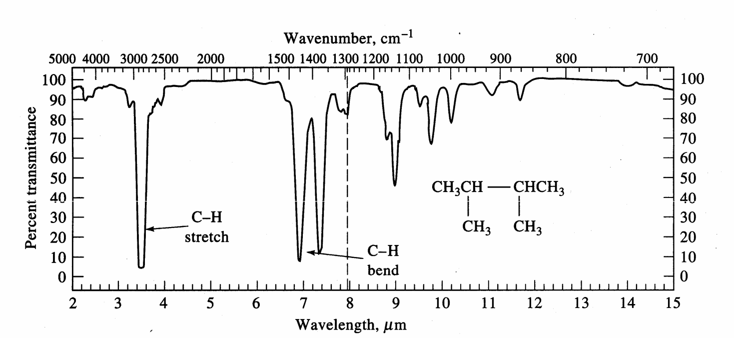
Infrared Spectroscopy

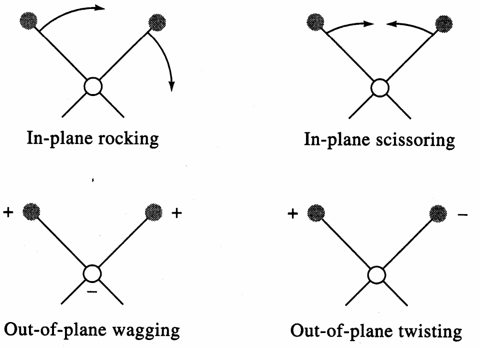


IR-spectrum of a typical organic compound

Characteristics:

- Transmittance rather than absorbance is measured
- The abscissa scale is not linear to wavenumber
- Infrared spectra are a result of the absorption of radiation which activates vibrations in molecules

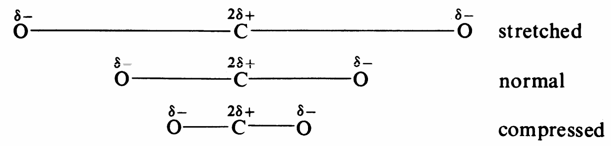
(a) Stretching vibrations

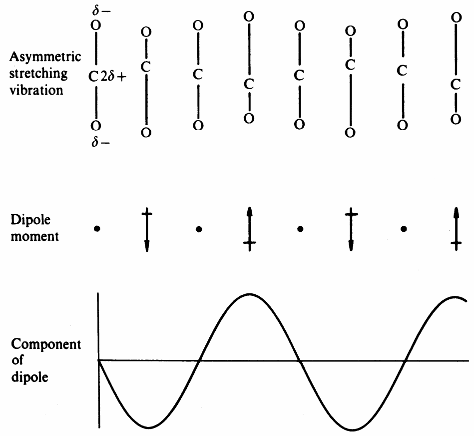


(b) Bending vibrations

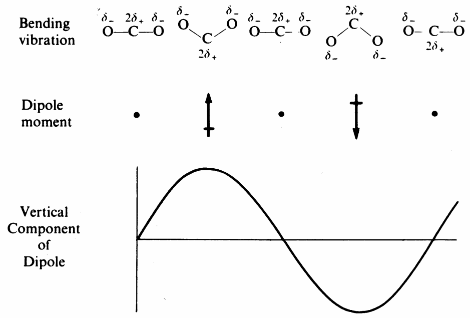
Types of molecular vibrations

- Vibrations of molecules can only be excited by radiation if the electric dipole moment changes during vibration (selection rule; *c.f.* Raman spectroscopy)



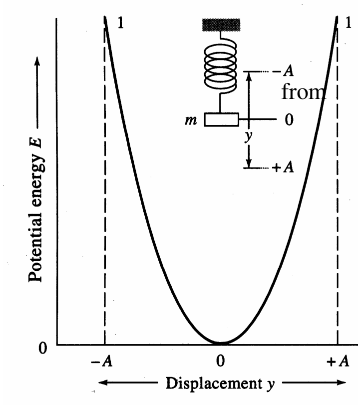


Mechanical model of a stretching vibration in CO$_2$



Mechanical model of a bending vibration in CO$_2$

Classical treatment (harmonic oscillator)



from $F = -k \cdot y$ and $dE = -F \cdot dy$

k: proportionality constant, force constant for the chemical bond (measure for its stiffness)
y: displacement

vibrational frequency: $\upsilon_m = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$

or for two masses connected with a spring

$$\upsilon_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

with the reduced mass $\mu : \mu = \dfrac{m_1 \cdot m_2}{m_1 + m_2}$

Example:

Calculate the approximate wavenumber of the fundamental absorption peak due to the stretching vibration of a carbonyl group.

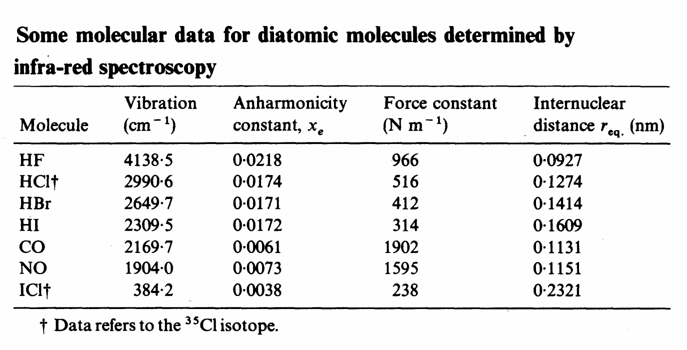
$$m_1(C) = \frac{12 \cdot 10^{-3}\,kg/mol}{6.0 \cdot 10^{23}\,atoms/mol} \cdot 1atom = 2.0 \cdot 10^{-26}\,kg$$

$$m_2(O) = 27 \cdot 10^{-26}\,kg$$

$$\Rightarrow \mu = \frac{2.0 \cdot 10^{-26}\,kg \cdot 2.7 \cdot 10^{-26}\,kg}{(2.0 + 2.7) \cdot 10^{-26}\,kg} = 1.1 \cdot 10^{-26}\,kg$$

$$\upsilon = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{\mu}} \qquad \Rightarrow \bar{\upsilon} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 5.3 \cdot 10^{-12} \cdot \sqrt{\frac{k}{\mu}}$$

$$= 5.3 \cdot 10^{-12}\,s/cm \cdot \sqrt{\frac{10^3\,N/m}{1.1 \cdot 10^{-26}\,kg}} = 1.6 \cdot 10^3\,cm^{-1}$$



Some molecular data for diatomic molecules determined by infra-red spectroscopy

Molecule	Vibration (cm^{-1})	Anharmonicity constant, x_e	Force constant ($N\,m^{-1}$)	Internuclear distance $r_{eq.}$ (nm)
HF	4138·5	0·0218	966	0·0927
HCl†	2990·6	0·0174	516	0·1274
HBr	2649·7	0·0171	412	0·1414
HI	2309·5	0·0172	314	0·1609
CO	2169·7	0·0061	1902	0·1131
NO	1904·0	0·0073	1595	0·1151
ICl†	384·2	0·0038	238	0·2321

† Data refers to the ^{35}Cl isotope.

Number of fundamental vibrations in polyatomic molecules

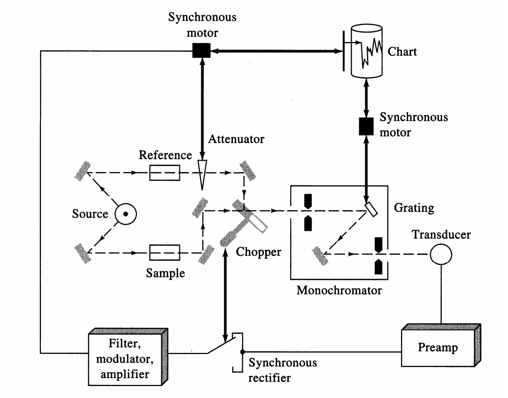
Non-linear molecules: **3 *N* – 6**

Linear molecules: **3 *N* - 5**

N: number of atoms

Instruments for IR-spectroscopy

Dispersive instruments (similar to UV-vis instruments, cell between source and monochromator)



FT-IR-instruments (high sensitivity, fast)

Filter photometers (for monitoring air pollutants CO_2, HCN, *etc.*)

Applications of IR-Spectroscopy

Qualitative Analysis

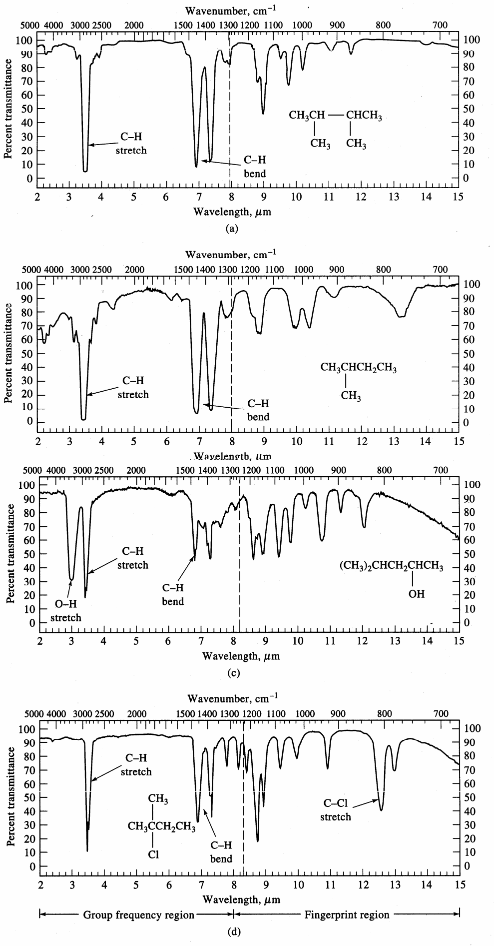
Group frequency region (3600 – 1200 cm^{-1}): identify characteristic groups

Fingerprint region (1200 – 600 cm^{-1}): characteristic for every compound

1.) Identification of compounds

by comparison with a database of spectra

2.) Identification of characteristic groups

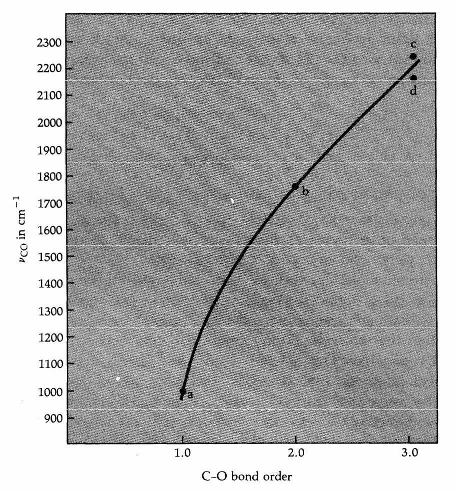


Group frequencies for some organic groups			
Bond	Type of compound	Frequency range (cm^{-1})	Intensity
O-H	Aliphatic and aromatic alcohols	3600-3000	Variable
N-H	Amines, amides	3600-3100	Medium
C-H	Alkanes	2850-2970	Strong
	alkenes	3010-3095	Medium
	Alkynes	3300	Strong
	Aromatic rings	3100-3010	medium
C≡N	Nitrile	2280-2210	strong
C≡C	Alkyne	2260-2100	Strong
C=O	Aldehydes, ketones, esters, …	1760-11690	Strong
-C=C-	alkenes	1670-1610	variable
-C=C-	Aromatic rings	1600-1500	variable
C-O	Alcohols, ethers, etc	1300-1050	strong
C-N	Amines, amides	1360-1180	strong

3.) Structural information

e.g. transition metal carbonyl complexes ($\nu_{CO} = 1850 – 2125\ cm^{-1}$)

a) bond order and $d\pi$ -$p\pi^*$ backbonding



$$\nu_{CO} = \frac{1}{2\pi c}\sqrt{\frac{k_{CO}}{\mu_{CO}}}$$

$\nu(CO) = 2170\ cm^{-1}$

$\nu(CO^+) = 2214\ cm^{-1}$

Complex	ν_{CO} (cm^{-1})
$Mn(CO)_6^+$	2090
$Cr(CO)_6$	2000
$V(CO)_6^-$	1860

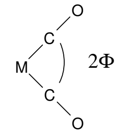
Complex	ν_{CO} (cm^{-1})
$Ni(CO)_4$	2046
$Co(CO)_4^-$	1883
$Fe(CO)_4^{2-}$	1788

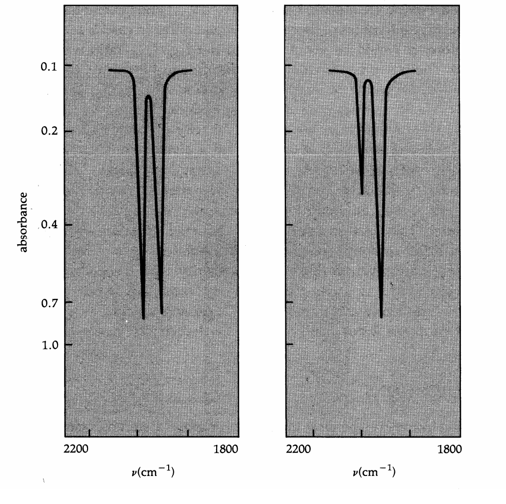
b) coordination geometry for complexes of the type $L_3M(CO)_2$

in phase vibration

out of phase vibration

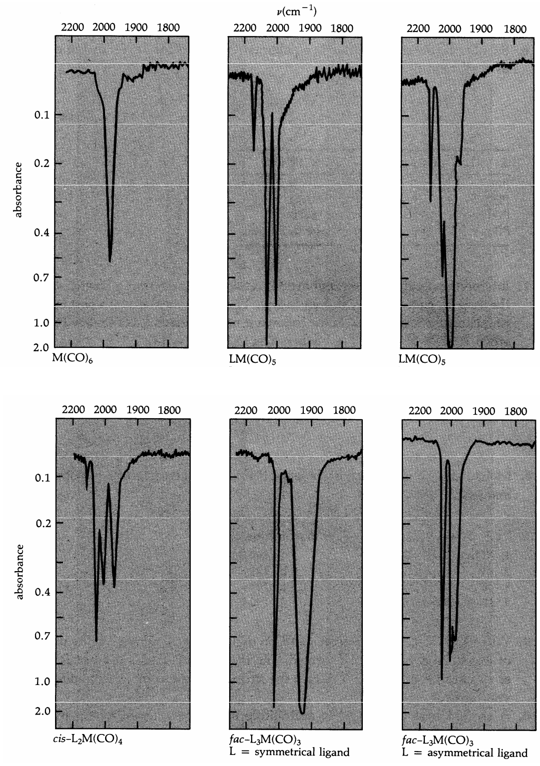
$I_{sym}/I_{asym} = \cot an^2\ \Phi$





Predicted relative intensities of $L_3M(CO)_2$ when 2Φ is 90° (a) and 120° (b)

c) geometrical structures of octahedral complexes $L_nM(CO)_{6-n}$



$M(CO)_6$ $LM(CO)_5$ $LM(CO)_5$

cis-$L_2M(CO)_4$

fac-$L_3M(CO)_3$
L = symmetrical ligand

fac-$L_3M(CO)_3$
L = asymmetrical ligand