Calculation of IR & NMR Spectra

(Measuring nuclear vibrations and spins)

2019

Lecture Outline

- **EM** spectrum

- **IR** – vibrations of nuclei on the electronic PES
  - Theory
  - Calculation scheme
  - Strengths & limitations
  - Calculations vs. experiment

- **NMR** – effect of electronic environment on nuclear spin transitions
  - Theory
  - Calculation of **shielding tensor**
  - Calculation vs. experiment
  - Advanced topic: Calculation of **spin-spin coupling**

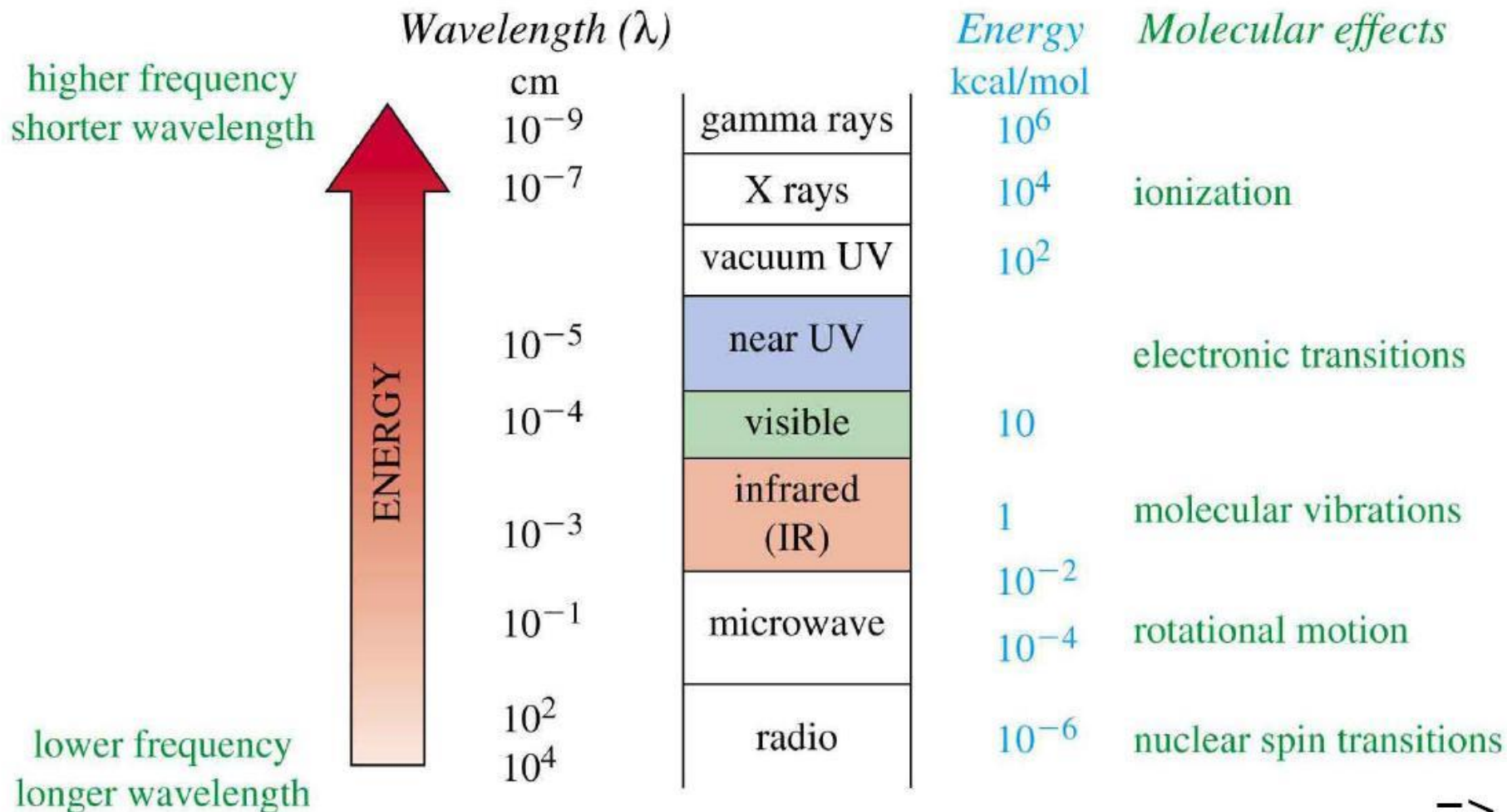# EM spectrum

Electromagnetic (EM) Spectrum

• <u>Examples</u>: X rays, UV, visible light, IR, microwaves, and radio waves.

• Frequency and wavelength are inversely proportional:

$$c = \lambda \nu$$

(c is the speed of light)

Energy per photon = hν, where h is Planck's constant.

The Spectrum and Molecular Effects

Wavelength (λ)		Energy	Molecular effects
cm		**kcal/mol**	
10^{-9}	gamma rays	10^6	
10^{-7}	X rays	10^4	ionization
	vacuum UV	10^2	
10^{-5}	near UV		electronic transitions
10^{-4}	visible	10	
10^{-3}	infrared (IR)	1	molecular vibrations
		10^{-2}	
10^{-1}	microwave	10^{-4}	rotational motion
10^2 10^4	radio	10^{-6}	nuclear spin transitions

higher frequency
shorter wavelength

ENERGY

lower frequency
longer wavelength

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IR spectroscopy

- *Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group and to confirm molecule-wide structure ("fingerprint").*
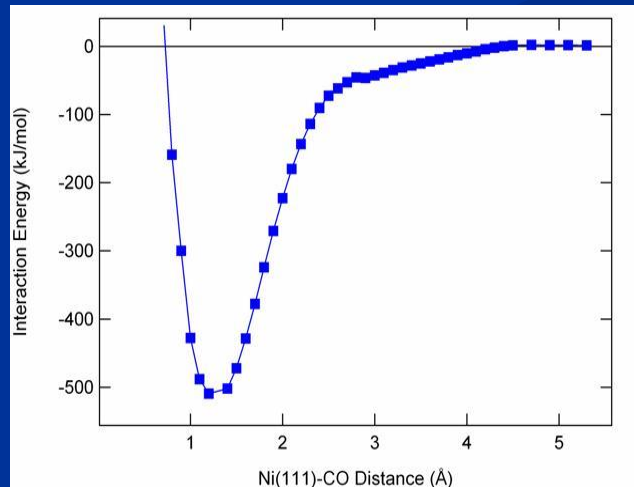
IR: Some theory

Born-Oppenheimer calculation of the PES:

$$H=H_e+H_n$$

$$\Psi=\Psi_e\,\Psi_n$$

$$(T_k+E_e(R))\,\Psi_n=E_n\,\Psi_n$$

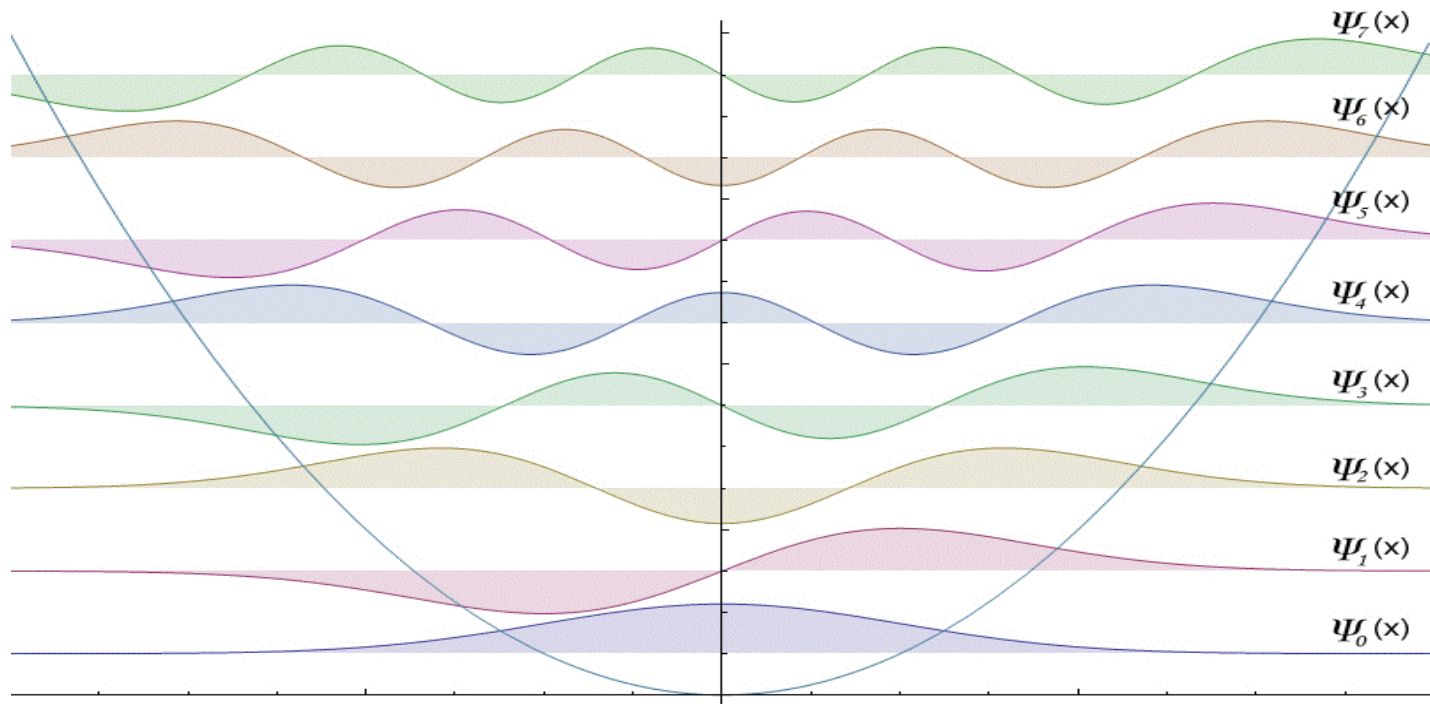# Separation of Vibrational and Rotational motion

(with good accuracy)

$$H_n = H_v + H_r$$
$$\Psi_n = \Psi_v \Psi_r$$
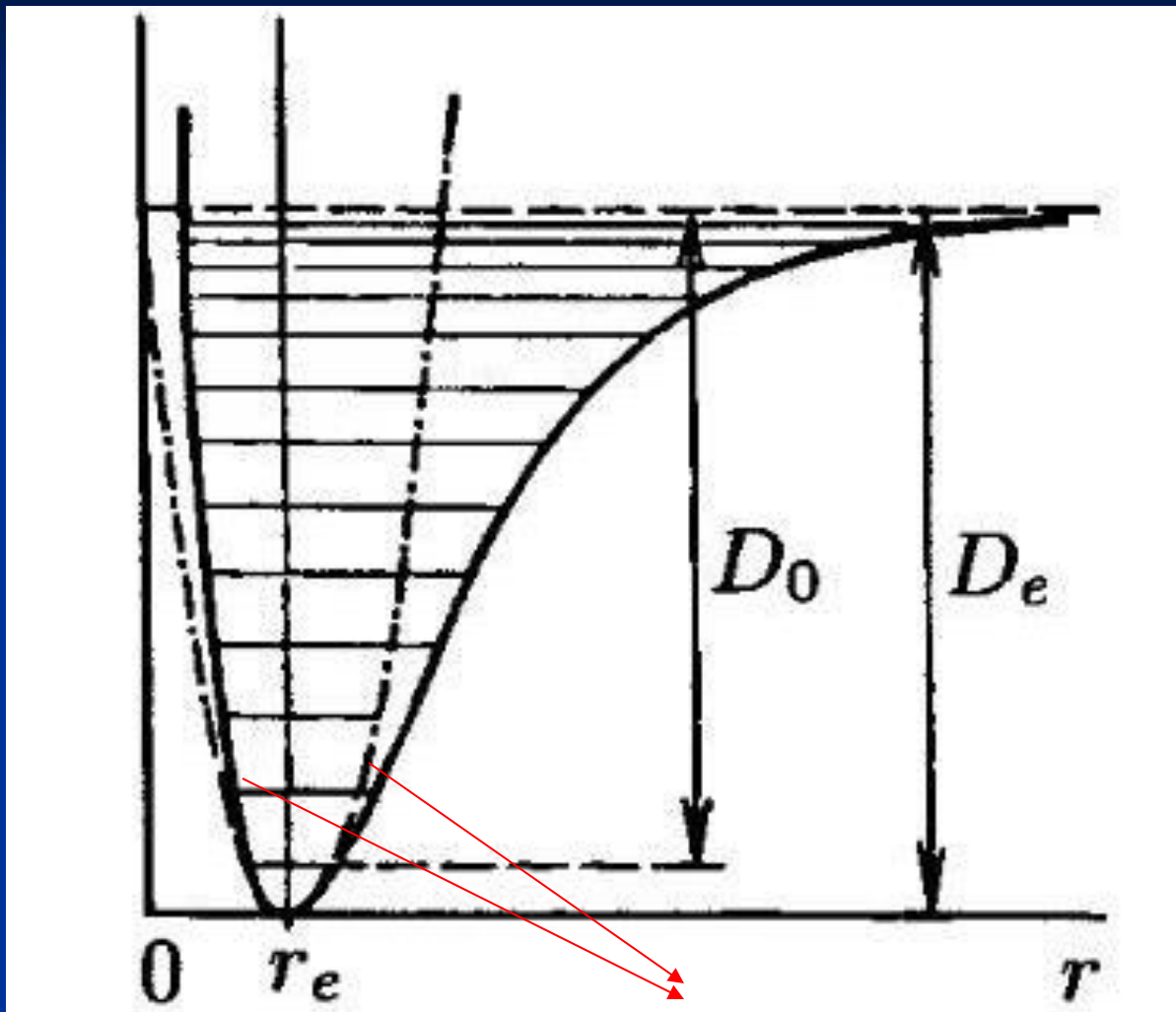
We are interested in the *vibrational* spectrum

Harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \,,$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

Diatomic molecule: 1-D PES

In the vicinity of r_e, the potential looks like a HO!!!

Harmonic approximation near the energy minimum

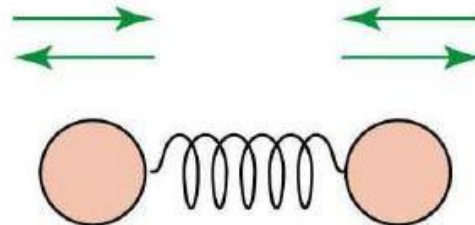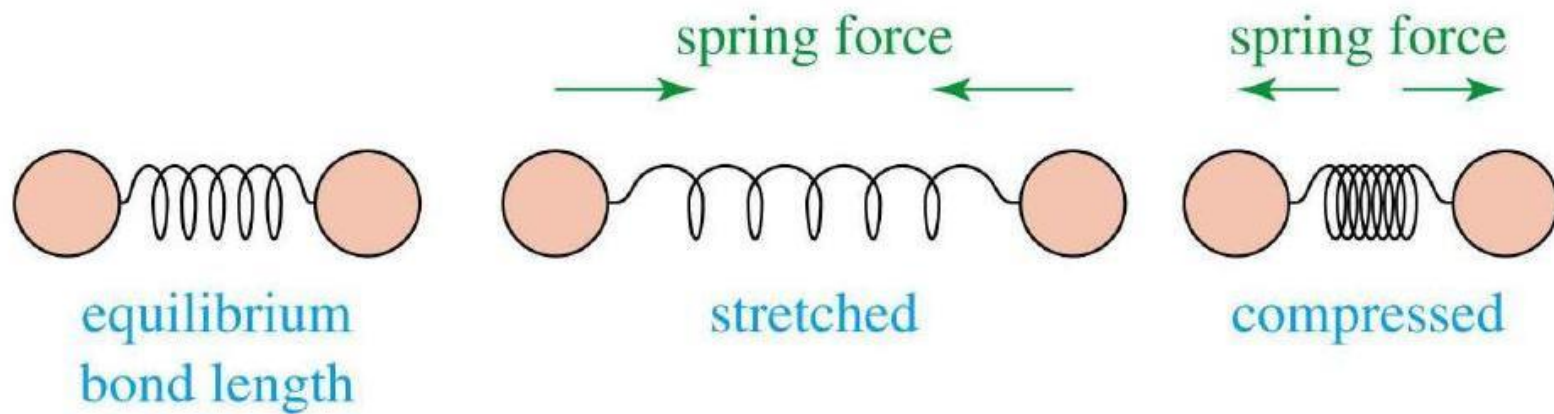$$V(x) = V(r_e) + V'(r_e)(r - r_e) + \frac{1}{2}V''(r_e)(r - r_e)^2 + ..$$

0

$$V(x) = \frac{1}{2}V''(r_e)(r - r_e)^2$$

Molecular vibrations

Covalent bonds vibrate at only certain allowable frequencies.

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How can we extract the vibrational frequencies (ω) if the potential is known?

$$V(x) = \frac{1}{2}mw^2x^2$$

$$w^2 = \frac{1}{m}\frac{d^2V(x)}{dx^2}$$

That's the potential from our previous calculations!!!

Steps of calculations

1. Calculate the potential $= V_e (R)$

2. Calculate ω^2

3. Work done! We know the spectrum

Polyatomic molecules

- Normal modes (classical)
- Question: how many internal degrees of freedom for molecule with N atoms ?
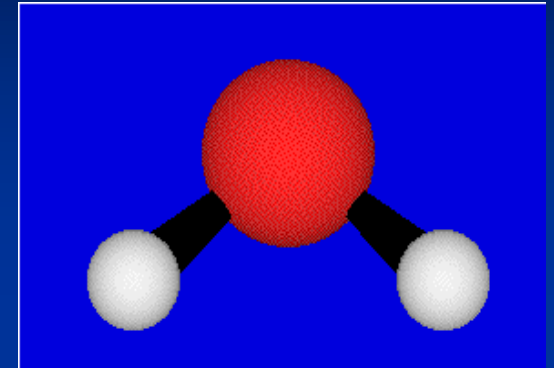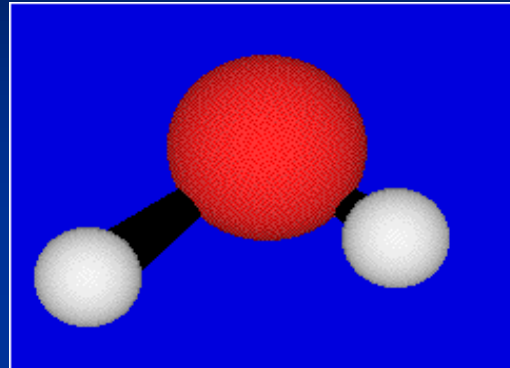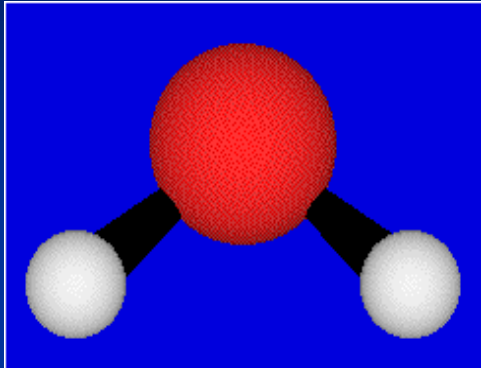
Answer:

$3N-5$ for linear molecule

$3N-6$ for nonlinear

Normal modes

For molecule with N atoms every vibration can be expand as a sum of *3N-6 (3N-5)* independent modes i.e. in the vicinity of the equilibrium geometry we have *3N-6* **independent** harmonic oscillators

(with frequencies $\omega_i=1...(3N-6))$.

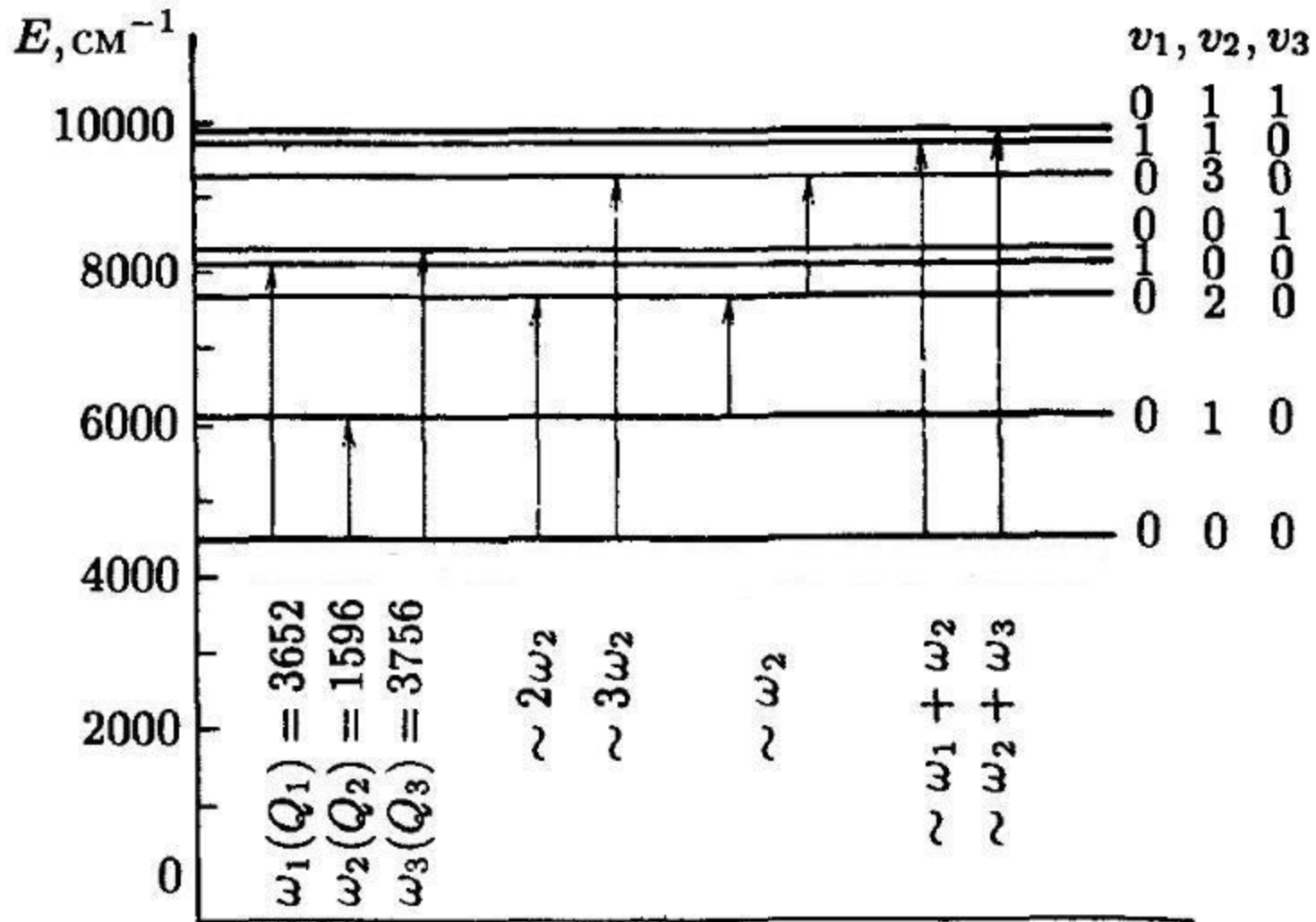$$E(v_1, v_2 .. v_{3N-6}) = \sum_{i=1}^{3N-6} hw_i\left(v_i + \frac{1}{2}\right)$$

Example: Water

Number of modes = 3x3-6 = 3

$$E(0, 0, 0) = \frac{1}{2} \sum_{i=1}^{3} h w_i = 4502 \, cm^{-1}$$

Transitions in state-space

Normal Mode Calculation

- The harmonic vibrational spectrum of the 3N-dim. PES:

$$V(R) = V(R_e) + V'(R_e)(R - R_e) + \tfrac{1}{2}V''(R_e)(R - R_e)^2 + \cdots + \tfrac{1}{n!}\left(\frac{d^n V}{dR^n}\right)_{R=R_e}(R - R_e)^n + \cdots$$

- Solve the B-O electronic Hamiltonian at each nuclear configuration to produce the PES, V(R):

$$\left(\hat{H}_e + V_{NN}\right)\psi_e = V\psi_e$$

- Create the force constant (k) matrix, which is the matrix of second-order derivatives: $\left(\dfrac{\partial^2 V}{\partial R_i \partial R_j}\right)_{eq.}$

- The mass-weighted matrix is the **Hessian**: $\omega^2 = \dfrac{k}{m} \Rightarrow \dfrac{1}{\sqrt{m_i m_j}}\left(\dfrac{\partial^2 V}{\partial R_i \partial R_j}\right)_{eq.} = H_{ij}$

- Diagonalize the Hessian to get **eigenvalues**, λ_k, and **eigenvectors**, l_{jk}:

$$\sum_{i,j=1}^{3N}\left(H_{ij} - \delta_{ij}\lambda_k\right)l_{jk} = 0$$

- Find the 3N roots of the **secular equation** $\left|H_{ij} - \delta_{ij}\lambda_k\right| = 0$

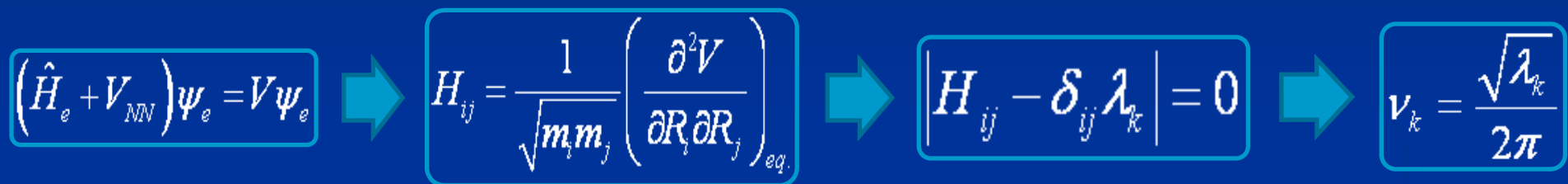- **Six of the roots should be zero** (rigid body degrees of freedom: Translation and rotation) The rest are vibrational modes. $\quad \nu_k = \dfrac{\omega_k}{2\pi} = \dfrac{\sqrt{\lambda_k}}{2\pi}$

Normal Mode Calculation

$$\left(\hat{H}_e + V_{NN} \right) \psi_e = V \psi_e$$

$$H_{ij} = \frac{1}{\sqrt{m_i m_j}} \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_{eq.}$$

$$\left| H_{ij} - \delta_{ij} \lambda_k \right| = 0$$

$$\nu_k = \frac{\sqrt{\lambda_k}}{2\pi}$$

Solve the electronic BO problem at each nuclear configuration to get PES.

The Hessian is the mass-weighted matrix of the second-order derivatives.

Diagonalize the Hessian by solving the secular equation, finding 3N roots, six (or five) of which aren't vibrations.

Vibrational frequencies are related to the square root of the eigenvalues.

- What would it mean if we got **too few non-zero roots**?
- When would we get one **negative vibrational frequency**?

Stretching Frequencies

Bond	Bond Energy [kcal (kJ)]		Stretching Frequency (cm^{-1})
Frequency dependence on atomic masses			
C—H	100	(420)	3000
C—D	100	(420)	2100
C—C	83	(350)	1200
Frequency dependence on bond energies			
C—C	83	(350)	1200
C=C	146	(611)	1660
C≡C	200	(840)	2200

C—H, C—D, C—C: heavier atoms

$\bar{\nu}$ decreases

C—C, C=C, C≡C: stronger bond

$\bar{\nu}$ increases

- Frequency decreases with increasing atomic weight.

- Frequency increases with increasing bond energy.

=>

Molecular Fingerprint

- Whole-molecule vibrations and bending vibrations are also quantized.

- No two molecules will give exactly the same IR spectrum (except enantiomers).

- Delocalized vibrations have lower energy (cf. "particle in a box"):

  - Simple stretching: 1600-3500 cm^{-1}.

  - Complex vibrations: 600-1400 cm^{-1}, called the "fingerprint region."

# An Alkane IR Spectrum
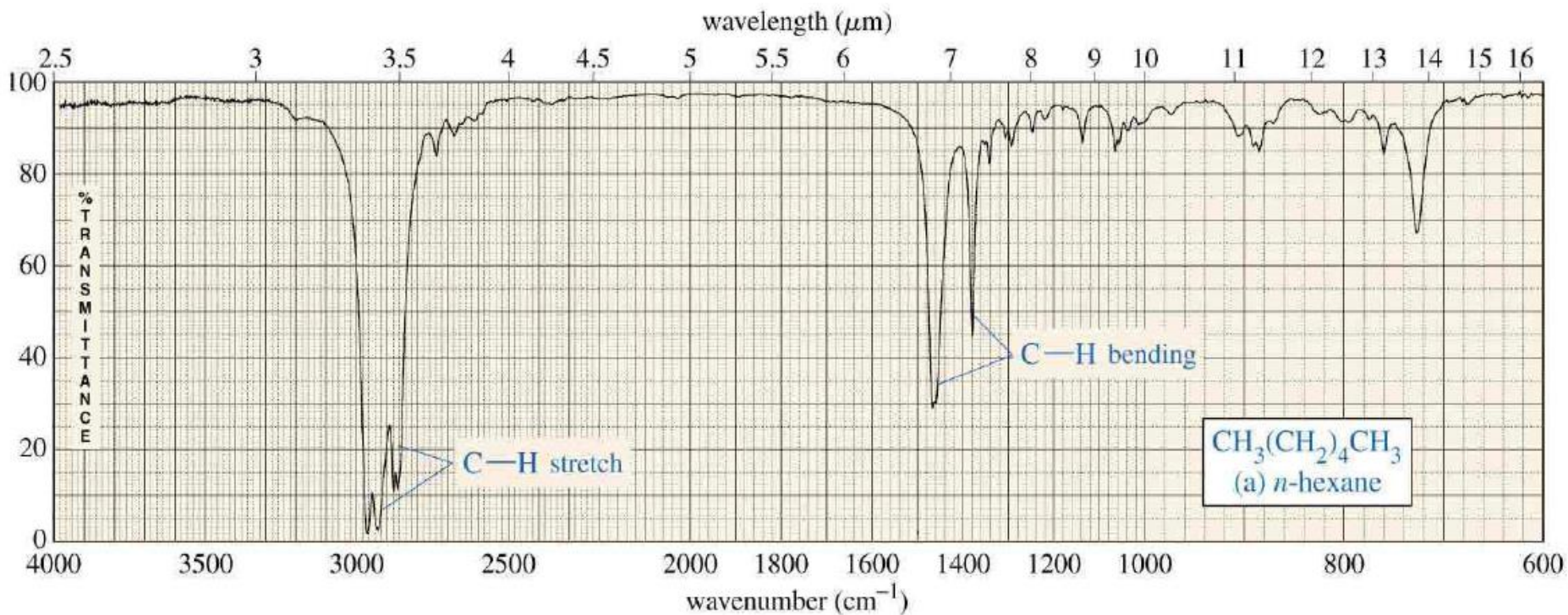
Summary of IR Absorptions
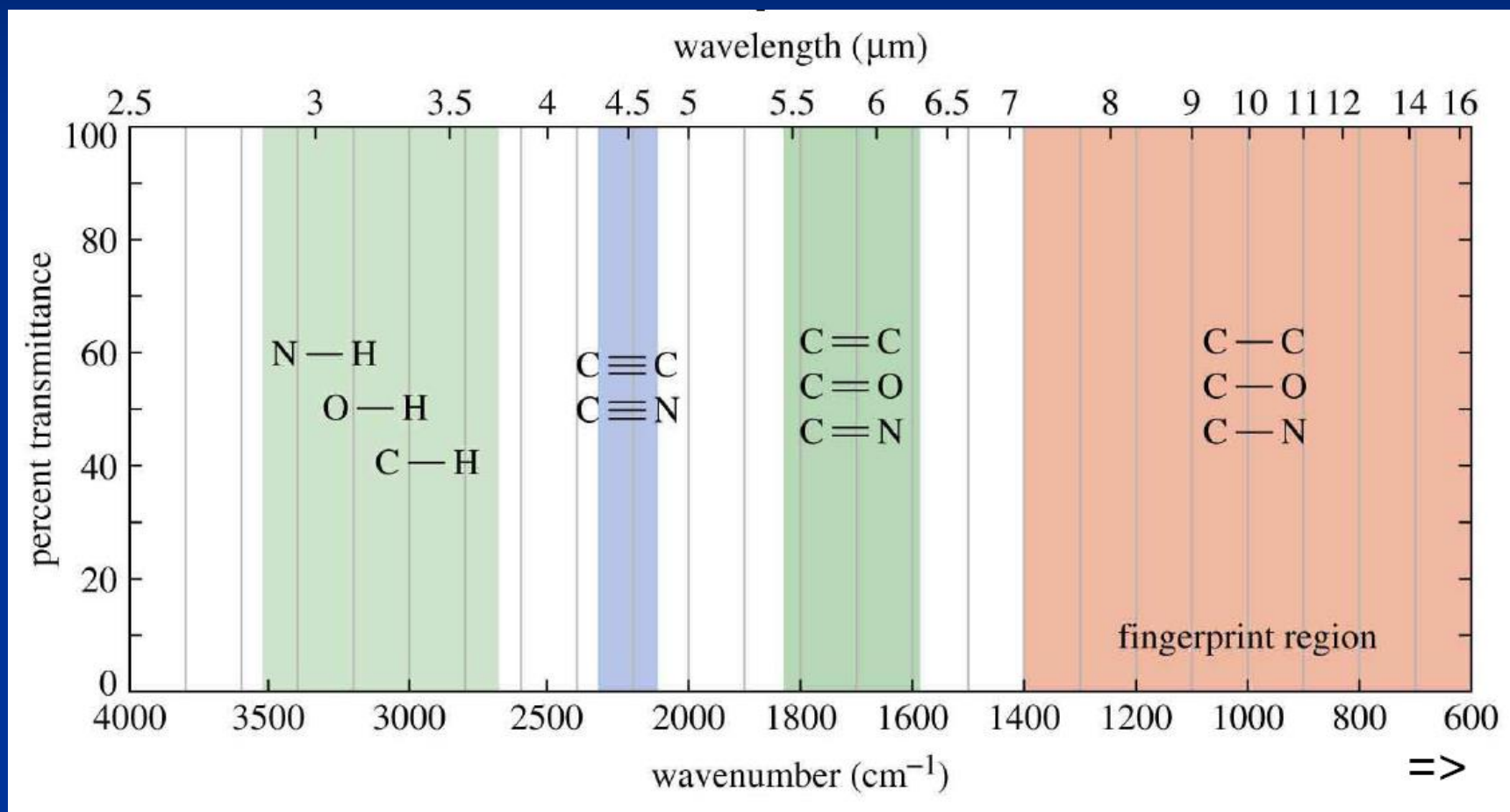
Strengths and Limitations

- IR alone cannot **determine** a structure.

- Some signals may be **ambiguous**.

- **Functional groups** are usually indicated.

- The **absence** of a signal is definite proof that the functional group is **absent**.

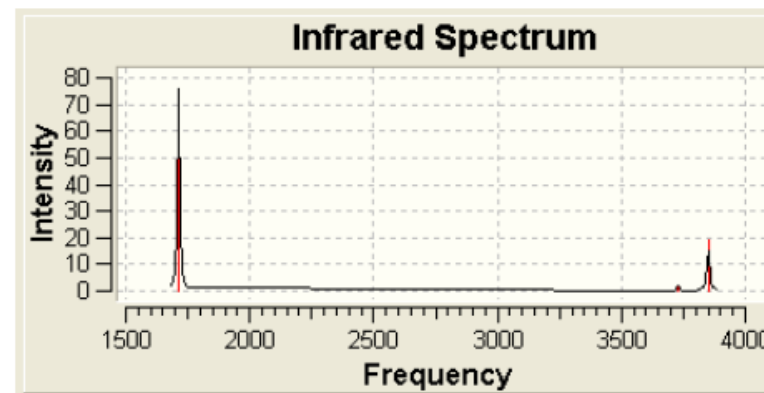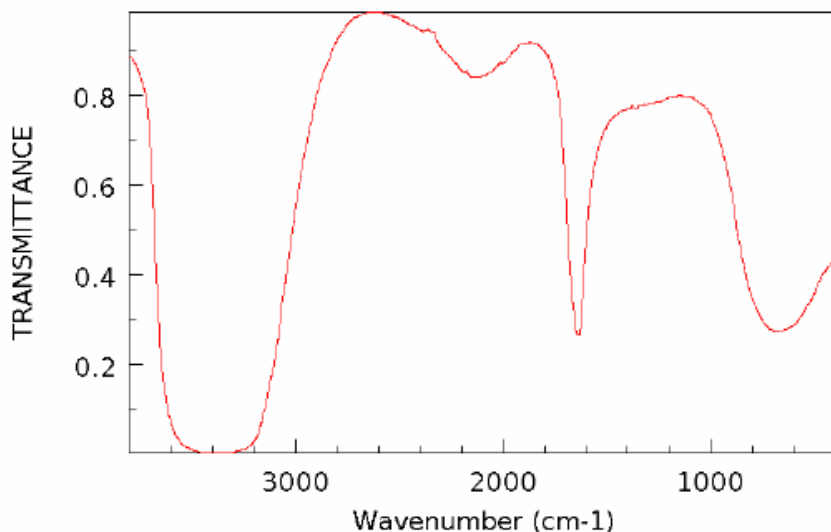- **Correspondence** with a known sample's IR spectrum confirms the identity of the compound.

IR Calculation vs. Experiment

Example:
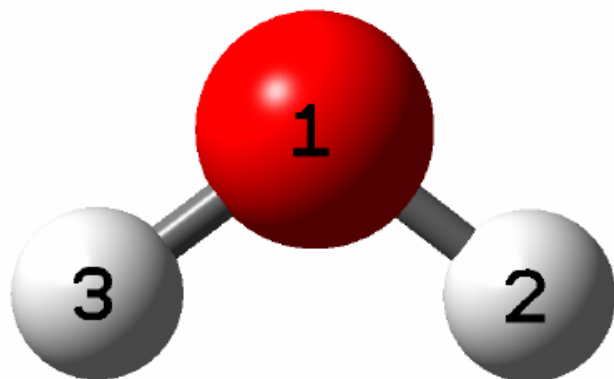
Method	DFT
Basis	6-31G(d)
Peak #	Freq. cm^{-1}
1	1712.8
2	3728.44
3	3850.58

WATER
INFRARED SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Infrared Spectrum
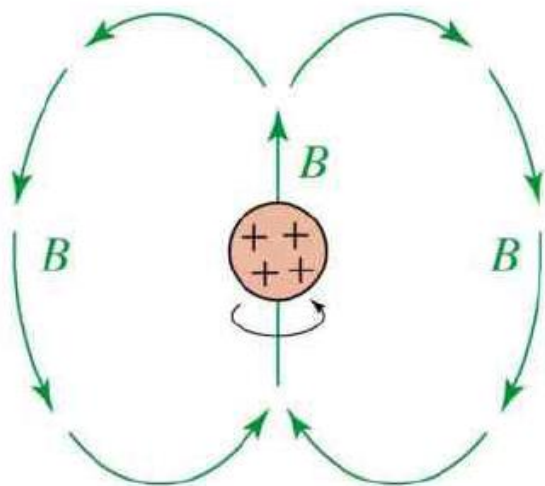
NMR *spectroscopy*
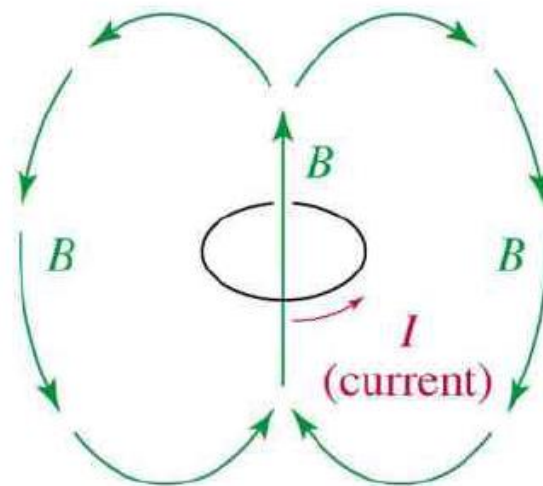
- ❑ Subatomic particles (electrons, protons and neutrons can be imagined as spinning on their axis.
- ❑ In many atoms these spins are paired against each other, such that the nucleus has no overall spin.
- ❑ Nuclear magnetic resonance is a physical phenomenon that base on magnetic property of an atom's nucleus.
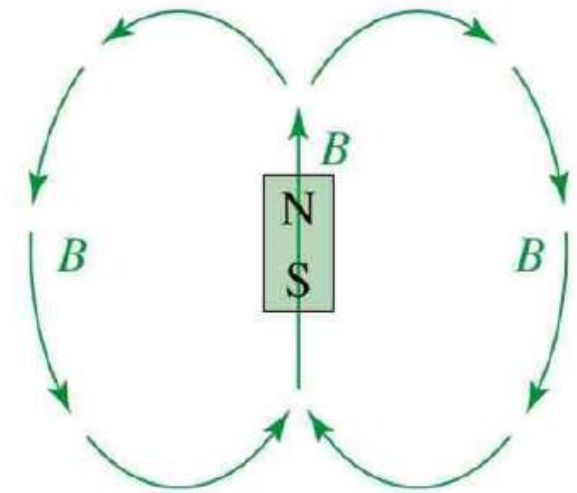
[1 Tesla = 10,000 Gauss ; earth 0.00005 Tesla]

spinning proton   loop of current   bar magnet

=>

Some theory

■ If the **nuclear spin** *I=0*, then the **nuclear angular momentum**, *p=0* (nucleus doesn't "spin").

■ If *I>0* then the nuclear angular momentum

$$p = \hbar I$$

■ Since the nucleus is charged and spinning, there is a **nuclear magnetic dipole moment**

$$\mu_n = \gamma_n p = \gamma_n \hbar I$$

Gyromagnetic ratio

Magnetic moment of a proton

$$\beta_n = \frac{e\hbar}{2m_p c}$$

$$\mu_n = g_n \beta_n I$$

Nucleus g factor

Length of vector $= |I| = \sqrt{I(I+1)}$

In the absence of magnetic field all $2I+1$ directions of the spin are equiprobable

Nuclear Spin

The rules for determining the net spin of a nucleus are as follows:

o If the number of neutrons and the number of protons are both even, then the nucleus has **NO** spin

o If the number of neutrons**+** the number of proton is odd, then the nucleus has **half-integer** spin (i.e.1/2, 3/2, 5/2).

o If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e 1,2,3).

- In the **presence of magnetic field**, there is an **interaction** between the field and the magnetic moment:
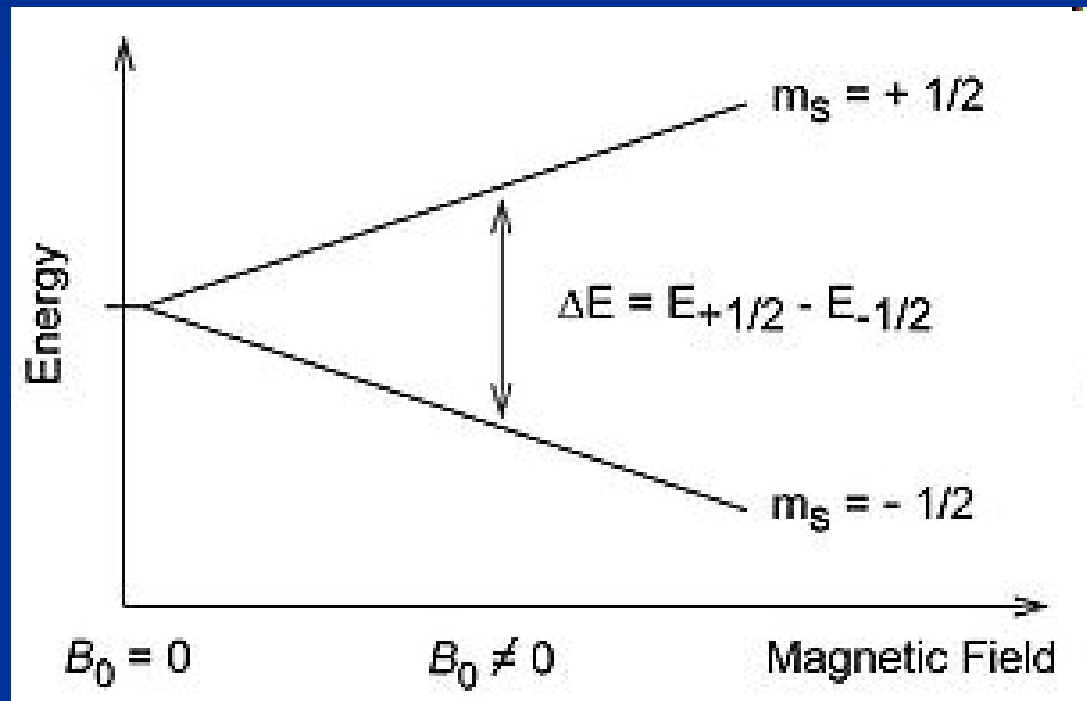
$$H = -\mu_n \cdot B$$

- If the field is in the **z direction**

$$H = -\gamma_n \hbar B I_z = -g_n \beta_n B I_z$$

There are *2I+1* values of I_z ⟹ There are *2I+1* values of energy

Example: proton

$$E_\alpha = -\mu_n \mathbf{B} = -\frac{1}{2}\gamma\hbar B = -\frac{1}{2}g_n\beta_n B \quad \text{и} \quad E_\beta = \frac{1}{2}\gamma\hbar B = \frac{1}{2}g_n\beta_n B,$$

Two Energy States

- The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

- A photon with the right amount of energy can be absorbed and

cause the spinning proton to flip.

Applied magnetic field
Each level is given a
magnetic quantum number *m*

This level are degenerate in
absence of external magnetic
field

β state

B_0

$hv = \Delta E$

α state
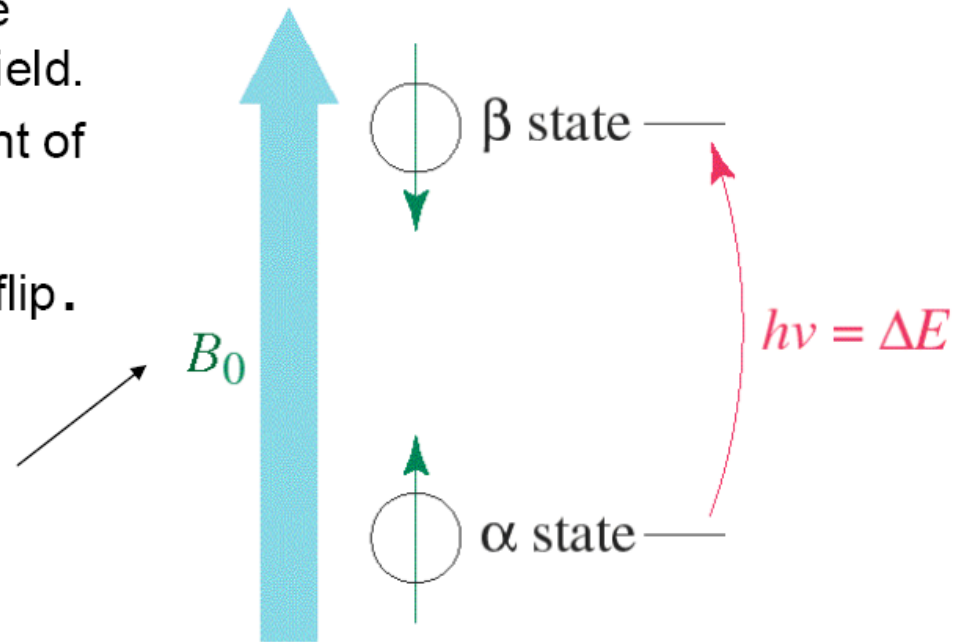
Calculating Transition energy

The difference in energy between levels (the transition) energy is given
By

$$|\Delta E| = \gamma \hbar B$$

The frequency of electromagnetic radiation is given by
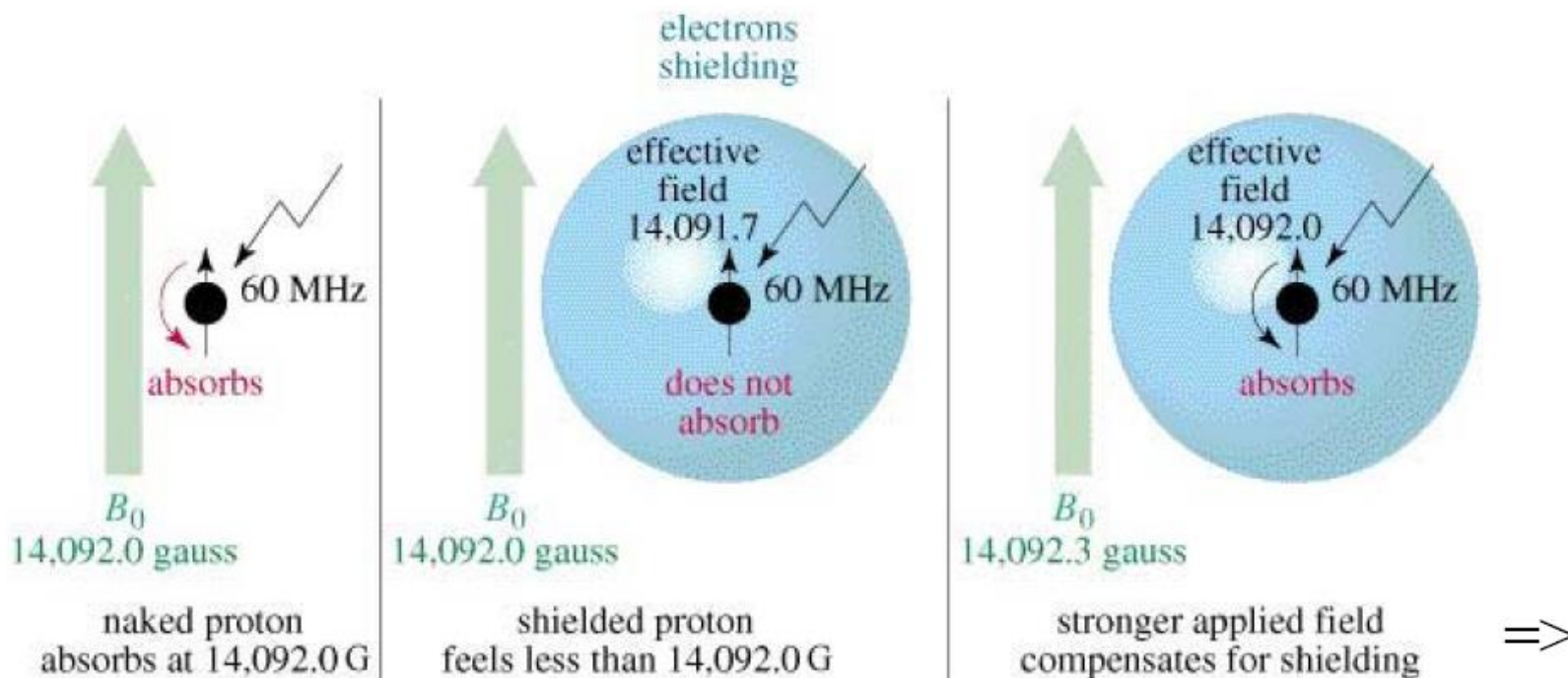
$$h\nu = \gamma \hbar B$$

$$\Rightarrow \nu = \frac{\gamma B}{2\pi}$$

Larmor freqency

γ is the gyromagnetic constant
(for each elements)

Shielding by the Electronic Environment

❑ The magnetic field at the nucleus is a results of number of effects, the most important of which is that the applied magnetic field induced motion of electron cloud near the nucleus in the molecule such that an additional magnetic field is set up in opposition to (and proportional to) the applied field. The nucleus is Shielded by electrons.

electrons shielding

effective field 14,091.7   60 MHz   does not absorb

effective field 14,092.0   60 MHz   absorbs

60 MHz   absorbs

B_0
14,092.0 gauss

B_0
14,092.0 gauss

B_0
14,092.3 gauss

naked proton absorbs at 14,092.0 G

shielded proton feels less than 14,092.0 G

stronger applied field compensates for shielding

=>

Shielding and Resonance Frequency

Shielding effects can be taken into account by the expression: $B = B_0 - \sigma_i B_0$

B_0 is the applied magnetic field strength and the σ_i is the shielding factor

$$\Rightarrow \nu_i = \frac{\gamma B_0}{2\pi} (1 - \sigma_i) \text{ [nucleus } i\text{]}$$
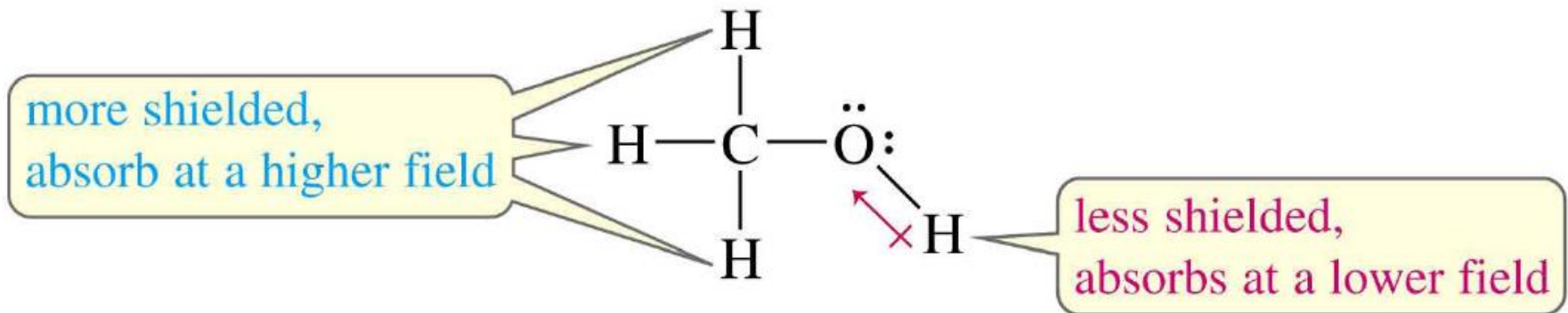
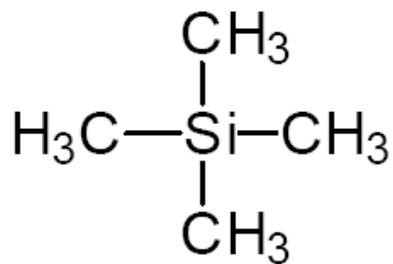$$\nu_{ref} = \frac{\gamma B_0}{2\pi} (1 - \sigma_{ref})$$

$$\nu_i - \nu_{ref} = \frac{\gamma B_0}{2\pi} (\sigma_{ref} - \sigma_i)$$

$$\Rightarrow \frac{\nu_i - \nu_{ref}}{\nu_{ref}} = \frac{\sigma_{ref} - \sigma_i}{1 - \sigma_{ref}} = 10^{-6} \delta_i \text{ chemical shift in } ppm$$

Protons in a Molecule

Depending on their chemical environment, protons in a molecule are shielded by different amounts.

Tetramethylsilane
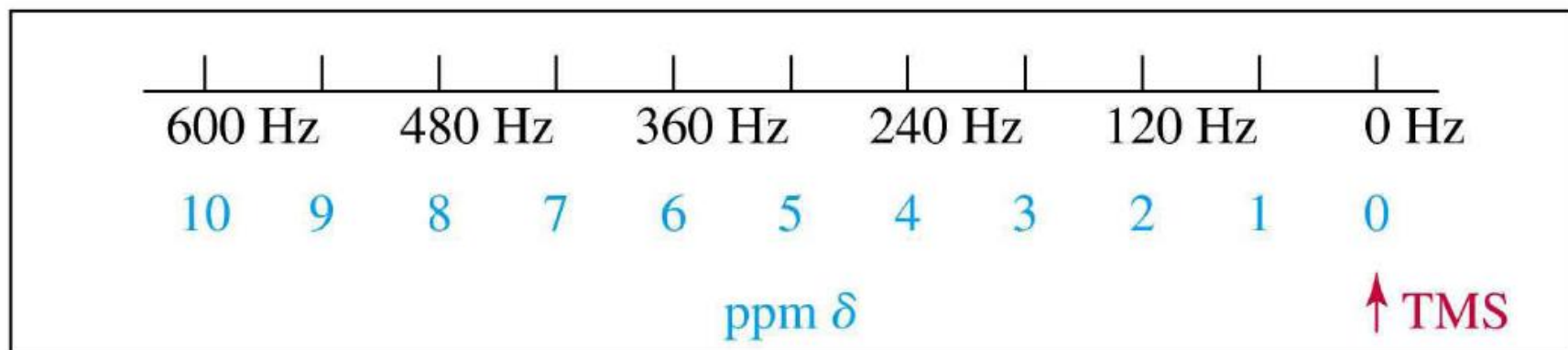
$$CH_3$$
$$H_3C—Si—CH_3$$
$$CH_3$$

- TMS is added to the sample.

- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.

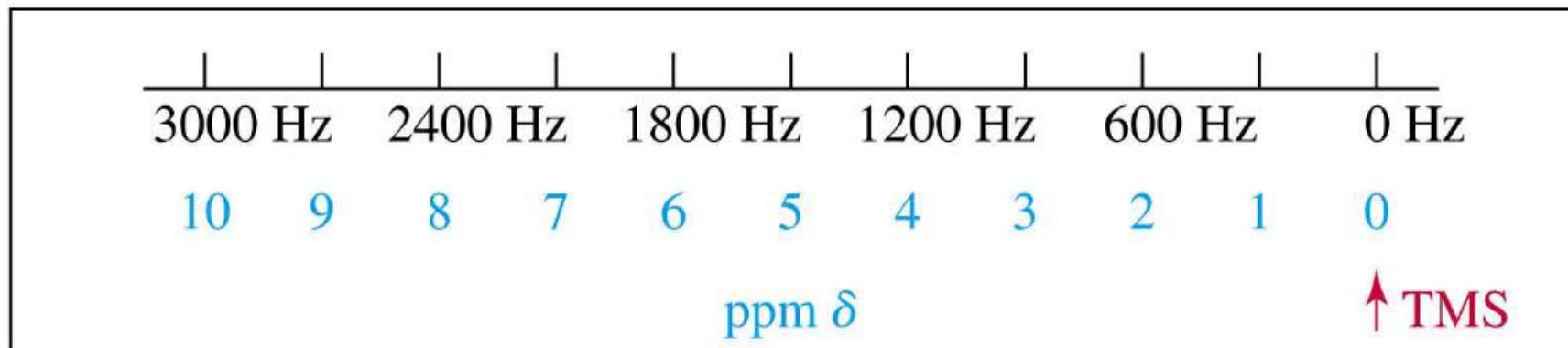- Organic protons absorb downfield (to the left) of the TMS signal.

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Delta Scale

chemical shift, ppm $\delta = \dfrac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$

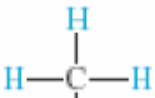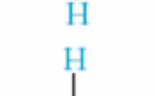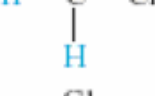| 600 Hz	480 Hz	360 Hz	240 Hz	120 Hz	0 Hz
10 9	8 7	6 5	4 3	2 1	0

ppm δ ↑ TMS

60 MHz

3000 Hz	2400 Hz	1800 Hz	1200 Hz	600 Hz	0 Hz
10 9	8 7	6 5	4 3	2 1	0

ppm δ ↑ TMS
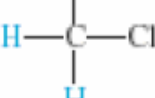
300 MHz

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Location of Signals
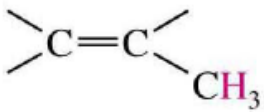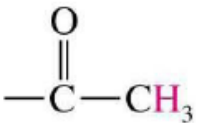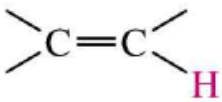
TABLE 13-2 Chemical Shifts of the Chloromethanes

Compound	Chemical Shift	Difference
H—C—H	δ0.2	
		2.8 ppm
H—C—Cl	δ3.0	
		2.3 ppm
H—C—Cl	δ5.3	
		1.9 ppm
H—C—Cl	δ7.2	

Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive.

- More electronegative atoms deshield more and give larger shift values.

- Effect decreases with distance.

- Additional electronegative atoms cause increase in chemical shift.
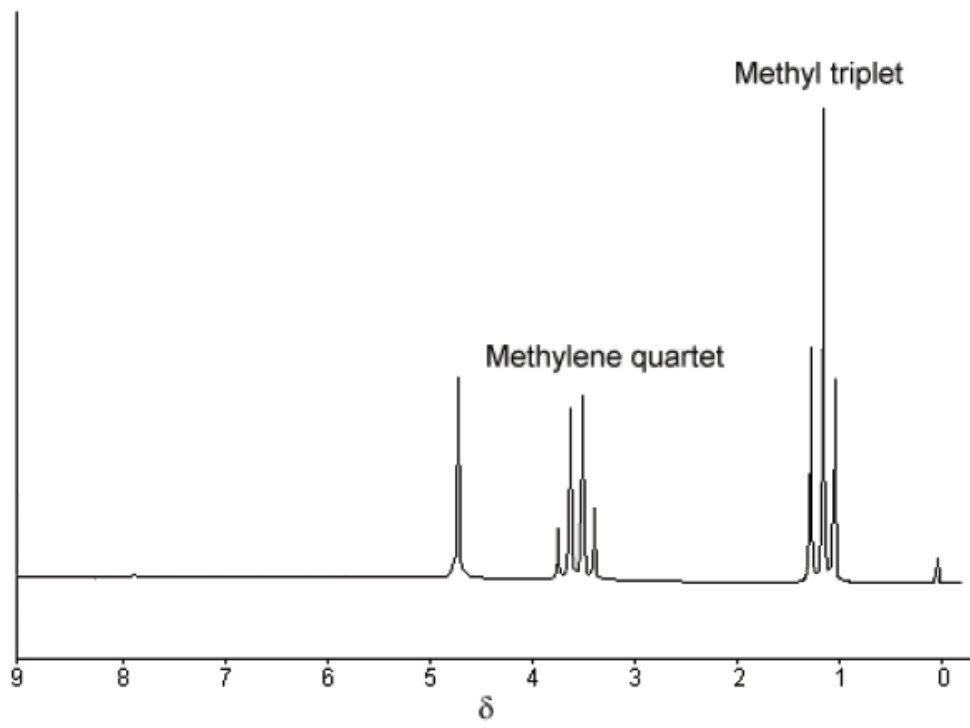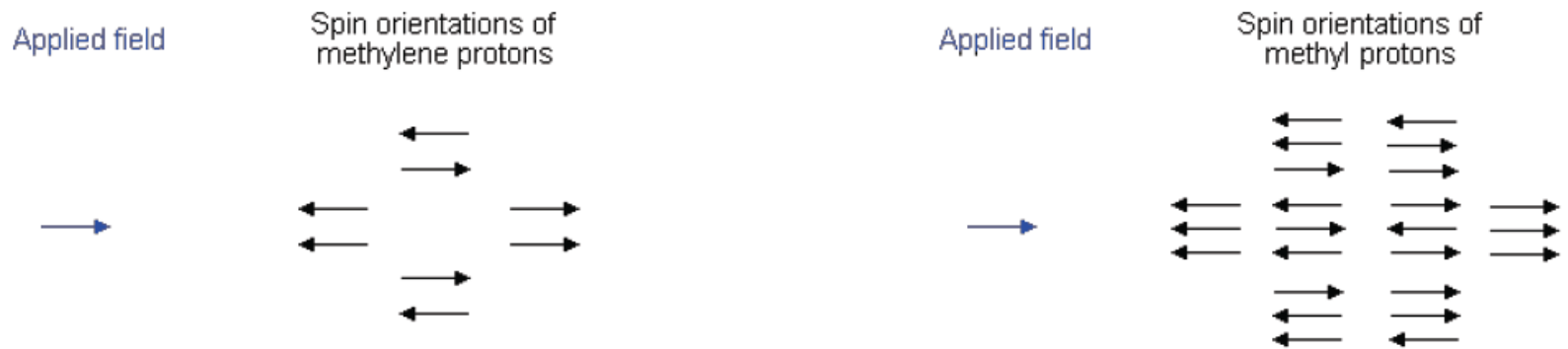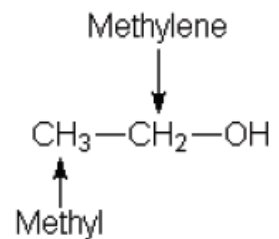
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Typical Values

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9	$>C=C<_{CH_3}$	1.7
alkane ($-CH_2-$)	1.3		
alkane $\left(-\overset{\vert}{C}H-\right)$	1.4	Ph$-$H	7.2
		Ph$-CH_3$	2.3
$-\overset{\overset{O}{\|\|}}{C}-CH_3$	2.1	R$-$CHO	9–10
		R$-$COOH	10–12
$-C\equiv C-H$	2.5	R$-$OH	variable, about 2–5
R$-CH_2-$X	3–4	Ar$-$OH	variable, about 4–7
(X = halogen, O)		R$-NH_2$	variable, about 1.5–4
$>C=C<_H$	5–6		

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

=>

Example: Ethanol (Spin-Spin coupling)

Methylene

CH_3-CH_2-OH

Methyl

Applied field

Spin orientations of methylene protons

Applied field

Spin orientations of methyl protons

Methyl triplet

Methylene quartet

δ

NMR Signals

- The *number* of signals shows how many different kinds of protons are present.

- The *location* of the signals shows how shielded or deshielded the proton is.

- The *intensity* of the signal shows the number of protons of that type.

- Signal *splitting* shows the number of protons on adjacent atoms.

Calculation of the Shielding Tensor

$$\{/k>^0, \varepsilon_k^0\}$$ → $$\phi$$ → $$\{/k>, \varepsilon_k\}$$ → $$\chi, \sigma$$

Calculate zero-field SCF

Choose gauge by which to enter the magnetic vector potential

Calculate new SCF for non-zero field.

Use the zero-field SCF results as the initial guess
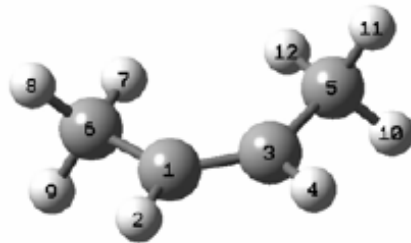
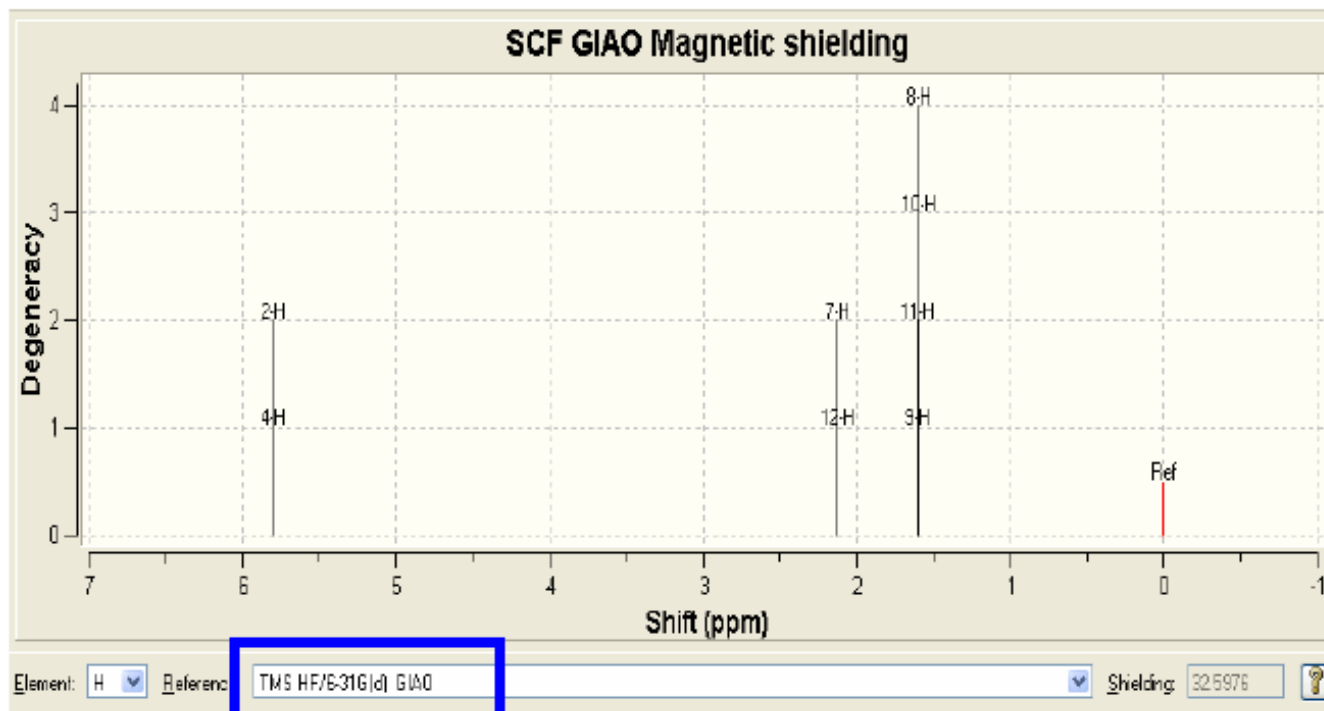Calculate shielding tensor, susceptibility, etc. using the non-zero field electron structure

Basic Calculation
(single molecule in gas phase)

Example:

Cis-2-butene עבור **NMR** ספקטרום

Calculation vs. Experiment
(single molecule in gas phase)

- Since the calculation is done on a static molecule, <u>no bond rotations</u> are possible (***number*** of sp^3 proton kinds may be different, e.g. H_3CNHF).

- The ***location*** of the signals is given relative to a reference material calculated separately, <u>at the same calculation level</u>.

- ***Linewidths*** are zero (no solvent or temperature effects, $T=0$).

- Signal ***splitting*** can be calculated separately, e.g. using G03:

Calc. of indirect dipole-dipole coupling

- Direct dipole-dipole coupling becomes negligible for **closed-shell** systems at high temperature (existence of **intermolecular collisions**).

- GAUSSIAN keyword option **NMR=SpinSpin**

Calculates **four** contributions to **isotropic** spin-spin coupling:

1. Paramagnetic spin-orbit coupling (PSO)
2. Diamagnetic spin-orbit coupling (DSO)
3. Spin-dipolar coupling (SD)
4. Fermi contact interaction (FC)

NMR: Summary

- ❑ NMR spectroscopy is a powerful and theoretically complex analytical tool for structure determination.
- ❑ It is used to study a wide variety of nuclei with non-zero nuclear spin (^1H, ^{13}C, ^{15}N…).
- ❑ In NMR we are performing experiments on the nuclei of atoms, not the electrons.
- ❑ The chemical environment of specific nuclei is deduced from information obtained about the nuclei.
- ❑ Transitions between energy levels for NMR dipoles occur in the radio-frequency range (transitions between energy levels for unpaired electron occur in the microwave range).
- ❑ Different methods for studying nuclear magnetic resonance were developed independently by Purcell and Bloch 1946.
- ❑ Nowadays Fourier transform spectrometers are used.