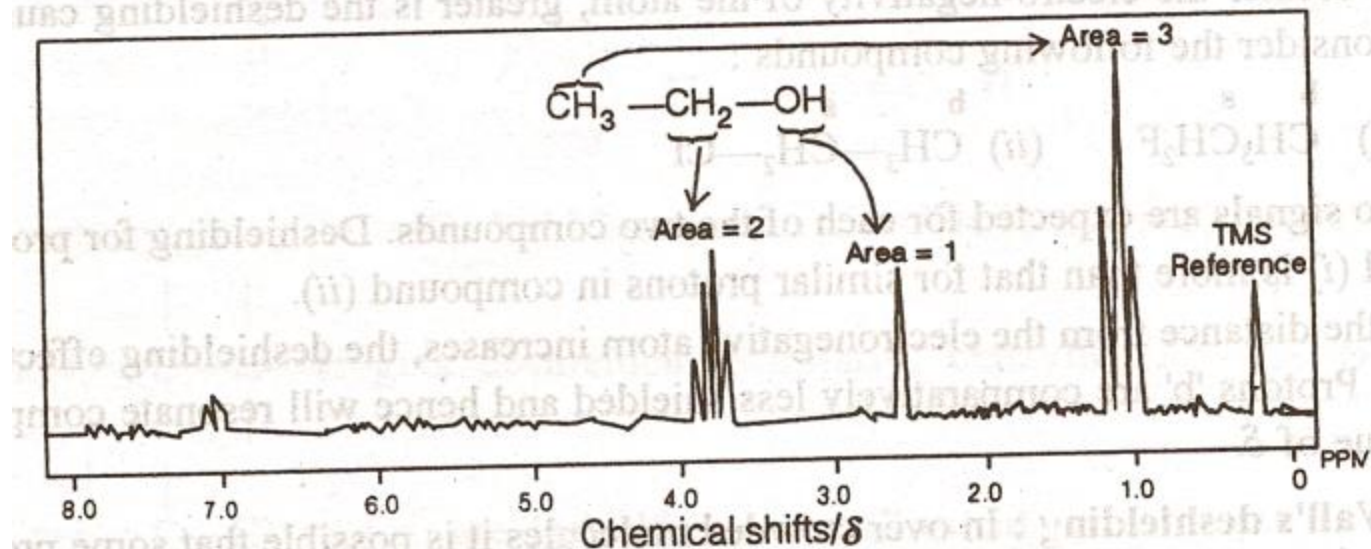


Spectroscopy



The spectrum shows 3-peaks, corresponding to the protons in —OH , $\text{—CH}_2\text{—}$, and —CH_3 respectively. The areas under the 3-peaks are in the ratio of 1:2:3 which correspond to the number of protons in OH , CH_2 and CH_3 . At high resolution, the main peak for $\text{—CH}_2\text{—}$ splits into three sub peaks, thereby indicating the presence of three protons on the adjacent carbon.

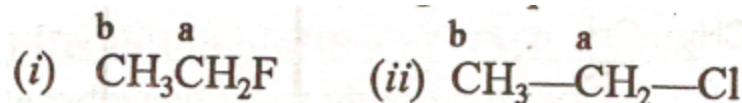
Spectroscopy

Factors Influencing Chemical Shift

- (i) Inductive effect
- (ii) van der Waals's deshielding
- (iii) Hydrogen bonding

(i) Inductive effect: A proton is said to be deshielded if it is attached to an electro-negative atom or group. Greater the electro-negativity of the atom, greater is the deshielding caused to the proton.

Example :



Two signals are expected for each of the two compounds. Deshielding for protons 'a' in compound (i) is more than that for similar protons in compound (ii). As the distance from the electronegative atom increases, the deshielding effect due to it decreases. Protons 'b' are comparatively less shielded .

Spectroscopy

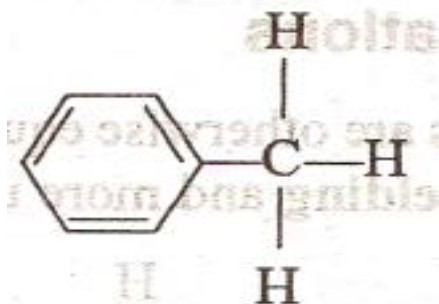
- (ii) van der Waals' deshielding :** In over crowded molecules it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of the bulky group (hindered group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate higher value of δ than expected in the absence of this effect.
- (iv) Hydrogen bonding :** If a hydrogen atom exhibits the property of hydrogen bonding in a compound, it will get deshielded due to the strongly electronegative atoms attached to it. As a result, absorption is shifted down- field.

Spectroscopy

Rules Governing the Splitting of Proton Signals

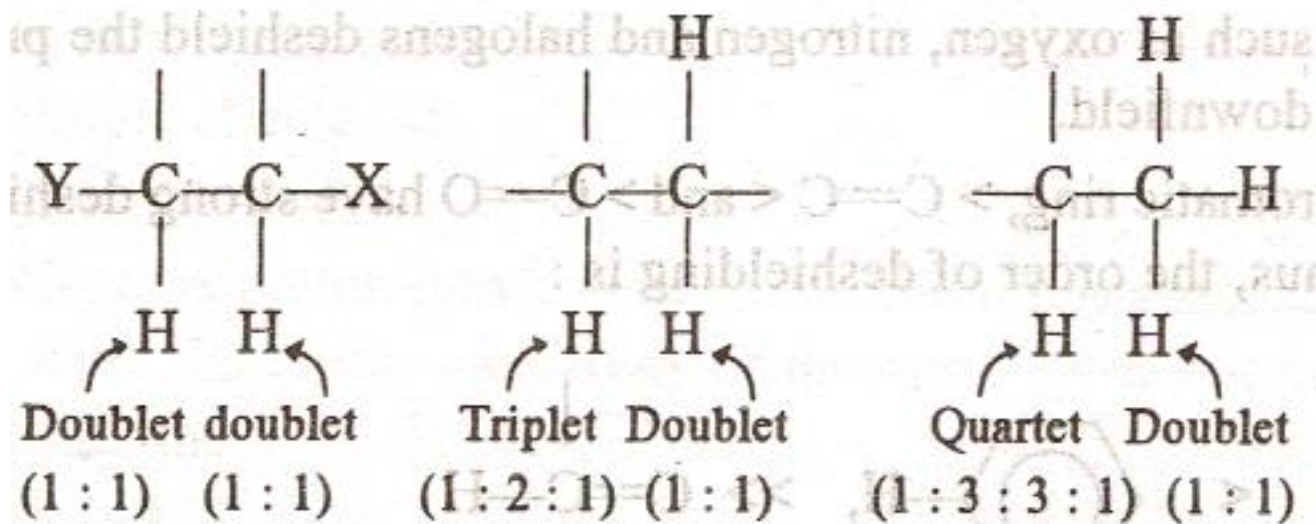
- (i) Splitting of a proton signal is caused only by neighbouring or vicinal protons (i.e., protons on adjacent carbon atoms) provided these are non-equivalent to the absorbing proton. Thus, there would be no splitting in the spectrum of ethylene chloride $\text{ClCH}_2\text{CH}_2\text{Cl}$ (since adjacent carbon has equivalent protons.)
- (ii) Splitting of one proton by another on the same carbon is rare because such protons are generally equivalent to each other.
- (iii) The mutual splitting of protons separated by more than two carbon atoms is very uncommon. Thus, there is no splitting of signals in toluene since the non-equivalent protons are separated by more than two carbon atoms.

Spectroscopy



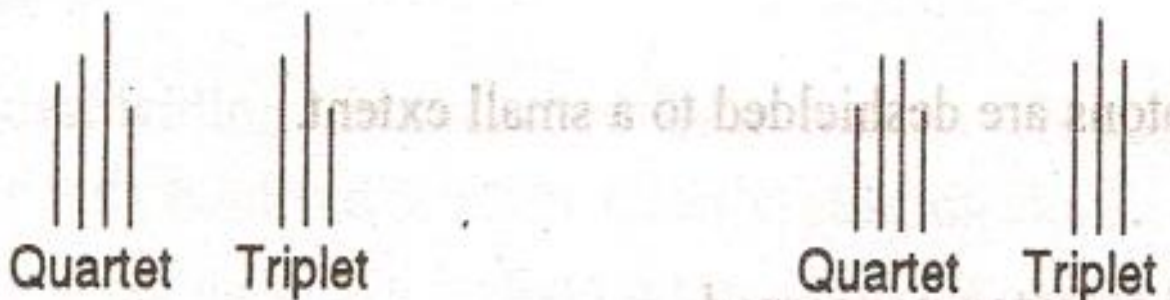
- (iv) The number of peaks (N) obtained after the splitting is one more than the number of vicinal protons (n), i. e.,
 $N = n + 1$. Thus, an NMR signal due to a proton is split into a doublet by one vicinal proton, into a triplet by two vicinal protons, into a quartet by three vicinal protons, into a quintet of four vicinal protons.

Spectroscopy



- (v) All the peaks of a given multiplet are not symmetrical. The inner peaks, i. e., the peaks near the other coupled multiplets, are relatively larger than the other peaks. Thus, in case of ethyl bromide, the triplet and quartet obtained are as :

Spectroscopy



Coupling Constant : The distance between the peaks in a multiplet is referred to as coupling constant. It is represented by the symbol 'J' and is expressed in the unit of Hertz.

This constant is a measure of the magnitude of the splitting effect. Unlike the chemical shifts, the 'J' values are independent of the applied magnetic field but depend on the molecular structure.

Spectroscopy

Application of NMR Spectroscopy :

- 1. Identification of substances:** Like infrared spectrum, the NMR spectrum of a substance often serves as the 'fingerprint' of the substance. If the NMR spectrum of a given sample is exactly the same as that of a known substance, its structural identity is established.
- 2. Qualitative analysis :** The NMR spectrum helps to establish the presence or absence of functional groups or other characteristic structural features of a given substance from their characteristic chemical shifts. Appearance of a signal at δ 9.5, is indicative of -CHO group in the sample.

Spectroscopy

- 3. Rate of reactions:** The NMR spectroscopy forms a means of studying certain reactions which are too fast for measurement by ordinary techniques. One such relation is the fast exchange of protons between two molecules having protons attached to electronegative atoms with lone pair of electrons.
4. Determination of molecular structure.
5. It is used to assay pharmaceutical formulations such as aspirin, Phenacetin and Caffeine.
6. It is used for the determination of fluorine content in plastics.

Spectroscopy

Advantages of NMR Spectroscopy

1. It is a totally non-destructive technique.
2. Compared to IR spectroscopy, it is much easier to study solid samples by this technique as a wide variety of solvents is available.
3. The NMR spectrometers used now-a-days are so improved that the spectra can be recorded as fast or even faster than IR spectra.
4. It is possible to have computer calculation of NMR spectra.