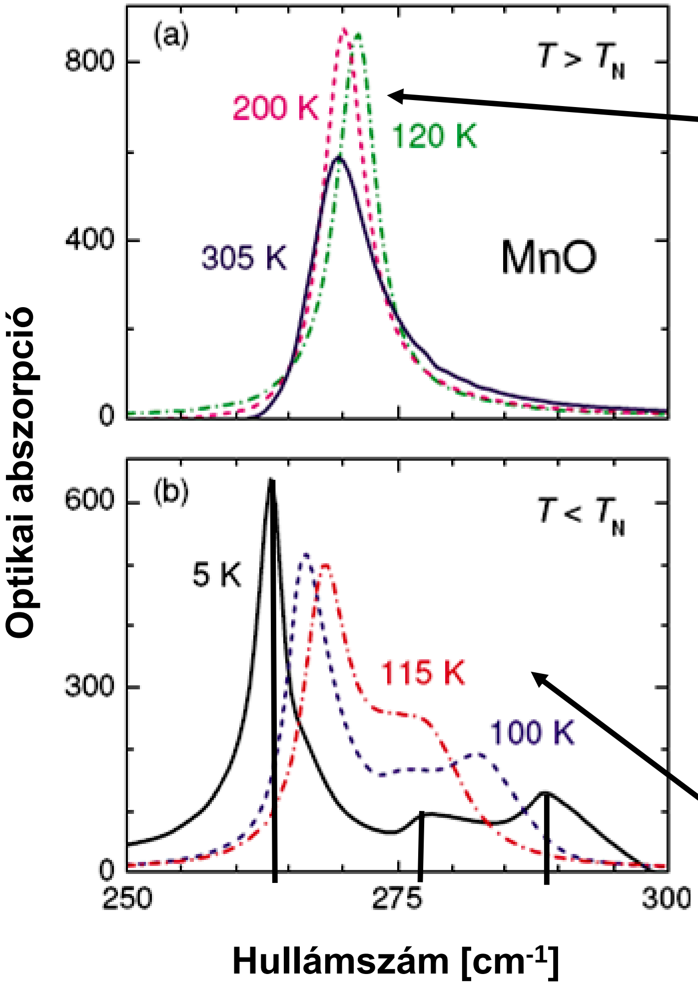




Vibrational spectroscopy

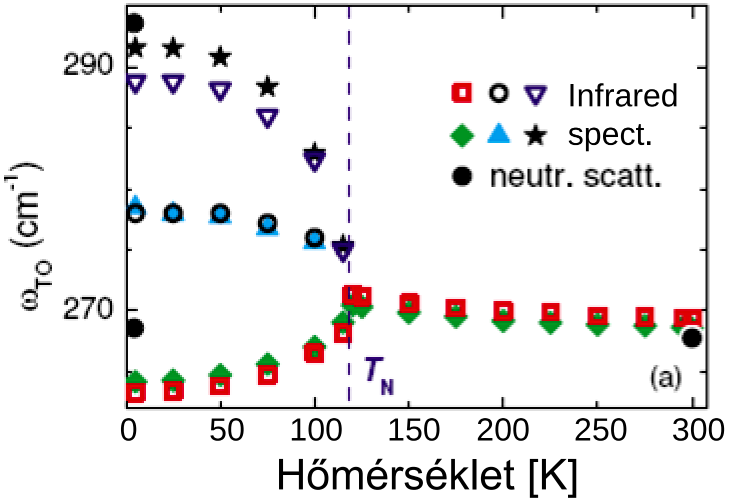
Symmetry lowering as seen by the vibrational modes

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



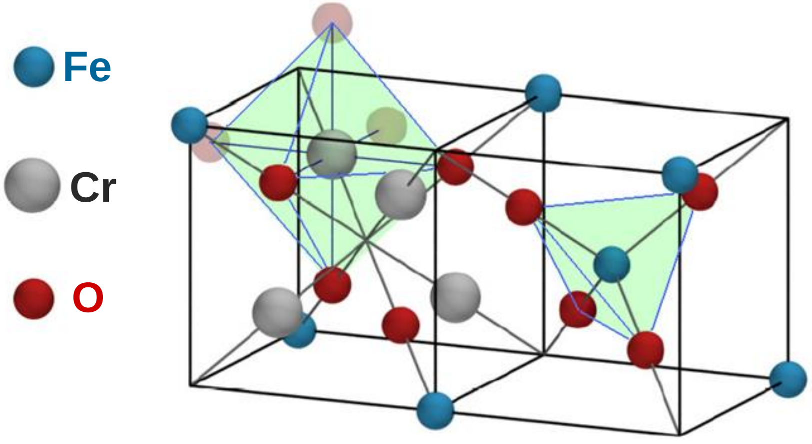
- 2 atoms in the unit cell: 3 acoustic + 3 optical branches
- $T>T_N$ 3× degeneracy, cubic phase
- $T<T_N$ no degeneracy, orthorhombic phase

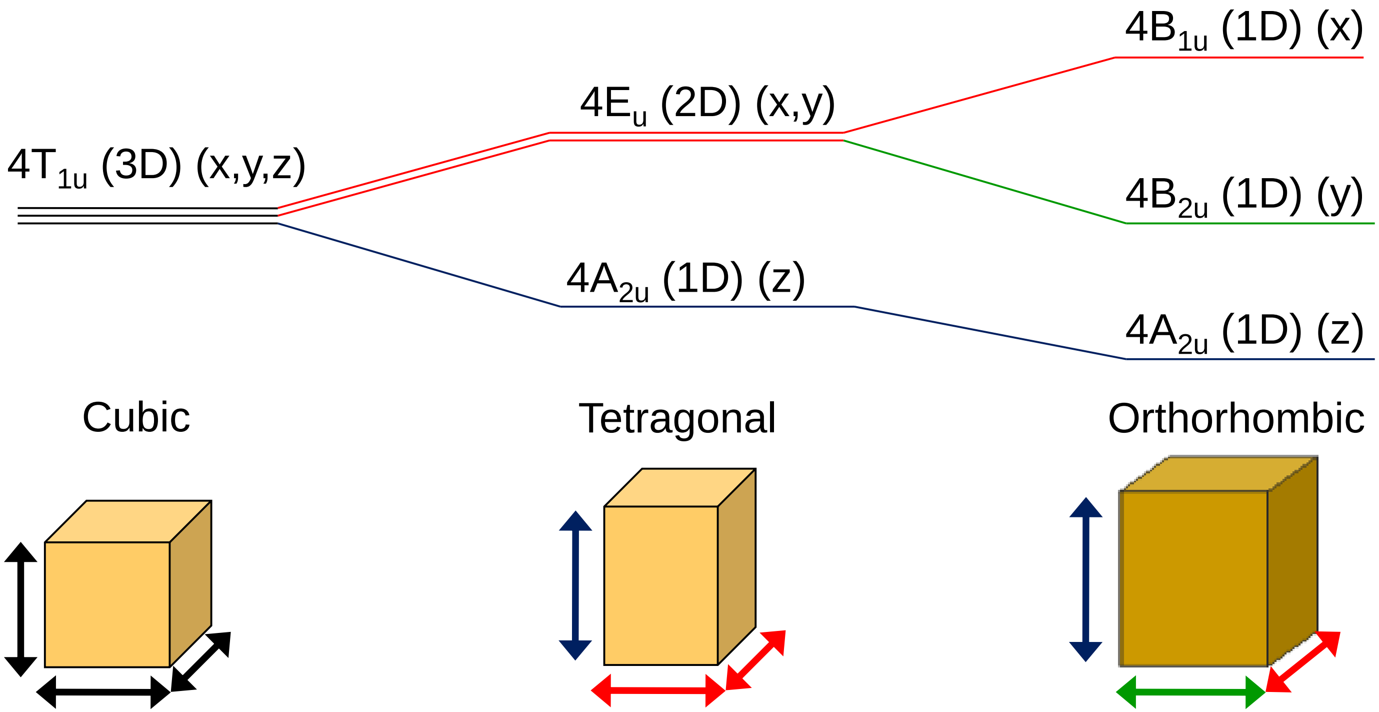
Physical Review B 77, 024421 (2008)

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



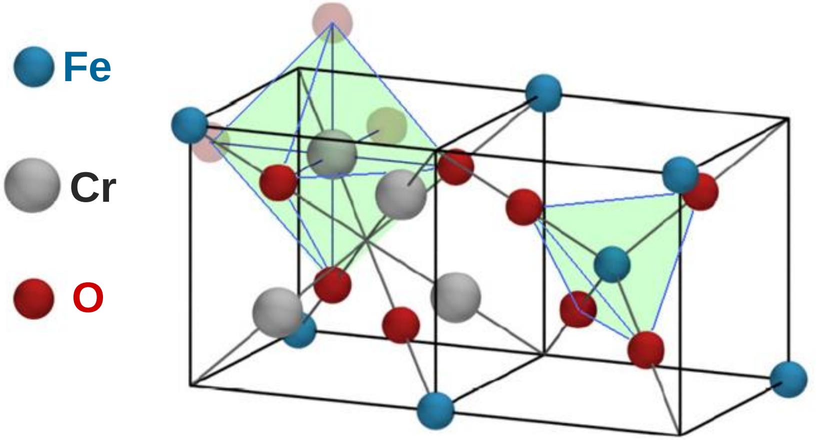


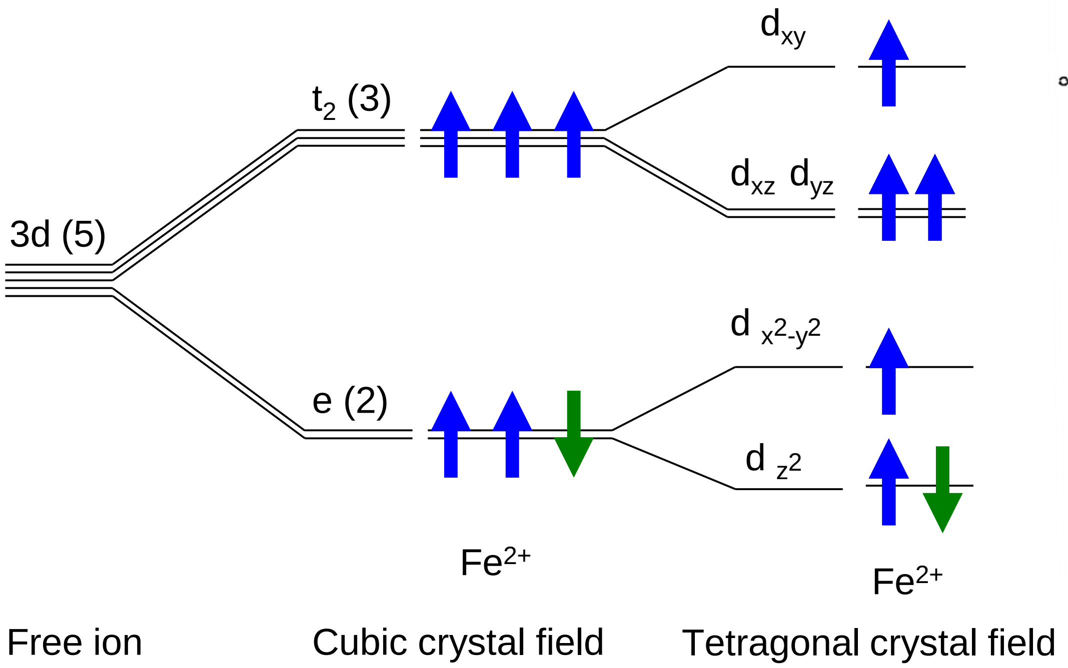
Vibrational spectroscopy

Symmetry lowering as seen by the vibrational modes

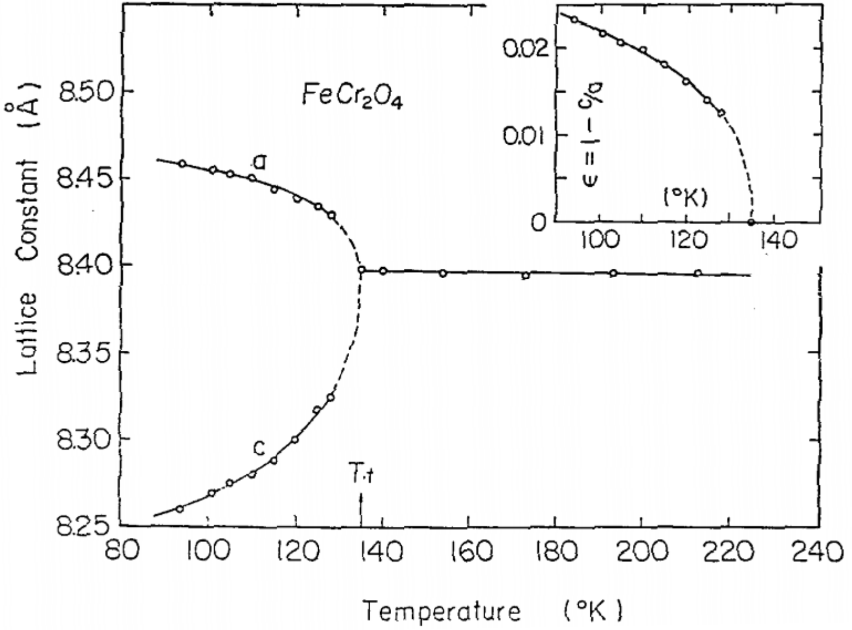
Fe^{2+} ions d shell is partially filled:

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





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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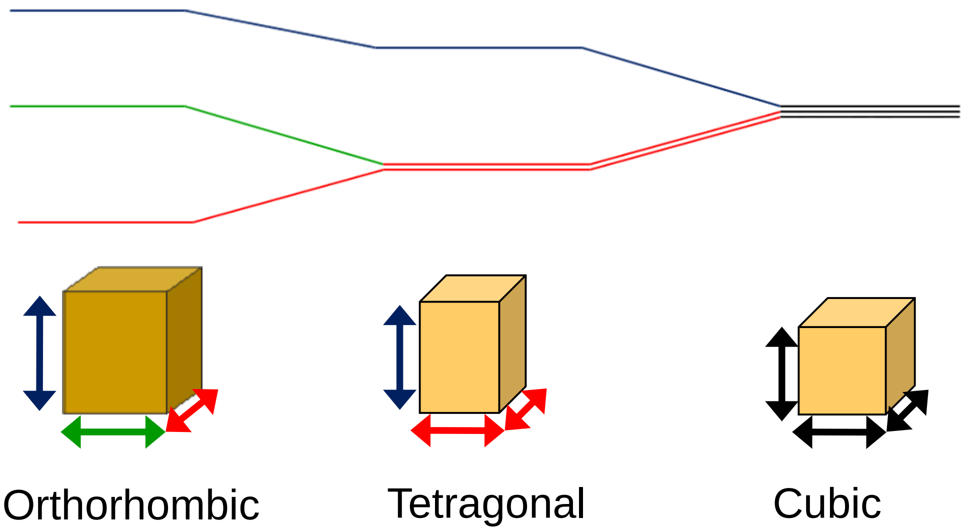
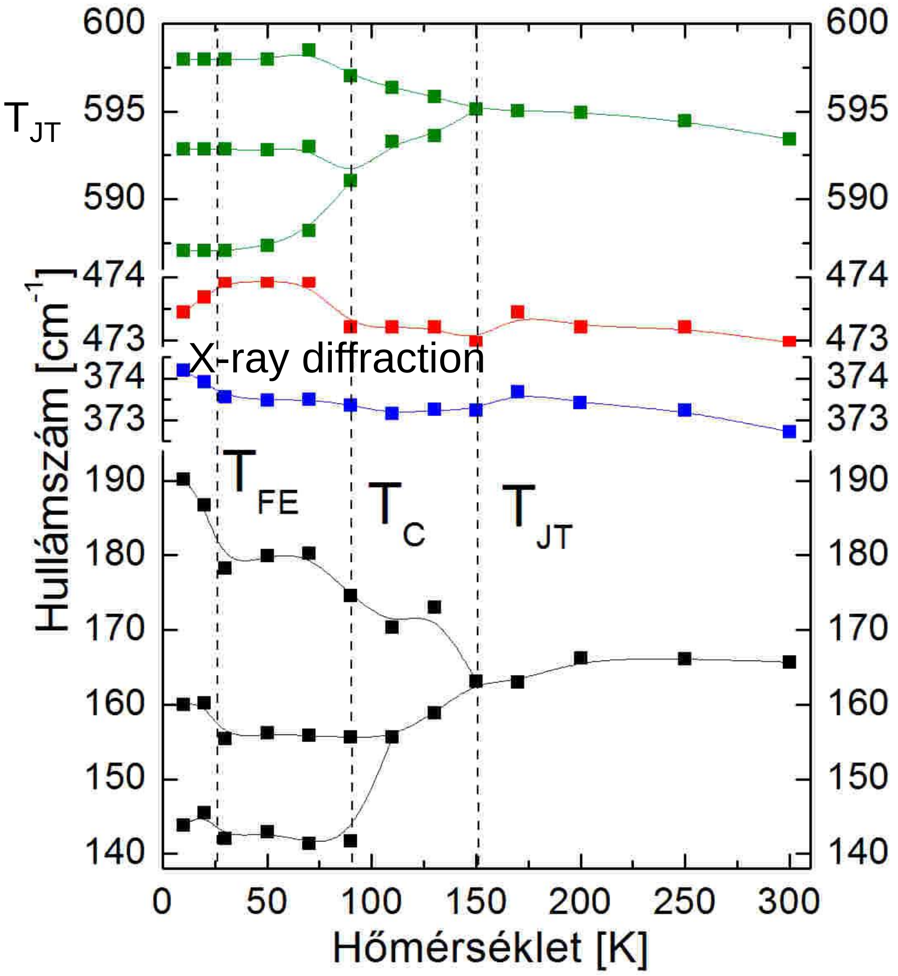
- Magnetic ordering, T_C

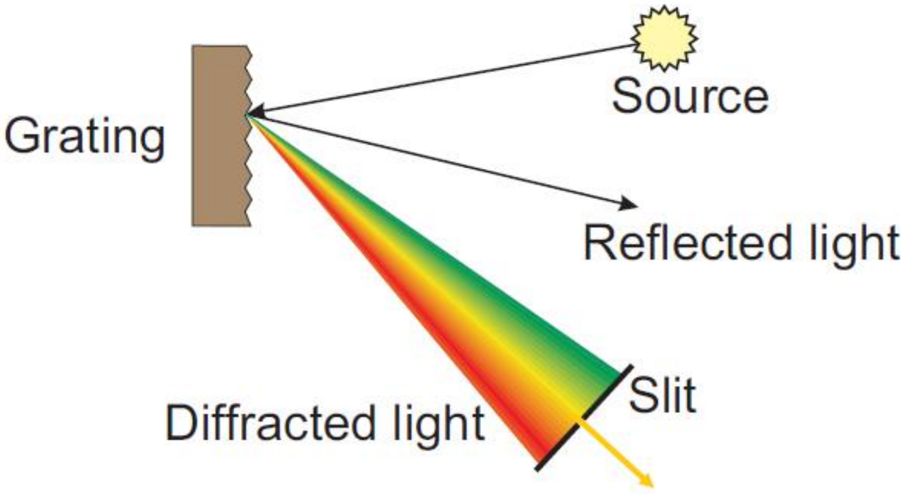




Bordács et al., Phys. Rev. Lett. **103**, 077205 (2009)

Vibrational spectroscopy

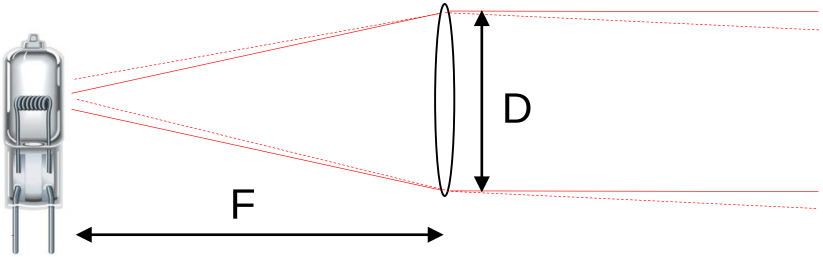
Grating spectrometer



Radiant flux: $\Phi = \iint_A \mathbf{S}\, d\mathbf{A}$

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

Brightness is conserved in an ideal loss-less optical system



$$B = \frac{\Phi}{A * \frac{\pi}{4}\frac{D^2}{F^2}} \quad = \quad B' = \frac{\Phi}{\pi\left(\frac{D}{2}\right)^2 * \frac{A}{F^2}}$$

✓

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] $\dfrac{\delta\lambda}{\delta L}$

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

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

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

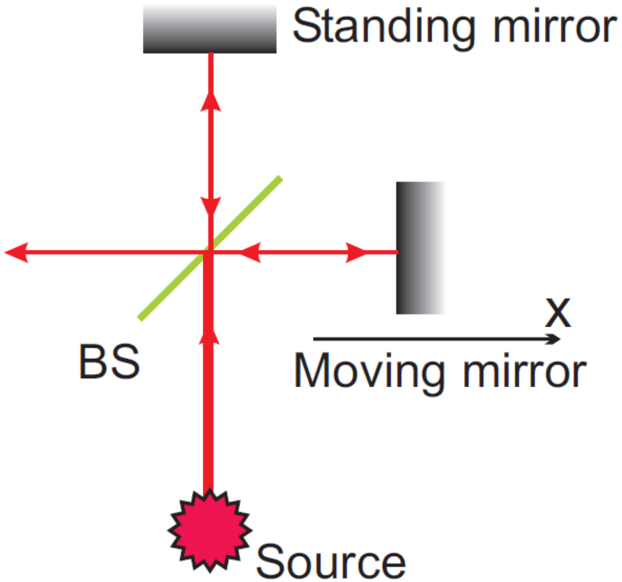
Vibrational spectroscopy

Fourier transform infrared (FT-IR) spectrometer

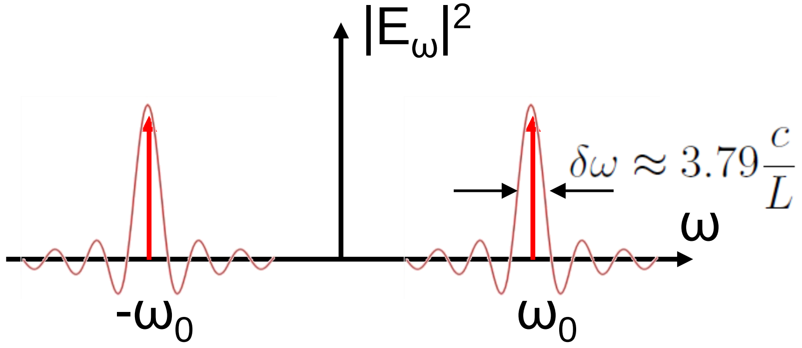
$$E_D = \int (\frac{E_\omega}{2} + \frac{E_\omega}{2} e^{i\frac{\omega}{c}2x}) e^{-i\omega t} \frac{d\omega}{2\pi}$$

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

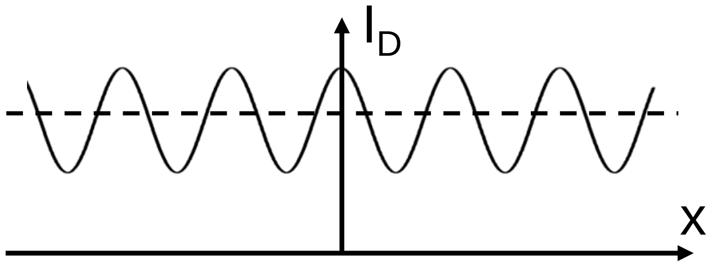
$$I_D(x) \simeq \frac{1}{2}\sqrt{\frac{\varepsilon_o}{\mu_o}} \frac{1}{2} \int |E_\omega|^2 \cos(\frac{\omega}{c}2x) \frac{d\omega}{2\pi}$$



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



$$\delta\omega \approx 3.79 \frac{c}{L}$$



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

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

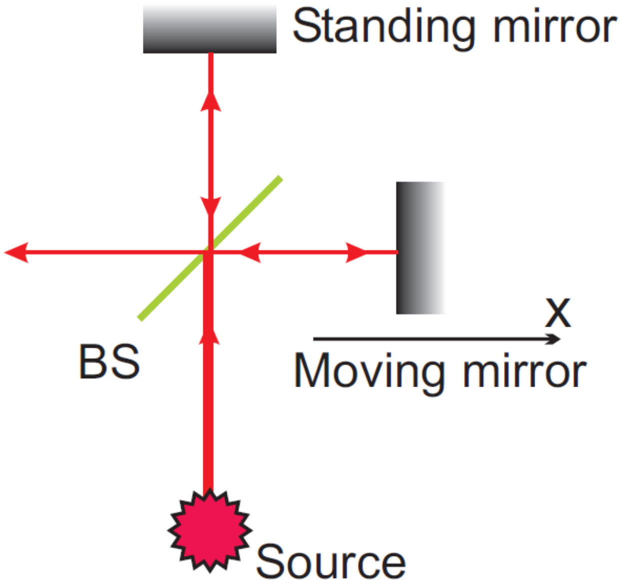
Vibrational spectroscopy

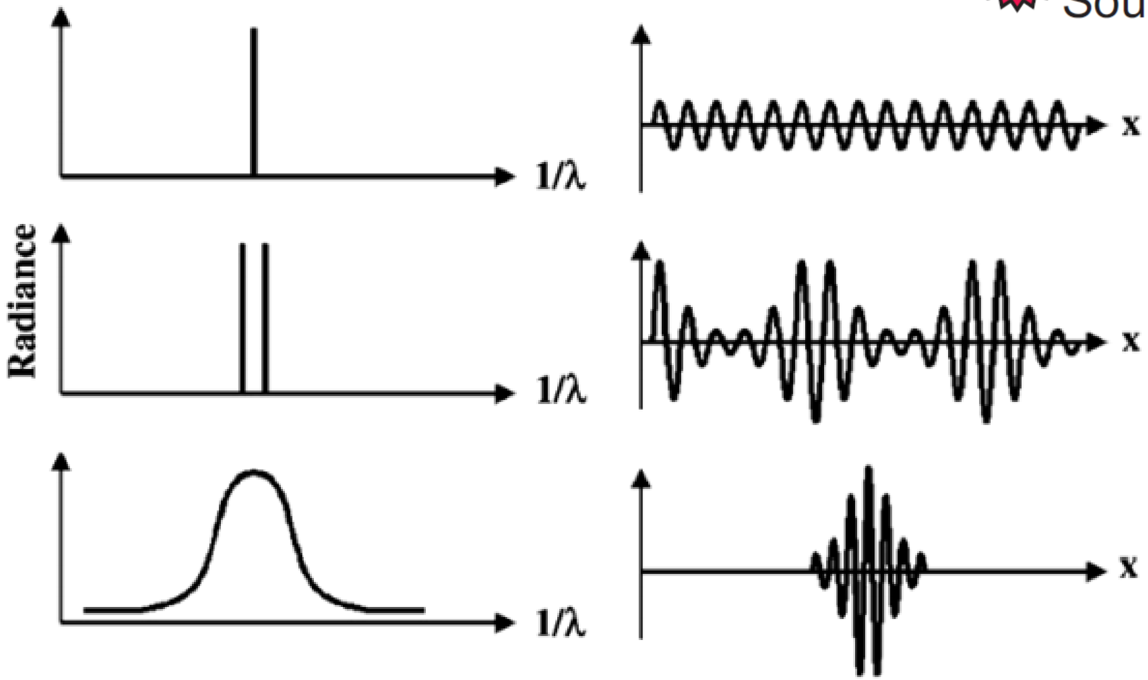
Fourier transform infrared (FT-IR) spectrometer

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

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

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

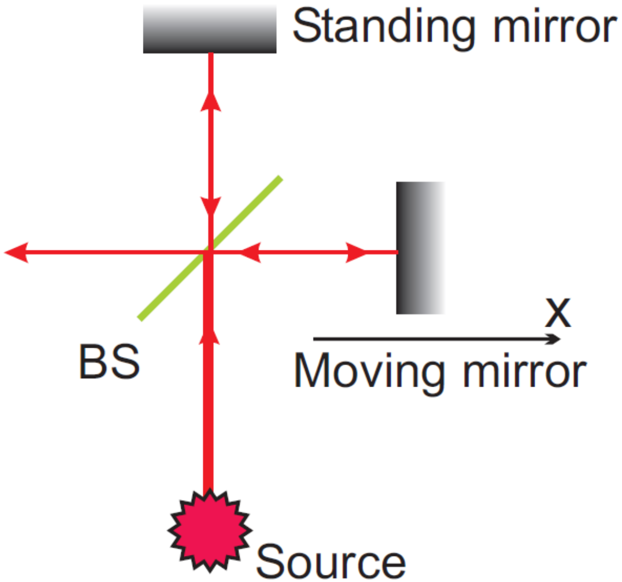




K-P. Mollmann and M. Vollmer Eur. J. Phys. 34 S123 (2013).

Vibrational spectroscopy

Fourier transform infrared (FT-IR) spectrometer



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

multiplex advantage

throughput advantage

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

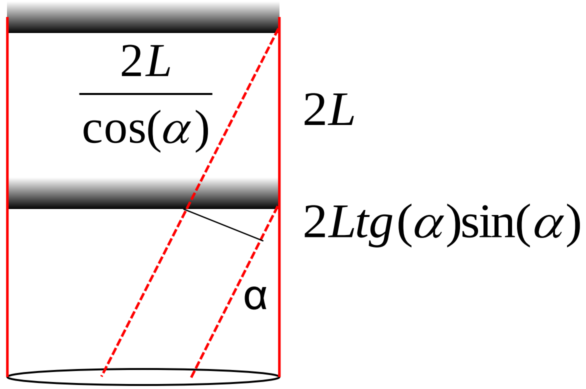
path difference = [deflected beam] - centered beam
when ξ~λ cancellation on the detector,
no point to further move the mirror

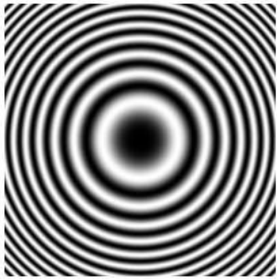
$$\lambda \approx L\alpha^2$$

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

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

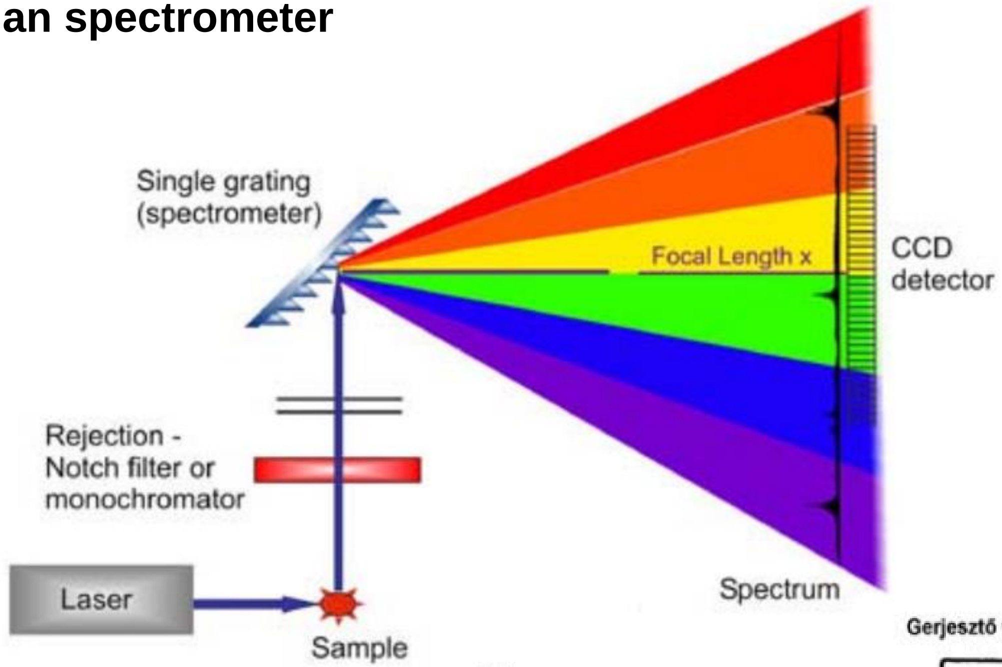
$$\frac{E_{FT}}{E_G} \propto \frac{F}{H} >> 1$$

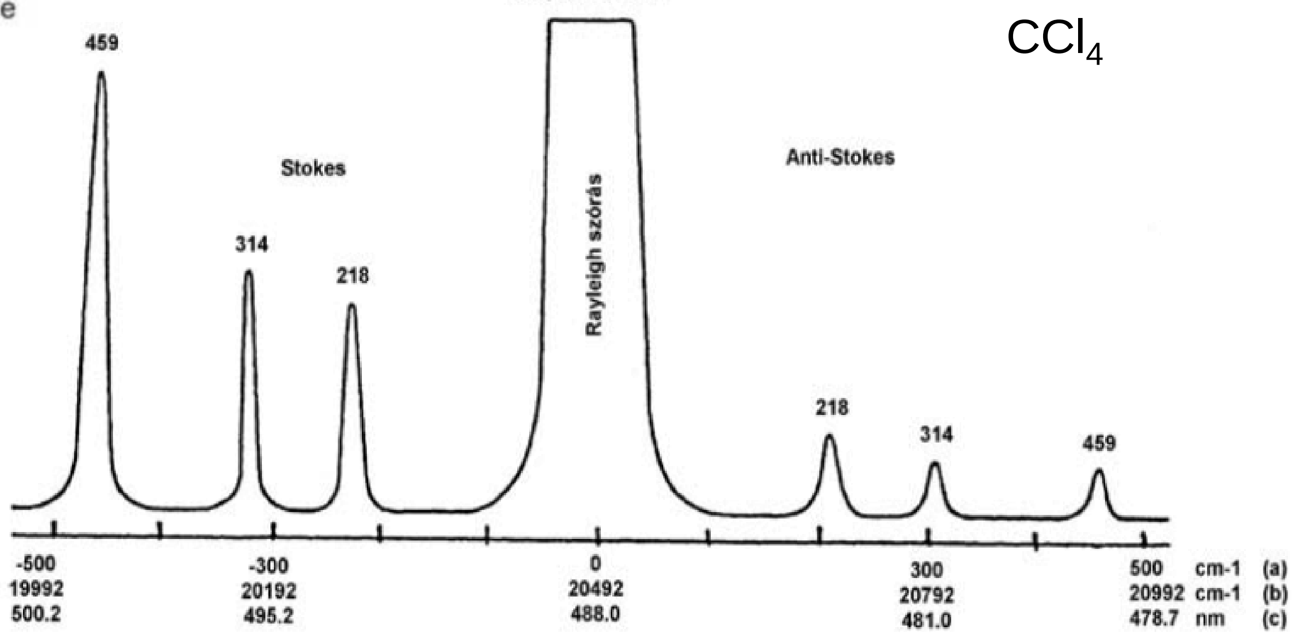




Vibrational spectroscopy

Raman spectrometer

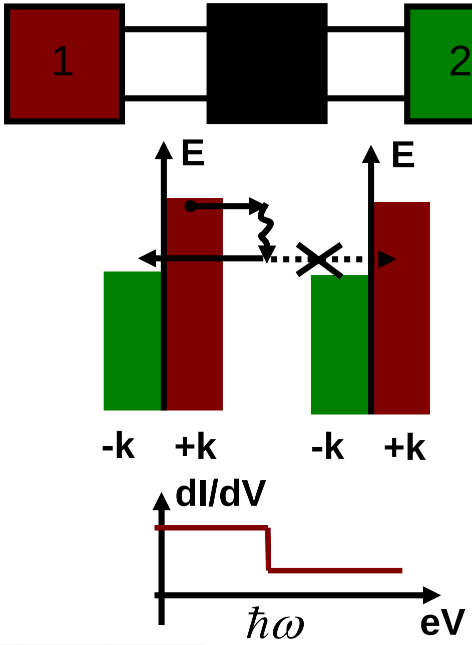


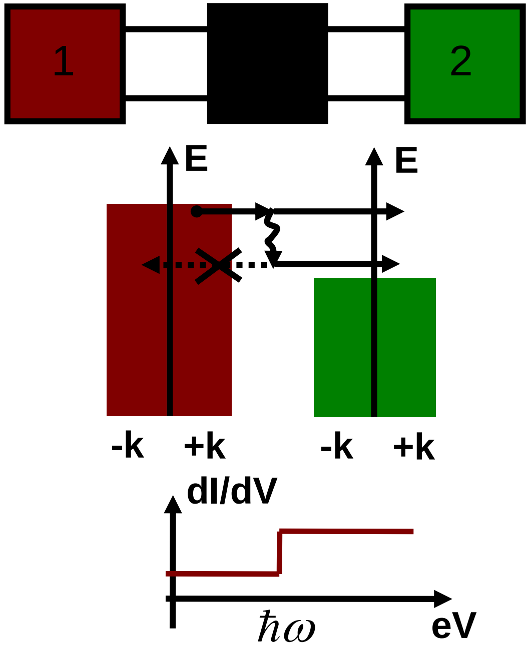


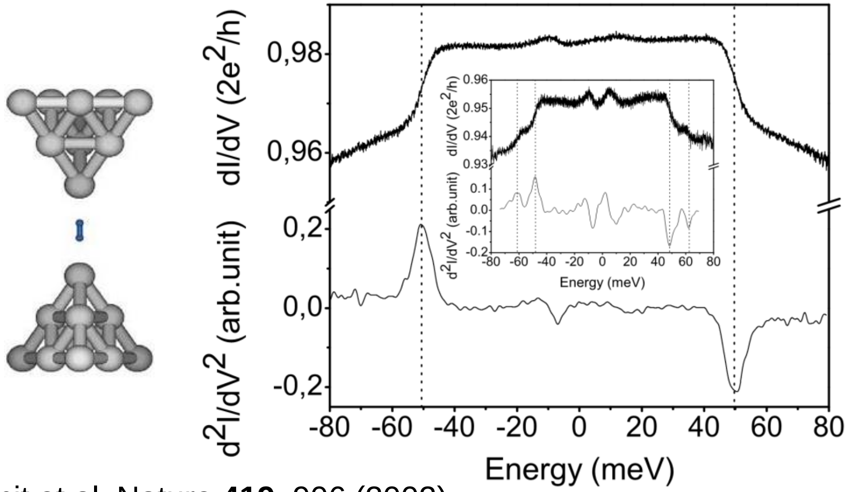
CCl_4

Vibrational spectroscopy

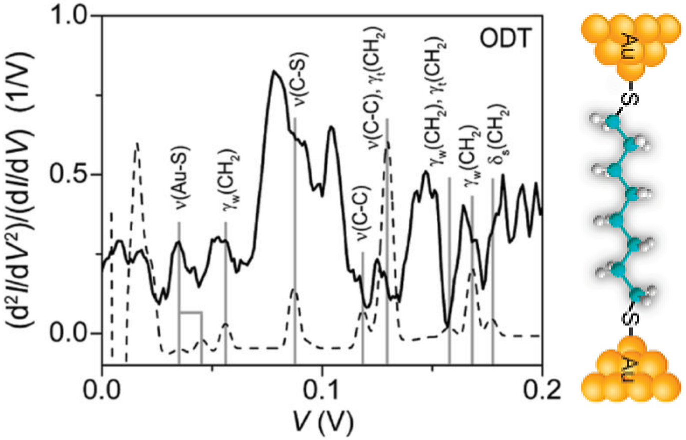
Molecular vibrations as seen by tunneling spectroscopy







Smit et al. Nature **419**, 906 (2002)

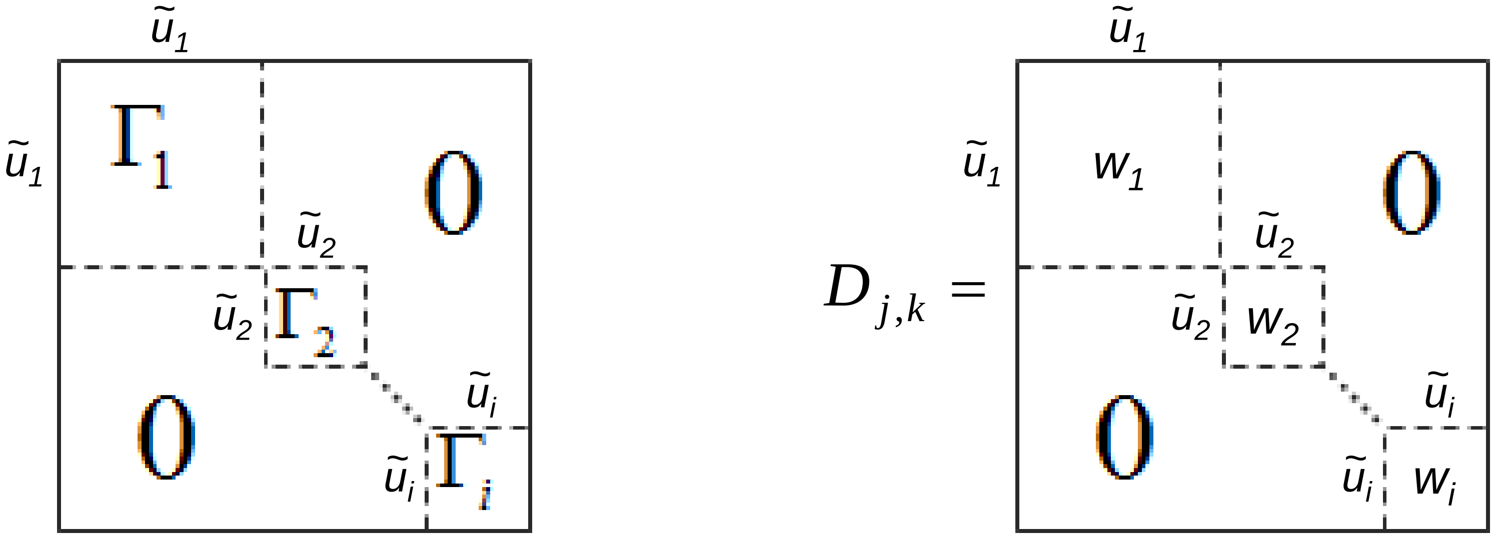


Kim et al. ACS Nano **5**, 4104 (2011)

Rezgési spektroszkópia

Szimmetriák szerepe a rezgési módusok meghatározásában

Szimmetria kvantumos megfogalmazásban: $\left[\hat{H}, g\right] = 0 \quad \forall g \in G$ Þ $\hat{H}, g$ közös sajátállapotok

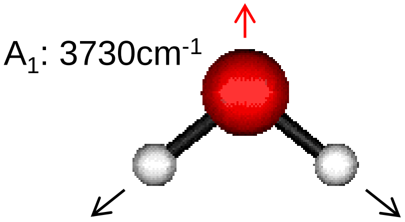


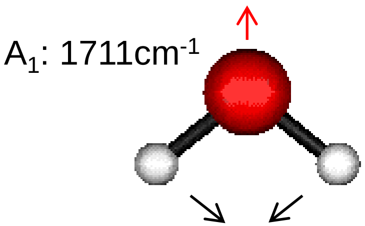
G_j-k a szimmetriacsoport invariáns alterei, $\hat{H}$-nak ezen altereken belül a sajátértékei megegyeznek

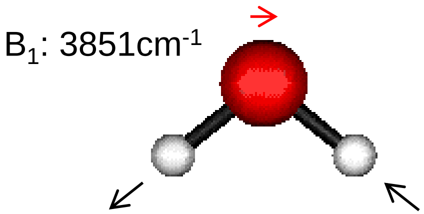
- A molekula szimmetriáinak ismeretében megadható, hogy hány darab, hányszorosan degenerált rezgési módus van, $D_{j,k}$ pontos alakjának ismerete nélkül!!!
- Megadható, hogy mely módusok infravörös ill. Raman aktvak ill. melyek csendes módusok

Rezgési spektroszkópia

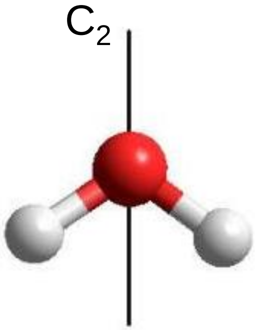
Vízmolekula: (N-2)×3=3 vibrációs módus

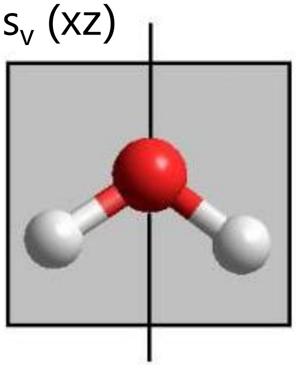


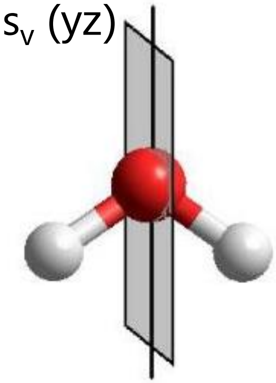




- Molekula pontcsoportja: a molekula összes szimmetriája az alapállapotában,
- Pontcsoport generátorai: a minimális számú szimmetria, melynek szorzataként a többi előáll,







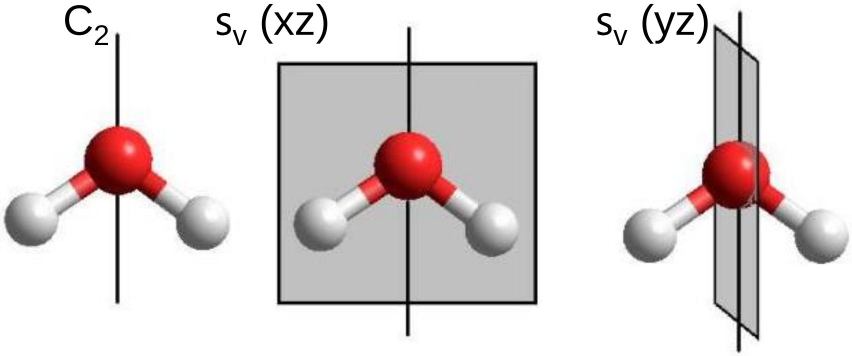
- Pontcsoport karaktertáblája:

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

a csoport invariáns alterei (polár- és axiálvektor)

Rezgési spektroszkópia

Recept módusszám és -karakter meghatározására



	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
H_2O	9	-1	3	1		

IR

rotációs

Raman

$$E=\begin{array}{c}\begin{matrix}\text{O}&\text{H1}&\text{H2}\end{matrix}\\\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\end{array}\otimes\begin{array}{c}\begin{matrix}x&y&z\end{matrix}\\\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\end{array}$$

$$C_2=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}\otimes\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$$

$$\sigma_v(xz)=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\otimes\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}$$

$$\sigma_v(yz)=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}\otimes\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

$\Gamma_{H_2O}=\bigoplus_i c_i\Gamma_i$, ahol $c_i=\frac{1}{h}\sum_{g\in G}\chi_{H_2O}(g)\chi_i^*(g)$ Þ

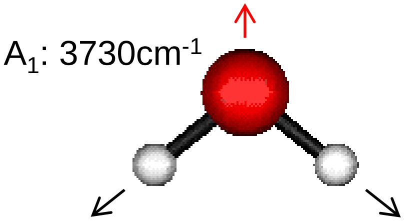
Összes módus: $\Gamma_{H_2O}=3A_1+A_2+3B_1+2B_2$

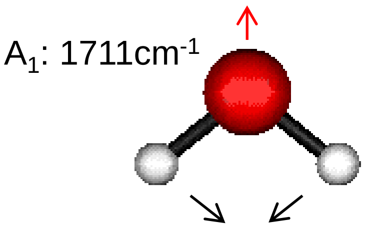
Rezgési módusok: $\Gamma^{vibr}_{H_2O}=\Gamma_{H_2O}-3\times transz-3\times rot=\boxed{2A_1+B_1}$

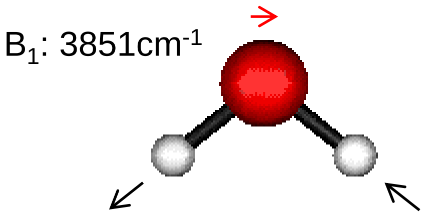
IR és Raman aktív

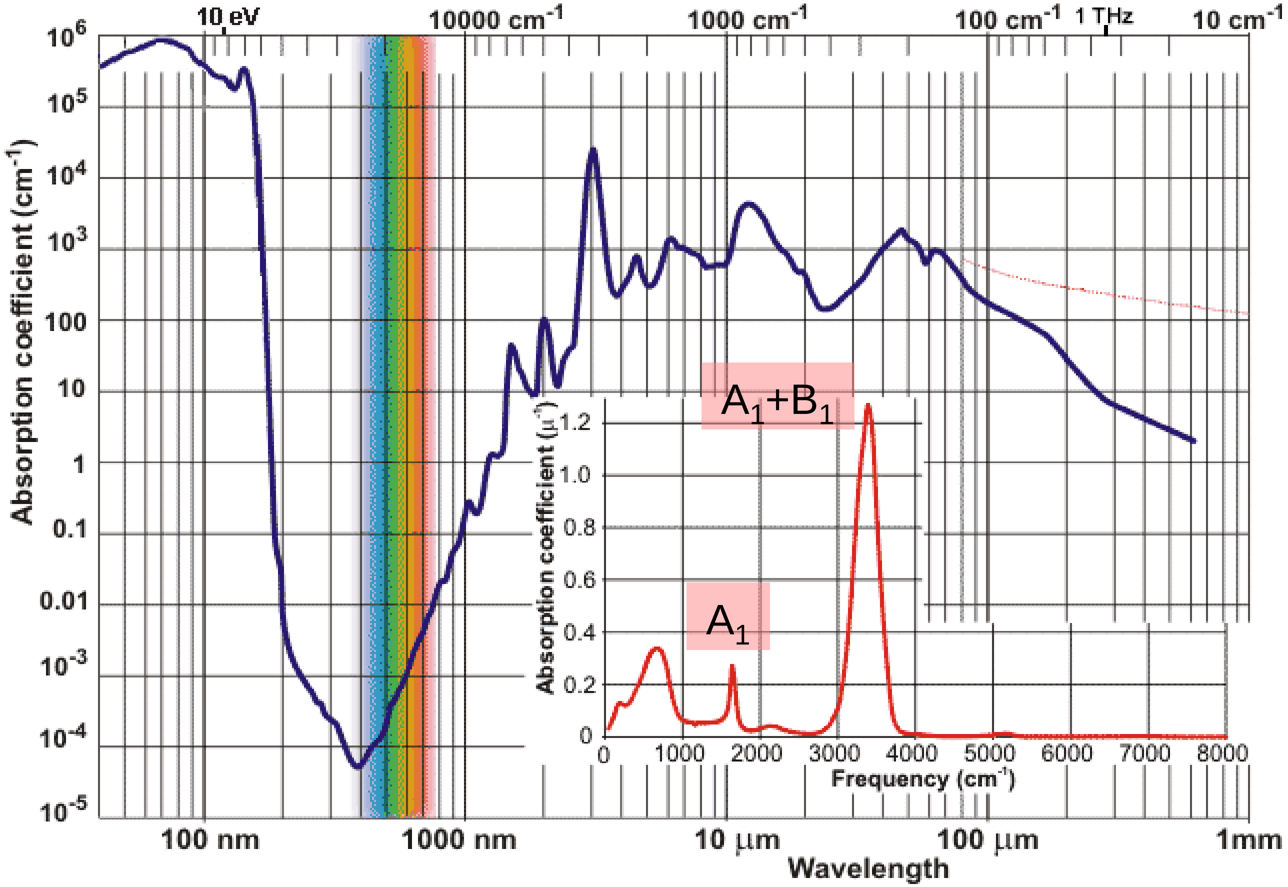
Rezgési spektroszkópia

http://www.chemtube3d.com/vibrationsH2O.htm









- Alacsony frekvenciákon rotációs módusok
- Környezet hatása, H-H kötések, ...
- Látható–közeli-infravörös ablak: szövetek átlátszósága
- Ultraibolya tartomány: elektronikus gerjesztések

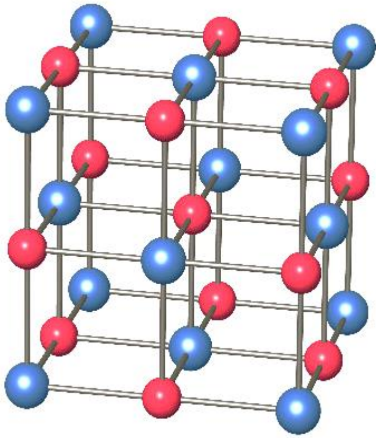
Rezgési spektroszkópia

Szimmetriaváltozás megnyilvánulása rezgési módusokban

MnO

- FCC rács 2 atomos bázissal, NaCl struktúra
- Antiferromágneses rendeződés T_N=118K-en (Nobel-díj, neutron szórás)
- Kristályrács szimmetriája köbösről trigonálisra csökken a mágneses rendeződés miatt

$Fm\bar{3}m$ Þ https://en.wikipedia.org/wiki/Space_group Þ $\bar{m}3m$ v. O_h



Character table for O_h point group

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 =(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		
MnO	6	-2	-2	2	-2	-6	-2	2	2	2		

Összes módus: $\Gamma_{MnO} = 2T_{1u}$

Vibrációs módus: $\Gamma_{MnO}^{vibr} = T_{1u}$

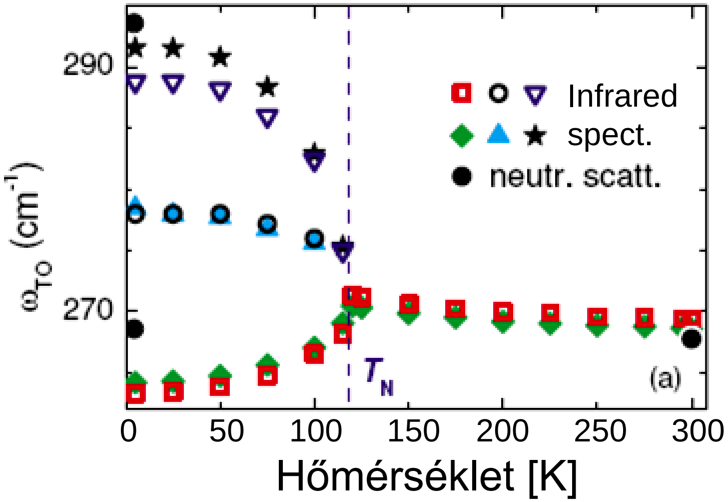
Rezgési spektroszkópia

Szimmetriaváltozás megnyilvánulása rezgési módusokban

MnO szimmetriája ~~trigonálisra~~ trigonálisnál alacsonyabbra csökken a mágneses rend miatt!!!

Character table for D_{3d} point group

	E	$2C_3$	$3C'_2$	i	$2S_6$	$3\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	-1	1	1	-1	R_z	
E_g	2	-1	0	2	-1	0	(R_x, R_y)	(x^2-y^2, xy) (xz, yz)
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	z	
E_u	2	-1	0	-2	1	0	(x, y)	
T_{1u}	3	0	-1	-3	0	1		



Vibrációs módus: $\Gamma^{vibr}_{MnO} = A_{2u} + E_u$

Subgroups of D_{3d} point group: C_s, C_i, C_2, C_3, D_3, C_{3v}, S_6

Character table for C_i point group

	E	i	linear, rotations	quadratic
A_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, xz, yz$
A_u	1	-1	x, y, z	

Character table for C_s point group

	E	σ_h	linear, rotations	quadratic
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

Character table for C_2 point group

	E	C_2	linear, rotations	quadratic
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	-1	x, y, R_x, R_y	yz, xz