

CHEMICAL SHIFTS

RESONANCE FREQUENCIES AND SHIELDING

- Thus far, we have specified the resonance condition as follows:

$$\nu_L = \nu_1 = \left| \frac{\gamma}{2\pi} \right| B_0, \Delta E = h\nu_1$$

- Because all nuclei of a particular type (i.e. all ^1H nuclei) have the same γ , this suggests that the resonance frequencies of all ^1H nuclei are the same (this would not be very interesting or useful)
- In molecules, nuclei are surrounded by electrons and other nuclei/atoms
- Thus, in diamagnetic molecules, the effective field (B_{eff}) at a given nucleus is (almost) always less than the actual (B_0) field

$$B_{\text{eff}} = B_0(1 - \sigma)$$

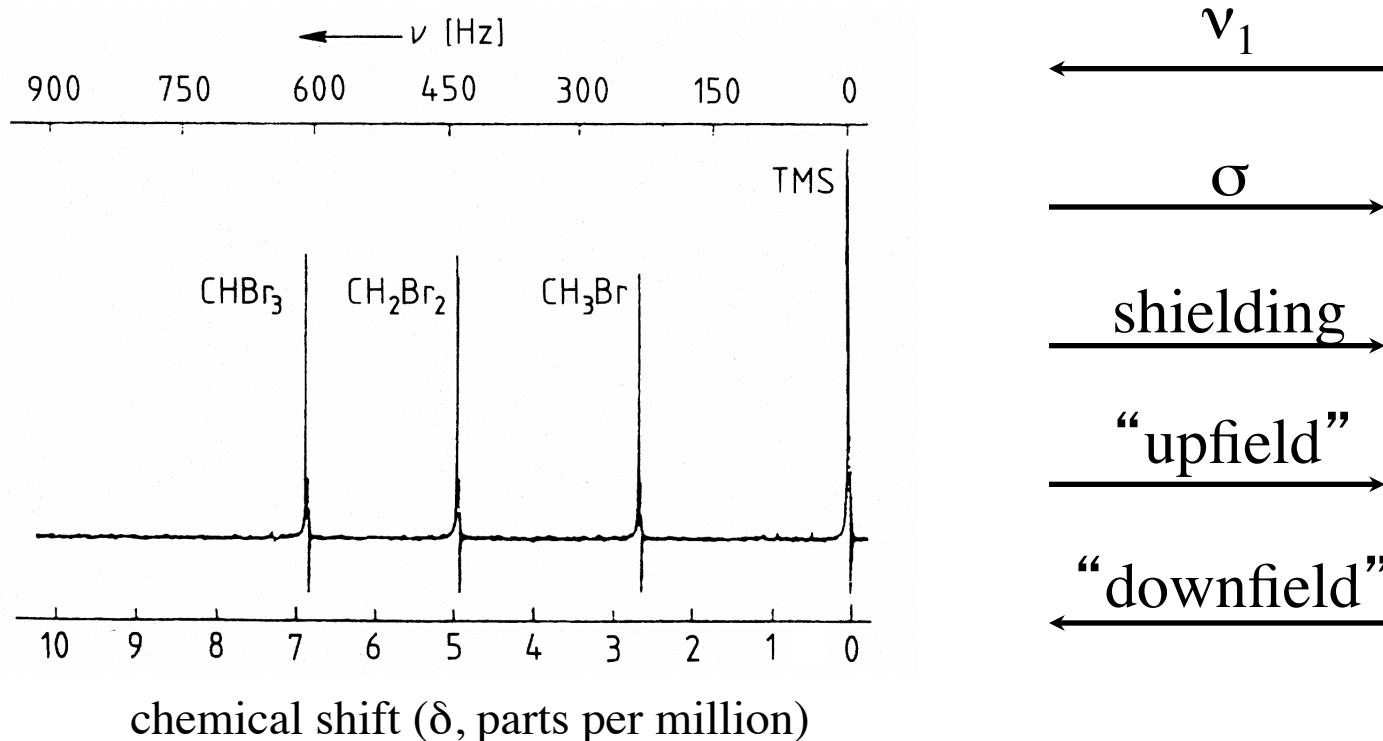
- Here σ (sigma) is the *shielding constant*
 - σ is dimensionless and independent of magnetic field strength
 - σ depends mostly on electronic structure: *highly shielded* means *high electron density*
- The new resonance condition thus is:

$$\nu_L = \nu_1 = \frac{\gamma}{2\pi}(1 - \sigma)B_0$$

RESONANCE FREQUENCIES AND SHIELDING

$$B_{eff} = B_0(1-\sigma) \quad \nu_L = \nu_1 = \frac{\gamma}{2\pi}(1-\sigma)B_0$$

- Now, ν_1 is proportional to B_0 and $(1-\sigma)$
- When the effective field (B_{eff}) that the nucleus experiences is significantly less than the actual field (B_0), the nucleus is said to be **shielded** (i.e. shielded from B_0)
 - so, increased σ = increased shielding = decreased frequency (ν_L or ν_1)
- Example: 1H deshielding by Br (90 MHz spectrometer)



CHEMICAL SHIFTS AND SHIELDING

- The frequency difference between two signals is dependent on B_0
 - this is inconvenient for comparing spectra acquired on different instruments at different B_0

$$\nu_{LA} = \frac{\gamma}{2\pi}(1-\sigma_A)B_0, \quad \nu_{LB} = \frac{\gamma}{2\pi}(1-\sigma_B)B_0, \quad \Delta\nu = \nu_{LA} - \nu_{LB} = \frac{\gamma B_0}{2\pi}(\sigma_B - \sigma_A)$$

- We can define a B_0 -*independent* parameter for expressing relative frequencies called the *chemical shift* (δ)

$$\delta_A = \frac{\nu_A - \nu_{\text{reference}}}{\nu_{\text{reference}}} \times 10^6$$

- The units of δ are parts per million (ppm)
- The denominator can be replaced by the instrument frequency (without introducing any error), and then any chemical shift difference can readily be determined

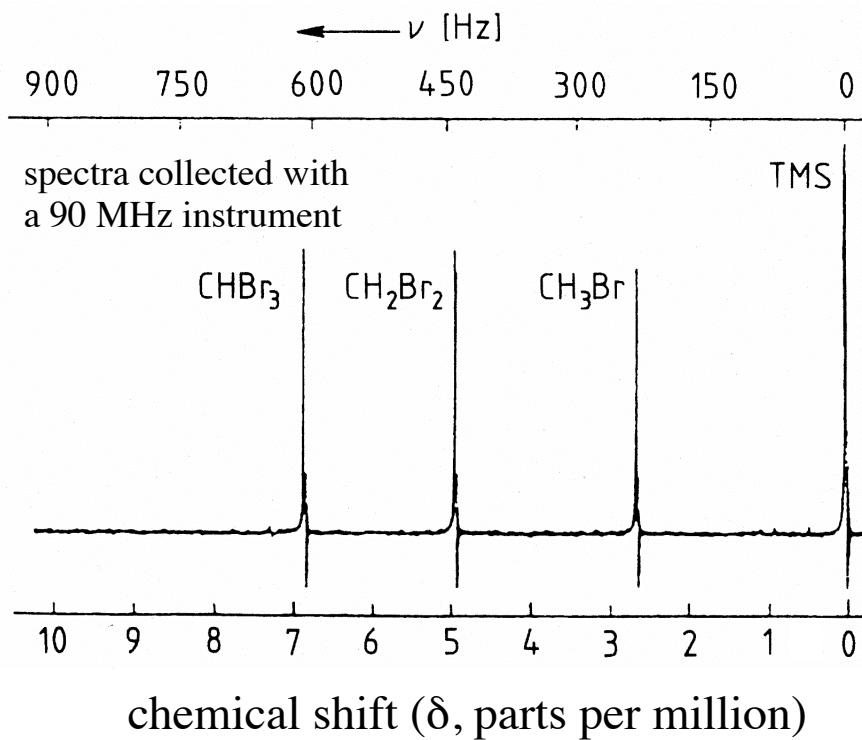
$$\Delta\delta = \frac{\Delta\nu}{\text{spectrometer frequency}} \times 10^6$$

- So, with a 400 MHz magnet, 1 ppm = 400 Hz, etc.
 - so $\Delta\delta$ is independent of magnetic field strength

CHEMICAL SHIFT REFERENCING AND RANGES

- Normally, chemical shifts are reported relative ($\Delta\delta$) to a chemical shift standard
-for ^1H , this is usually TMS (tetramethylsilane)

$$\delta_{\text{TMS}} = 0$$



- Example: CH_2Br_2

$$\Delta\delta = \frac{450 \text{ Hz}}{90 \text{ MHz}} \times 10^6 = 5 \text{ ppm}$$

ORIGINS OF SHIELDING

- The B_0 field induces current in the electron cloud surrounding nuclei, which in turn induces a local magnetic field
- The local induced magnetic field opposes the B_0 field (thus, $B_{\text{eff}} < B_0$)
- Shielding is thus dependent on the electron density distribution around the nucleus
- Lamb's equation describes the electron density ρ at a distance r from the nucleus

$$\sigma = \frac{4\pi e^2}{3mc^2} \int_0^\infty r\rho(r)dr$$

- Only valid for spherical charge density / electrons near to nucleus (s electrons)
- Examples:

He (2 1s electrons)	59.93×10^{-6}
H (~2 1s electrons)	60×10^{-6}
Ne (10 s electrons)	547×10^{-6}
- To account for non-spherical charge density (atoms in molecules, p orbitals, etc.), other terms are necessary.
- Thus, the term discussed above, which accounts for spherical charge density (s orbitals) and opposes B_0 , is called the diamagnetic component (σ^{dia}) of the shielding factor

ORIGINS OF SHIELDING

- A term to account for non-spherical charge density is necessary
- This term is called the “paramagnetic” shielding term, σ^{para}

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}}$$

- This shielding term is finite when the charge density is asymmetric
- The sign is opposite to σ^{dia} (so σ^{dia} and σ^{para} effects can attenuate or cancel one another)
- σ^{para} is inversely proportional to the square of the mass and the electronic excitation energy for low-lying excited levels

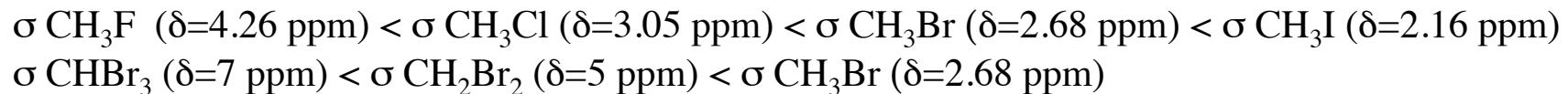
$$\sigma^{\text{para}} \propto \frac{1}{m^2 \Delta E}$$

- In heavy atoms, including ^{13}C , there are low-lying excited states, so that ΔE is small (not so for ^1H , for example), so this term can become important
- This is why the chemical shift ranges for heavier atoms are often much larger than for lighter atoms

$^1\text{H}, ^2\text{H}$:	~ 10 ppm	^{19}F	~ 1300 ppm
^{13}C	~ 300 ppm	$^{59}\text{Co}, ^{195}\text{Pt}$	$\sim 10,000$ ppm
$^{15}\text{N}, ^{31}\text{P}$	~ 500 ppm		

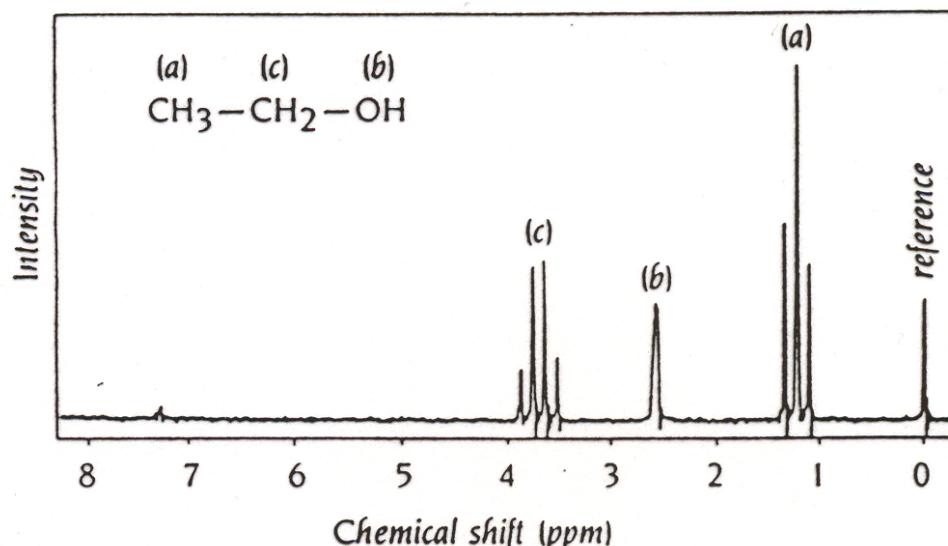
NEIGHBORING GROUP EFFECTS ON SHIELDING

- Inductive Effects:
 - chemical shift correlates with electronegativity of neighboring groups
 - electronegative groups deshield neighboring nuclei



- Electronegativity of oxygen shifts
- CH_2- of ethanol downfield

- Electronegativity of carbon chain increases as chain length increases

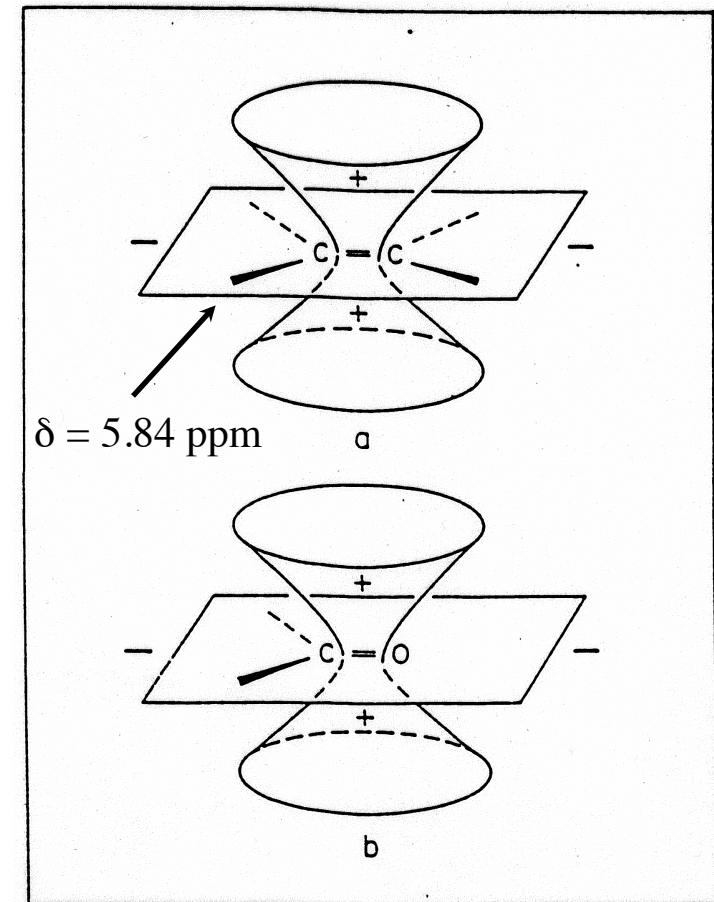
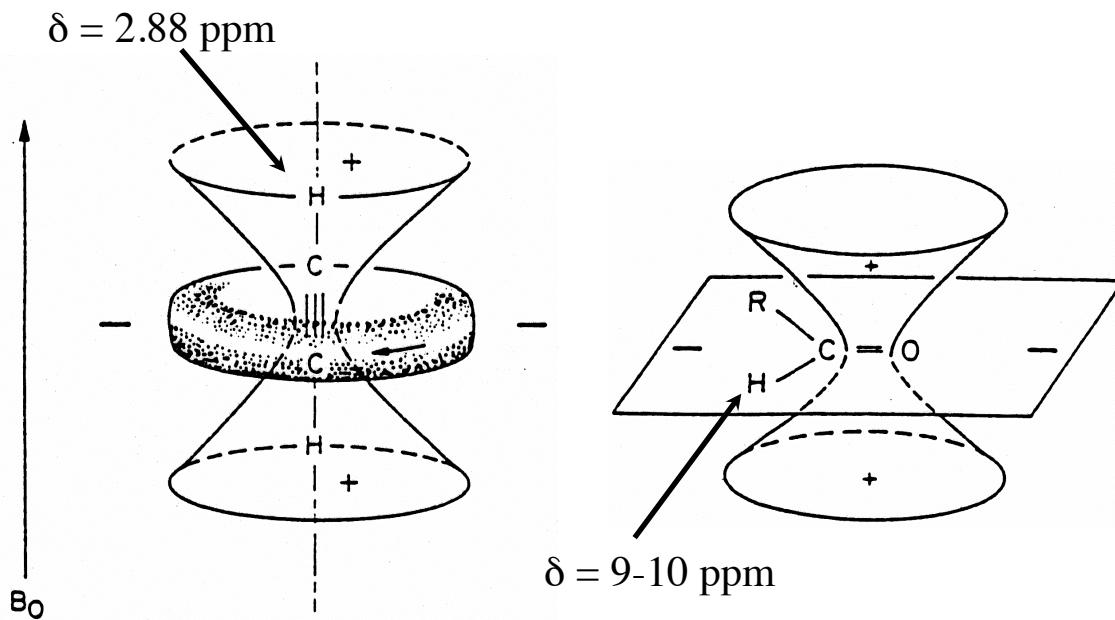


$\delta = 0.23 \text{ ppm}$	$\text{H}-\text{CH}_3$
$\delta = 0.80 \text{ ppm}$	$\text{H}-\text{CH}_2-\text{CH}_3$
$\delta = 0.91 \text{ ppm}$	$\text{H}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

NEIGHBORING GROUP EFFECTS ON SHIELDING

- Magnetic anisotropy effects:
 - chemical bonds are often magnetically anisotropic
 - thus, magnetic moments in these bonds induced by the B_0 field are not necessarily equal for different orientations of the bond
 - so, shielding of neighboring groups is dependent on their location with respect to the bond

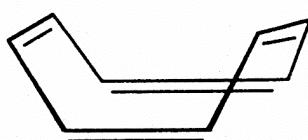
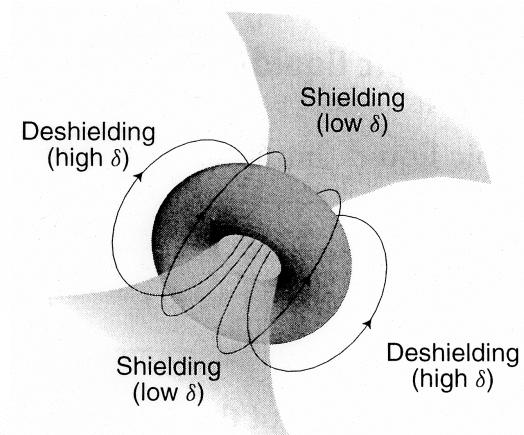
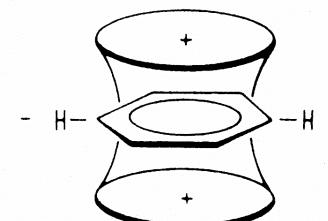
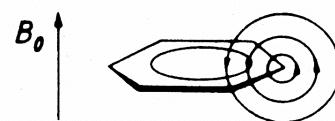
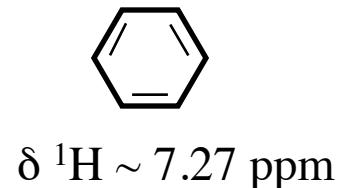
Ethane:	1.96 ppm
Ethylene	5.84 ppm
Acetylene	2.88 ppm



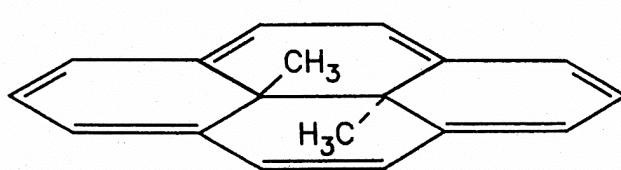
NEIGHBORING GROUP EFFECTS ON SHIELDING

- Magnetic anisotropy effects:

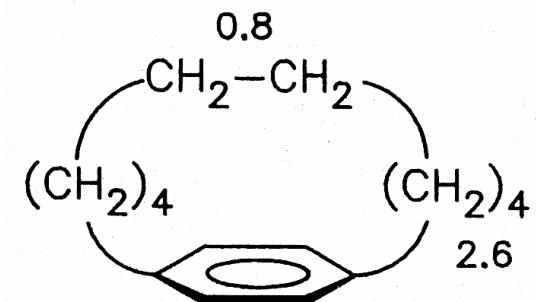
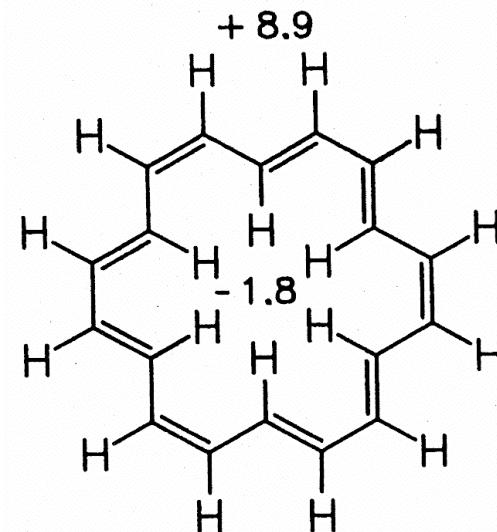
- π electrons in ring systems (i.e. benzene) support induced electron currents that differentially shield/deshield neighboring nuclei depending on location (called *ring-current shift*)



$$\delta(\text{H}) = 5.7$$



$$\delta(\text{CH}_3) = -4.25$$

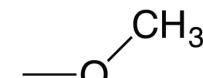
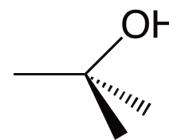
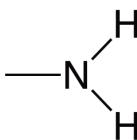


OTHER EFFECTS: MESOMERIC (RESONANCE) EFFECTS

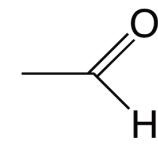
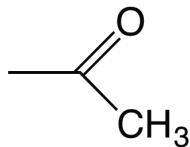
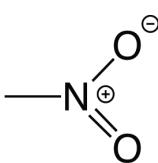
- “Mesomeric” effects are substituent effects resulting in shielding (+M) or deshielding (-M) effects explained on the basis of resonance or resonance structures of substituted compounds

Examples:

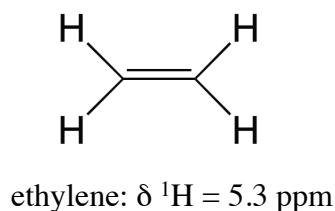
+ M substituents:



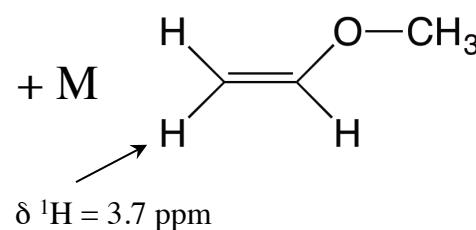
- M substituents:



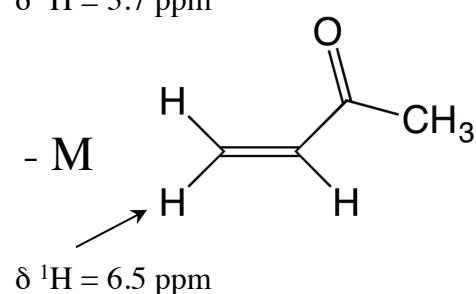
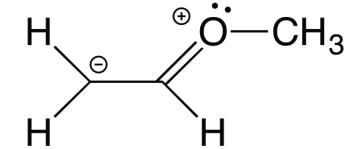
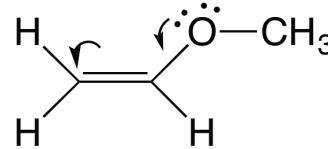
- Substituted ethylenes: chemical shifts indicate methoxy is electron releasing group (resonance)



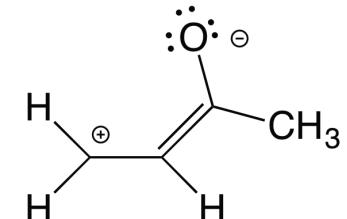
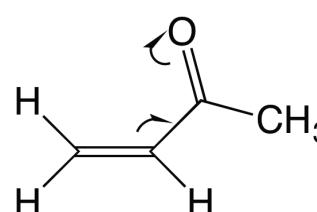
ethylene: $\delta^1\text{H} = 5.3 \text{ ppm}$



$\delta^1\text{H} = 3.7 \text{ ppm}$

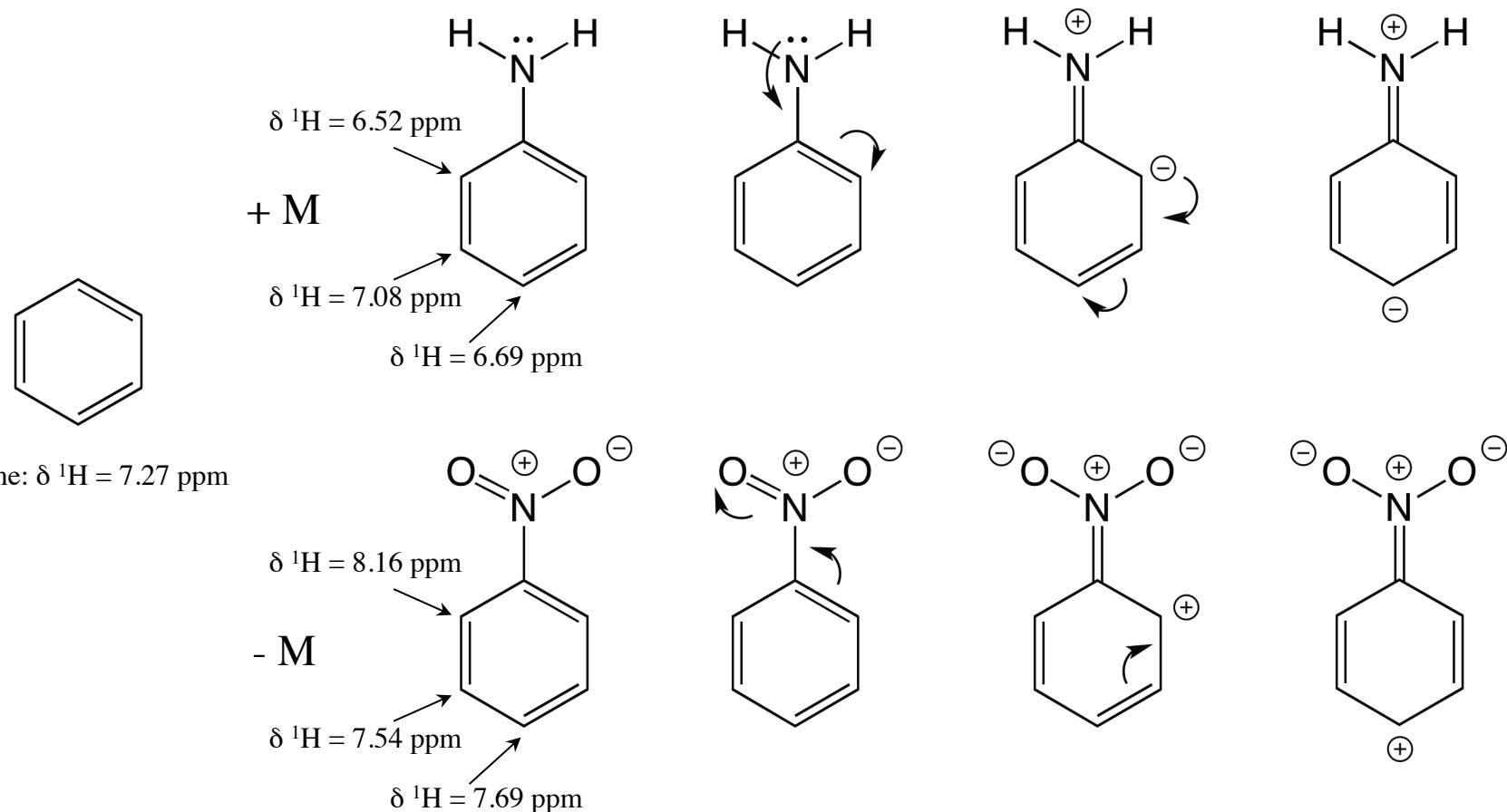


$\delta^1\text{H} = 6.5 \text{ ppm}$



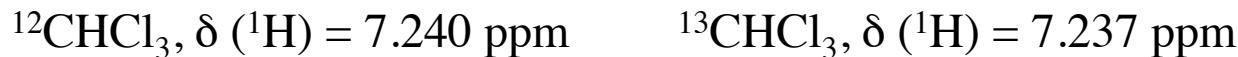
OTHER EFFECTS: MESOMERIC (RESONANCE) EFFECTS

- “Mesomeric” effects of substituents are very important in aromatic compounds

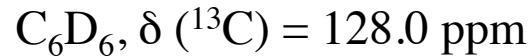
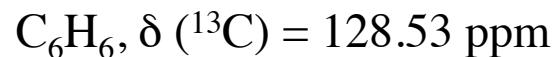


OTHER EFFECTS: ISOTOPE EFFECTS

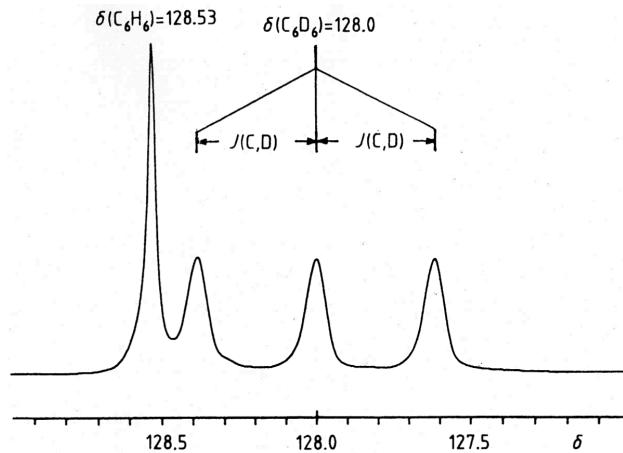
- Substituting ^{13}C for ^{12}C can have a measurable, but small, effect on ^1H chemical shifts



- Substituting ^2H (D) for ^1H (H) can have significant effects on ^{13}C chemical shifts



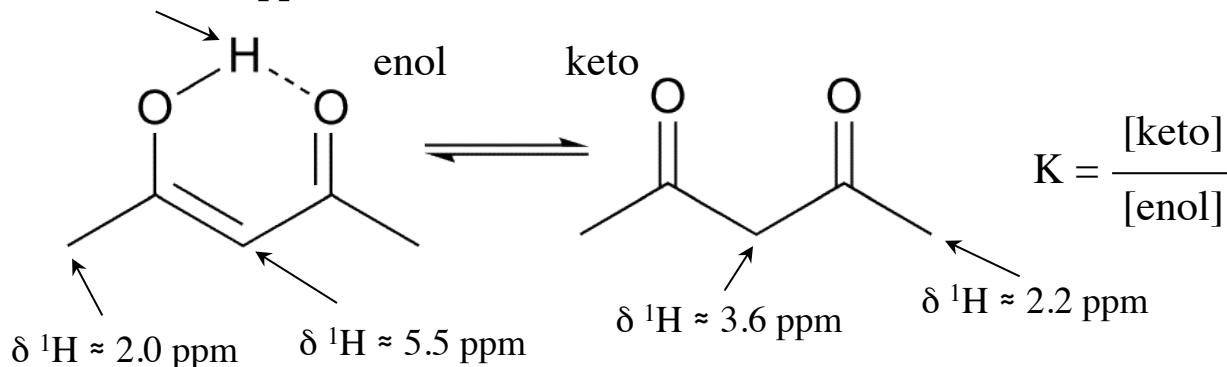
-qualitatively, the C-H bond is longer than the C-D bond, so the ^{13}C nucleus is less highly shielded by the neighboring hydrogen in C-H, so the ^{13}C chemical shift is more downfield



OTHER EFFECTS: HYDROGEN BONDING / SOLVENT EFFECTS

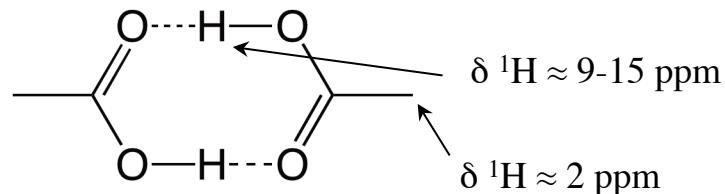
- Hydrogen bonded ^1H nuclei can have very high (downfield) chemical shifts
- Solvent polarity can dictate H-bonding and chemical shift
 - intramolecular H-bond example: acetyl acetone and keto-enol tautomerism

**** $\delta ^1\text{H} = 15.4 \text{ ppm}$ ****



Solvent	K
water	5
DMSO	0.5
THF	0.14
toluene	0.1
cyclohexane	0.024

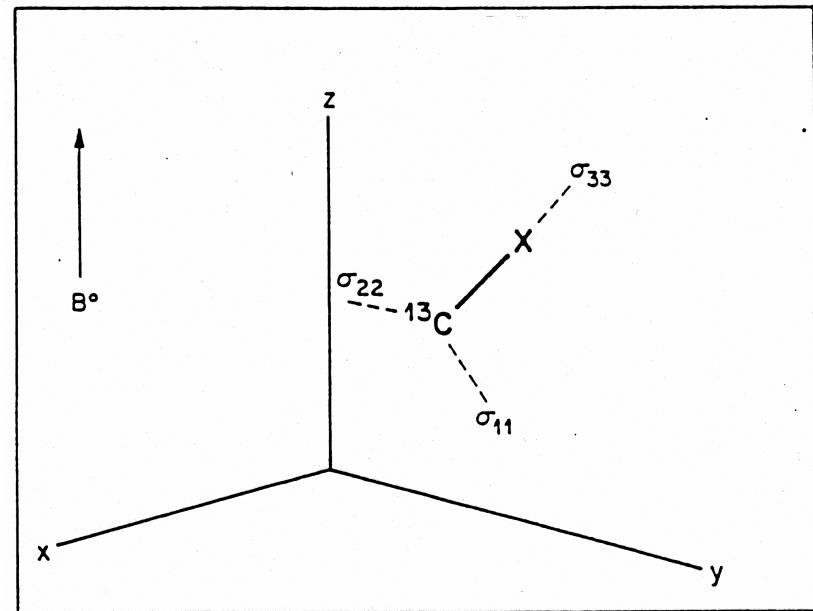
- intermolecular H-bond example: carboxylic acids are strongly H-bonded in non-polar solvents



- Warning: ^1H chemical shifts of hydroxyl groups are highly variable due to interactions with solvent (are highly temperature and concentration dependent)

CHEMICAL SHIFT ANISOTROPY

- The electron density distribution around a nucleus (in a molecule) is generally not spherically symmetric
- Therefore, the value of the shielding constant σ is dependent on the orientation of the molecule with respect to B_0
- This can be described by a tensor that relates the molecular orientation to the orientation of B_0



- The average, or isotropic, shielding is defined as the average of the trace elements of the tensor:

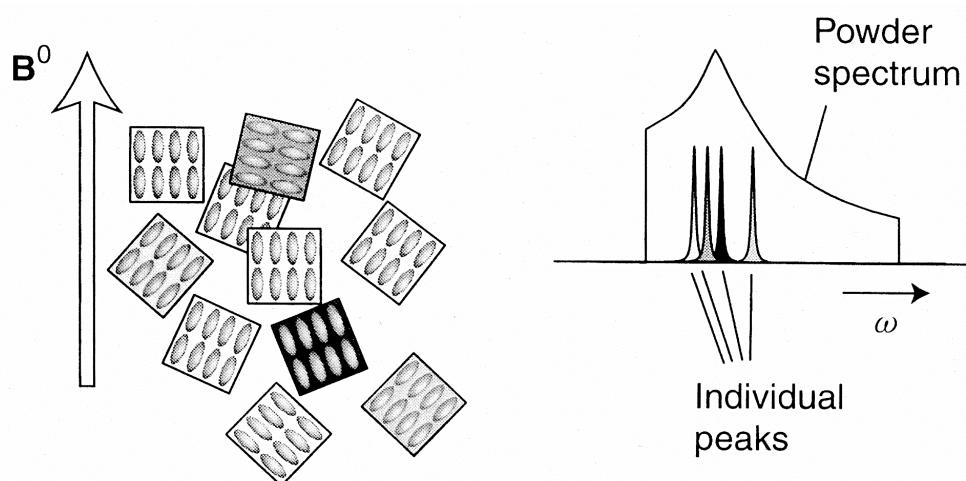
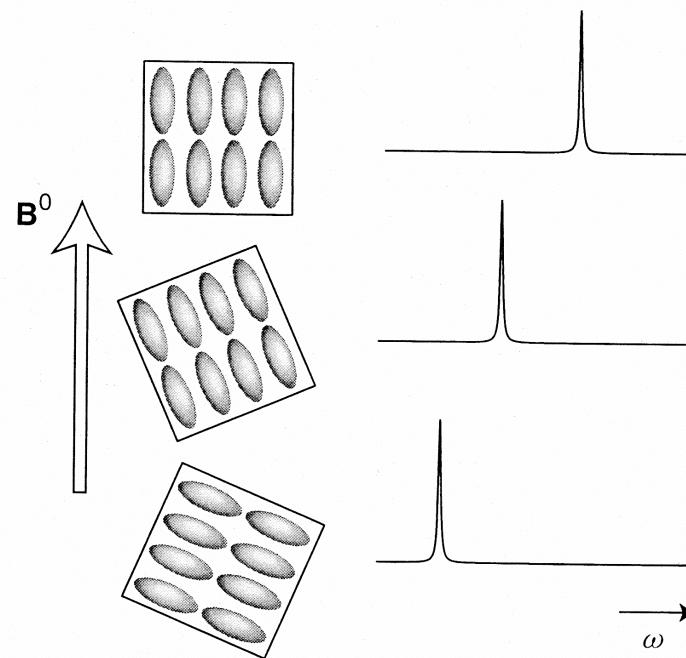
$$\sigma_{iso} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3}$$

- For molecules in solution, each molecule samples all possible orientations rapidly, so $\sigma = \sigma_{iso}$

- Above: orientation defines effective field. If σ_{33} , for instance, is aligned with B_0 , then $B_0 = (1-\sigma_{33})B_0$

CHEMICAL SHIFT ANISOTROPY

- In a crystal (right), if all molecules are oriented in the same direction, the observed chemical shift will depend simply on the orientation of the crystal in B_0



- In a powder (left), each crystallite contributes a peak at its own chemical shift, and the observed peak is a superposition of all peaks (and thus is very broad)