5. INTERPRETATION AND ASSIGNMENT OF IR AND RAMAN SPECTRA

Introduction

- Masses (atomic weight)
- Force constants
- Geometry (bond angles, distances)

These molecular parameters:

a) determine the band position and
b) allow to calculate the form and frequencies of all normal modes.

Examples:

1.

$H^{35}Cl$	2886 cm^{-1}	$F(XCl) = 4.81$ Ncm^{-1}
$D^{35}Cl$	2091 cm^{-1}	
$T^{35}Cl$	1739 cm^{-1}	

2. CC stretching force constants

CH_3-CH_3	4.50	(993 cm^{-1}, Raman)
CH_2=CH_2	9.60	(1623 cm^{-1}, Raman)
CH≡CH	15.6	(1974 cm^{-1}, Raman)

3. CH_2Cl-CH_2Cl C-Cl stretching vibrational (cm^{-1}):

gauche: 653 (R)   656 (IR)
trans: 753 (R)   (- IR)

For complicated (big) molecules the calculations become very complex, so **empirical** methods are frequently used.

Certain sub molecular groups, e.g. $-CH_3$, $-NO$, $-COO^-$, $-C\equiv N$, $-SCN$, C_6H_5- etc. consistently produce bands in a characteristic frequency region of the vibrational spectrum. These bands are characteristic **GROUP FREQUENCIES**.

Example:

	Common bands	Not common bands
n-heptane	characteristic	e.g. 1150-1350 cm^{-1} region
n-octane	to n-alkanes	characteristic bands
n-nonane	(CH_3, CH_2, groups)	of chain length

The non common bands as so-called
FINGERPRINT BANDS, because they are characteristic of individual compound.

In order to understand the origin of group frequencies, some knowledge is necessary about theory of normal vibrations.

5.1. Basic ideas of theory of vibrations

The **diatomic molecules** have is only one stretching vibration (ν) which can be calculated very sample way using atomic masses (m_1, and m_2) and force constant (F):

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{F}{\mu}} = \frac{1}{2\pi c}\sqrt{F\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}, \quad cm^{-1}$$

where $\mu = \dfrac{m_1 \cdot m_2}{m_1 + m_2}$ the reduced mass.

F is the force constant (Ncm^{-1} = mdyn/Å)
When F is in Ncm^{-1}, and m_i are atomic weight, than

$$\frac{1}{2\pi c} = 1302.8 \text{ sec/cm}, \quad (6.025.10^{23})^{1/2}/2\,\pi c$$

The force constant can be calculated as

$$F = 4\,\pi^2 c^2 \nu^2\,\mu = 0.589148\,\mu\,(\nu/1000)^2, \quad Ncm^{-1}$$

$$\left(\frac{4\cdot(3.14)^2\cdot(3x10^{10})^2}{6.025\cdot10^{23}} = 0.589148\right)$$

In **polyatomic molecules** the situation is more complicated because all the nuclei perform their own harmonic oscillations.

Since the atom can, move in three directions (x, y, z) an N-atom molecule has 3N degrees of freedom of motion.

The 3N includes three (3T) translations and three rotations (3R) of the whole molecule.

This the vibrational degrees of freedom is 3N-6 or 3N-5 for linear molecules.

(One rotation along the axis is inactive.)

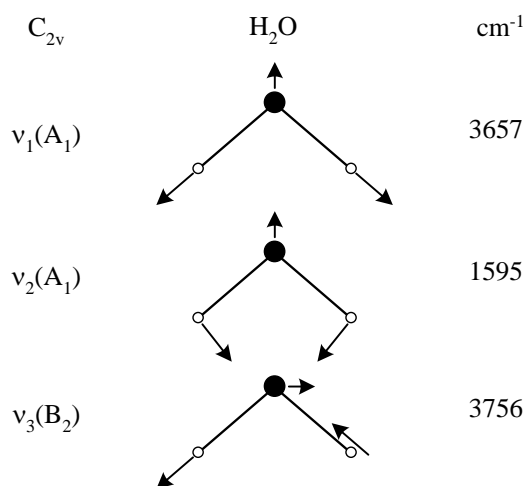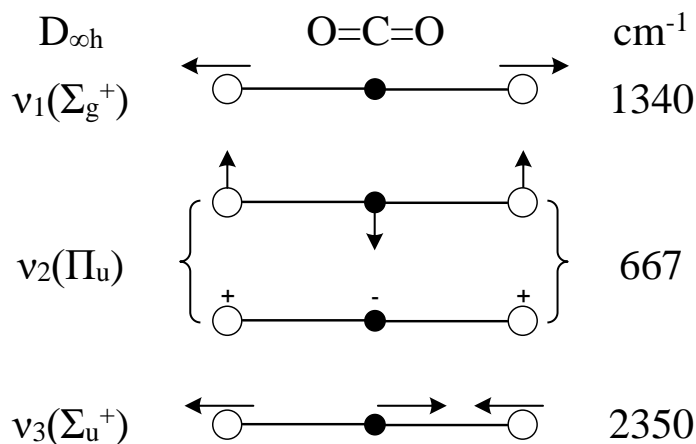In the case of H_2O molecule, we have 3x3 - 6 = 3 normal vibrations shown below.

C_{2v}	H_2O	cm^{-1}
$\nu_1(A_1)$		3657
$\nu_2(A_1)$		1595
$\nu_3(B_2)$		3756

Figure below illustrate the normal modes of CO_2 molecule

$D_{\infty h}$	O=C=O	cm^{-1}
$\nu_1(\Sigma_g^+)$		1340
$\nu_2(\Pi_u)$		667
$\nu_3(\Sigma_u^+)$		2350

Normal modes of vibration in CO_2 (+ and – denote vibrations going upward and downward, respectively, in direction perpendicular to the paper plane).

How can we calculate these vibrations?

5.1.1. Normal coordinates and normal frequencies

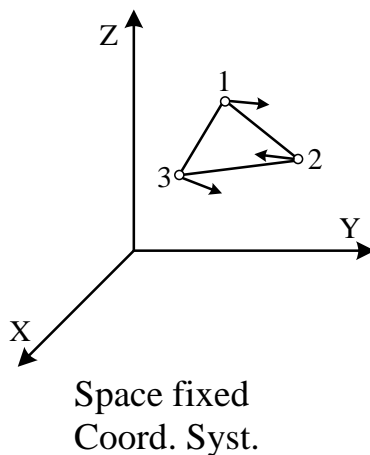T – function of the velocities ($\dot{q}$)
V – function of the displacement (q)

Newton's equation in Lagrangian from:

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) + \left(\frac{\partial V}{\partial q_i}\right) = 0 \qquad\qquad i = 1, 2, ..., N$$

N – number of atoms

Kinetic energy of molecules

Displacement vectors (ξ_i)

Atoms	Δx	Δy	Δz
1	ξ_1	ξ_2	ξ_3
2	ξ_4	ξ_5	ξ_6
3	ξ_7	ξ_8	ξ_9

3N

Space fixed
Coord. Syst.

Mass weighted Cartesian coordinates

$$\sqrt{m_1}\ \xi_1 = q_1$$

$$\sqrt{m_2}\ \xi_2 = q_2$$

....

$$\sqrt{m_3}\ \xi_3 = q_3$$

$$T = \frac{1}{2}\sum_i^{3N} \dot{q}_i^2 \qquad , \qquad 1, 2, ..., 3N$$

$$T = \frac{1}{2}\{\dot{q}\}\|\dot{q}\|$$

Potential energy of molecules

- No analytical expression

$$V = E_e^{vib} - E_e^{eq} \qquad \text{(very general)}$$

For small displacements:
Expand V in a Tailor's power series

$$V = f(q)_0$$

$$V = V_0 + \sum_i^{3N}\left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \frac{1}{2}\sum_{i,j}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \frac{1}{6}\sum_{i,j,k}^{3N}\left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_0 q_i q_j q_k + ...$$

Special conditions:
$V = 0$ (arbitrary)

$$\left(\frac{\partial V}{\partial q_i}\right)_0 = 0 \quad \text{(equilibrium)}$$

In harmonic approximation

$$V = \frac{1}{2}\sum_{i,j}^{3N} f_{ij} q_i q_j$$

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0$$

$$\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 = \left(\frac{\partial^2 V}{\partial q_j \partial q_i}\right)_0$$

$f_{ij} = f_{ji}$

$$V = \frac{1}{2}\{q\}F_q\|q\|$$

$$F_q \begin{vmatrix} f_{11} & f_{12} & \cdots & f_{1,3N} \\ f_{21} & f_{22} & \cdots & f_{2,3N} \\ \cdots & \cdots & \cdots & \cdots \\ f_{3N,1} & f_{3N,2} & \cdots & f_{3N,3N} \end{vmatrix}$$

Newton's equation

$$\left(\frac{\partial T}{\partial \dot{q}_i}\right) = \sum_i^{3N} \dot{q}_i \qquad , \qquad \frac{d}{dT}\left(\frac{\partial T}{\partial \dot{q}_i}\right) = \sum_i^{3N} \ddot{q}_i$$

$$\left(\frac{\partial V}{\partial q}\right) = \frac{1}{2}\sum_{ij}^{3N} f_{ij}q_j + \sum_i^{3N} f_{ii}q_j$$

$$\qquad\qquad\qquad\qquad\qquad i \neq j \qquad\qquad i=j$$

$$\sum_i^{3N} \ddot{q}_i + \frac{1}{2}\sum_{ij}^{3N} f_{ij}q_j + \sum_i^{3N} f_{ii}q_i = 0$$

$$\ddot{q}_i + \frac{1}{2}\sum_j^{3N} f_{ij}q_j + f_{ii}q_j = 0 \qquad i = 1,2,...,3N$$

$$\ddot{q}_i + f_{ii}q_j = 0 \qquad i = 1,2,...,3N$$

$$q_i = q_i^0 \qquad \sin(2\pi c\nu_i t + \varphi_i) \qquad i = 1,2,...,3N$$

$$\nu_i$$
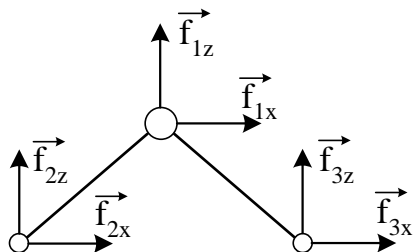
$$\varphi_i$$

$$q_i^0$$
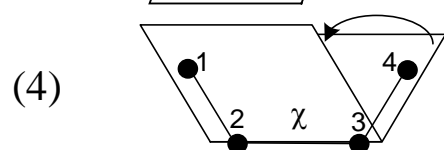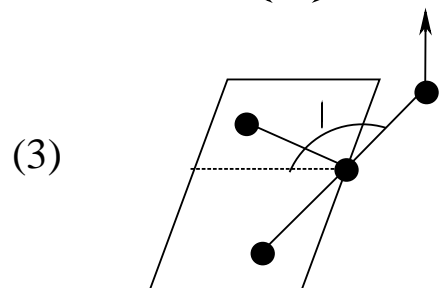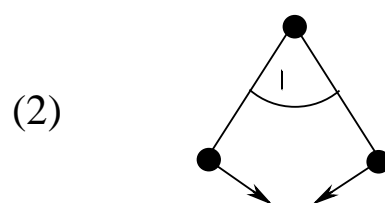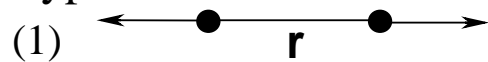
(1) $f_{ij} = 0$

(2)
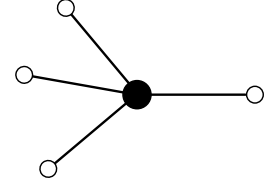
(3) $6\lambda i = 0$ (3T + 3R)
                          (3T + 2R) linear

5.1.2. Internal coordinates

Characteristic to molecular structure
Types:

(1)

r

(2)

(3)

(4)

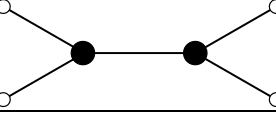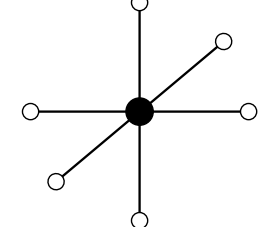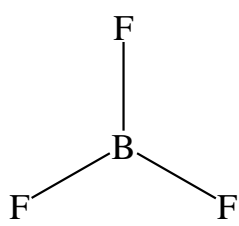| Molecule	Rotational axes	Rotation	Translation	Vibration
Linear				
Symmetric Top				
Asymmetric Top				
Spherical Top				
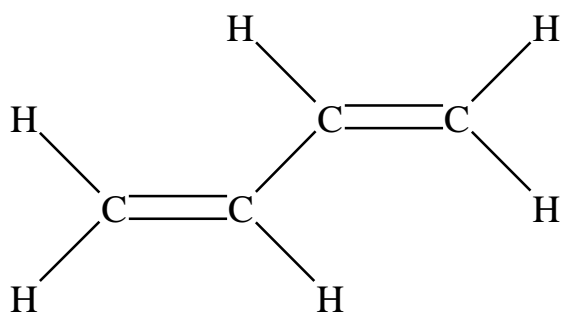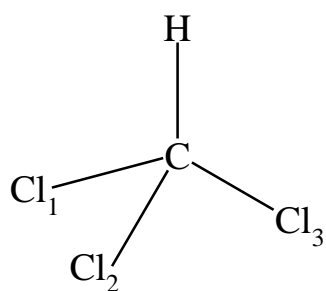
Further examples for introducing internal coordinates:

Molecule	Coordinates	Total Nº of coord.	3N-6 3N-5	Redundant
O═══C═══O				
H────C═══C────H				
F B F F				

The V and T in terms of internal coordinates

$$\left.\begin{array}{c} \Delta r \\ \Delta\alpha \\ \rho \end{array}\right\} \quad \text{Cartesian } \vec{q}_j \text{ displacements}$$

$$\underbrace{}_{r_i}$$

$$r_i = \vec{b}_{ij}\,\vec{q}_i$$

$$r_1 = \vec{b}_{11}\vec{q}_1 + \vec{b}_{12}\vec{q}_2 + \cdots + \vec{b}_{1,N}\,\vec{q}_N$$

$$r_2 = \vec{b}_{21}\vec{q}_1 + \vec{b}_{22}\vec{q}_2 + \cdots + \vec{b}_{2,N}\,\vec{q}_N$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$r_{(3N-6)} = \vec{b}_{n_1}\vec{q}_1 + \vec{b}_{n_2}\vec{q}_2 + \cdots + \vec{b}_{n,N}\vec{q}_N$$

$$\underbrace{}_{n} \qquad\qquad \underbrace{}_{\substack{\text{scalar} \\ \text{product}}}$$

$$\|r\| = \vec{B}\,\|\vec{q}\|$$

Opposite way:

$$\vec{q} = \sum_i \vec{b}'_{ji} \, r_i$$

$$\vec{q}_1 = \vec{b}'_{11} \, r_1 + \vec{b}'_{12} \, r_2 + \cdots + \vec{b}'_{1n} \, r_n \qquad n = 3N - 6$$

$$\vec{q}_2 = \vec{b}'_{21} \, r_1 + \vec{b}'_{22} \, r_2 + \cdots + \vec{b}'_{2n} \, r_n$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\vec{q}_N = \vec{b}'_{N_1} \, r_1 + \vec{b}'_{N_2} \, r_2 + \cdots + \vec{b}'_{N,n} \, r_n$$

$$\|\vec{q}\| = \vec{B}' \|r\|$$

Transformation of $\vec{q} - s$ to r coordinates:
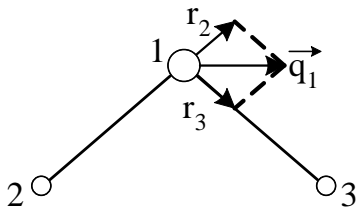
Potential energy

$$V = \frac{1}{2} \{\vec{q}\} \, F_q \, \|\vec{q}\| = \frac{1}{2} \{r\} \underbrace{\tilde{\vec{B}}' F_q \, \vec{B}'}_{F \text{ (internal)}} \|r\|$$

a. $V = \dfrac{1}{2} \{r\} \, F \, \|r\|$

b. $F = \tilde{\vec{B}}' F_q \, \vec{B}'$

Kinetic energy

$$T = \frac{1}{2} \{\vec{p}\} M^{-1} \|\vec{p}\| \qquad \vec{p}\ momentum$$

$$M^{-1} = \begin{bmatrix} \dfrac{1}{m_1} & & & 0 \\ & \dfrac{1}{m_2} & & \\ & & \ddots & \\ 0 & & & \dfrac{1}{m_N} \end{bmatrix}$$

m_i – atomic mass (i=1, 2, …, N)
$\vec{p}$ - its momentum

$$T = \frac{1}{2} \{p\} \underbrace{\vec{B}\ M^{-1}\tilde{\vec{B}}}_{G} \|p\|$$

a. $T = \dfrac{1}{2} \{p\}\ G\ \|p\|$

b. $G = \vec{B}\ M^{-1}\tilde{\vec{B}}$

5.1.3. Normal coordinates

Problem in Schrödinger equation: $r_i\, r_j$ cross terms

Transformation

$r_1 = l_{11}\, Q_1 + l_{12}\, Q_2 + \ldots\ldots + l_{1m}\, Q_n$ $\qquad\qquad n = 3N\text{-}6$

$r_2 = l_{21}\, Q_1 + l_{22}\, Q_2 + \ldots\ldots + l_{2m}\, Q_n$

$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$

$r_n = l_{n1}\, Q_1 + l_{n2}\, Q_2 + \ldots\ldots + l_{nm}\, Q_n$

$$\|r\| = L\|Q\| \qquad \{r\} = \{Q\}\tilde{L}$$

$$\|\dot{r}\| = L\|\dot{Q}\| \qquad \{\dot{r}\} = \{\dot{Q}\}\tilde{L}$$

$$T = \frac{1}{2}\{\dot{r}\}\, G^{-1}\, \|\dot{r}\|$$

$$T = \frac{1}{2}\{\dot{Q}\}\underbrace{\tilde{L}\, G^{-1}\, L}_{E}\|\dot{Q}\| = \frac{1}{2}\{\dot{Q}\}\|\dot{Q}\|$$

$$V = \frac{1}{2}\{r\}\, F\|r\| = \frac{1}{2}\{Q\}\underbrace{\tilde{L}FL}_{\Lambda}\|Q\| = \frac{1}{2}\{Q\}\Lambda\|Q\|$$

(1) $\tilde{L}G^{-1}L = E$ ⎫

$\quad\quad\quad\quad\quad\quad\quad\quad$ Properties of **L**

(2) $\tilde{L}FL = \Lambda$ ⎭

From (1) $\quad \tilde{L} = L^{-1}G \quad \rightarrow \quad$ to (2)

$L^{-1} G F L = \Lambda$

G F L = Λ L

Computation:

Calculate G (masses, bond lengths and angles)

Construct F (transferability)

Diagonalise G:

$\tilde{L}_1 G L_1 = \mu$ (eigenvalues)

Multiply F:
$\sqrt{\mu}\,\tilde{L}_1 F L_1 \sqrt{\mu} = F'$

Diagonalise F':
$\tilde{L}_2 F' L_2 = \Lambda$ (eigenvalues)

$L = L_1 \sqrt{\mu}\, L_2 \quad$ (eigenvectors)

Examples: for introduction of internal coordinates

(H_2O_2)

(NH_3)

(BF_3)

(HCN)

(C_4H_2)

$[C_2O_4]^{2-}$

B_2Cl_4

C_2H_6

$[SO_4]^{2-}$

$[PtCl_4]^{2-}$

BrF_5

UF_6

$[Pt_2Cl_6]^{2-}$
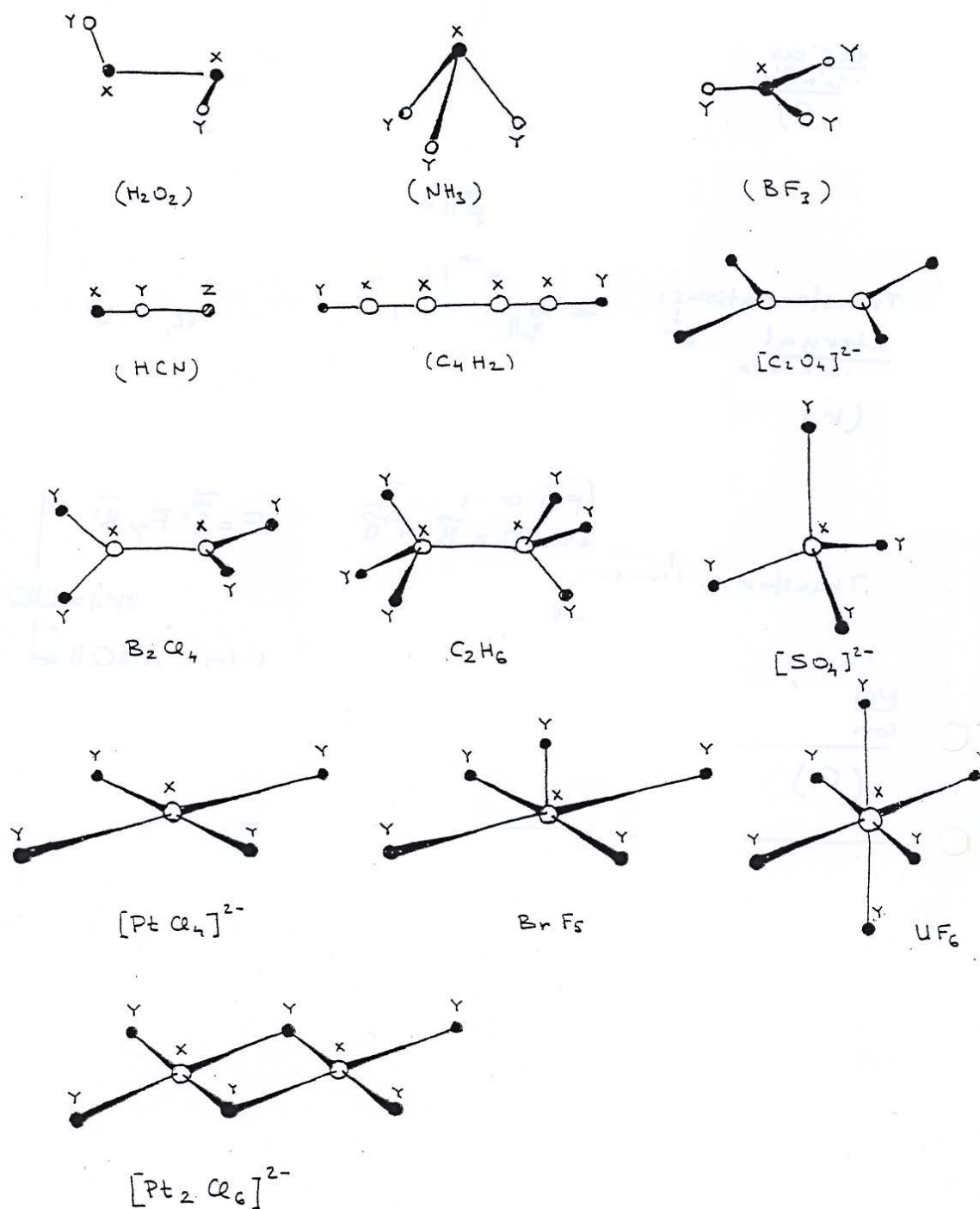
5.1.4. Calculation and characterisation of kinetic energy matrix

Atomic masses
Molecular geometry $\Bigg\}$ $\Longrightarrow$ G-matrix

$$G = \vec{B}\,M^{-1}\tilde{\vec{B}}$$

$$\cdots G = B_x M^{-1}\tilde{B}_x + B_y M^{-1}\tilde{B}_y + B_z M^{-1}\tilde{B}_z$$

G-matrix for water type molecule:

Internal coordinates: r_1, r_2, α
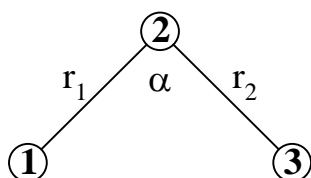
G-matrix in internal coordinates:

r_1	r_2	α
$\mu_1+\mu_3$	$\mu_3\cos\varphi$	$-\mu_3\,\sigma_{23}\sin\varphi$
	$\mu_1+\mu_3$	$-\mu_3\,\sigma_{13}\sin\varphi$
Sym.		$-\mu_1\,\sigma_{13}^2 + \mu_2\,\sigma_{23}^2 + \mu_3(\sigma_{13}^2 + \sigma_{23}^2 - 2\sigma_{13}\,\sigma_{23}\cos\varphi)$

    μ_i – inverse masses of atom i
    σ_{ij} – inverse bond lengths between atoms i and j
    φ – is the bond angle

G-matrix

$$G_{rr}^2 = \mu_1 + \mu_2$$

    r

$$G_{rr}^1 = \mu_1 \cos \phi$$

    rr

$$G_{r\phi}^2 = -\rho_{23}\mu_2 \sin \phi$$

    rα

$$G_{r\phi}^1 \begin{pmatrix} 1 \\ 1 \end{pmatrix} = -(\rho_{13} \sin \phi_{213} \cos \psi_{234} \\ + \rho_{14} \sin \phi_{214} \cos \psi_{243})\mu_1$$

    rα

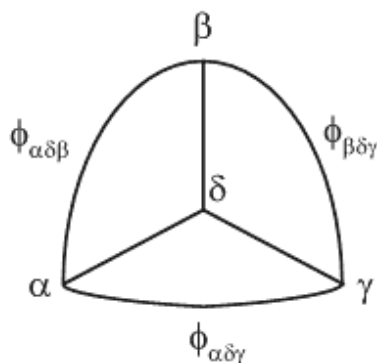$$G_{\phi\phi}^3 = \rho_{12}^2\mu_1 + \rho_{23}^2 \mu_3 + (\rho_{12}^2 + \rho_{23}^2 \\ - 2\rho_{12}\rho_{23} \cos \phi)\mu_2$$

    α

$$G_{\phi\phi}^2 \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (\rho_{12}^2 \cos \psi_{314})\mu_1 + [(\rho_{12} - \rho_{23} \cos \phi_{123} \\ - \rho_{24} \cos \phi_{124})\rho_{12} \cos \psi_{314} \\ + (\sin \phi_{123} \sin \phi_{124} \sin^2 \psi_{314} \\ + \cos \phi_{324} \cos \psi_{314})\rho_{23}\rho_{24}]\mu_2$$

    ρ

Here, the atoms surrounded by a double circle are those common to both coordinates. The symbols μ and ρ denote the reciprocals of mass and bond distance, respectively. The spherical angle $\psi_{\alpha\beta\gamma}$ is defined as

$$\cos \psi_{\alpha\beta\gamma} = \frac{\cos \phi_{\alpha\delta\gamma} - \cos \phi_{\alpha\delta\beta} \cos \phi_{\beta\delta\gamma}}{\sin \phi_{\alpha\delta\beta} \sin \phi_{\beta\delta\gamma}}$$

Solid angles involving positions α, β, γ, and δ.
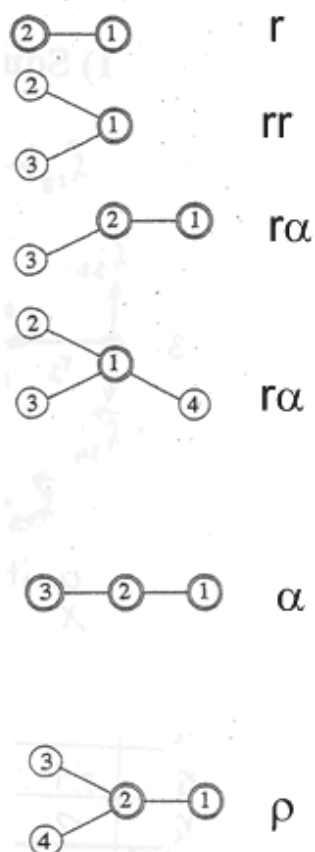
Special properties of matrix G

1.
   - Identical coordinates → identical matrix elements
   - Diagonal elements are always positive and bigger than off-diagonal ones

2. No common atom, no interaction term

3. Planar molecules:

   > 2N-3 in-plane
   > N-3 o.-o.p.

$$B_x = \begin{bmatrix} b_x \\ \cdots \\ 0 \end{bmatrix} \quad B_y = \begin{bmatrix} b_y \\ \cdots \\ 0 \end{bmatrix} \quad B_z = \begin{bmatrix} 0 \\ \cdots \\ b_z \end{bmatrix}$$

$$G \text{ (in-plane)} = B_x M^{-1} \tilde{B}_x + B_y M^{-1} \tilde{B}_y$$
$$G \text{ (o.o.p.)} = B_z M^{-1} \tilde{B}_z$$
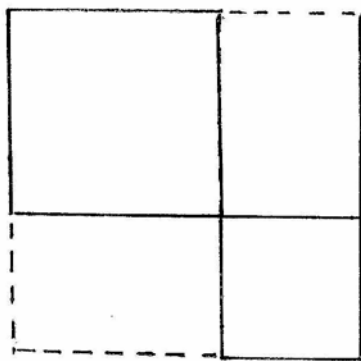
4. Redundancy conditions
a. Branching redundancies
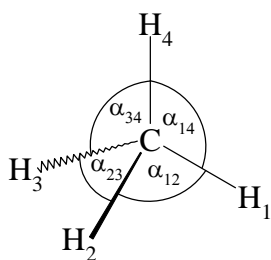
Structure of G-matrix:

Redundancy: $\sum_{i=1}^{6} \alpha_i = 0$

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'CH$_4$'

MATRIX G IN INTERNAL COORDINATES

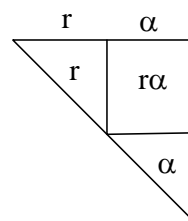|	r_1	r_2	r_3	r_4	α_{23}	α_{13}	α_{12}	α_{14}	α_{24}	α_{34}
ROW 1	1.075419	-.027752	-.027752	-.027752	.072014	.072014	.072014	-.072014	-.072014	-.072014
ROW 2	-.027752	1.075419	-.027752	-.027752	.072014	-.072014	-.072014	-.072015	.072014	.072014
ROW 3	-.027752	-.027752	1.075420	-.027752	-.072013	.072014	-.072013	.072014	-.072014	.072014
ROW 4	-.027752	-.027752	-.027752	1.075420	-.072013	-.072013	.072014	.072014	.072014	-.072014
ROW 5	.072014	.072014	-.072013	-.072013	1.857037	-.417542	-.417542	-.186869	-.417541	-.417541
ROW 6	.072014	-.072014	.072014	-.072013	-.417542	1.857034	-.417542	-.417541	-.186869	-.417541
ROW 7	.072014	-.072014	-.072013	.072014	-.417542	-.417542	1.857034	-.417541	-.417541	-.186869
ROW 8	-.072014	-.072015	.072014	.072014	-.186869	-.417541	-.417541	1.857034	-.417542	-.417542
ROW 9	-.072014	.072014	-.072014	.072014	-.417541	-.186869	-.417541	-.417542	1.857034	-.417542
ROW 10	-.072014	.072014	.072014	-.072014	-.417541	-.417541	-.186869	-.417542	-.417542	1.857034

SUMMARY

(1) It means, that the vibrations of a polyatomic molecule have been **separated** to the vibrational motion of 3N-6 **oscillators.** If the vibrational frequency of two or three oscillators are identical, then the two (or more) vibrations are said to be **degenerate**. The energy expression then has a form
$E_i = hcv_i (\Sigma v_{ik} + \alpha_i/2)$

(2) The complicated vibrational motions have been separated into 3N-6 **normal** vibrations along Q_i coordinate.

(3) The vibrations along the Q_i normal coordinates mathematically refer to an **one-dimensional** motion, which is basically identical with the motions of diatomic molecules, but here Q_i represents a linear combination of internal coordinates.

(4) For each given solution $\lambda_k = 4\pi^2 c^2 v_k^2$ of the secular equation, i.e. for each normal coordinate Q_k, the molecule undergoes a simple motion in which all the nuclei move **in phase** with the same frequency v_k, but with **different amplitudes**, Q^0_k. In other words, all the nuclei will pass through the equilibrium position at the same time, reach their maximum displacement in a given direction, pass again through the equilibrium position, reach their maximum displacement in the opposite direction and so forth.

   Mode of motions of this kind is called a **normal mode of vibrations** or simply a **normal vibration** and the frequency associated with it is call ed a **normal** or **fundamental** frequency of vibrations. Normal modes of H_2O

$$Q_1(r_1+r_2) \qquad Q_2(\alpha) \qquad Q_3(r_1-r_2)$$
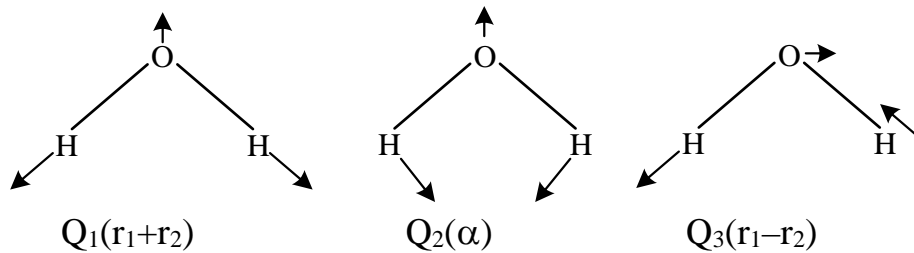
Normal or fundamental frequencies

   The relative 'length of the arrows can be chosen so that they give the relative amplitudes of displacements of the individual nuclei. If this is done in the proper scale, then each drawing will represent the normal coordinate as well.
(5) The theoretical ca1culation of vibrations simply lead to the determination of the G and F matrices.

Selected Force Constants and Bond Orders (according to Siebert) of Organic and Inorganic Compounds

Bond A–B	Force Const. f (N cm^{-1})	Bond Order	Compound	Bond A–B	Force Const. f (N cm^{-1})	Bond Order	Compound
H–H	5.14	0.77	H_2	H–O	7.40	1.0	HO^-
Li–Li	1.24	1.2	Li_2	H–F	8.85	1.1	HF
B–B	3.58	1.2	B_2	H–Al	1.76	0.60	AlH_4^-
C–C	16.5	3.2	HCCH	H–Si	2.98	0.84	SiH_4
N–N	22.42	3.2	N_2	H–P	3.11	0.82	PH_3
O–O	11.41	1.4	O_2	H–S	4.29	1.0	H_2S
F–F	4.45	0.58	F_2	H–Cl	4.81	1.0	HCl
Na–Na	0.17	0.24	Na_2	H–Ge	2.81	0.82	GeH_4
Si–Si	4.65	2.0	Si_2	H–As	2.85	0.81	AsH_3
Si–Si	~1.7	~0.9	Si_2H_6	H–Se	3.51	0.93	H_2Se
P–P	5.56	2.1	P_2	H–Br	3.84	0.98	HBr
P–P	2.07	0.95	P_4	H–Sn	2.03	0.76	SnH_4
S–S	4.96	1.7	S_2	H–Sb	2.09	0.77	SbH_3
S–S	2.5	0.99	S_8	H–I	2.92	0.97	HI
Cl–Cl	3.24	1.1	Cl_2	C–H	5.50	1.0	CH_4
Ni–Ni	0.11	0.2	Ni solid	C–B	3.82	1.1	$B(CH_3)_3$
As–As	3.91	1.8	As_2	C–C	16.5	3.2	HCCH
Se–Se	3.61	1.6	$^{80}Se_2$	C–C	9.15	1.9	H_2CCH_2
Br–Br	2.36	1.1	Br_2	C–C	7.6	1.7	C_2H_6
Rb–Rb	0.08	0.2	Rb_2	C–C	4.4	1.1	H_3CCH_3
Cd–Cd	1.11	1.0	Cd_2^{2+}	C–N	18.07	3.0	HCN
Sb–Sb	2.61	1.9	Sb_2	C–N	11.84	2.1	CN_2^{2-}
Te–Te	2.37	1.7	Te_2	C–N	6.54	1.3	$NNCH_2$
I–I	1.70	1.2	I_2	C–O	18.56	2.8	CO
Hg–Hg	1.69	1.5	Hg_2^{2+}	C–O	15.61	2.4	CO_2
Pb–Pb	4.02	3	Pb_2	C–O	12.76	2.0	OCH_2
Bi–Bi	1.84	1.6	Bi_2	C–O	7.86	1.3	CO_3^{2-}
H–B	2.75	0.68	BH_3	C–O	5.1	0.96	$O(CH_3)_2$
H–C	5.50	1.0	CH_4	C–F	6.98	1.1	CF_4
H–N	7.05	1.1	NH_3	C–P	8.95	2.4	HCP
H–O	8.45	1.1	H_2O	C–S	7.67	2.0	CS_2

Selected Force Constants and Bond Orders (according to Siebert) of Organic and Inorganic Compounds

Bond A–B	Force Const. f (N cm^{-1})	Bond Order	Compound	Bond A–B	Force Const. f (N cm^{-1})	Bond Order	Compound
C–S	3.3	1.0	$S(CH_3)_2$	O–O	6.18	0.89	O_2^-
C–Cl	3.12	0.93	CCl_4	O–O	5.70	0.83	O_3
C–Ni	2.91	1.2	Ni_4CO	O–Na	~3.2	~1.1	Na–OH
C–Ni	1.43	0.68	NiCO	O–Mg	3.5	1.1	MgO
C–Se	5.94	1.8	CSe_2	O–Al	5.66	1.5	AlO
C–Br	2.42	0.86	CBr_4	O–Al	3.8	1.1	$Al(OH)_4^-$
C–Rh	2.4	1.2	$(Rh(CN)_6)^{3-}$	O–Si	9.25	2.1	SiO
C–Ag	2.0	0.99	$(Ag(CN)_2)^-$	O–Si	4.75	1.2	SiO_4^{-4}
C–I	1.69	0.79	CI_4	O–P	9.41	2.0	PO
N–H	7.05	1.1	NH_3	O–P	6.16	1.4	PO_4^{3-}
N–B	7.2	1.6	BN_2^{3-}	O–S	10.01	2.0	SO_2
N–C	18.07	3.0	HCN	O–Cl	4.26	1.0	ClO_2^-
N–N	22.42	3.2	N_2	O–Cl	3.30	0.82	ClO^-
N–N	16.01	2.4	N–NNH	O–Ca	2.85	1.2	CaO
N–N	13.15	2.0	$N-N-N^-$	O–Ti	7.19	2.4	TiO
N–O	25.07	3.1	$N-O^+$	O–V	7.36	2.3	VO
N–O	17.17	2.3	NO_2^+	O–Cr	5.82	1.9	CrO
N–O	15.49	2.1	NO	O–Mn	5.16	1.6	MnO
N–O	15.18	2.0	ONCl	O–Fe	5.67	1.7	FeO
N–O	11.78	1.7	NNO	O–Cu	2.97	0.93	CuO
N–F	4.16	0.66	NF_3	O–Ge	7.53	1.8	^{74}GeO
N–Si	3.8	1.1	$((CH_3)_3Si)_2NH$	O–Se	6.45	1.5	SeO
N–S	12.54	2.5	NSF_3	O–Mo	3.05	1.2	Ba_2CaMoO_6 (solid)
N–S	8.3	1.9	HNSO	O–Ru	6.70	2.2	RuO_4
N–S	3.1	0.87	H_3N-SO_3	O–Ag	2.00	0.79	AgO
O–Li	1.58	0.66	LiO	O–Sn	5.53	1.7	SnO
O–Be	7.51	1.8	BeO	O–Te	5.31	1.6	TeO
O–B	13.66	2.5	BO	O–Ba	3.79	1.8	BaO
O–B	6.35	1.3	BO_3^3	O–Ce	6.33	2.6	CeO
O–O	16.59	2.0	O_2^+	O–Pr	5.68	2.4	PrO
O–O	11.41	1.4	O_2	O–Nd	3.5	1.6	$NdAc_3 \cdot H_2O$ (polymer)

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5.2. Principles of the origin of group frequencies

Number of functional groups exhibit characteristic bands in IR and Raman spectra which can be characteristic by
1. frequency
2. frequency and intensity.

Origin of characteristic bands:
- Similar atoms (with identical masses) form groups in similar geometric arrangement.
- The transferability of force constants means identical force constant set for similar groups in different molecules. Part of G and F matrix for CH_3 and CH_2 groups:
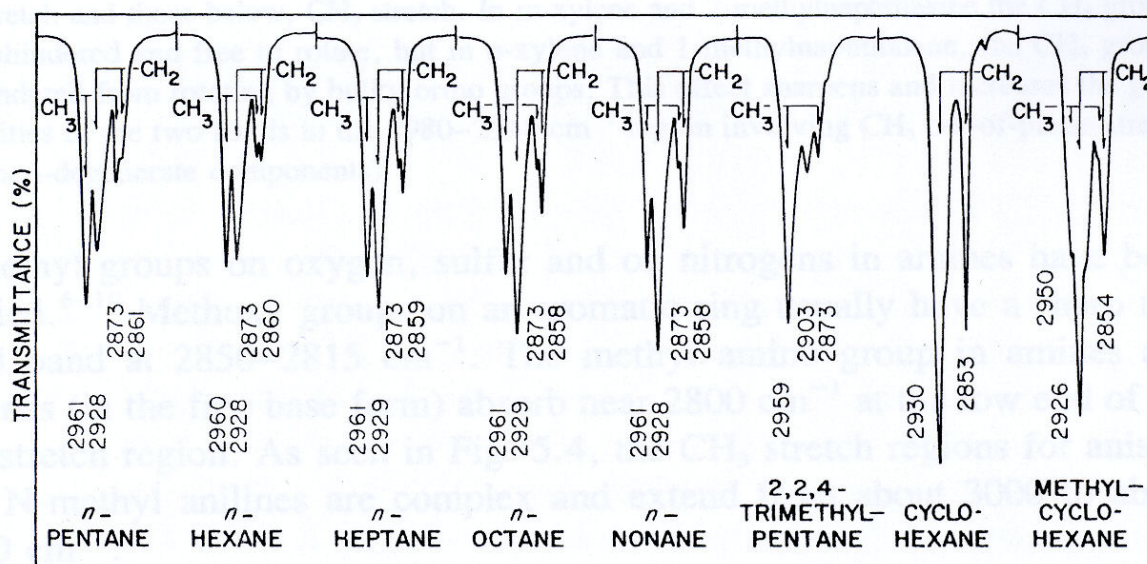
	CH_3			CH_2				CH_3			CH_2	
	r_1	r_2	r_3	q_1	q_2 q_2			r_1	r_2	r_3	q_1	q_2
G =	a	b	b			F =		f_r	f_{rr}	f_{rr}		
	b	a	b					f_{rr}	f_r	f_{rr}		
	b	b	a					f_{rr}	f_{rr}	f_r		
				a	b						f_q	f_{qq}
				b	a						f_{qq}	f_q

Bond lengths: ~1.09 Å
Bond angles: ~109.47° (tetrahedral)

After diagonalization of G and F matrices the calculated frequencies will be close to:

	Wavenumber (cm^{-1})	
ν CH$_3$ asym str	2960, s	degenerate
ν CH$_3$ asym str	2960, s	
ν CH$_3$ sym str	2870, w	
ν CH$_2$ asym str	2926, s	
ν CH$_2$ sym str	2853, w	

The infrared spectra of some alkanes in the CH stretch region.

Factors influencing characteristic frequencies:
- mass effects (isotope substitution, or changing e.g. Cl, Br, I substituents)
- electron affinity of substituents (changing the force constant)
- steric effects (ring strain, isomers, conformations, steric hinderance, co planarity etc.)

- tautomeria (keto-enol)
- external conditions
    - ◆ state (solid, liquid, gas)
    - ◆ temperature
    - ◆ crystal modification
    - ◆ solvent effect
    - ◆ concentration
    - ◆ association (H-bonding, adsorption, cage effect, matrix effect)

Characteristic X-H stretching frequencies

The hydrogen stretching vibrations are mechanically independent of the rest of the molecule and tend to make good group frequencies. (See Table below).

1.) Reduced mass changing very little
   $\mu(BH) = 0.9087$ $\mu(IH)$ =   1.008
   (1.008 is the atomic weight of H)
2.) Therefore the most of the shift is caused by changes in the X-H force constants from F(AlH)=1.9 till F(HF)=8.8 Ncm^{-1}.

Approxymate X-H stretching frequencies (cm^{-1}) and force constants (mdynes/Å)

BH	CH	NH	OH	FH
2500	3000	3400	3600	3960 cm^{-1}
3.4	4.9	6.4	7.2	8.8 mdynes/Å
AlH	SiH	PH	SH	ClH
1820	2150	2350	2570	2890
1.9	2.6	3.2	3.8	4.8
	GeH	AsH	SeH	BrH
	2070	2150	2300	2560
	2.5	2.7	3.1	3.8
	SnH	SbH		IH
	1850	1890		2230
	2.0	2.1		2.9

3.) Force constants increase as the electronegativity of X increases.

4.) Change in hybridisation (changing the special arrangement of electrons).
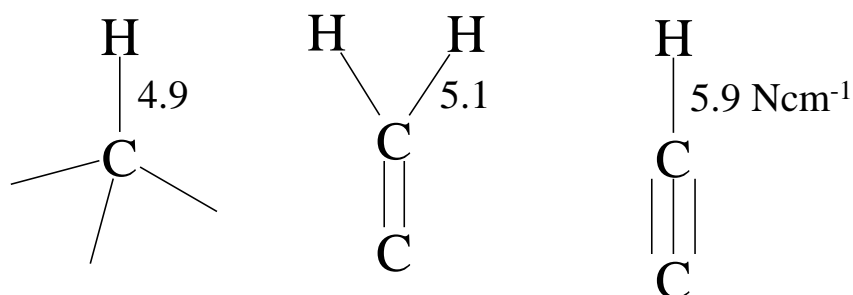
5.) Hydrogen bonding (NH, OH, FH)

5.3. Group frequencies of organic molecules

Spectra-structure correlations are similar in IR and Raman spectra. The band intensities are different:

1.) Center of inversion (alternatively)
2.) C=O, OH groups are strong in IR
3.) S-H, N-H, N=O are strong in Raman

By comparing the infrared spectra of two substances thought to be identical, you can establish whether they are, in fact, identical. In case if their infrared spectra coincide peak for peak (absorption for absorption), in most cases the two substances will be identical.
A second and more important use of the infrared spectrum is to determine structural information about the molecule. The absorption of each type of bond (N–H, C–H, O–H, C–X, C=O, C–O, C–C, C=C, C≡C, C≡N, and so on) are regularly found only in certain small portion of the vibrational infrared region. A small range of absorption can be defined for each type of bond.
See Characteristic stretching frequencies in the next Table.

5.3.1. Hydrocarbons

Hydrocarbons contain only C–H, C–C (C=C, C≡C) bonds but there is plenty of information to be obtained from the IR and Raman spectra

Characteristic group frequencies of some stretching modes

| 4000 | 3000 | 2400 | 2000 | 1500 | 1000 | 200 cm⁻¹ |

vOH 3760-3520 - ... (1800)
   monomer   dimer

vNH 3500-3300 - ... (1900)
   monomer   dimer

vCH: ≡C-H ~3300
   =C-H 3100-3000
   –C-H 3000-2800

vS-H 2600-2550
   vP-H 2440-2275
   vSi-H 2260-2100

vC≡N
vC≡C
vX=Y=Z
(C,N,O,S)

vC=O
vC=C
vC=N
+
Aromatic C-C str.

δCH, δNH
δOH

vS=O
vC=S

vN–O
vC–C
vC–O
vC–F

vC–X (Cl, Br, I)

δC-C-N
δC-C-C

γNH
γOH
γ=CH
γC=O

τC–C

Localized modes ← →

Fingerprint region, (strongly coupled modes)

249
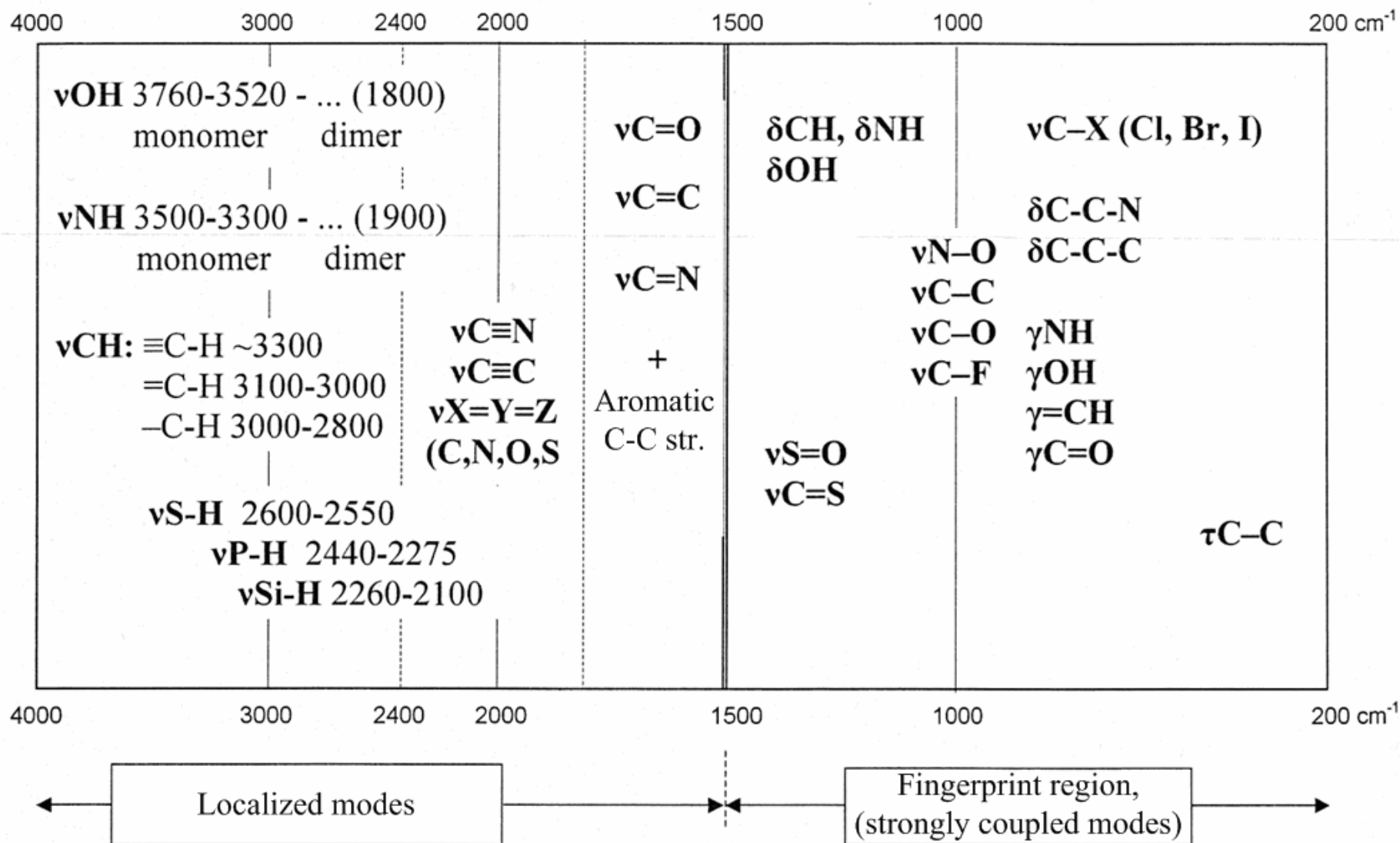
Aliphatic hydrocarbons

They contain: $-CH_3$ (C_{3v})
$\qquad\qquad\quad >CH_2$ (C_{2v})
$\qquad\qquad\quad \gg CH$ (C_{3v})

Methyl groups

Internal coordinates
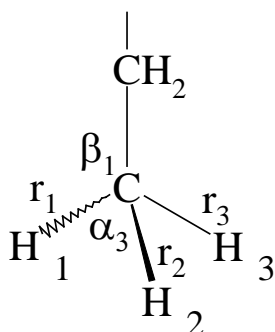
Linear combination of internal coordinates	Absorption region (cm^{-1}) $-CH_2-CH_3$
$\nu_a(CH_3) = 2r_1 - r_2 - r_3$	2985(25)
$\nu_a'(CH_3) = r_2 - r_3$	2970(30)
$\nu_s(CH_3) = r_1 + r_2 + r_3$	2905(65)
$\delta_a(CH_3) = 2\alpha_1 - \alpha_2 - \alpha_3$	1465(20)
$\delta_a'(CH_3) = \alpha_2 - \alpha_3$	1445(25)
$\delta_s(CH_3) = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3$	1380(20)
$\rho(CH_3) = 2\beta_1 - \beta_2 - \beta_3$	1100(95)
$\rho'(CH_3) = \beta_2 - \beta_3$	1080(80)
$\tau(CH_3) = \chi$ (coordinates)	230(105)

Methyl groups
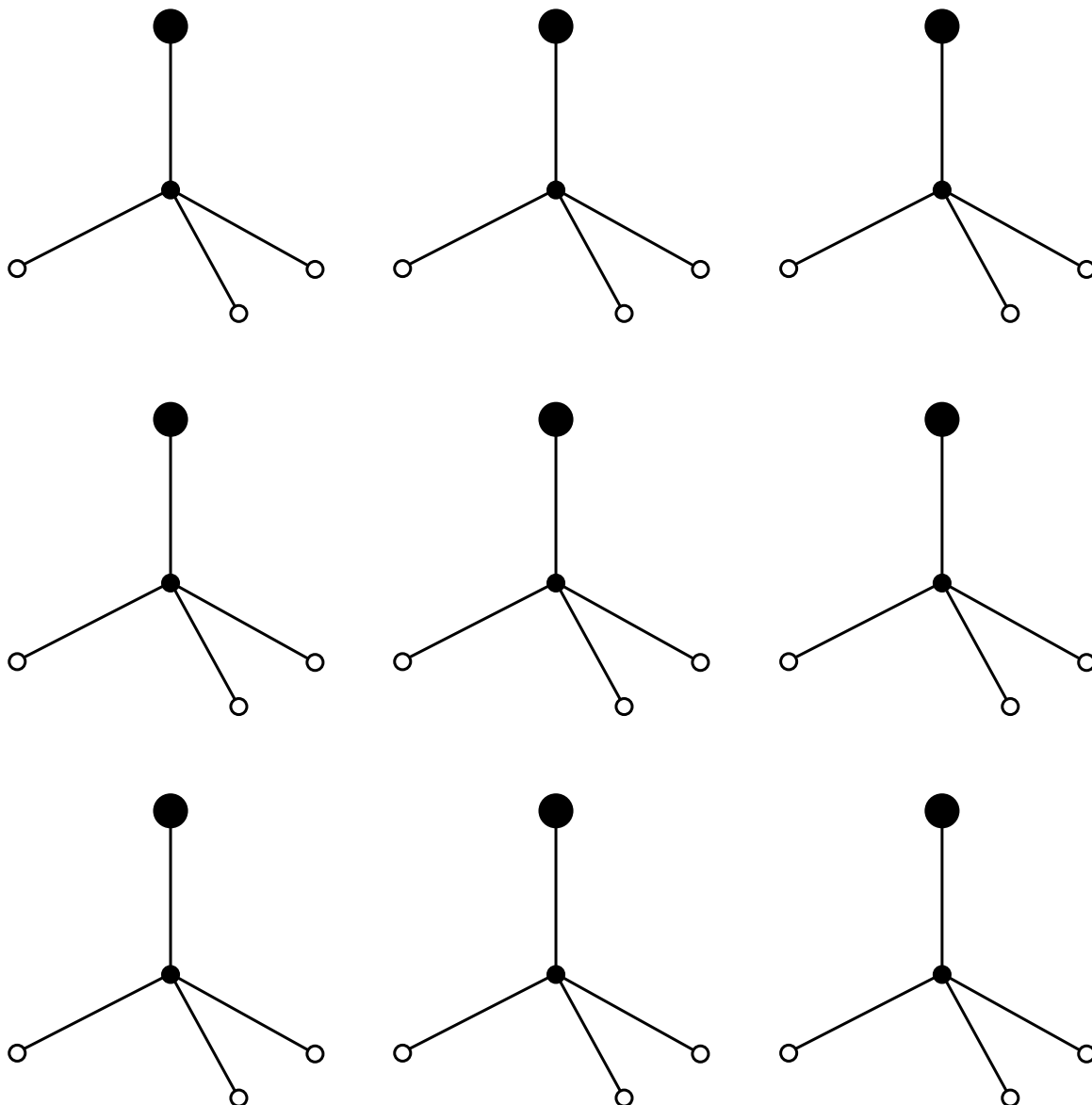
$\nu_a(CH_3) > \nu_s(CH_3) > \delta_a(CH_3) > \delta_s(CH_3) > \rho(CH_3) > \nu(CCl)$
$\sim2960 \qquad \sim2870 \qquad \sim1460 \qquad \sim1380 \qquad \sim1000 \qquad \sim700 \text{ cm}^{-1}$
Characteristic (strong) bands

Special features of CH stretching:
   1.) $\nu_a(CH_3)$ as a double degenerate mode can be splitted.
   2.) Separation between ν_a and ν_s is about 100 cm^{-1} (without Fermi resonance).
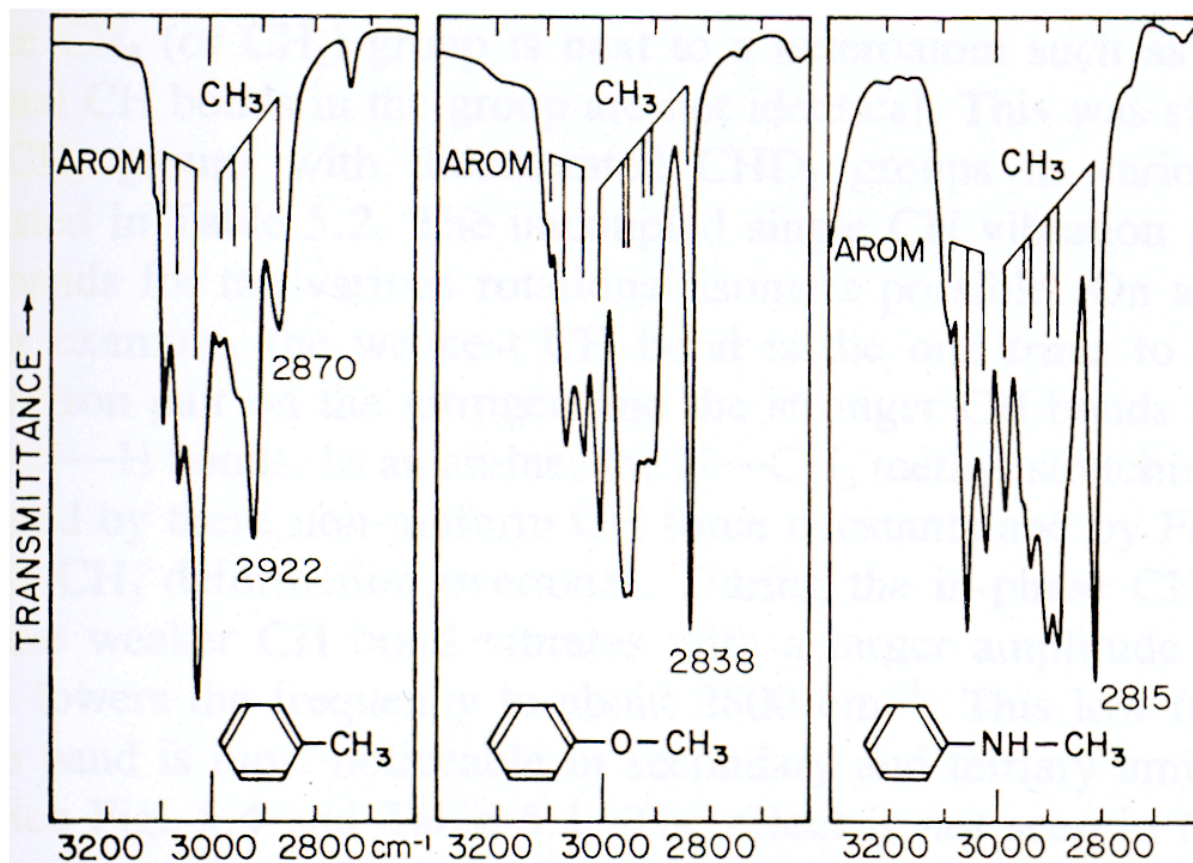
IR spectra in the CH stretching region
            a.)   Bands above 3000 cm^{-1}
            b.)   Splitting of $\nu_a(CH_3)$ (~2970, 2940 cm^{-1}, is weak)
            c.)   Fermi resonance, 2x1448 cm-1
            d.)   Sharp isolated band at 2838 cm^{-1} (methoxy) and 2815 cm^{-1} (N-methyl aniline)

CH₃ deformation vibrations
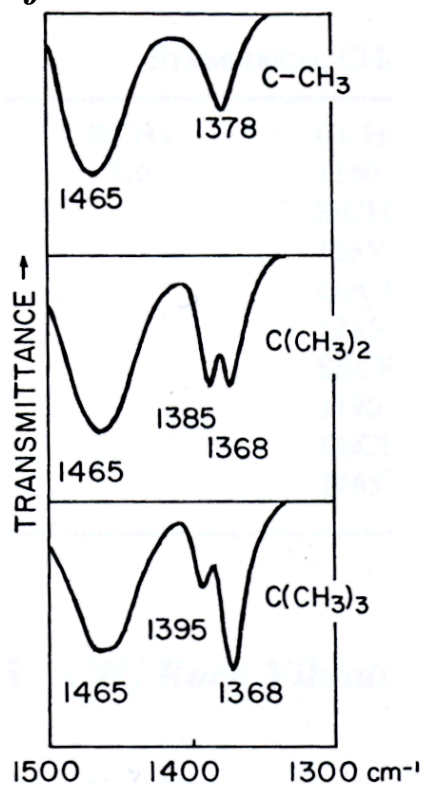
CH$_3$ deformation bands of alkanes

X-sensitive vibrations of X–CH$_3$ groups

Symmetrical CH$_3$ deformation frequencies (cm^{-1}) (±20 cm^{-1})

BCH$_3$	CCH$_3$	NCH$_3$	OCH$_3$	FCH$_3$
1310	1380	1410	1445	1475
	SiCH$_3$	PCH$_3$	SCH$_3$	ClCH$_3$
	1265	1295	1310	1355
	GeCH$_3$	AsCH$_3$	SeCH$_3$	BrCH$_3$
	1235	1250	1282	1305
	SnCH$_3$	SbCH$_3$		ICH$_3$
	1190	1200		1252
	PbCH$_3$			
	1165			

Effects: – electronegativity – mass

CH₃ rocking vibrations (degenerate)

⪢ Si–CH₃	855 – 765 cm⁻¹	(1.90) (electronegativities)
⪢ P–CH₃	960 – 860 cm⁻¹	(2.19)
–S–CH₃	1030 – 950 cm⁻¹	(2.58)
F–CH₃	1182 cm⁻¹	(3.98)
Cl–CH₃	1017 cm⁻¹	(3.16)
Br–CH₃	955 cm⁻¹	(2.96)
I–CH₃	882 cm⁻¹	(2.66)

Electronegativity / mass effect

Mixing with C–C stretching vibrations

Methylene group vibrations

Internal coordinates
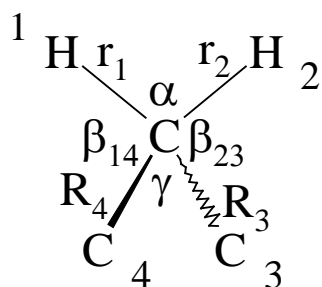
Linear combination of internal coordinates	Absorption region (cm⁻¹) −CH₂−**CH₂**−CH₃
$\nu_a(CH_2) = r_1 - r_2$	2935(35)
$\nu_s(CH_2) = r_1 + r_2$	2865(25)
$\delta(CH_2) = 2\alpha - \beta_{13} - \beta_{14} - \beta_{23} - \beta_{24}$	1460(20)
$\omega(CH_2) = \beta_{13} - \beta_{14} - \beta_{23} + \beta_{24}$	1335(30)
$t(CH_2) = \beta_{13} - \beta_{14} + \beta_{23} - \beta_{24}$	1245(45)
$\rho(CH_2) = \beta_{13} + \beta_{14} - \beta_{23} - \beta_{24}$	780(55)

Symmetric stretch ($\sim$2853 cm^{-1})	
Scissoring ($\sim$1450 cm^{-1})	Wagging ($\sim$1250 cm^{-1})
Asymmetric stretch ($\sim$2926 cm^{-1})	
Rocking ($\sim$720 cm^{-1}) IN-PLANE	Twisting ($\sim$1250 cm^{-1}) OUT-OF-PLANE
STRETCHING VIBRATIONS	**BENDING VIBRATIONS**
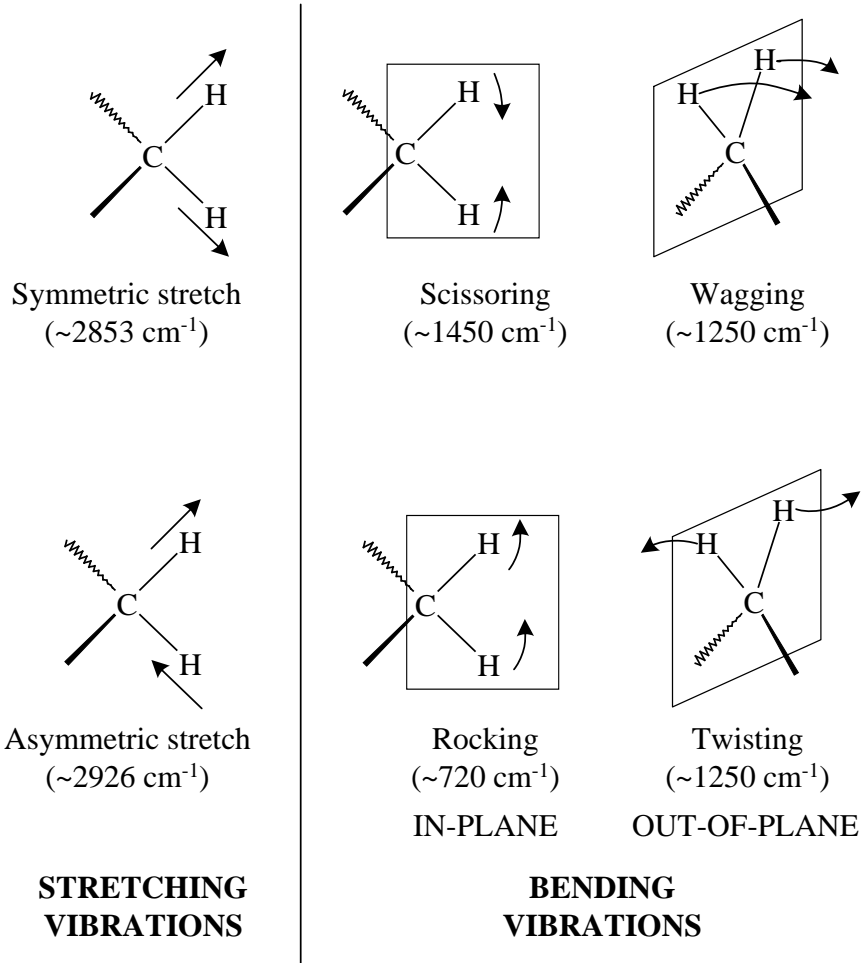
Asymmetric stretch, $\nu_a(CH_2)$: 2925 $\pm$ 10
Symmetric stretch, $\nu_s(CH_2)$: 2855 $\pm$ 10
Both are in very characteristic positions.

	N-CH_2CH_3	P-CH_2CH_3	C-CH_2CH_3	Si-CH_2CH_3	X-CH_2CH_3
ν_a:	2940	2940	2968	2980	3010
ν_s:	2850	2885	2887	2885	2945
½(ν_a+ ν_s)	2895	2913	2928	2918	2978

	△	▢	⬡
ν_a:	3103	2987	2927
ν_s:	3025	2880 (FR)	2852
½(ν_a+ ν_s)	3064	2933	2890

CH₂ deformation vibrations

Scissoring is very close to $\delta_a(CH_3)$ (1465 ± 20 cm^{-1})

X*=	Ph	C=C	C≡C	C=O	S
δ (CH_2)	1450	1435	1430	1410	1400

*X–CH_2Cl group.

CH₂ wag vibrations are spread over a region. These exhibit a special pattern for long CH_2 chains.
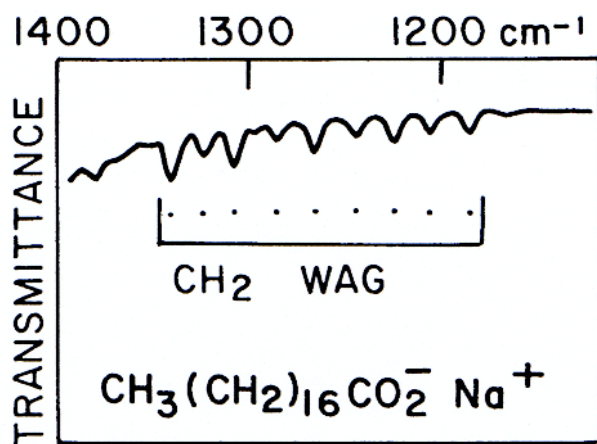
CH$_2$ wag band progression sodium stearate
(range 1350 – 1180 cm^{-1})

Similarly to $\delta_s(CH_3)$ and $\rho(CH_3)$ the $\omega(CH_2)$ shows the same sensitivity to substituent electronegativity:

	–CH$_2$Cl	–CH$_2$S–	–CH$_2$Br	–CH$_2$I
$\omega(CH_2)$	1275	1250	1230	1170 cm^{-1}
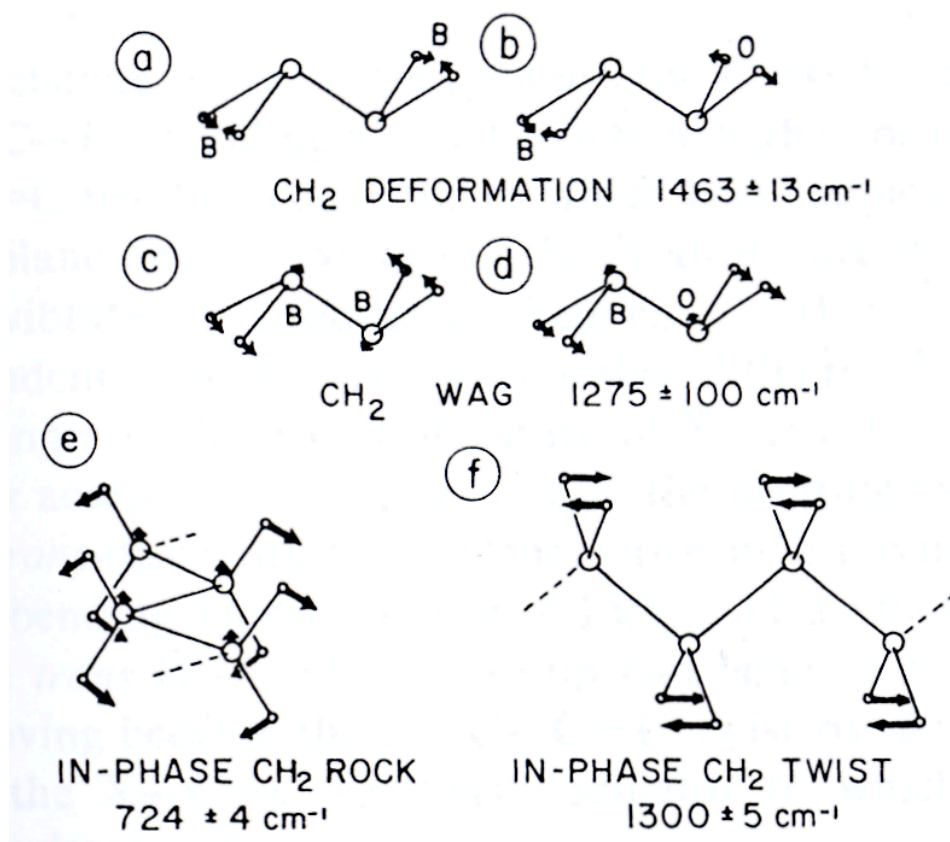
Vibrations of the –CH$_2$–CH$_2$– group.

CH$_2$ rock vibrations have very characteristic weak, medium bands around 720 cm^{-1}. In crystalline state the CH$_2$ rock, ρ(CH$_2$), band splits.

	Splitting of ρ(CH$_2$) modes in crystalline, long CH$_2$ chain.
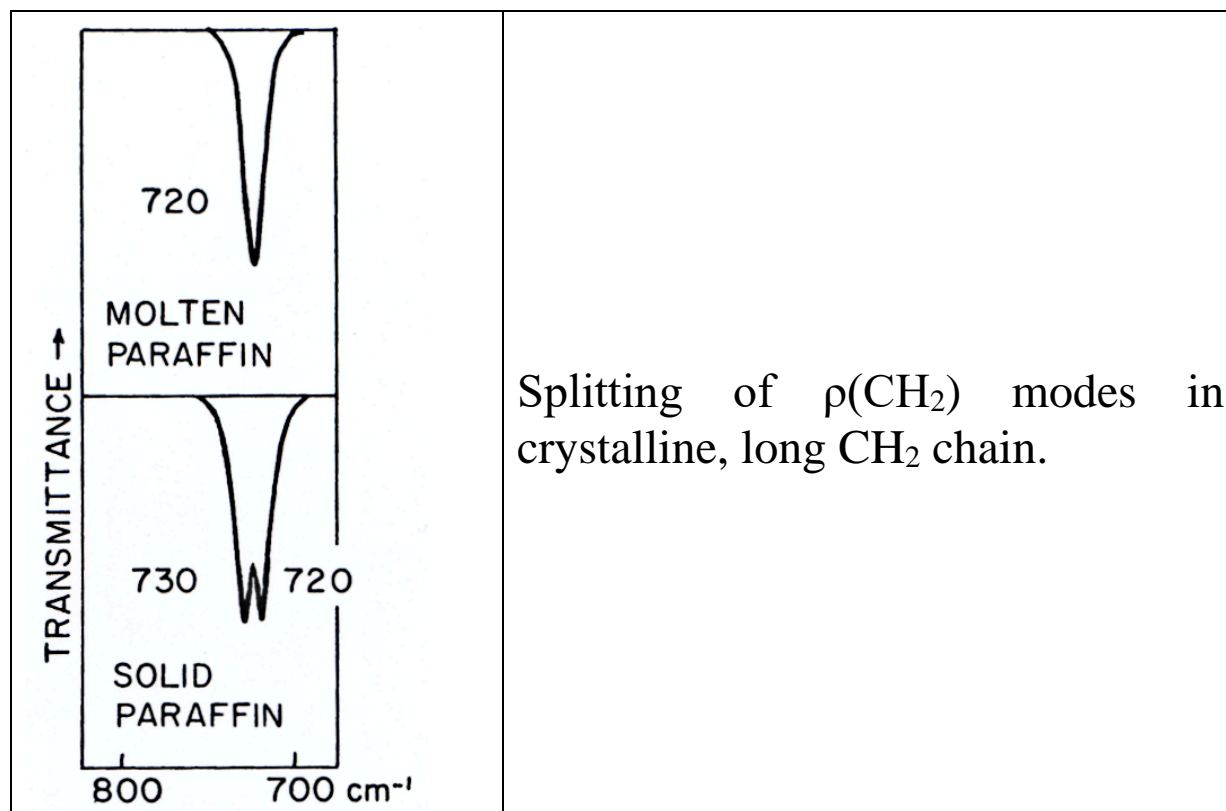
Carbon hydrogen group

Internal coordinates
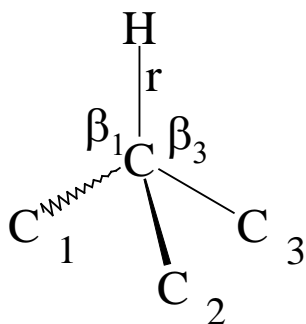
Linear combination of internal coordinates	Absorption region (cm^{-1}) (isopropyl)
ν (CH) = r	2930(20)
γ(CH) = $\beta_2 - \beta_3$	1325(25)
β(CH) = $2\beta_1 - \beta_2 - \beta_3$	1285(45)

The $>$CH group exhibit bands at ~2900 and ~ 1330 cm^{-1} as stretching and bending modes, respectively.

SPECTRAL REGIONS FOR THE CH GROUP (IN cm^{-1})

—O—CH	*ortho*-formates			
	Acetals, *Sec*-peroxides	1350–1315 medium		
—N—CH	Substituted amine			
HO—CH	*Sec*-alcohol free	1410–1350	1300–1200	
	Sec-alcohol bonded	1440–1400	1350–1285	
—CHO	Aldehyde	2900–2800	2775–2695	1420–1370
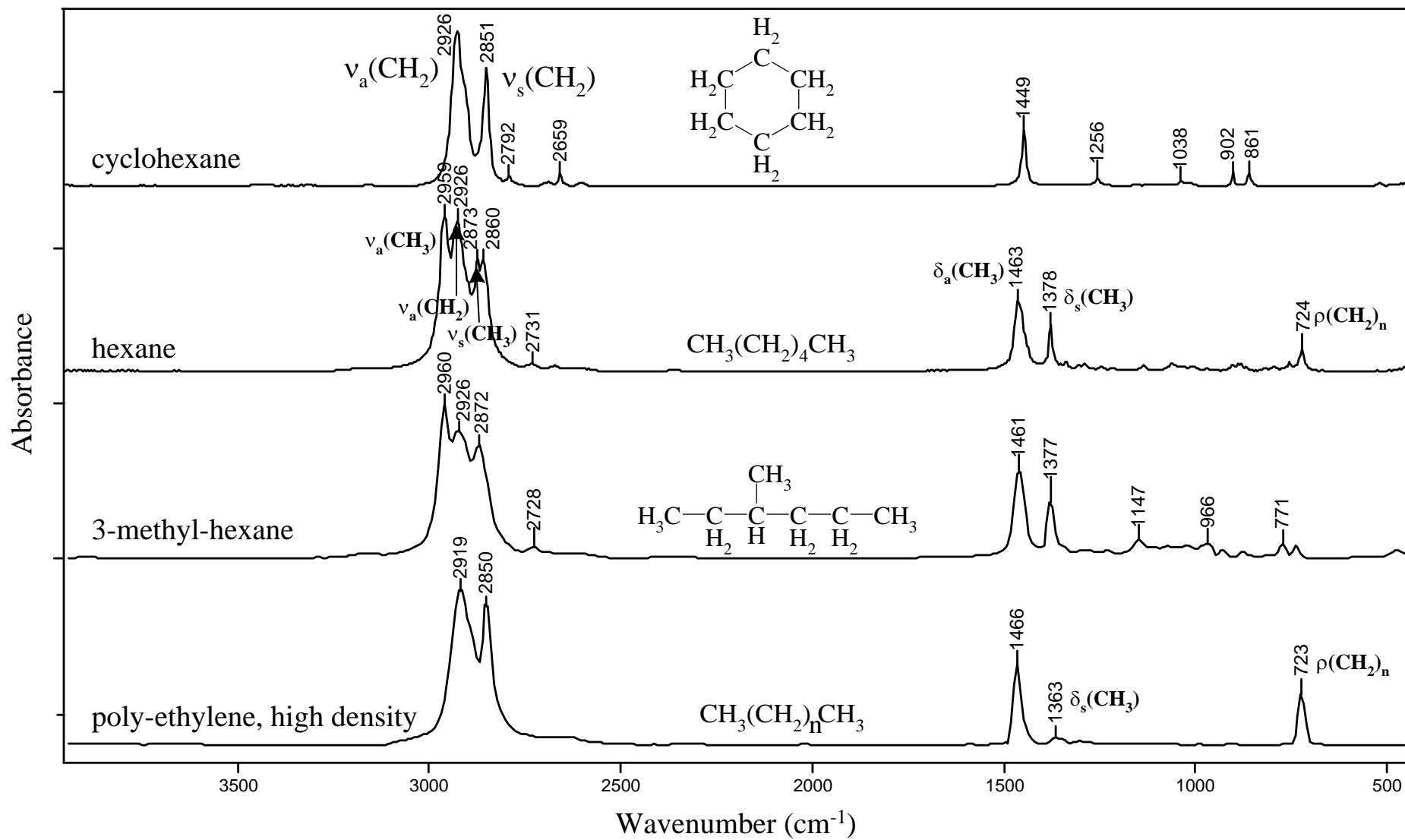
ALKANES

The spectrum is usually simple, with few peaks.

C—H   Stretch occurs around 3000 cm^{-1}.

In alkanes (except strained ring compounds), sp^3 C—H absorption always occurs at frequencies less than 3000 cm^{-1}.

If a compound has vinylic, aromatic, acetylenic, or cyclopropyl hydrogens, the C—H absorption is greater than 3000 cm^{-1}. These compounds have sp^2 and sp hybridizations.

CH$_2$ Methylene groups have a characteristic bending absorption of approximately 1465 cm^{-1}.

CH$_3$ Methyl groups have a characteristic bending absorption of approximately 1375 cm^{-1}.

CH$_2$ The bending (rocking) motion associated with four or more CH$_2$ groups in an open chain occurs at about 720 cm^{-1} (called a long-chain band).

C—C   Stretch not interpretatively useful; many weak peaks.

ALKENES

Noncyclic olefins

   I. The CH stretchings are above 3000 cm^{-1} (sp^2) in 3100–3000 cm^{-1} region
   II. The C=C stretch: 1680–1630 cm^{-1}
       a) IR-variable, Raman-strong
       b) 1680–1665 cm^{-1} *trans-*, *tri-* and *tetra-* subst.
       c) 1660 – 1630 cm^{-1} *vinyl-*, *cis-*, *vinylidine*.
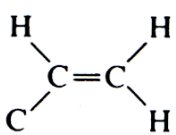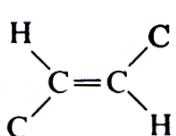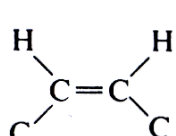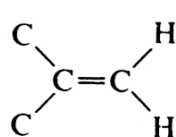   III. Out-of-plane CH deformation vibrations are very good group frequencies (1000–650 cm^{-1})

OUT-OF-PHASE CH$_2$ STRETCH 3080 cm^{-1}

"TRANS" CH WAG 990 cm^{-1}

CH STRETCH 3010

CH$_2$ WAG 910

IN-PHASE CH$_2$ STRETCH 2985

"CIS" CH WAG 630

C=C STRETCH 1640

TRANS CH WAG 970

CH$_2$ DEFORMATION 1415

CH$_2$ WAG 890

CH ROCK 1300

CIS CH WAG 680

CH$_2$ ROCK 1075

CH WAG 825
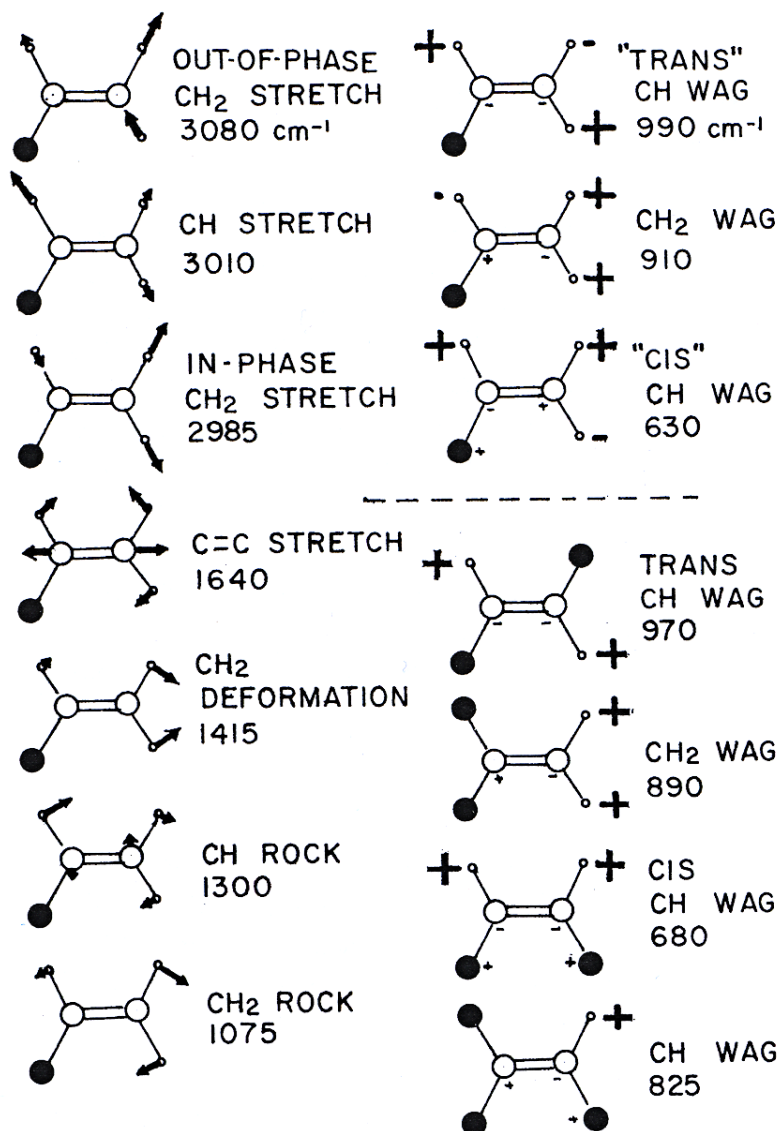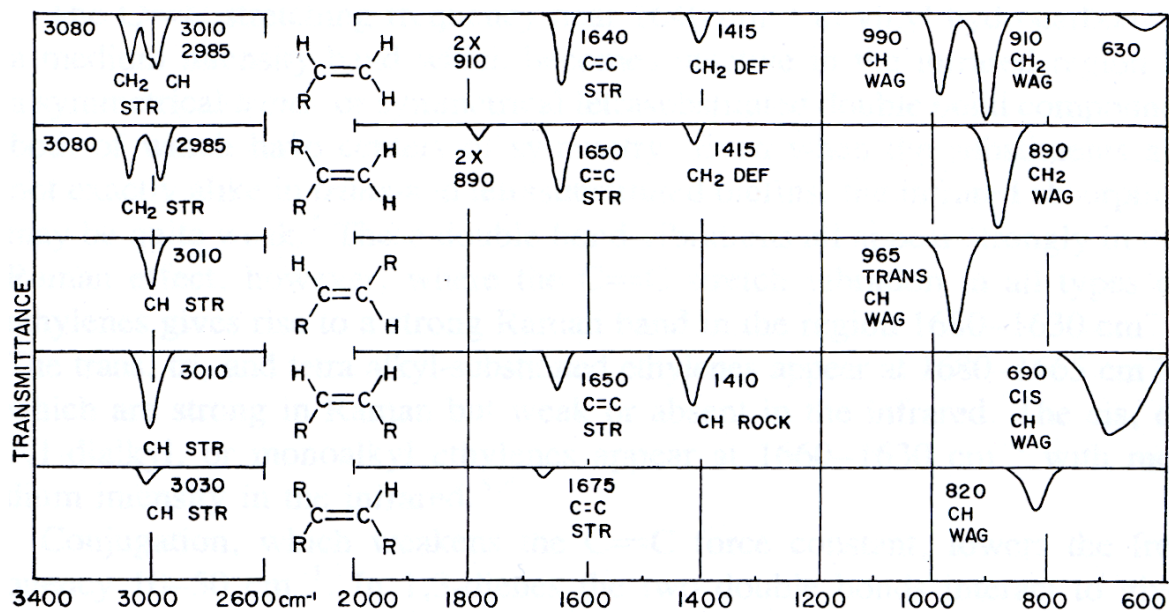
Olefin vibrations
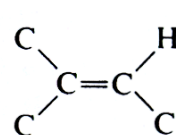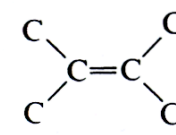
General IR spectra expected for ethylenes with alkane substituents.
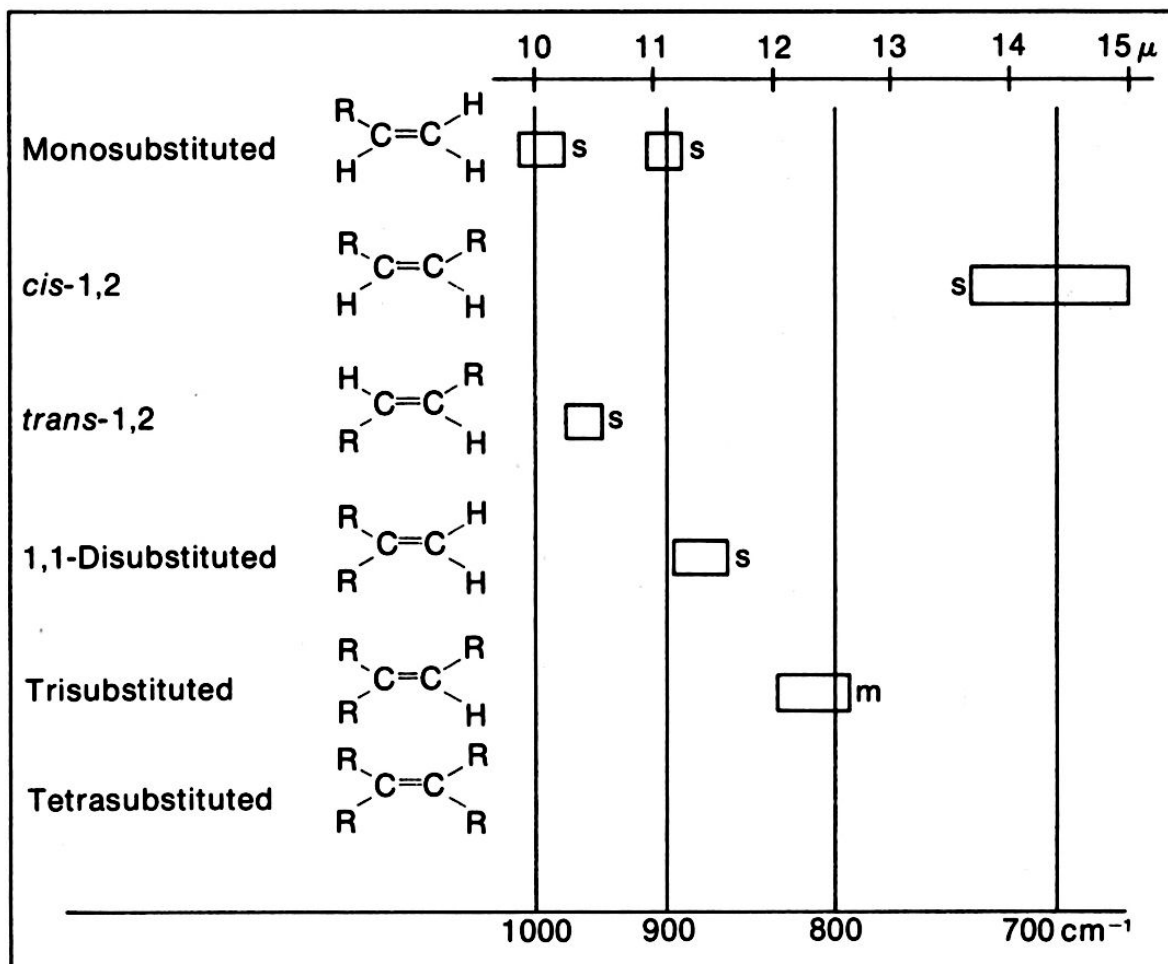
The C—H out-of-plane bending vibrations for substituted alkenes.

Vinyl	3100–3070	Medium CH$_2$ asymmetric stretch
	3025–3012	Medium CH stretch
	1840–1805	Medium 2 × CH$_2$ wag
	1648–1638	Medium C=C Stretch
	1420–1412	Medium CH$_2$ deformation
	995– 985	Strong *trans* CH wag
	910– 905	Strong CH$_2$ wag
trans	3020–2995	Medium CH stretch
	1678–1668	Weak or absent (strong Raman band) C=C stretch
	980– 965	Strong *trans* CH wag
cis	3020–2995	Medium CH stretch
	1662–1631	Medium C=C stretch
	1429–1397	Medium CH rock
	730– 650	Medium to strong *cis* CH wag
Vinylidine	3100–3070	Medium CH$_2$ asymmetric stretch
	1792–1775	Medium 2 × CH$_2$ wag
	1661–1639	Medium C=C stretch
	895– 885	Strong CH$_2$ wag
Trisubstituted	3050–2990	Weak CH stretch
	1692–1667	Weak C=C stretch
	840– 790	Medium to strong CH wag
Tetrasubstituted	1680–1665	Weak or absent (strong Raman band) C=C stretch

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$$\underset{\displaystyle \overset{|}{\diagup}}{C}=\underset{\displaystyle \overset{H\oplus}{\diagdown H\oplus}}{C}$$
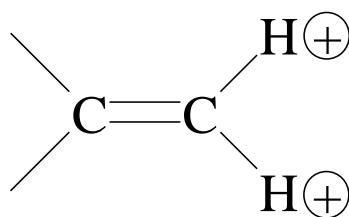
CH$_2$ WAGGING FREQUENCIES (IN cm^{-1})

R—O—CO—CH=CH$_2$	961
N≡C—CH=CH$_2$	960
R—CH=CH$_2$	910
Cl—CH=CH$_2$	894
R—CO—O—CH=CH$_2$	870
R—CO—N—CH=CH$_2$	840
R—O—CH=CH$_2$	813

$$\underset{\displaystyle N\equiv C}{\overset{\displaystyle N\equiv C}{\diagdown}}C=CH_2 \qquad 985$$

$$\underset{\displaystyle R-O-CO}{\overset{\displaystyle R}{\diagdown}}C=CH_2 \qquad 939$$

$$\underset{\displaystyle Cl}{\overset{\displaystyle N\equiv C}{\diagdown}}C=CH_2 \qquad 916$$

$$\underset{\displaystyle R}{\overset{\displaystyle R}{\diagdown}}C=CH_2 \qquad 890$$

$$\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\diagdown}}C=CH_2 \qquad 867$$

$$\underset{\displaystyle R-O}{\overset{\displaystyle R}{\diagdown}}C=CH_2 \qquad 795$$

$$\underset{\displaystyle R-O}{\overset{\displaystyle R-O}{\diagdown}}C=CH_2 \qquad 711$$

$$
\begin{array}{c}
\overset{\oplus}{\text{H}} \qquad\qquad \text{R} \\
\backslash \qquad\qquad / \\
\text{C} == \text{C} \\
/ \qquad\qquad \backslash \\
\text{R}' \qquad\qquad \text{H}\oplus
\end{array}
$$

Trans-CH WAGGING FREQUENCIES (IN cm^{-1})

$(CH_3)_3Si-CH=CH_2$	1009
$R-CH=CH_2$	990
$R-O-CO-CH=CH_2$	982
$R-CO-N-CH=CH_2$	972
$R-O-CH=CH_2$	960
$R-CO-O-CH=CH_2$	950
$Cl-CH=CH_2$	938
$R-O-CO-CH=CH-CO-O-R$ *trans*	976
$CH_3-CH=CH-CO-O-R$ *trans*	968
$R-CH=CH-R$ *trans*	964
$CH_3-CH=CH-C\equiv N$ *trans*	953
$CH_3-CH=CH-Cl$ *trans*	926
$Cl-CH=CH-C\equiv N$ *trans*	920
$Cl-CH=CH-Cl$ *trans*	892

ν(=CH)   ν(C=C)   γ(CH)

1-hexene

2-methyl-1-pentene

trans-2-pentene

cis-2-pentene

2-methyl-2-butene

2,3-dimethyl-2-butene

Absorbance

Wavenumber (cm^{-1})
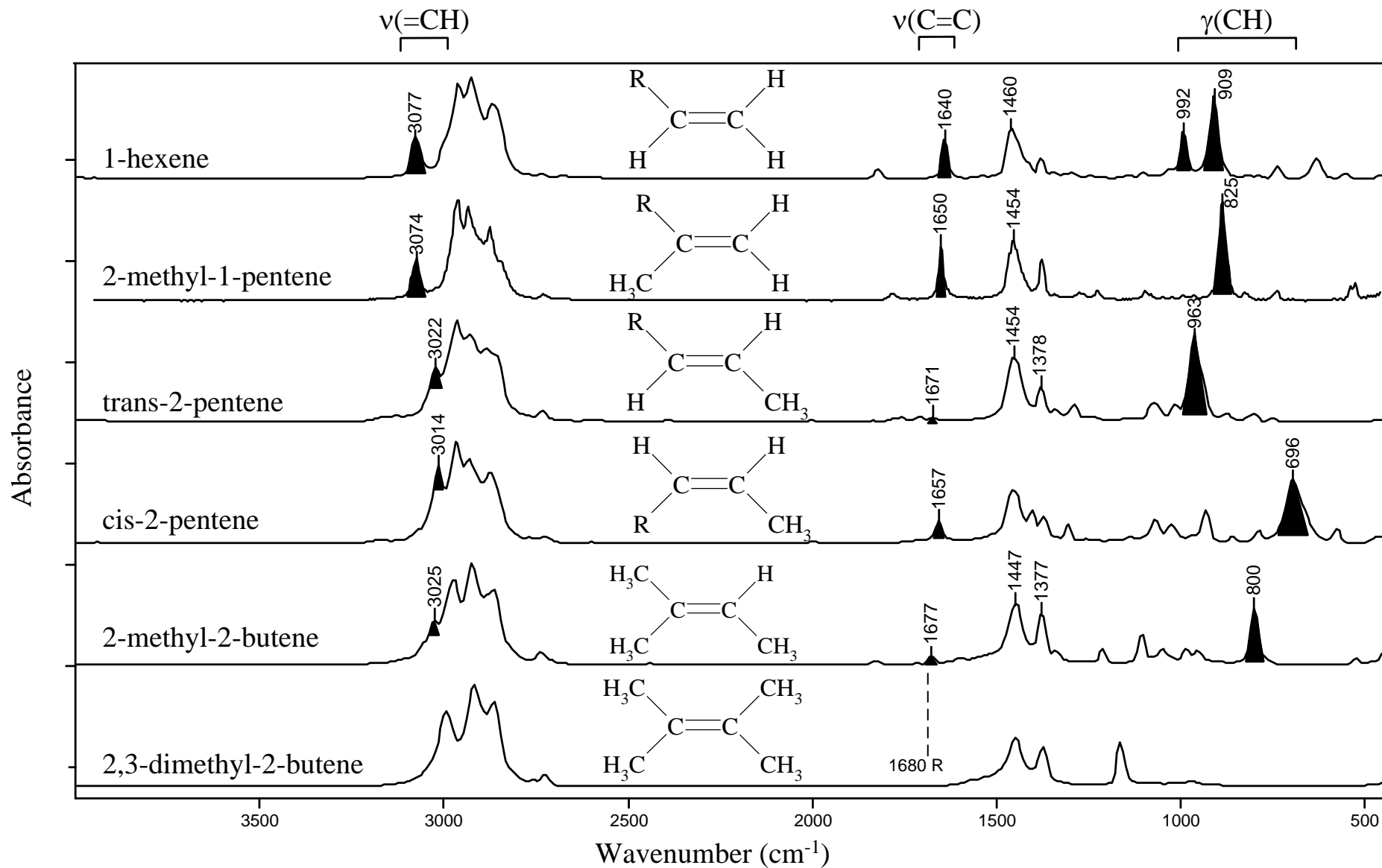
External cyclic C=C

Increasing $\nu(C=C)$ – increasing interaction with the C–C bonds

| 1940 cm^{-1} | 1780 | 1678 | 1657 | 1655 | 1651 |

Exo double bonds
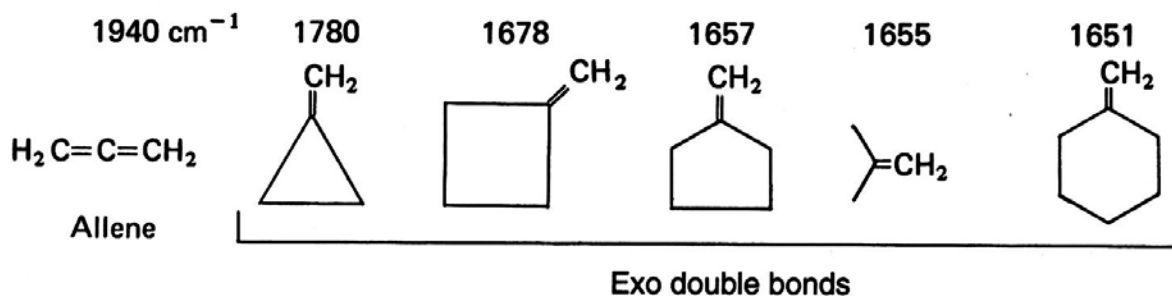
(a) Strain moves the peak to the left.

(b) Ring fusion moves the absorption to the left.

1687 cm^{-1} 1668 cm^{-1}
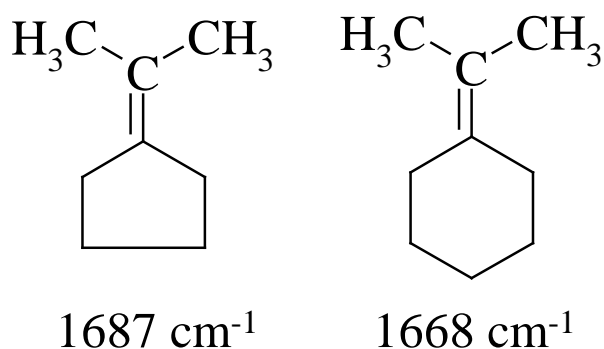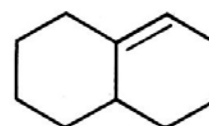
Internal cyclic C=C

It is similar to noncyclic *cis* counterpart (1660–1630 cm^{-1}).
As the ring gets smaller, the C=C / C–C interaction decreases.
This interaction is minimum at 90° (cyclobutane)
(Stretch–stretch interaction term $G_{RR} = \mu_c \cdot \cos\varphi$)

1656 cm^{-1}	1788 cm^{-1}	1883 cm^{-1}
1566 cm^{-1}	1641 cm^{-1}	1675 cm^{-1}
1611 cm^{-1}	1650 cm^{-1}	1679 cm^{-1}
1646 cm^{-1}	1675 cm^{-1}	1681 cm^{-1}
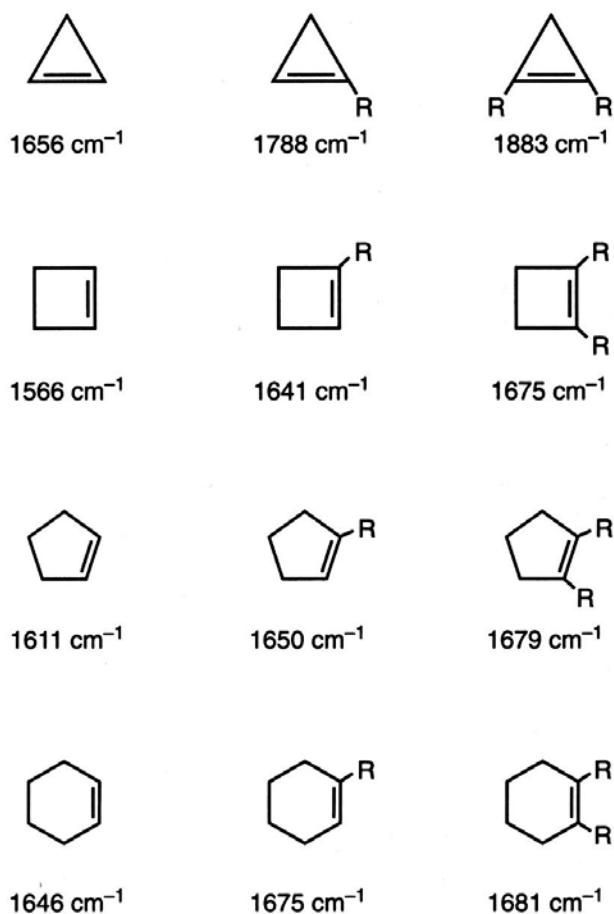
Effects of ring size and alkyl substitution (R=CH$_3$)

Triple bonds and accumulated double bonds

Frequency range: 2300–1900 cm^{-1}
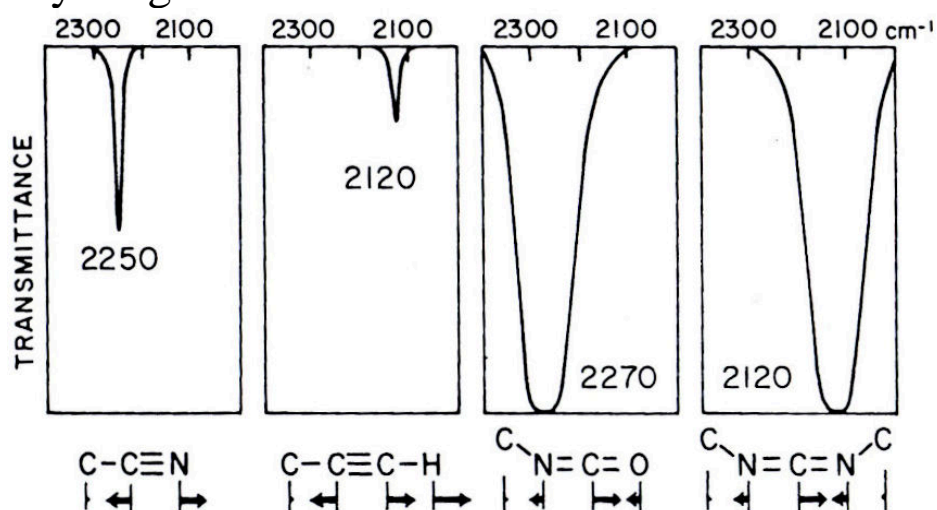
Bands expected for various triple bond and cumulated double bond stretching vibrations
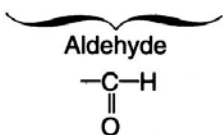
≡C—H stretch	3340–3267 cm^{-1}	Strong
C≡C stretch	2140–2100	Weak[1] in hydrocarbons
Overtone CH wag	1375–1225	Weak–broad
≡C—H wag	700–610	Strong–broad
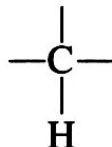
The 2300–1900 cm^{-1} Region

—C≡C—H	2140–2100 cm^{-1}	Weak–variable
—C≡C—	2260–2190	Very weak-variable
C=C=CH$_2$	2000–1900	Strong
CH$_2$—C≡N	2260–2240	Medium weak
C=C—C≡N	2235–2215	Medium
aryl-C≡N	2240–2220	Variable
—C≡N→O	2304–2288	Strong
—N=C=O	2275–2263	Very strong
—S—C≡N	2170–2135	Medium strong
—N=C=S	2150–2050	Very strong
>N—C≡N	2225–2175	Strong
—N=C=N—	2150–2100	Very strong
>C=C=N—	2050–2000	Very strong
—CH=$\overset{+}{N}$=$\overset{-}{N}$	2132–2012	Very strong
--N=$\overset{+}{N}$=$\overset{-}{N}$	2170–2080	Very strong
aryl-$\overset{+}{N}$≡N	2309–2136	Medium
—$\overset{+}{N}$≡$\overset{-}{C}$	2165–2110	Strong
>C=C=O	2200–2100	Very strong
[C≡N]$^-$	2200–2070	Medium
[Fe(C≡N)$_6$]$^{4-}$	2010	Medium
[Fe(C≡N)$_6$]$^{3-}$	2100	Medium
[N=C=O]$^-$	2220–2130	Strong
[N=C=S]$^-$	2090–2020	Strong
metal(CO)	2170–1900	Strong

Summary of the CH stretching of different hydrocarbons.

| 3300 cm⁻¹ | 3100 | 3000 | 2850 | 2750 |

$3300\ cm^{-1}$ 3100 3000 2850 2750

Acetylenic ≡C—H	Vinyl =C—H	Aliphatic C—H	Aldehyde
	Aromatic =C—H	(see Table 2-6)	—C—H
	Cyclopropyl —C—H		‖
			O

sp sp^2 sp^3

←——— Strain moves absorption to left

←——— Increasing *s* character moves absorption to left

Stretching Vibrations for Various *sp³*-Hybridized C—H Bonds

Group		Stretching Vibration (cm^{-1})	
		Asymmetric	**Symmetric**
Methyl	CH_3—	2962	2872
Methylene	—CH_2—	2926	2853
Methine	—$\overset{\displaystyle \mid}{\underset{\displaystyle H}{C}}$—	2890	Very weak