

# Calculation of IR & NMR Spectra

Measuring nuclear vibrations and spins

Computational Chemistry Lab

Inbal Oz

2018



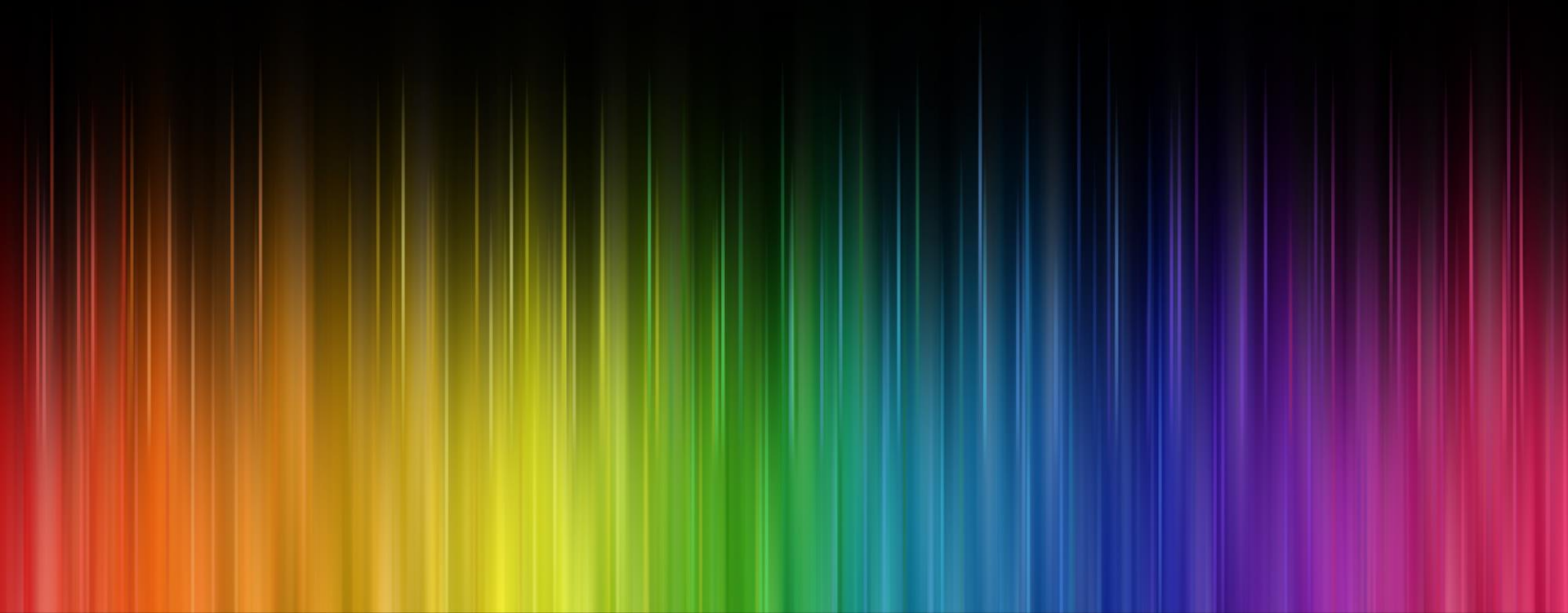
TEL AVIV אוניברסיטת  
UNIVERSITY תל אביב

# Lecture Outline

- **EM** spectrum
- **IR** – vibrations of nuclei on the electronic PES
  - Review of theory
  - Calculation scheme
  - Calculations vs. experiment
- **NMR** – effect of electronic environment on nuclear spin transitions
  - Review of theory
  - Calculation of shielding tensor
  - Worked example (calculation vs. experiment)



# The Electromagnetic Spectrum



# Electromagnetic (EM) Spectrum

- Frequency and wavelength are inversely proportional,

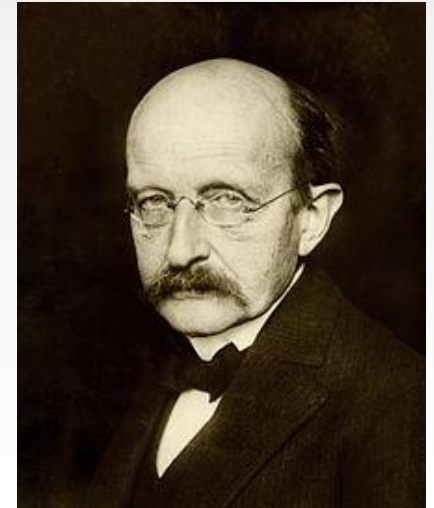
$$c = \lambda\nu,$$

where  $c$  is the speed of light.

- Planck's relation:

$$E = h\nu = \frac{hc}{\lambda},$$

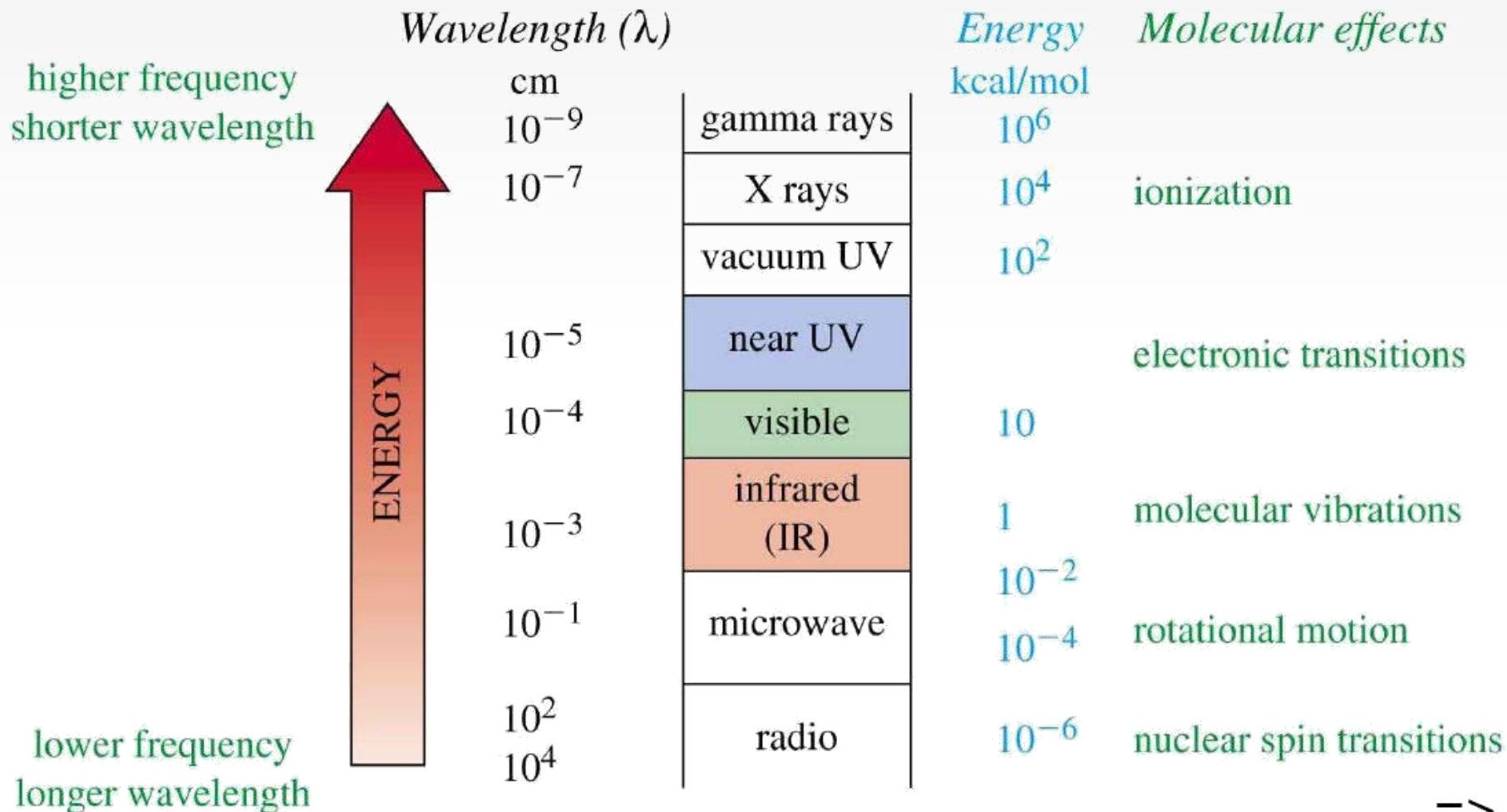
where  $h$  is Planck's constant.



Max Planck  
1858 –1947



# The Spectrum and Molecular Effects



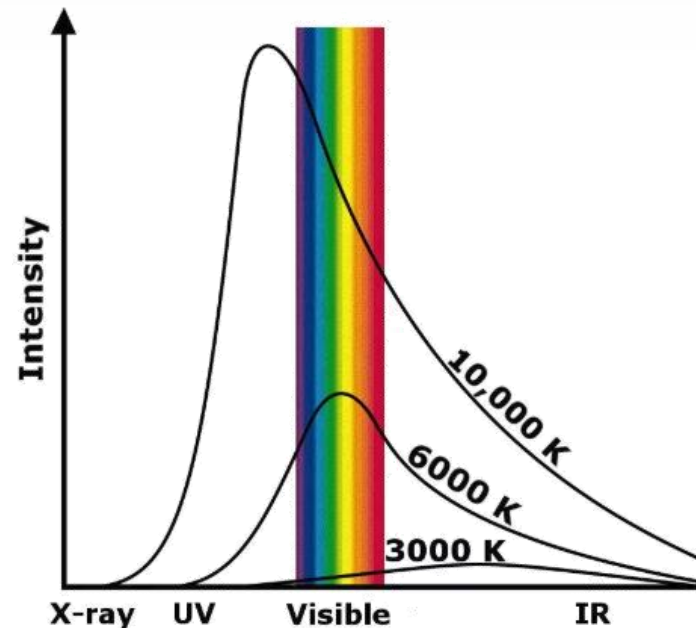
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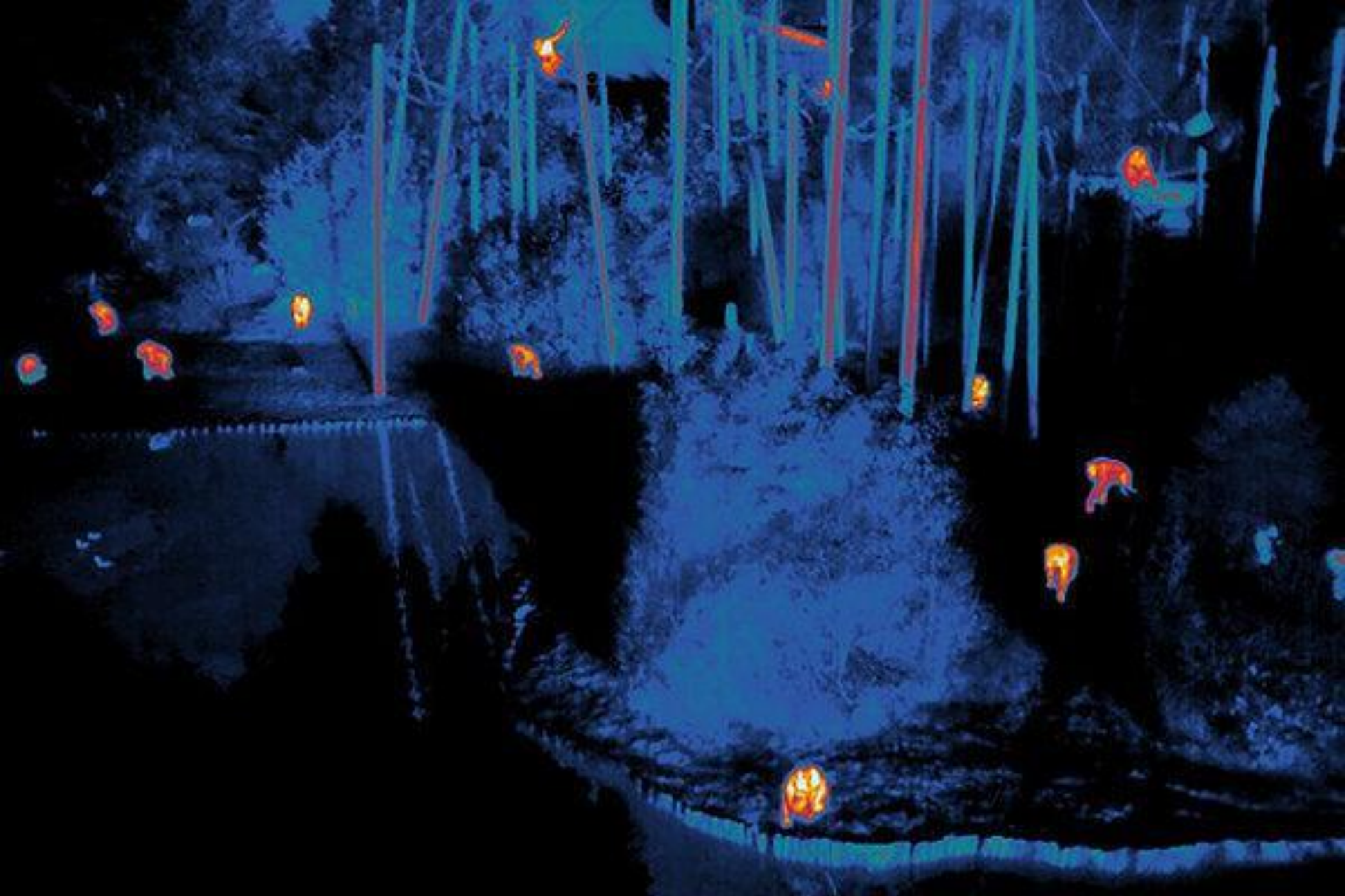
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# Infrared Radiation

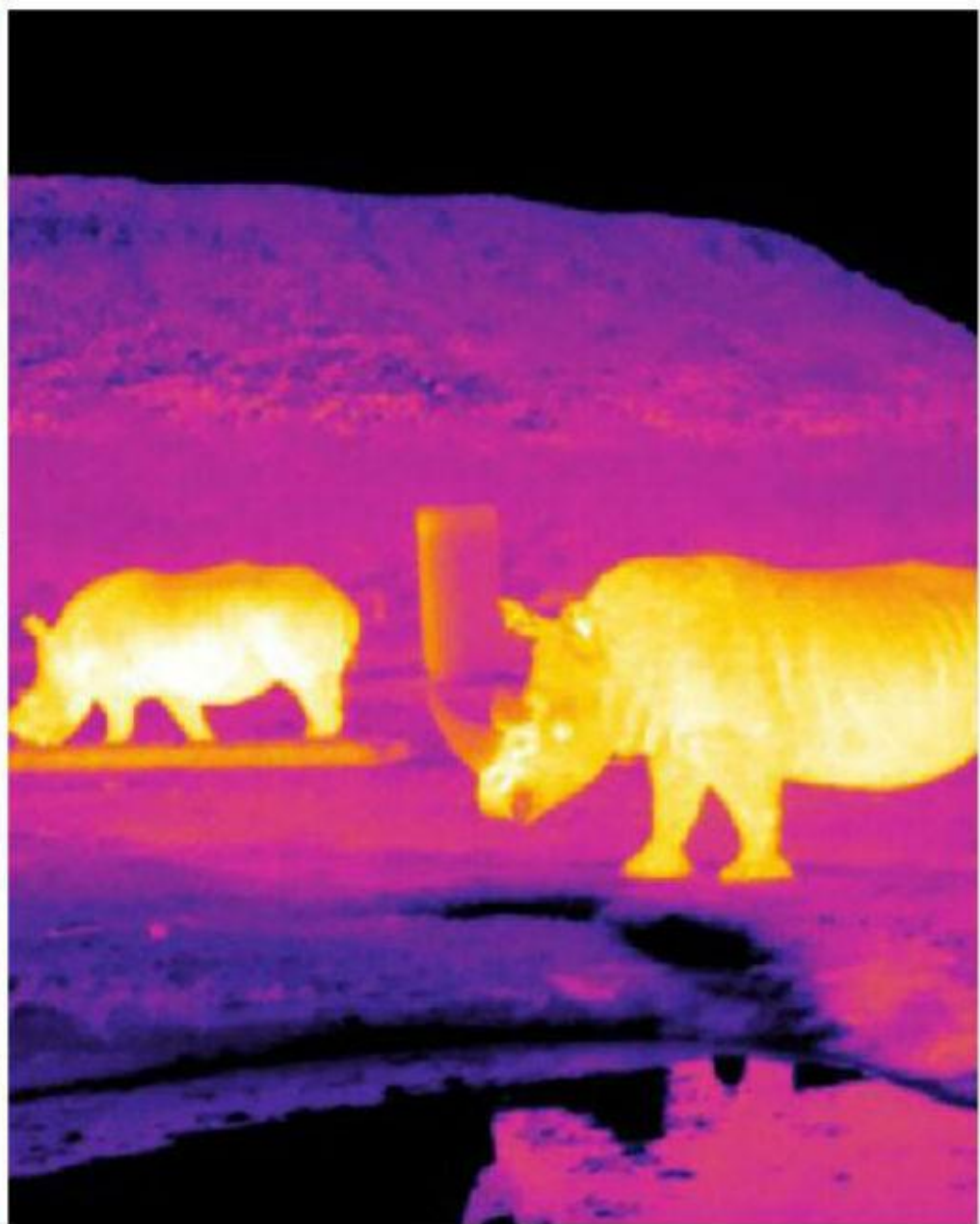
- Infrared radiation is emitted or absorbed by molecules when they change their rotational-vibrational movements.
- It excites vibrational modes in a molecule through a change in the dipole moment.





The research team has been working with a local safari park and zoo to film and photograph animals, like these chimpanzees, to build up a reference library of different animals. Credit Endangered Wildlife Trust/LJMU





Rhinos observed as part of the tests. The researchers found that, like stars, animals have a recognizable thermal footprint. Credit Endangered Wildlife Trust/LJMU

# Review of Theory

Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule.

→ used to determine the functional group and to confirm molecule-wide structure (“fingerprint”).



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# Review of Theory

Born-Oppenheimer calculation of the PES:

$$H = H_e + H_n$$



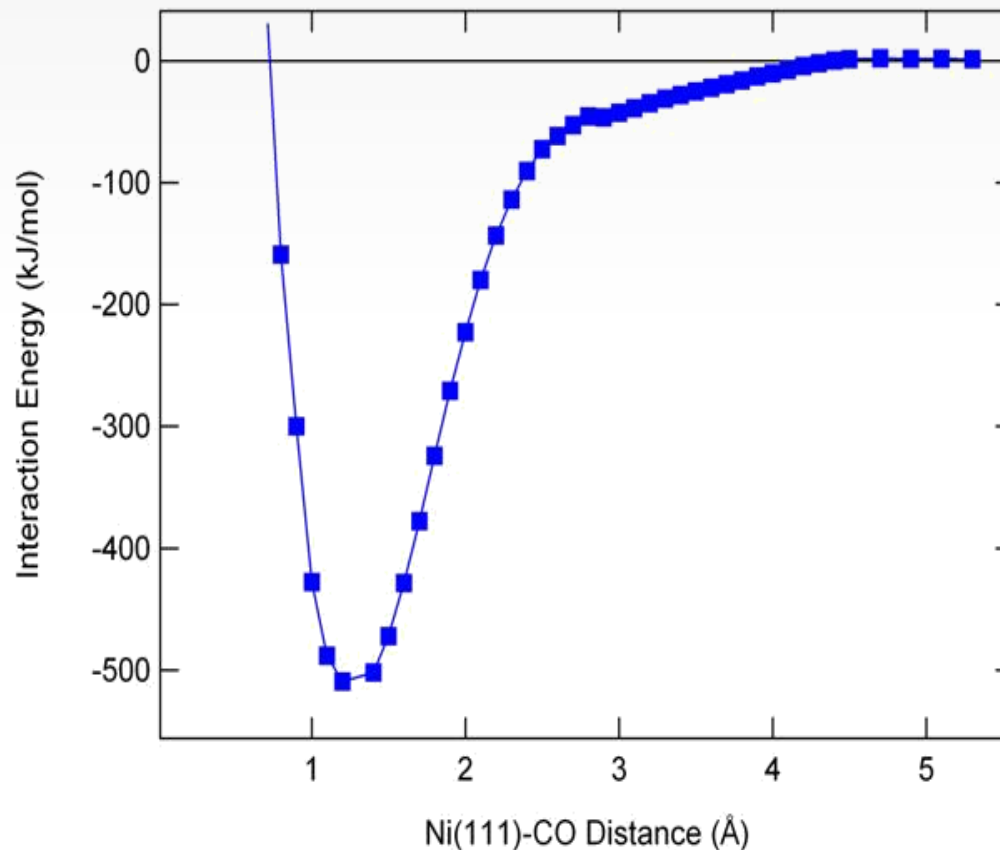
$$\Psi = \Psi_e \Psi_n$$



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

# Review of Theory

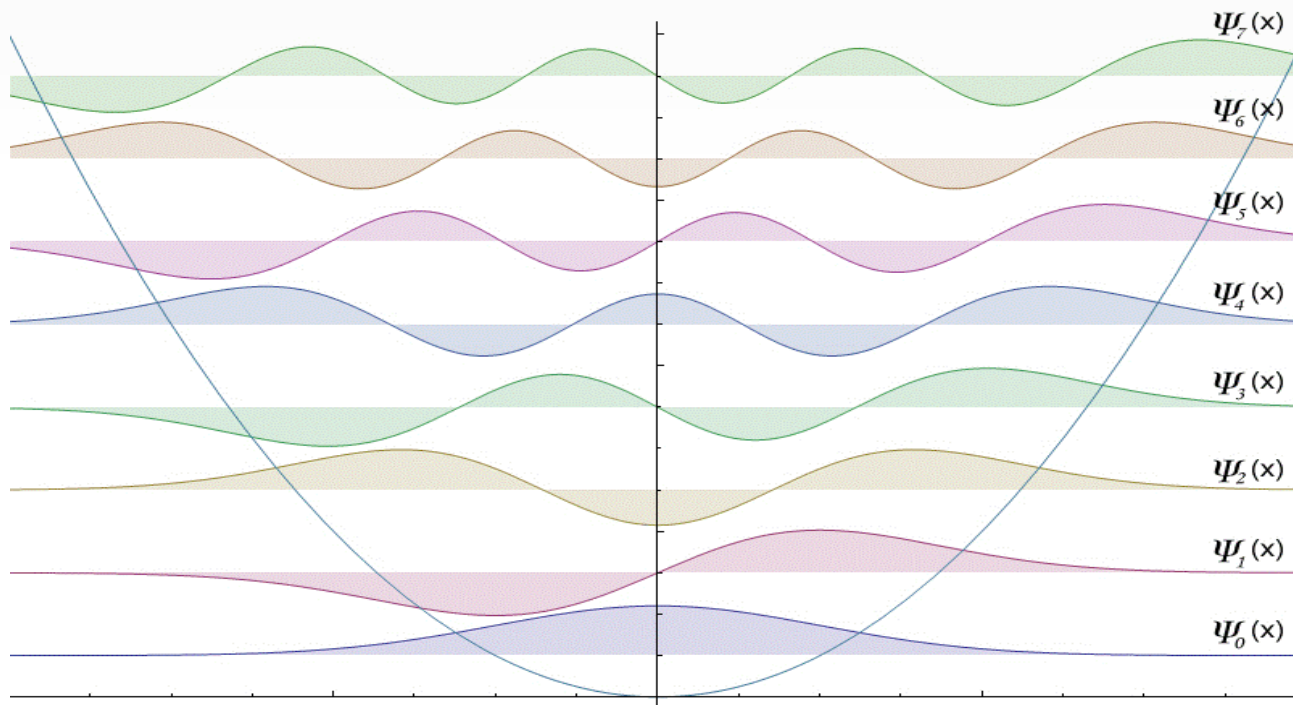
Born-Oppenheimer calculation of the PES:



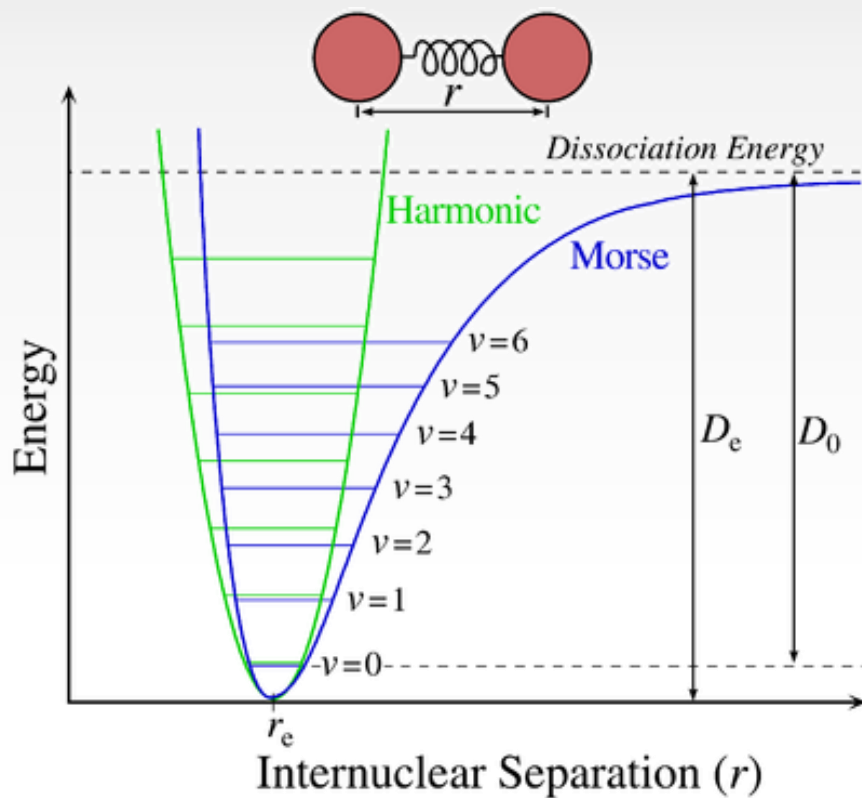
# Harmonic oscillator

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

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



# Extracting the Resonant Frequency



In the vicinity of  $r_e$  the potential looks like a harmonic oscillator.

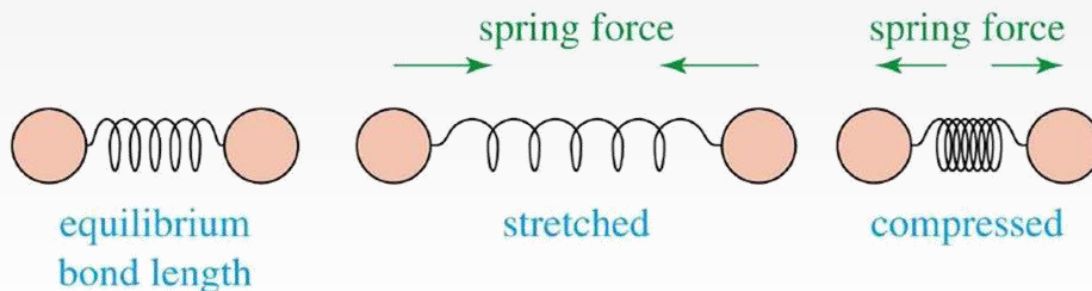
$$V(x) = V(r_e) + V'(r_e)(r - r_e) + \frac{1}{2}V''(r_e)(r - r_e)^2 + ..$$

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



# Extracting the Vibrational Frequencies

Covalent bonds vibrate at only certain allowable frequencies.



Calculate the potential energy surface.

Calculate the harmonic potential,

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

Extract the vibrational frequency,

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





# Normal modes

- For a molecule with  $N$  atoms we have  $3N$  degrees of freedom ( $x, y, z$ ).
- Out of those:
  - 3 belong to the location of the center of mass.
  - 3 (or 2 for a linear molecule) belong to rotation.
- In the vicinity of the equilibrium geometry we have  $3N - 6$  ( $3N - 5$ ) independent harmonic oscillators  
(with frequencies  $\omega_i = 1 \dots (3N - 6)$ ).

$$E = \sum_{i=1}^{3N-6} \hbar \omega_i \left( n_i + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots$$



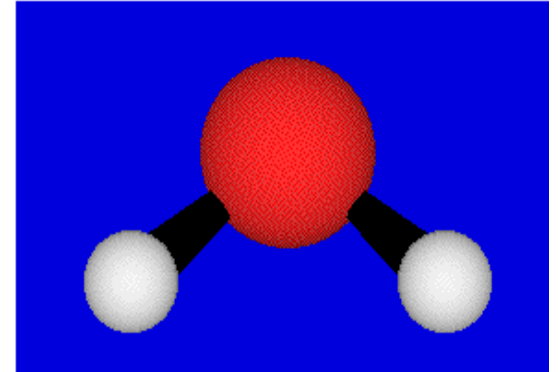
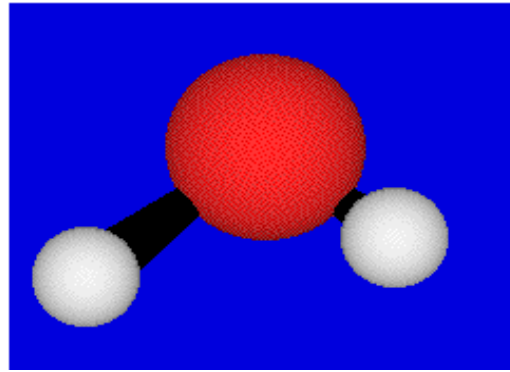
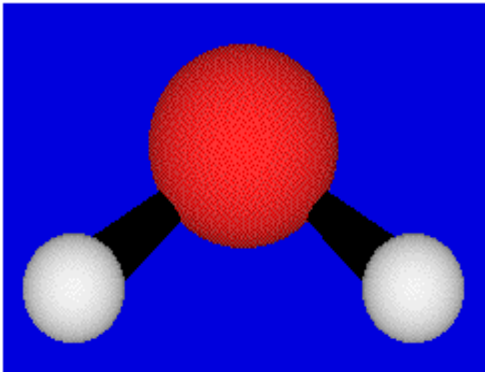
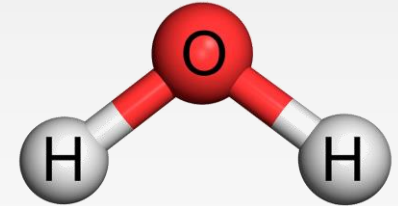
# Example: Water Molecule

- Number of atoms:  $N = 3$ .

- Linear?

→ No.

- Number of normal modes:  $N = 3N - 6 = 9 - 3 = 3$ .



# Normal Mode Calculation

PES

Solve the BO electronic Hamiltonian at each nuclear configuration to get the PES

K matrix

Create the  
matrix of

$$E - E_0 = k(q - q_0)^2$$
$$\Rightarrow \frac{d^2 E}{dq^2} = 2k .$$

which is the

$$\left. \frac{\partial^2 V}{\partial R_i \partial R_j} \right)_{eq.}$$

Hessian

Mass weighted:  $\omega^2 = \frac{k}{m} \Rightarrow \frac{1}{\sqrt{m_i m_j}} \left( \frac{\partial^2 V}{\partial R_i \partial R_j} \right)_{eq.} = H_{ij}$



# Normal Mode Calculation

Eigenvalues

Diagonalize the Hessian to get eigenvalues,  $\lambda_k$ , and eigenvectors,  $l_{jk}$ :

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

Roots

Six (five) of the roots should be zero, and the rest are vibrational modes.

$$v_k = \frac{\omega_k}{2\pi} = \frac{\sqrt{\lambda_k}}{2\pi}$$



# Normal Mode Calculation

- What would it mean if we got too few non-zero roots?
  - Calculation hasn't converged.
- Too many?
  - It is actually non-zero, but very small. (we may use more iterations or a different method)
- When would we get one negative eigenvalue of the Hessian?
  - Saddle point.
- What does a complex eigenvalue of the Hessian?
  - Our calculation hasn't converged.



# General Trends

- The vibration frequency is

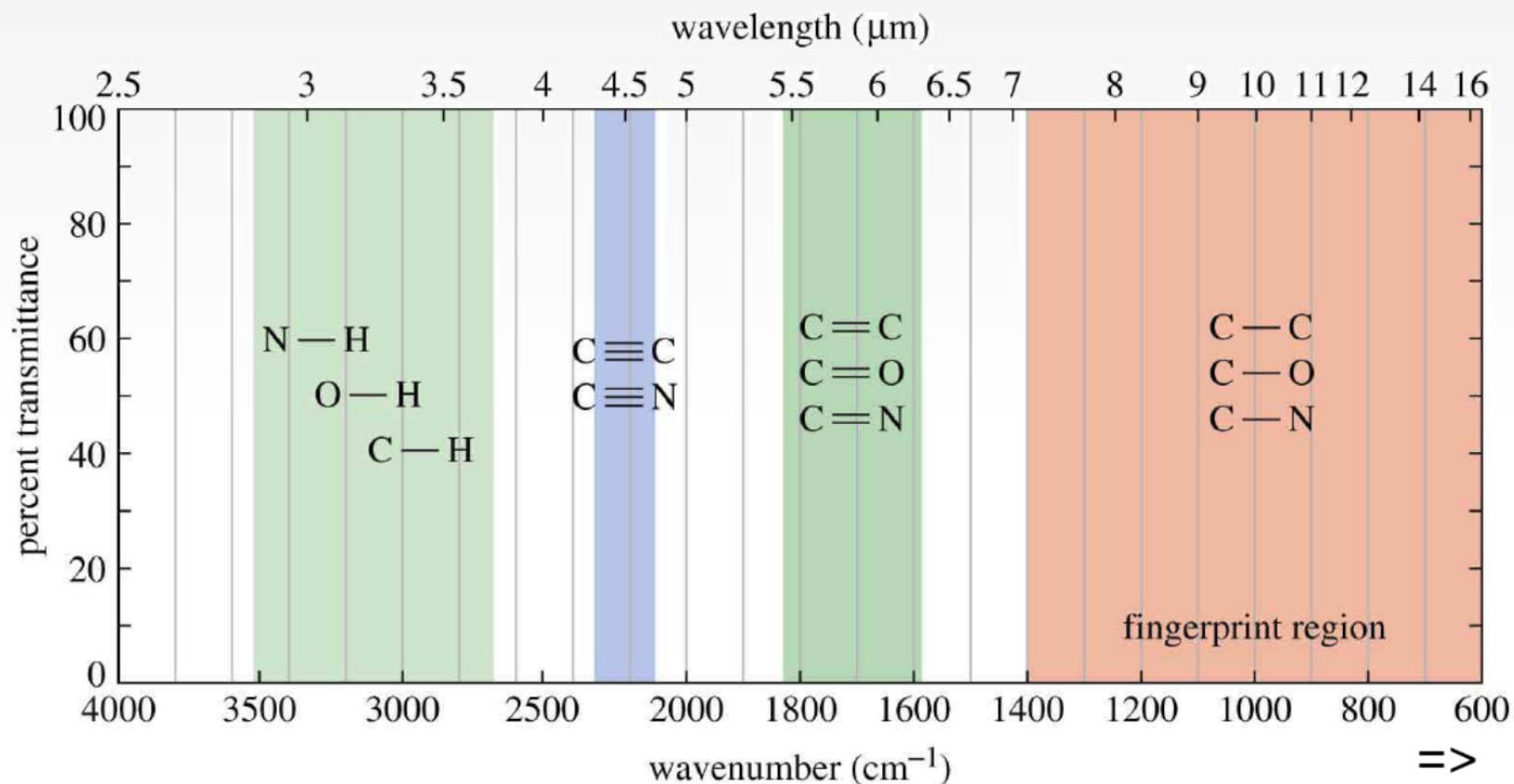
$$\omega = \sqrt{\frac{k}{m}}$$

- Frequency decreases with increased atomic weight.
- Frequency increases with bond energy.

| Bond   | Bond Energy<br>[kcal (kJ)] | Stretching Frequency<br>(cm <sup>-1</sup> ) |
|--|----------------------------|---|
| <i>Frequency dependence on atomic masses</i> |                            |   |
| C—H  | 100 (420)                  | 3000  |
| C—D  | 100 (420)                  | 2100  |
| C—C  | 83 (350)                   | 1200  |
|  | ↓ heavier atoms            | ↓ $\bar{\nu}$ decreases                     |
| <i>Frequency dependence on bond energies</i> |                            |   |
| C—C  | 83 (350)                   | 1200  |
| C=C  | 146 (611)                  | 1660  |
| C≡C  | 200 (840)                  | 2200  |
|  | ↓ stronger bond            | ↓ $\bar{\nu}$ increases                     |



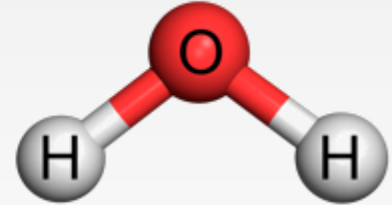
# Summary of IR Absorptions



# Example: Water

- The experimental IR gives

$$\begin{aligned}\hbar\omega_1 &= 1000 \text{ cm}^{-1} \\ \hbar\omega_2 &= 1500 \text{ cm}^{-1} \\ \hbar\omega_3 &= 2200 \text{ cm}^{-1}\end{aligned}$$



- What is the energy of the ground state?

$$E = \sum_{i=1}^{3N-6} \hbar\omega_i \left( n_i + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots$$

$$\begin{aligned}E_1(0,0,0) &= \hbar\omega_1 \left( 0 + \frac{1}{2} \right) + \hbar\omega_2 \left( 0 + \frac{1}{2} \right) + \hbar\omega_3 \left( 0 + \frac{1}{2} \right) \\ &= 500 + 750 + 1100 = 2350 \text{ cm}^{-1}\end{aligned}$$





# Final Notes

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



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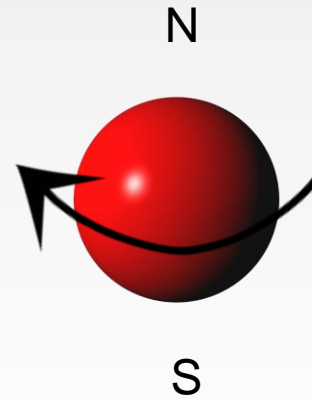
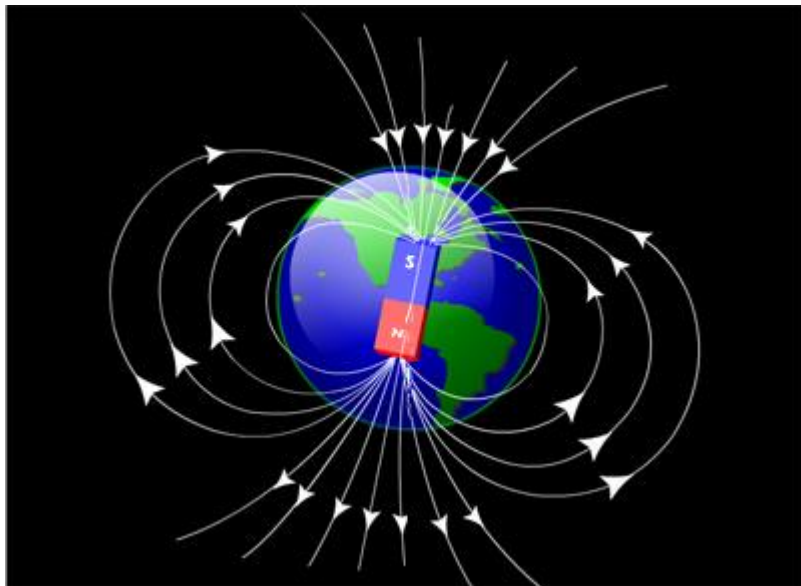
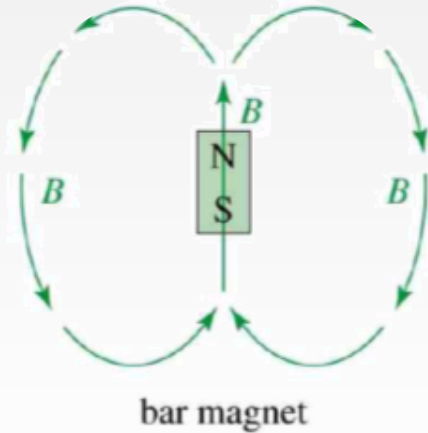


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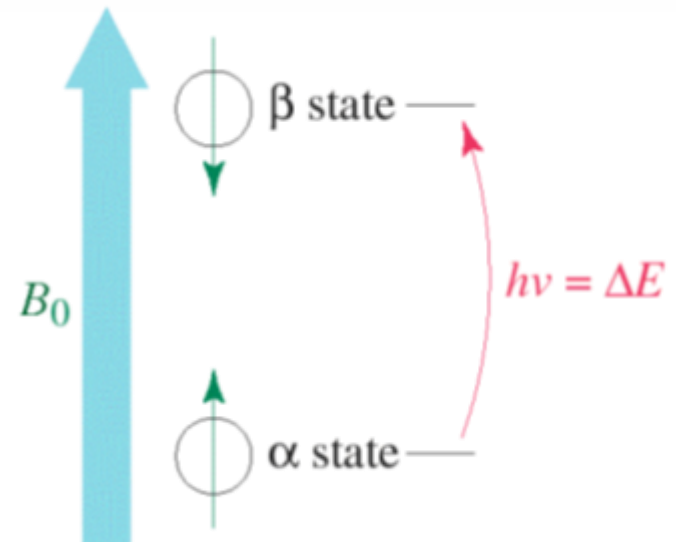
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# Review of theory

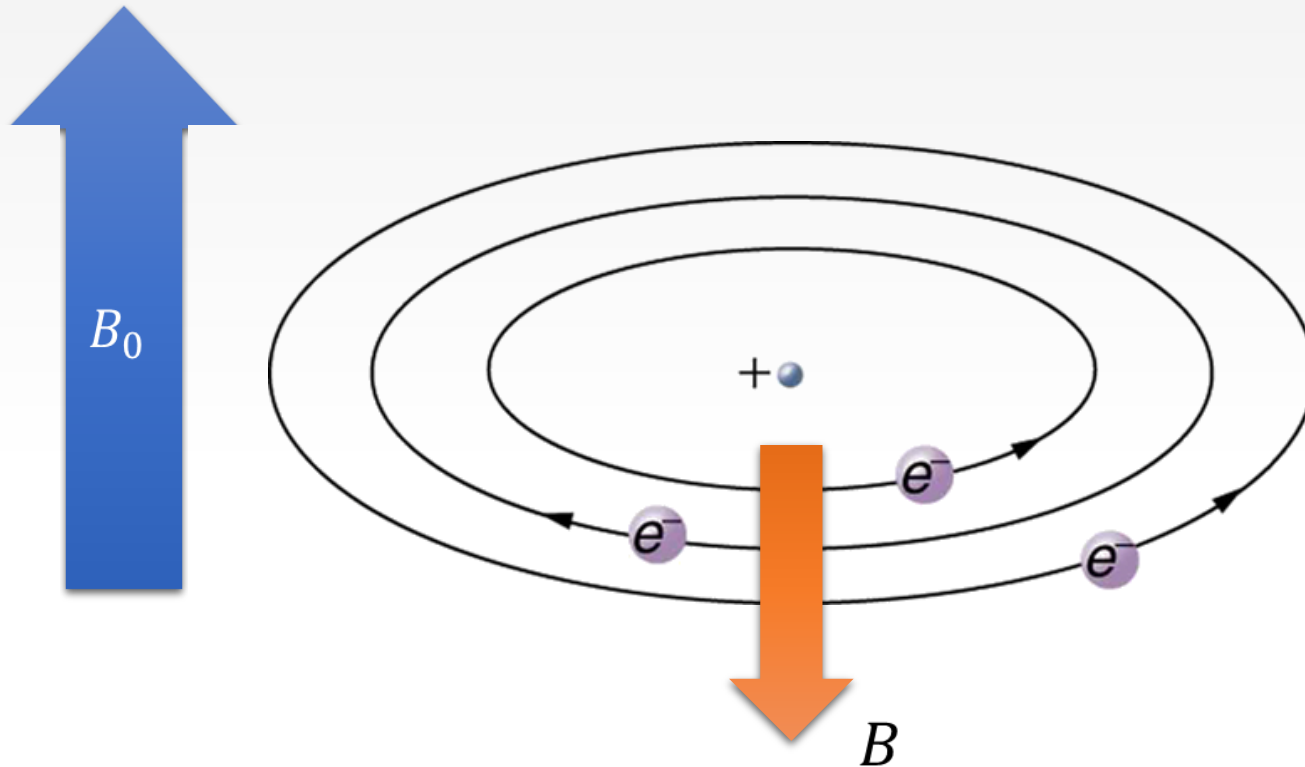


Any moving charge creates a magnetic field.



# Shielding

Any moving charge creates a magnetic field.



→ Shielding of proton.

# Terminology

- $s$  – total spin. Fermions:  $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ , Bosons:  $0, 1, 2, \dots$
- $\mu_n$  - the magnetic moment represents the magnetic strength of a given magnet.
- The magnetic moment is related to the angular momentum through the gyromagnetic ratio,

$$\gamma_n = \frac{e}{2m_p} g_n$$

$$g_n = +5.585694702$$

$$\mu_n = \gamma_n S$$

If  $s = 0$ , the particle does not react to a magnetic field.

- $S$  – spin angular momentum.

$$S = \hbar \sqrt{s(s+1)}$$

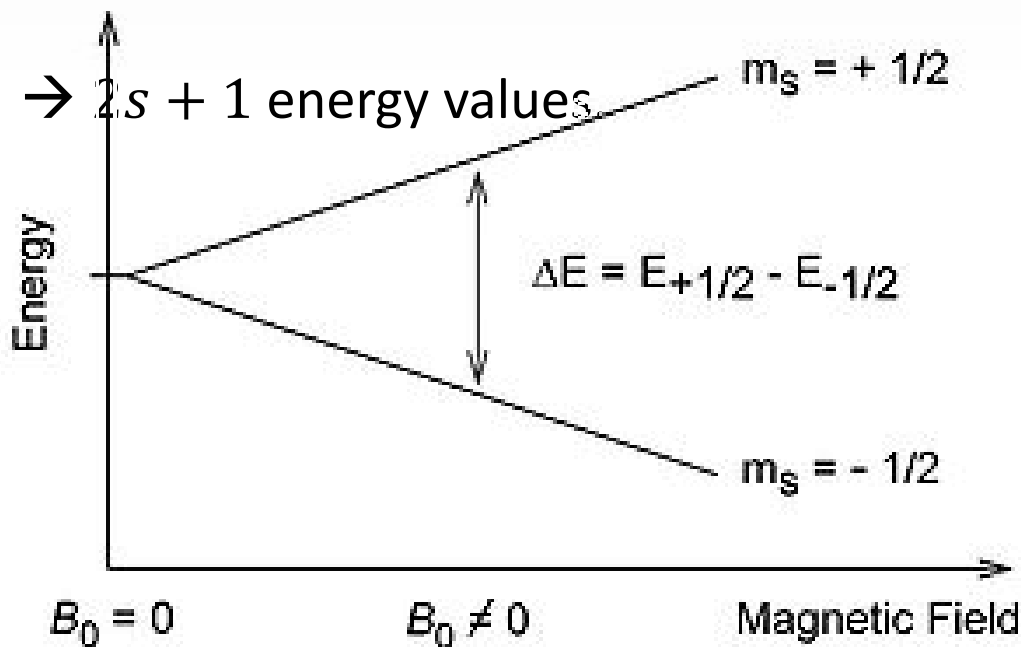


# Terminology

- In the presence of a magnetic field,  $E = -\mu_n B$ .

$$\mu_n = \gamma_n S$$

$$S = \hbar \sqrt{s(s+1)}, \quad -s, \dots, s$$



$$E_\alpha = -\mu_n B = -\frac{1}{2} \gamma \hbar B = -\frac{1}{2} g_n \beta_n B$$

$$E_\beta = \frac{1}{2} \gamma \hbar B = \frac{1}{2} g_n \beta_n B,$$

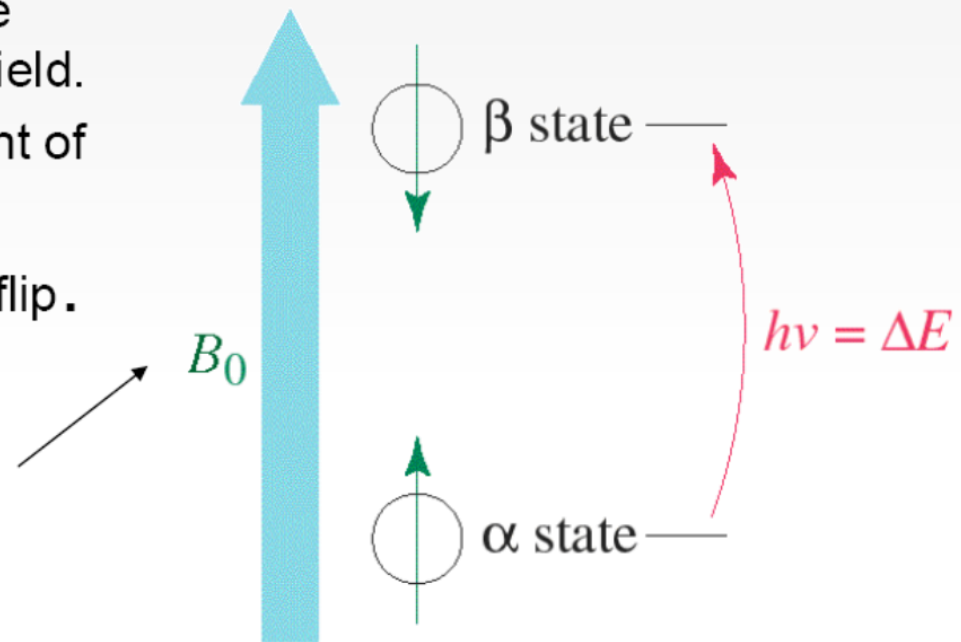


# Two Energy States

- 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






## 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

$$h\nu = \gamma \hbar B$$

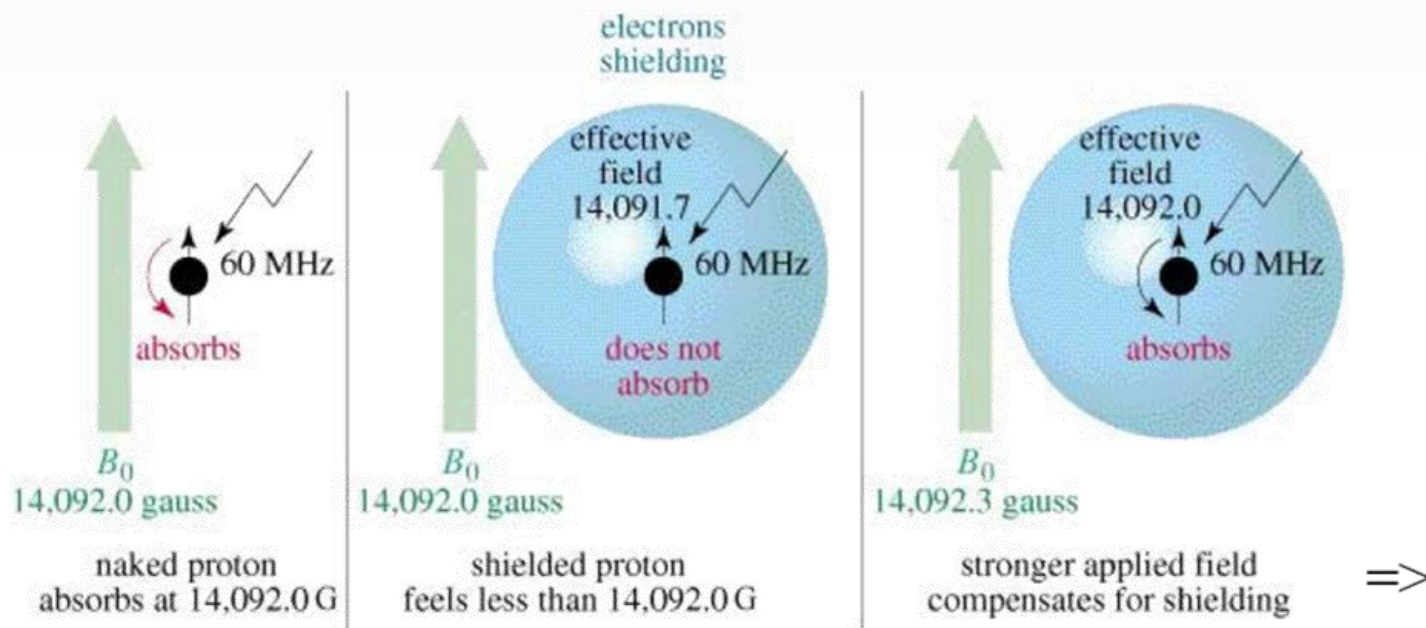
$$\Rightarrow \nu = \frac{\gamma B}{2\pi}$$


Larmor frequency

$\gamma$  is the gyromagnetic constant  
(for each element)

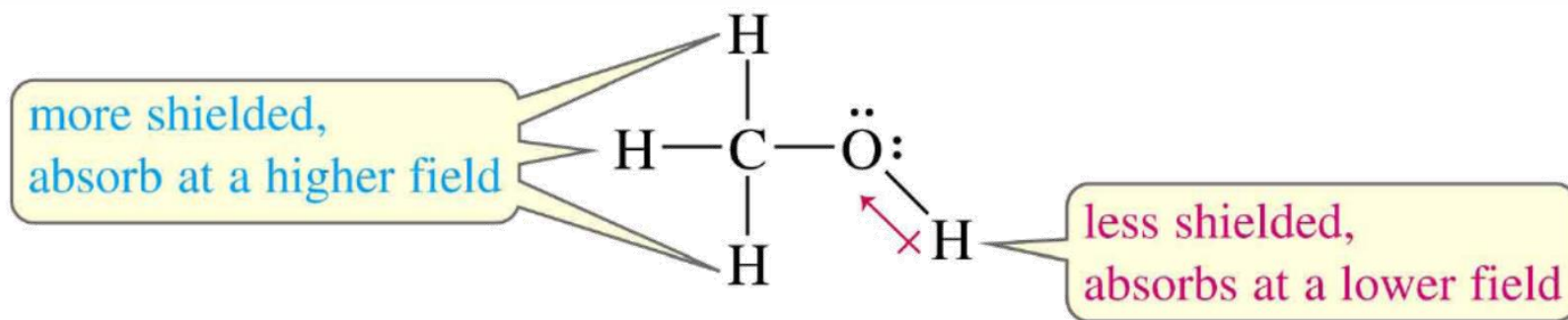
# Shielding and Resonance Frequency

- The magnetic field at the nucleus is a result 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.



# Protons in a Molecule

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



=>

# Shielding and Resonance Frequency

- Shielding effects can be taken into account by the expression:

$$B = B_0 - \sigma_i B_0$$

where  $B_0$  is the applied magnetic field strength and  $\sigma_i$  is the shielding factor.

- The effective shift is then:

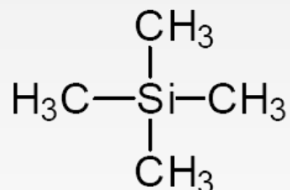
$$\Rightarrow \nu_i = \frac{\gamma B_0}{2\pi} (1 - \sigma_i) \text{ [nucleus } i \text{]}$$

$$\nu_{ref} = \frac{\gamma B_0}{2\pi} (1 - \sigma_{ref})$$

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

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



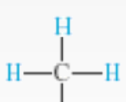
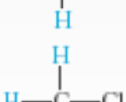
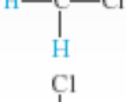
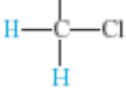


# Tetramethylsilane

- 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.

=>

# Location of Signals

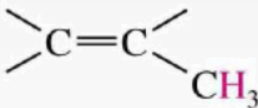
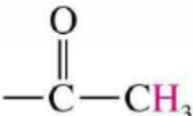
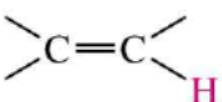
| Compound  | Chemical Shift | Difference |
|---|----------------|------------|
|  | 80.2           |            |
|  | 83.0           | 2.8 ppm    |
|  | 85.3           | 2.3 ppm    |
|  | 87.2           | 1.9 ppm    |

*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.

=>

# Typical Values

| Type of Proton  | Approximate $\delta$ | Type of Proton  | Approximate $\delta$  |
|---|----------------------|---|-----------------------|
| alkane ( $-\text{CH}_3$ )   | 0.9                  |  | 1.7                   |
| alkane ( $-\text{CH}_2-$ )  | 1.3                  | Ph—H  | 7.2                   |
| alkane ( $-\overset{ }{\text{C}}\text{H}-$ )  | 1.4                  | Ph—CH <sub>3</sub>  | 2.3                   |
|    | 2.1                  | R—CHO   | 9–10                  |
| $-\text{C}\equiv\text{C}-\text{H}$  | 2.5                  | R—COOH  | 10–12                 |
| R—CH <sub>2</sub> —X  | 3–4                  | R—OH  | variable, about 2–5   |
| (X = halogen, O)  |                      | Ar—OH   | variable, about 4–7   |
|  | 5–6                  | R—NH <sub>2</sub>   | variable, about 1.5–4 |

*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.



# 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.





# Shielding and Resonance Frequency

- Shielding effects can be taken into account by the expression:

$$B = B_0 - \sigma_i B_0$$

where  $B_0$  is the applied magnetic field strength and  $\sigma_i$  is the shielding factor.

- The effective shift is then:

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

$$\nu_{ref} = \frac{\gamma B_0}{2\pi} (1 - \sigma_{ref})$$

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

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



# Calculation of the Shielding Tensor

$$\{|k\rangle^0, \varepsilon_k^0\}$$



$$\phi$$



$$\{|k\rangle, \varepsilon_k\}$$



$$\sigma = \frac{\partial^2 E_{elec}}{\partial B \partial \mu_n}$$

Calculate zero-field SCF.

Choose gauge by which to enter the magnetic vector potential.

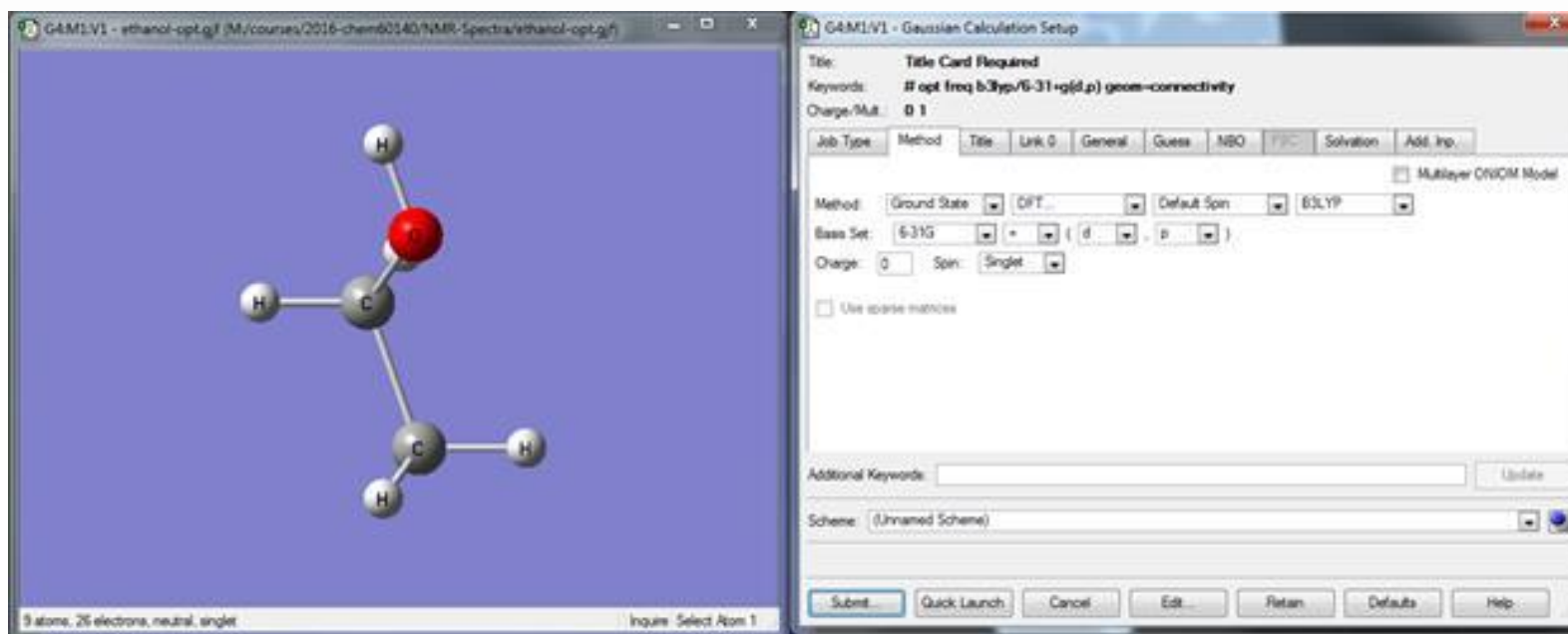
Calculate new SCF for non-zero field.  
Use the zero-field SCF results as the initial guess.

Calculate shielding tensor using the non-zero field electron structure.



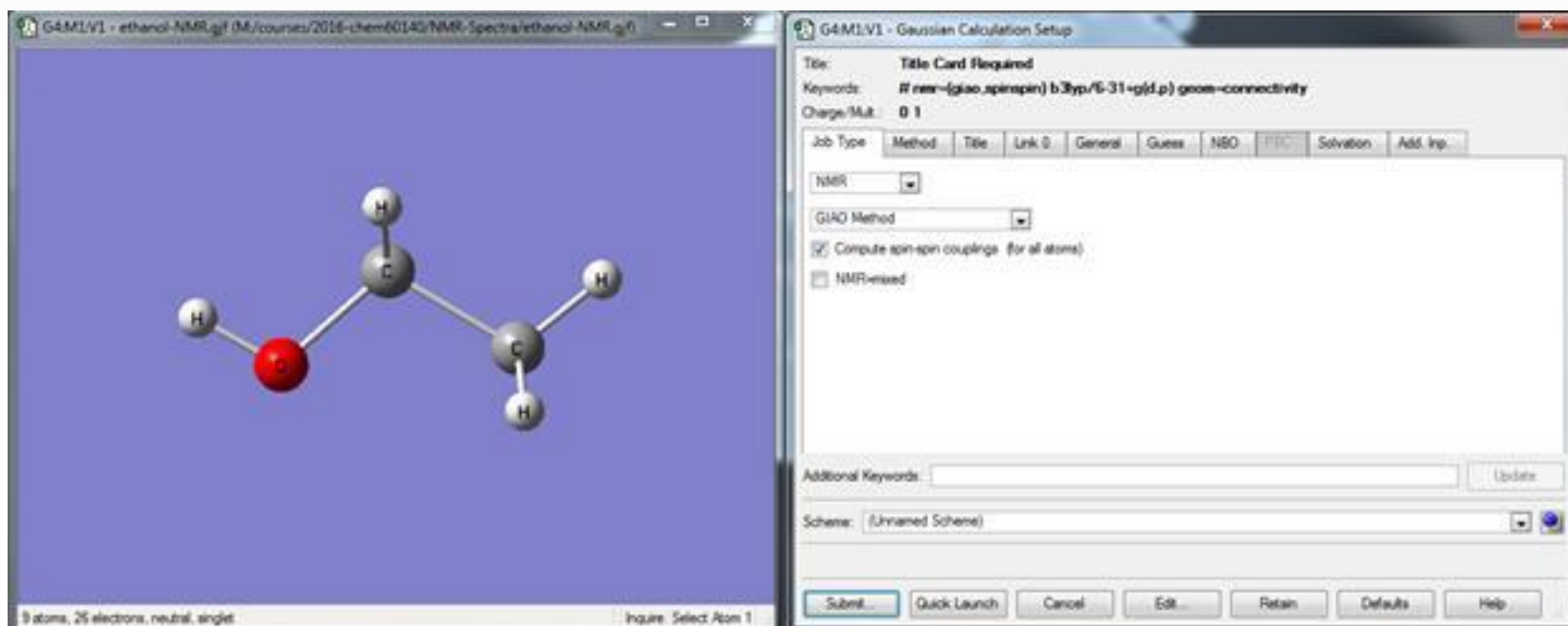
# Worked Example

- NMR spectra, and particularly spin-spin coupling constants, are sensitive functions of molecular geometry.
- We start with the computed NMR spectrum of a single molecule of ethanol.
- B3LYP/6-31+G(d,p) geometry optimization using a reasonable initial guess geometry:



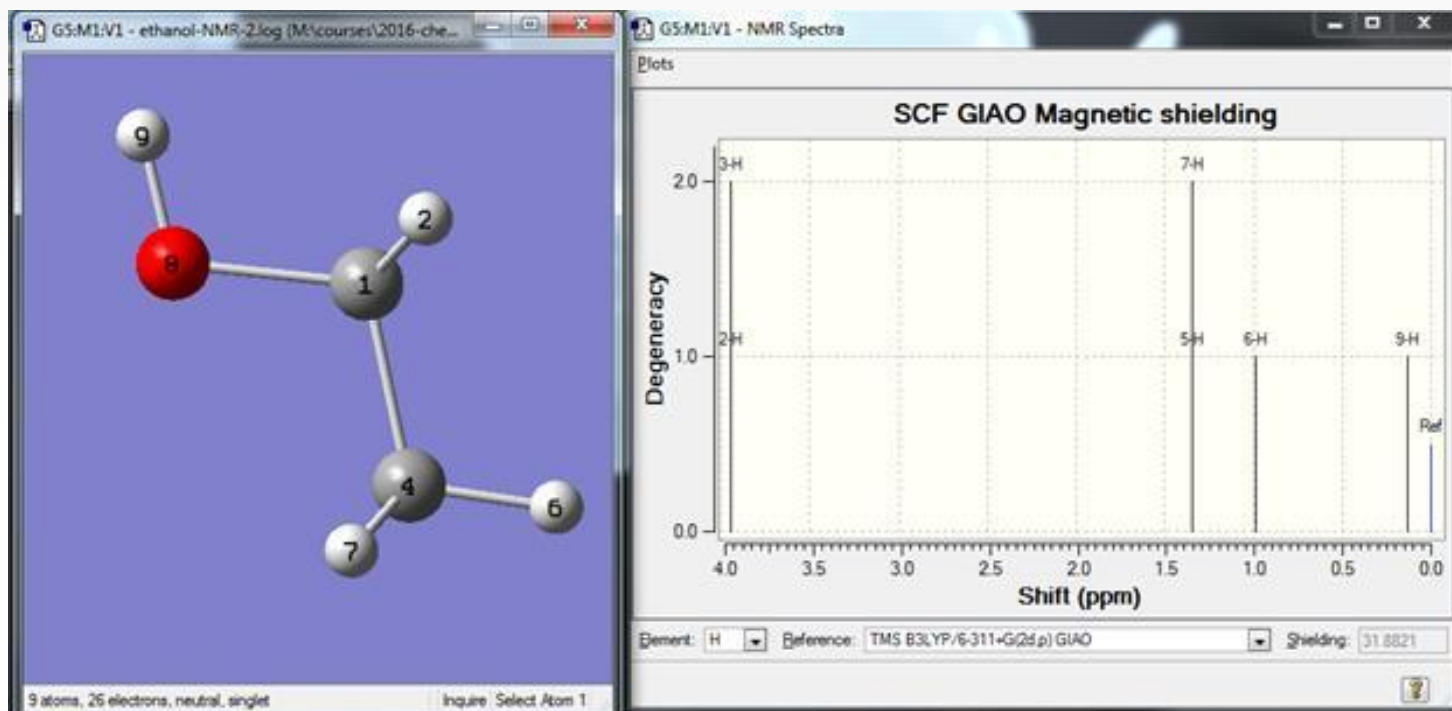
# Worked Example

- We run the geometry optimization.
- Once complete, we use the computed optimized geometry and set up a calculation with "Job Type" equal to "NMR". (default GIAO method, calculate spin-spin couplings between all atoms).



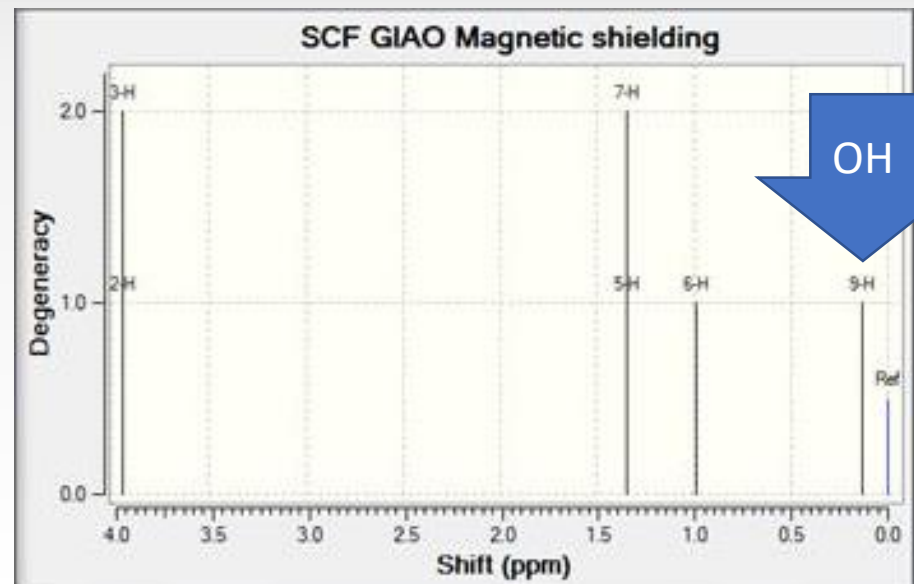
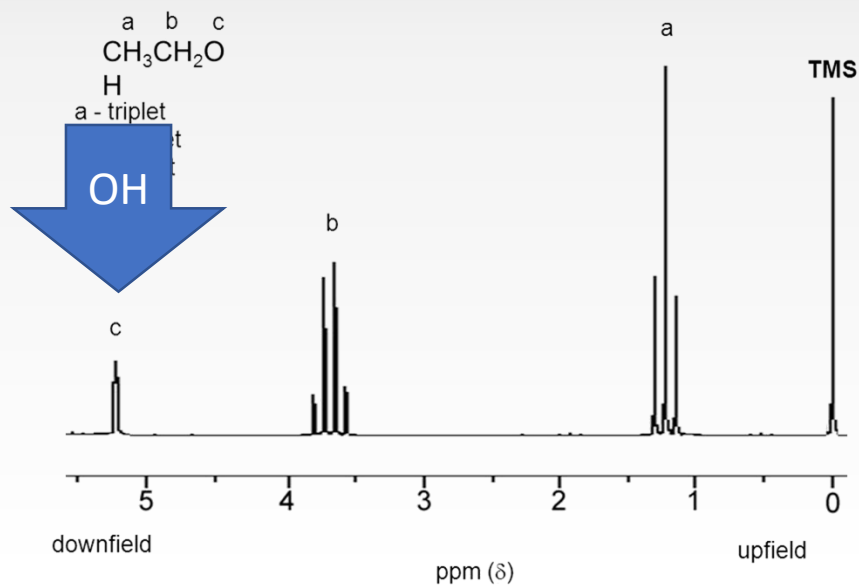
# Worked Example

- The predicted spectrum is indexed by the "number" of each atom, which comes from their order in the original input file. Use "View"=>"Labels" to see these numbers. (For example: the OH hydrogen is atom number 9).





# Worked Example



NMR spectrum of ethanol dissolved in chloroform at 89.56 MHz, taken from the SDBS.

- OH hydrogen is more shielded than in the experiment.
- This is because our **gas phase** calculation does not account for **hydrogen bonding** to solvent seen in this experiment.



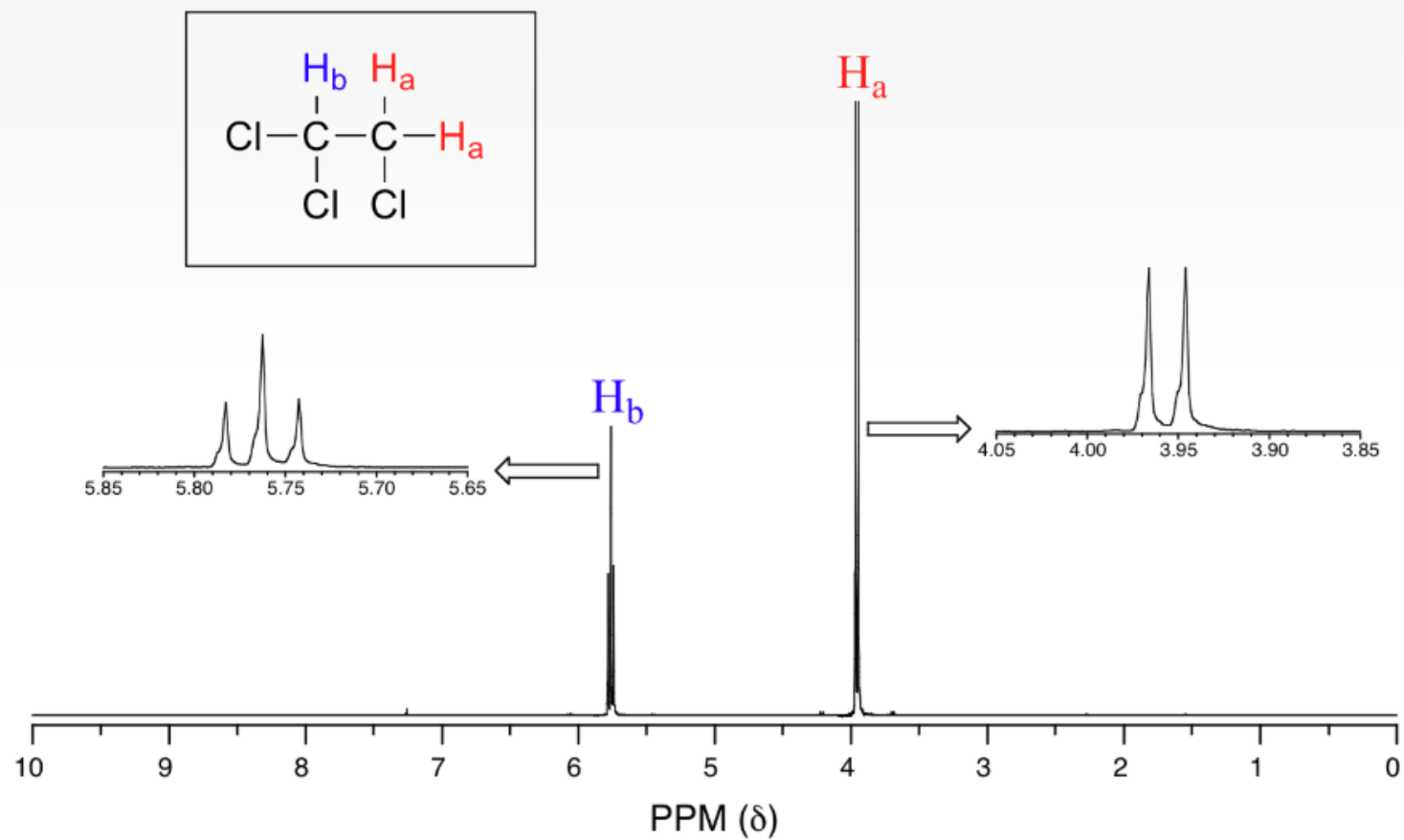




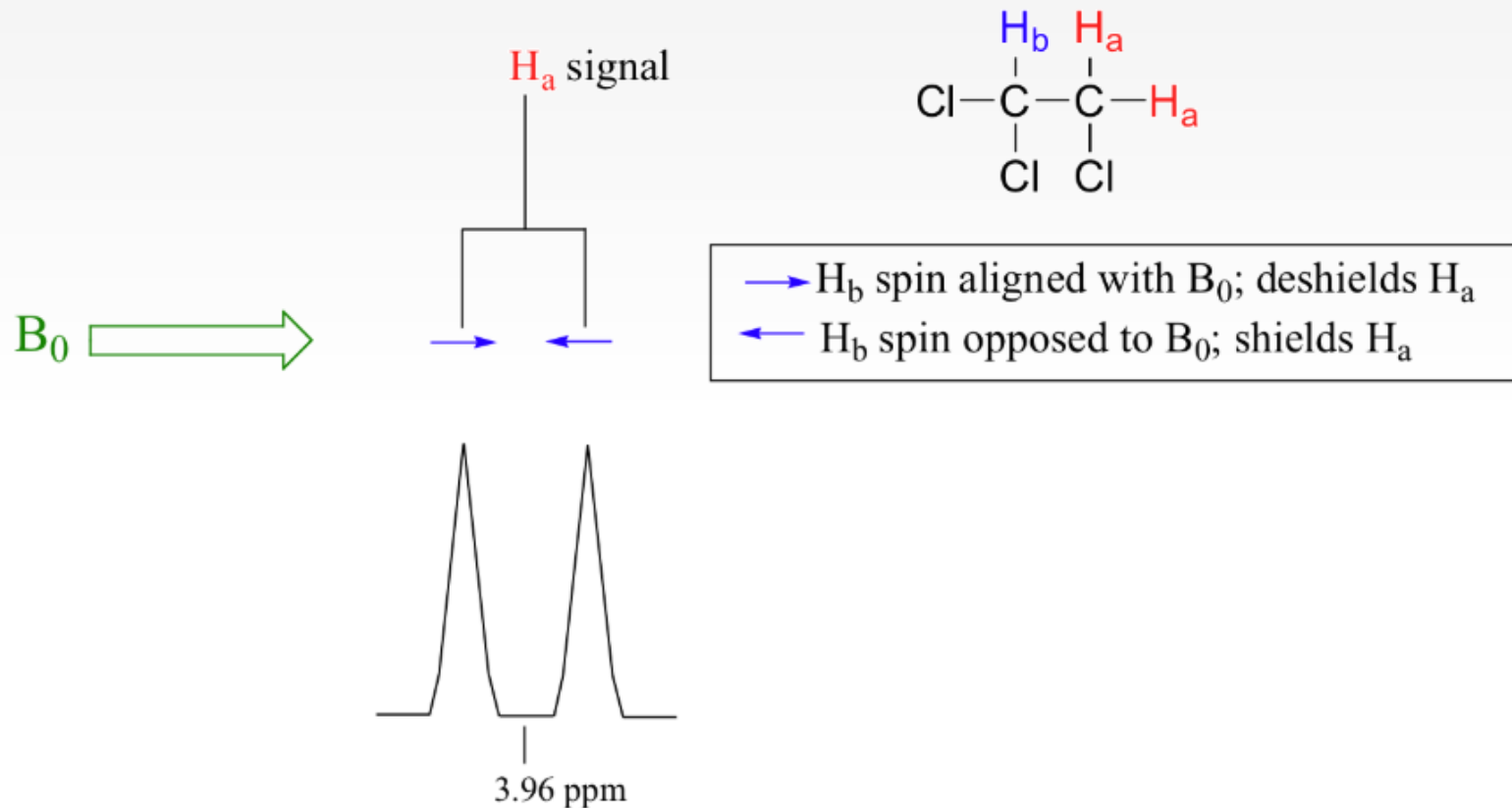


# Spin-Spin Coupling

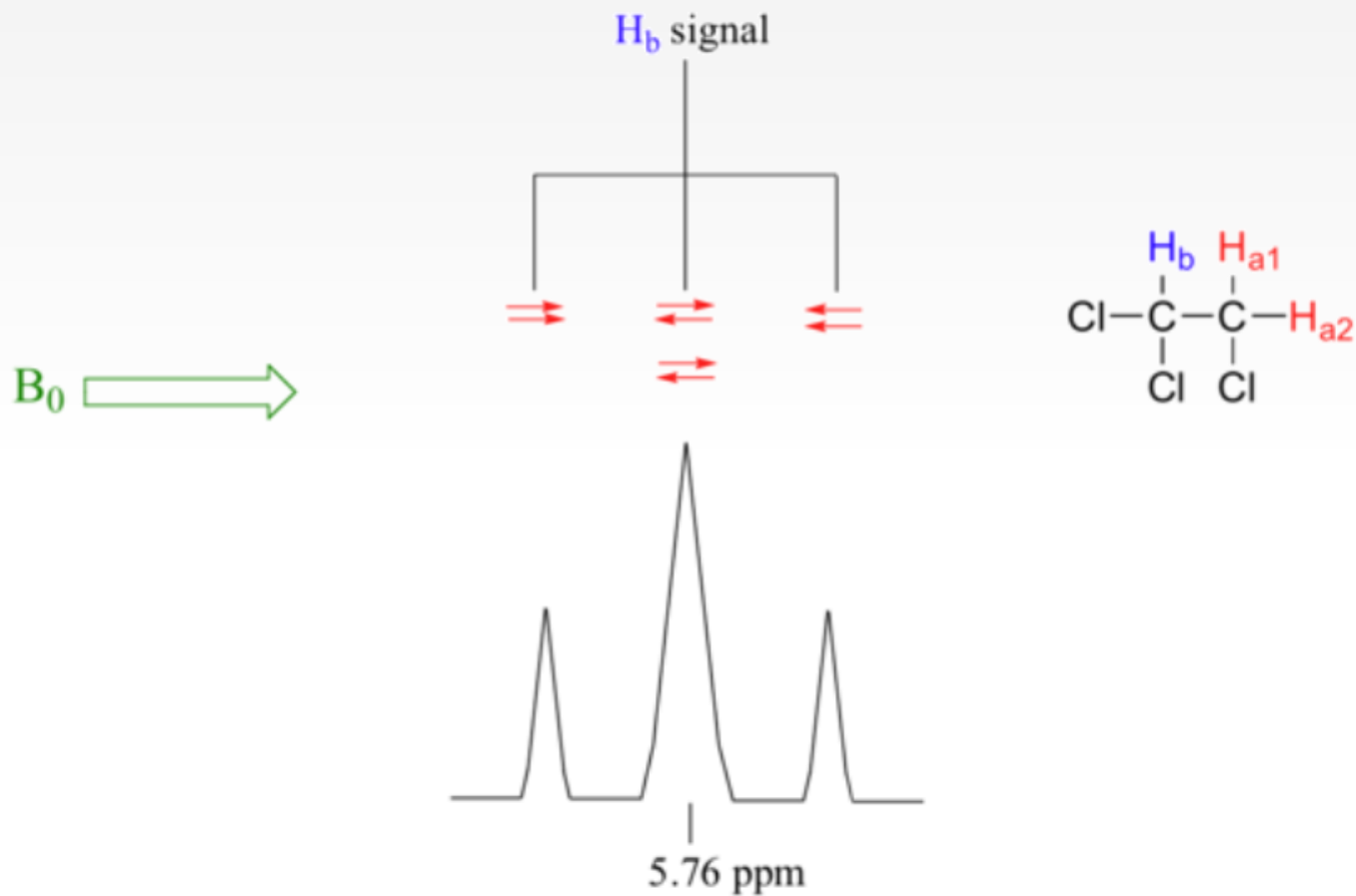
Example: 1,1,2-trichloroethane



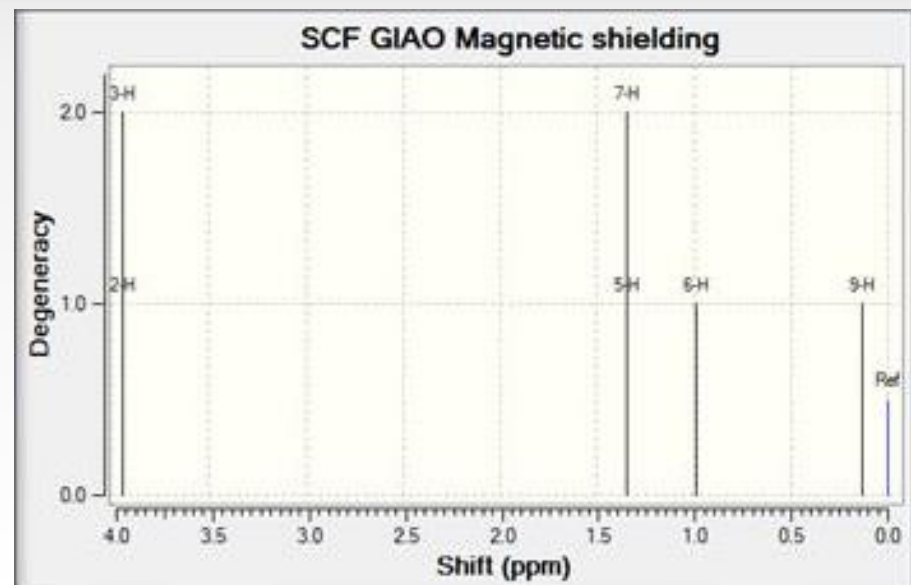
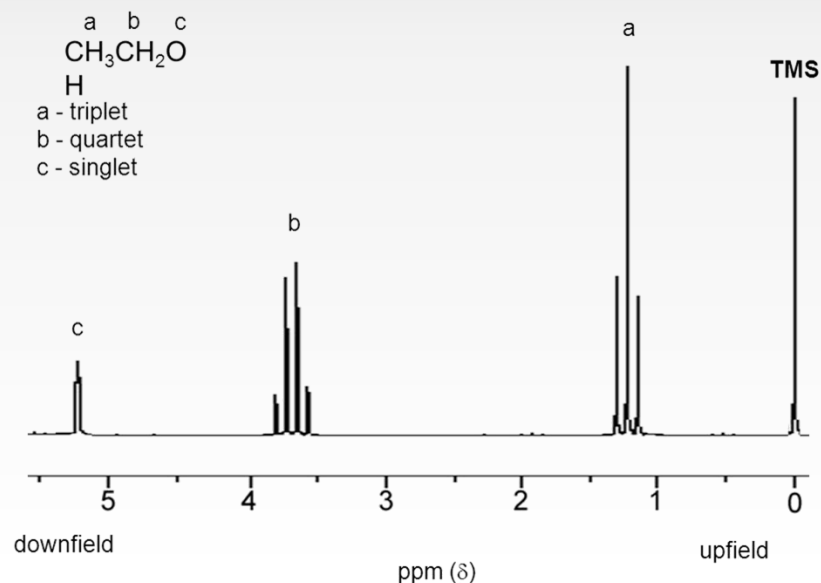
# Spin-Spin Coupling



# Spin-Spin Coupling



# Worked Example



NMR spectrum of ethanol dissolved in chloroform at 89.56 MHz, taken from the SDBS.

- Gaussian's "SpinSpin" option will calculate spin-spin couplings between all atoms.
- While GaussView won't display the results directly, one can simply use "Results"=>"Stream Output File" and search for "Total nuclear spin-spin coupling J (Hz)



# Calculation vs. Experiment

- Since the calculation is done on a static molecule, no bond rotations are possible.
- The location of the signals is given relative to a reference material calculated separately, at the same calculation level.
- Linewidths are zero (no solvent or temperature effects,  $T=0$ ).
- Splitting is not shown by default.

