S.O.S. IN ENVIRONMENTAL CHEMISTRY
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Carbon-13 NMR

- The ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules - does not have a nuclear magnetic moment, and thus is NMR-inactive. Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons.

PRINCIPLE OF NMR

- The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the lower energy to a higher energy level . The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its lower level, energy is emitted at the same frequency. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.

KEY POINTS OF NMR

- Because of its charge and spin, a nucleus can behave like a magnet.
- NMR spectroscopy operates by applying magnetic filed to nuclei and then measuring amount of energy necessary to put various nuclei in resonance.
- Nuclei in different environment (shielded or deshielded) requires different amount of energy to bring them into resonance.
- An NMR spectrum provides signal or peak representing the energy necessary to bring each nuclei into resonance.

- The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton, meaning that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals. This, combined with the low natural abundance of ^{13}C, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels.
- Unlike ^{1}H-NMR signals, the area under a ^{13}C-NMR signal cannot be used to determine the number of carbons to which it corresponds. This is because the signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene (CH_2) peaks. Peak integration is generally not useful in ^{13}C-NMR spectroscopy, except when investigating molecules that have been enriched with ^{13}C isotope

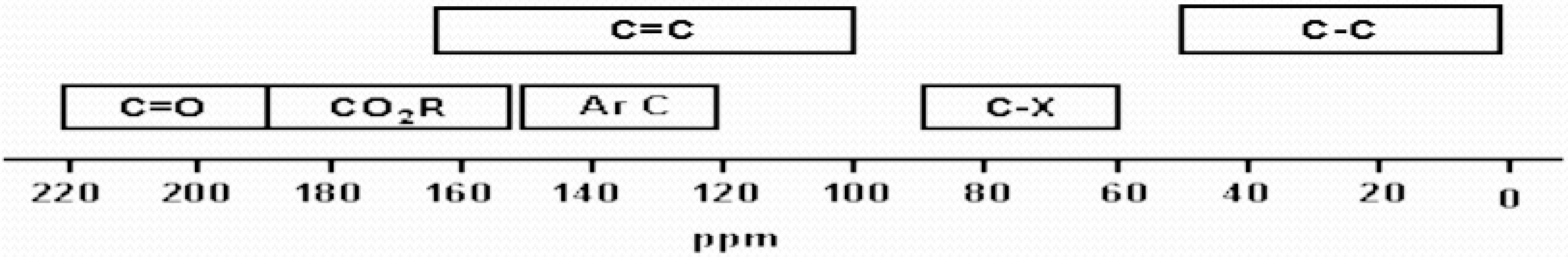
CARBON-13, NUMBER OF SIGNALS

- The number of signals in a carbon-13 spectrum gives the number of different types of carbon atoms in a molecules.

CARBON-13 CHEMICAL SHIFTS

- Carbon-13 chemical shifts are mainly most affected by the electronegativity of groups attached to the carbon.

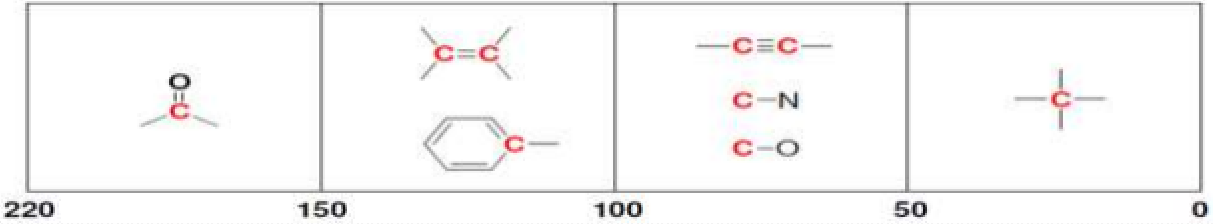
Chemical Shift



where X implies an electronegative heteroatom *e.g.* O

Carbon-13 chemical shifts are most affected by,

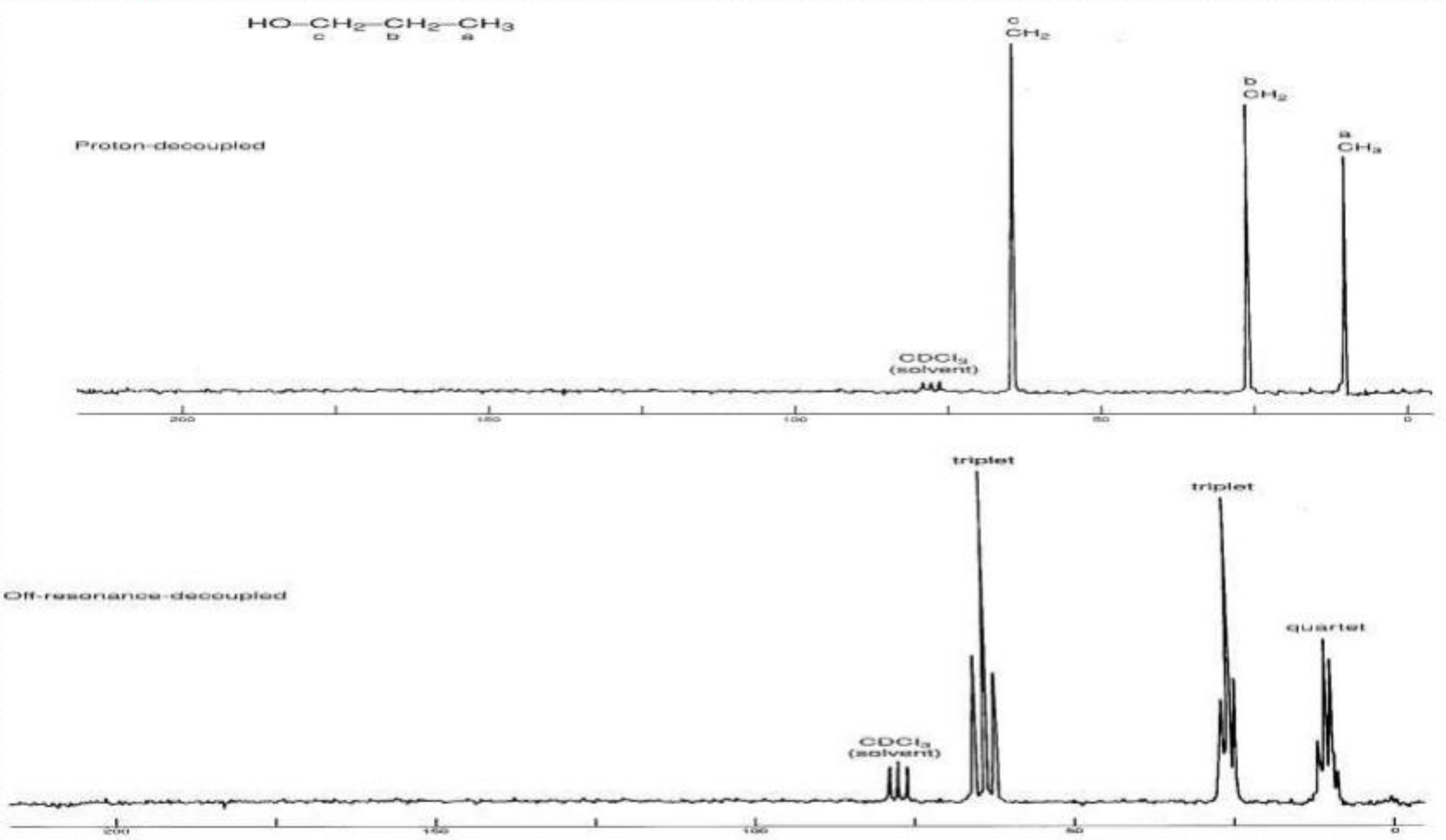
- Hybridiasation state of carbon & Electronegative group attached to carbon.



Off-Resonance Decoupling

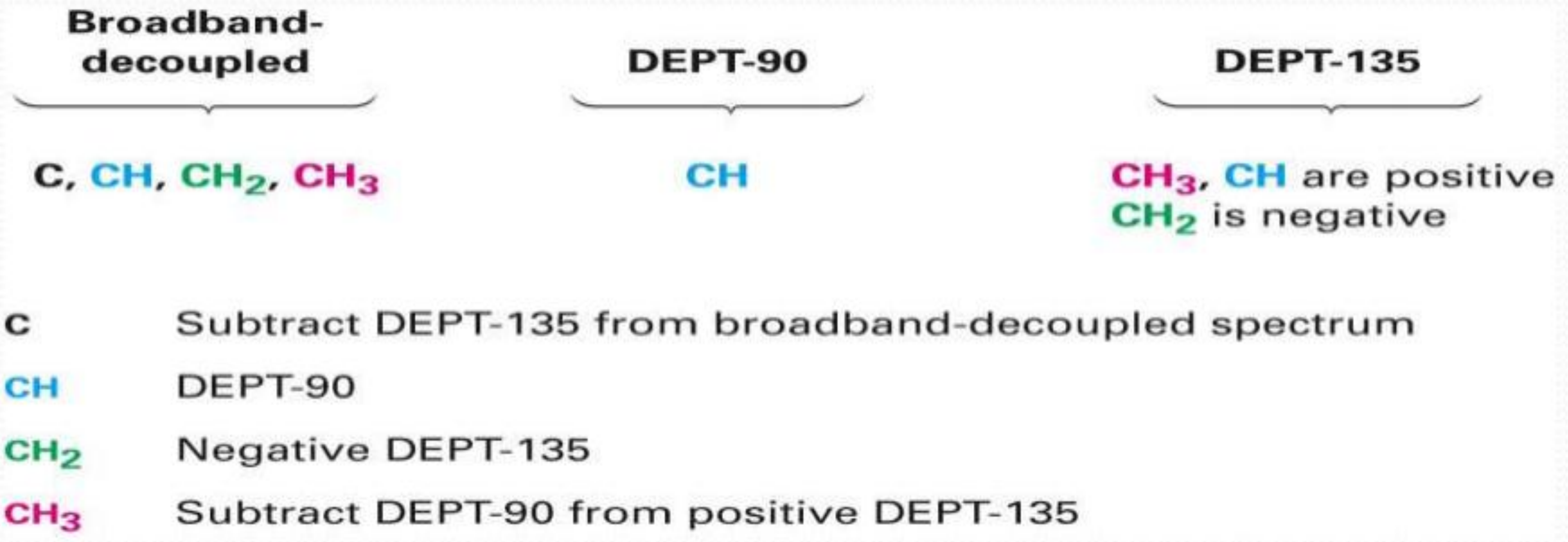
- Off-Resonance decoupling simplifies the spectrum by allowing some of the splitting information to be retained.
- In this technique only the 13C nuclei are split by the protons directly bounded to them and not by any other protons i.e., one observes only one bond coupling 13C - 1H
- The coupling between each carbon atom and each hydrogen attached directly to it, s observed acc to n+1 rule.
- Use of off-resonance decoupled spectra has been replaced by use of DEPT 13C NMR

Example: Propanol



DEPT ^{13}C NMR Spectroscopy

- Distortionless Enhancement by Polarization Transfer (DEPT-NMR) experiment
- Run in three stages



Broadband-decoupled	DEPT-90	DEPT-135
C, CH, CH_2, CH_3	CH	CH_3, CH are positive CH_2 is negative

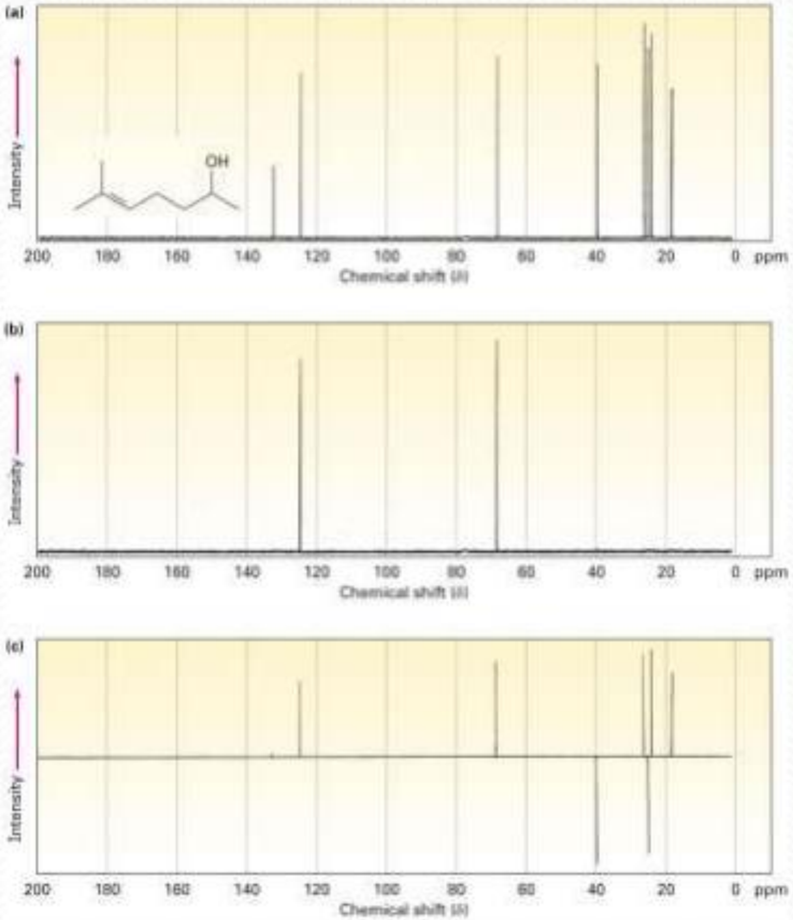
C	Subtract DEPT-135 from broadband-decoupled spectrum
CH	DEPT-90
CH_2	Negative DEPT-135
CH_3	Subtract DEPT-90 from positive DEPT-135

Example: 6methylhept-5-en-2-ol

(a) Ordinary broadband-decoupled spectrum showing signals for all eight of 6-methylhept-5-en-2-ol

(a) DEPT-90 spectrum showing signals only for the two C-H carbons.

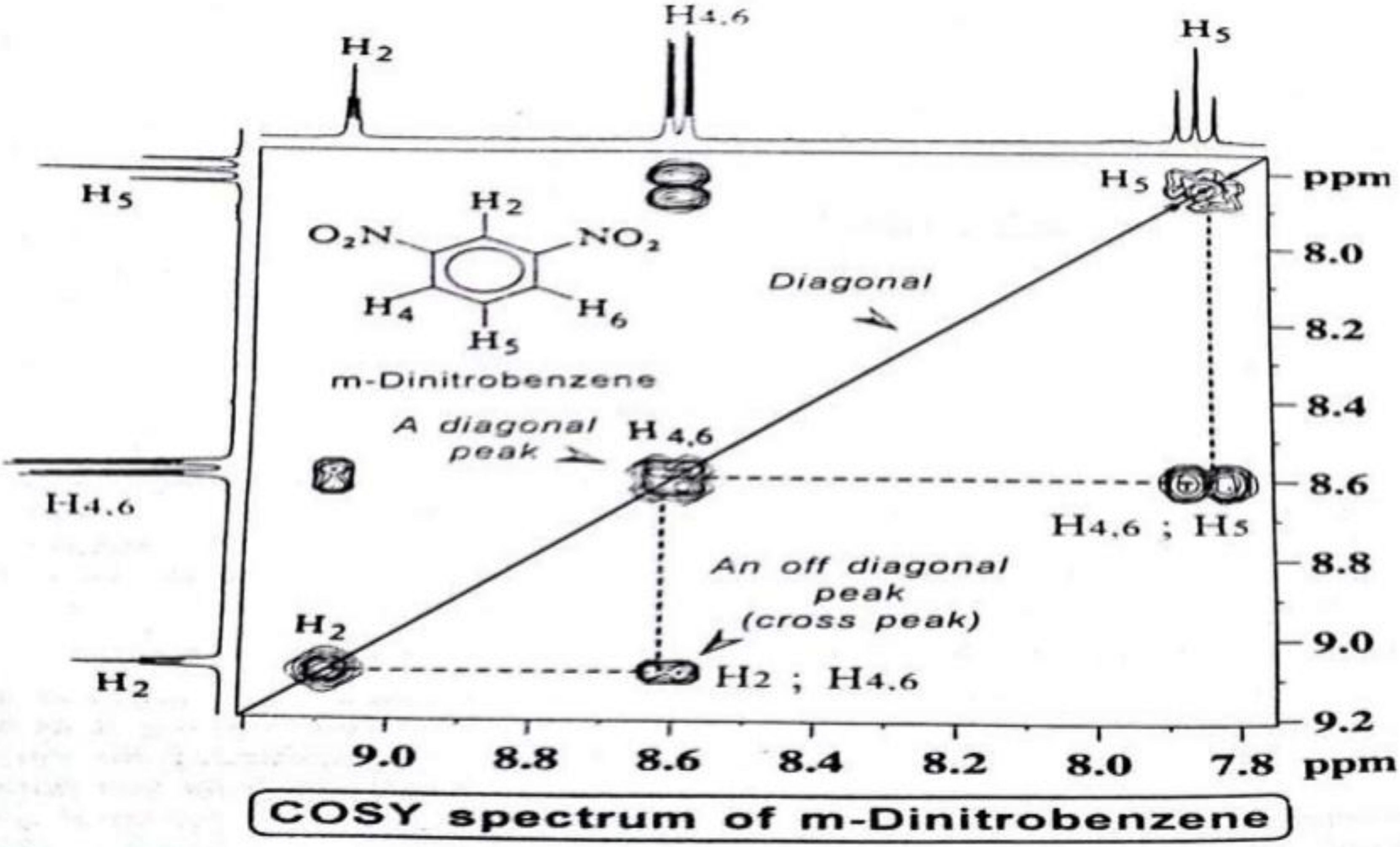
(b) DEPT-135 spectrum showing positive signals for the two CH carbons and the three CH_3 carbons and negative signals for the two CH_2 carbons.



COSY Spectrum

- 2D NMR spectra have two frequency axes and one intensity
- The common 2D spectra are 1 H - 1H shift correlations known as COSY Spectrum.
- COSY identifies pair of protons which are coupled to each other.
- The compound is identified using a contour plot One dimensional counterpart of a given peak on the diagonal lies directly below that peak on each axis
- The presence of cross peak normally indicates protons giving the connected resonance on the diagonal are geminaly or vicinally coupled.

COSY Spectrum of m-dinitrobenzene



COSY spectrum of m-Dinitrobenzene

Applications of 13C NMR

- CMR is a noninvasive and nondestructive method,i.e,especially used in repetitive In-vivo analysis of the sample without harming the tissues .

- CMR, chemical shift range(0-240 ppm) is wider compared to H-NMR(0-14 ppm), which permits easy separation and identification of chemically closely related metabolites.

- C-13 enrichment, which the signal intensities and helps in tracing the cellular metabolism.

- CMR technique is used for quantification of drugs purity to determination of the composition of high molecular weight synthetic polymers.