The Shapes and Structures of Molecules

Michaelmas 2005 – Dr Peter Wothers

- **Nuclear Spin & NMR**

Mass of nucleus	**Proton number**	**Neutron number**	**Nuclear spin**
Odd			Half-integral
Even	Odd	Odd	Integral
Even	Even	Even	Zero

The number of nuclear spin states, s, of a nucleus with spin I is given by

$$s = 2I + 1$$

The NMR signal from a particular nuclear environment is split into η lines by coupling to n nuclei*, where

$$\eta = 2nI + 1$$

**the n nuclei are equivalent to each other, but are not equivalent to the nucleus from which the signal is received*

Coupling

Coupling is **not** observed between equivalent nuclei

The coupling constant between nuclei Y and Z, through x bonds, is denoted

$$^{x}J_{Y-Z}$$

and is measured in Hz

- ## Typical ^{13}C NMR Chemical Shifts (δ)

0-50 ppm – sp^3 carbons
50-100 ppm – sp^3 carbons attached to electronegative atoms
100-150 ppm – sp^2 carbons
150-200 ppm – sp^2 carbons attached to electronegative atoms

Finer details
Small shifts (e.g. 0 ppm) are said to be 'upfield'
Large shifts (e.g. 200 ppm) are said to be 'downfield'

For sp^3 carbons, the number of hydrogen atoms attached influences δ – 1°< 2°< 3°< 4° due to inductive effect of alkyl groups

For sp^3 carbons, an attached electronegative atom deshields the carbon and thus increases its chemical shift – if the atom is nitrogen, the shift is generally below 50 ppm but above 30 ppm. If the atom is oxygen or fluorine it is usually above 50 ppm.

Carbons that are **sp** hybridized are found around **75-100 ppm**

Acid derivatives find their quaternary carbonyl carbon around **160-170 ppm**

Incidentally, quaternary carbons exhibit a smaller peak (a less intense signal) for reasons not explained

Ketones' carbonyl carbons are found just above **200 ppm**

Aldehydes' carbonyl carbons are found just below **200 ppm**

- ## Infrared Spectroscopy

The stretching frequency of a bond between two atoms, A and B, with masses m_A and m_B, is given by

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} \quad \text{where} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

ν – stretching frequency
f – force constant (a measure of bond strength)
μ – reduced mass of A–B system

- **Typical IR absorption frequencies**

- **Quantum numbers**

Any electron in an atom is specified by four unique quantum numbers. The observed fact that no two electrons can share the same four quantum numbers is part of the Pauli exclusion principle.

The principal quantum number, n, takes on integral values: 1, 2, 3, 4, etc. and determines the shell an electron is in

The angular momentum quantum number, l, takes on integral values from 0 to $(n-1)$

The magnetic quantum number, m_l, takes on integral values from $+l$ to $-l$

The spin angular momentum quantum number, m_s, takes on values from $+s$ to $-s$. Since for an electron, s = ½, m_s = +½ or −½.

Quantum number	**Symbol**	**Values**
Principal	n	Non-zero positive integers e.g. 1, 2, 3, 4, etc.
Angular momentum	l	Integers from 0 to $(n-1)$

Magnetic	m_l	Integers from $+l$ to $-l$
Spin angular momentum	m_s	−½ or +½

- ## Schrödinger Equation

In general the Schrödinger Equation may be written

$$\hat{H}\psi = E\psi$$

where $\hat{H}$ is the Hamiltonian operator, ψ is the wavefunction and E is energy associated with the wavefunction

For the hydrogen atom, the Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

where

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\hbar = \frac{h}{2\pi}$$

and where e is the elementary charge, $\mathrm{m_e}$ is the mass of the electron and ε_0 is the vacuum permittivity

In spherical polar coordinates,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2}\sin^2\theta\frac{\partial^2}{\partial\phi^2}$$

The Bohr radius is given by

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

The wavefunction may be denoted as a function of 3D space

$$\psi_{n,l,m} = (x, y, z)$$

The energy of a wavefunction is given by

$$E_n = \frac{-m_e e^4}{8\varepsilon_0^2 h^2}\cdot\frac{z^2}{n^2}$$

In terms of the Rydberg constant, R_h, this is written

$$E_n = -R_h \cdot \frac{z^2}{n^2}$$

- **Orbital nodes**

The number of nodes in an atomic orbital is determined by its principal quantum number and its angular momentum quantum number

$$\text{Total nodes } = n - 1$$

$$\text{Angular nodes } = l$$

$$\text{Radial nodes } = n - l - 1$$

- **Orbital overlap**

The best overlap is observed between orbitals with:

- Similar size
- Similar energy
- Correct symmetry