

# Spectroscopy

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## SUMMARY

Section 13.1 Structure determination in modern-day organic chemistry relies heavily on instrumental methods. Several of the most widely used ones depend on the absorption of electromagnetic radiation.

Section 13.2 Absorption of electromagnetic radiation causes a molecule to be excited from its most stable state (the *ground* state) to a higher energy state (an *excited* state).

### *Spectroscopic method*

Nuclear magnetic resonance

Infrared

Ultraviolet-visible

### *Transitions between*

Spin states of an atom's nucleus

Vibrational states

Electronic states

Mass spectrometry is not based on absorption of electromagnetic radiation, but monitors what happens when a substance is ionized by collision with a high-energy electron.

## *<sup>1</sup>H Nuclear Magnetic Resonance Spectroscopy*

Section 13.3 In the presence of an external magnetic field, the  $\alpha$  and  $\beta$  nuclear spin states of a proton have slightly different energies.

Section 13.4 The energy required to “flip” the spin of a proton from the lower energy spin state to the higher state depends on the extent to which a nucleus is shielded from the external magnetic field by the molecule's electrons.

Section 13.5 Protons in different environments within a molecule have different **chemical shifts**; that is, they experience different degrees of shielding. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) from tetramethylsilane (TMS). Table 13.1 lists characteristic chemical shifts for various types of protons.

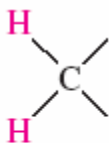
Section 13.6 In addition to *chemical shift*, a  $^1\text{H}$  NMR spectrum provides structural information based on:

*Number of signals*, which tells how many different kinds of protons there are

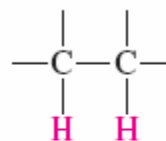
*Integrated areas*, which tells the ratios of the various kinds of protons

*Splitting pattern*, which gives information about the number of protons that are within two or three bonds of the one giving the signal

Section 13.7 **Spin–spin splitting** of NMR signals results from coupling of the nuclear spins that are separated by two bonds (*geminal coupling*) or three bonds (*vicinal coupling*).



Geminal hydrogens  
are separated by two bonds



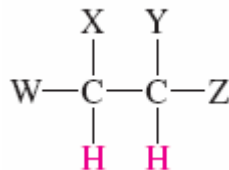
Vicinal hydrogens  
are separated by three bonds

In the simplest cases, the number of peaks into which a signal is split is equal to  $n + 1$ , where  $n$  is the number of protons to which the proton in question is coupled. *Protons that have the same chemical shift do not split each other's signal.*

Section 13.8 The methyl protons of an ethyl group appear as a *triplet* and the methylene protons as a *quartet* in compounds of the type  $\text{CH}_3\text{CH}_2\text{X}$ .

Section 13.9 The methyl protons of an isopropyl group appear as a *doublet* and the methine proton as a *septet* in compounds of the type  $(\text{CH}_3)_2\text{CHX}$ .

Section 13.10 A *doublet of doublets* characterizes the signals for the protons of the type shown (where W, X, Y, and Z are not H or atoms that split H themselves).



Section 13.11 Complicated splitting patterns can result when a proton is unequally coupled to two or more protons that are different from one another.

Section 13.12 Splitting resulting from coupling to the OOH proton of alcohols is not normally observed, because the hydroxyl proton undergoes rapid intermolecular exchange with other alcohol molecules, which “decouples” it from other protons in the molecule.

Section 13.13 Many processes such as conformational changes take place faster than they can be detected by NMR. Consequently, NMR provides information about the *average* environment of a proton. For example, cyclohexane gives a single peak for its 12 protons even though, at any instant, 6 are axial and 6 are equatorial.

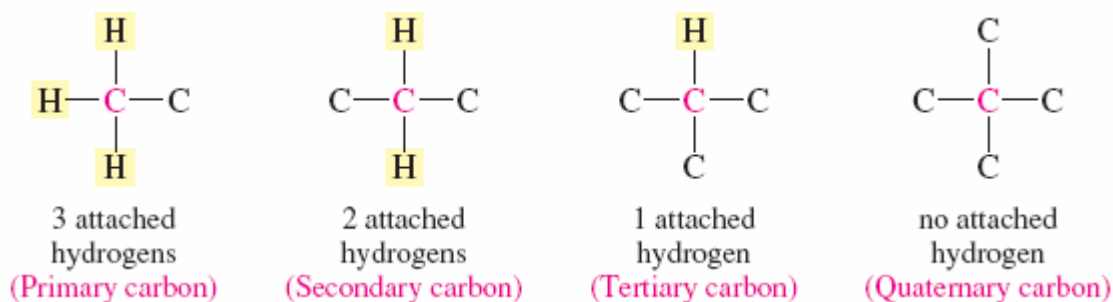
### *<sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy*

Section 13.14 <sup>13</sup>C has a nuclear spin of 1/2 but only about 1% of all the carbons in a sample are <sup>13</sup>C. Nevertheless, high-quality <sup>13</sup>C NMR spectra can be obtained by pulse FT techniques and are a useful complement to <sup>1</sup>H NMR spectra.

Section 13.15 <sup>13</sup>C signals are more widely separated from one another than proton signals, and <sup>13</sup>C NMR spectra are relatively easy to interpret. Table 13.3 gives chemical shift values for carbon in various environments.

Section 13.16 <sup>13</sup>C NMR spectra are rarely integrated because the pulse FT technique distorts the signal intensities.

Section 13.17 Carbon signals normally appear as singlets, but several techniques are available that allow one to distinguish among the various kinds of carbons shown.



Section 13.18 One of the special techniques for distinguishing carbons according to the number of their attached hydrogens is called **DEPT**. A series of NMR measurements using different pulse sequences gives normal, nulled, and inverted peaks that allow assignment of primary, secondary, tertiary, and quaternary carbons.

Section 13.19 2D NMR techniques are enhancements that are sometimes useful in gaining additional structural information. A <sup>1</sup>H-<sup>1</sup>H COSY spectrum reveals which protons are spin-coupled to other protons, which helps in determining connectivity. A HETCOR spectrum shows the COH connections by correlating <sup>13</sup>C and <sup>1</sup>H chemical shifts.

### *Infrared Spectroscopy*

Section 13.20 IR spectroscopy probes molecular structure by examining transitions between vibrational energy levels using electromagnetic radiation in the  $625\text{--}4000\text{-cm}^{-1}$  range. The presence or absence of a peak at a characteristic frequency tells us whether a certain *functional group* is present. Table 13.4 lists IR absorption frequencies for common structural units.

### ***Ultraviolet-Visible Spectroscopy***

Section 13.21 Transitions between electronic energy levels involving electromagnetic radiation in the 200–800-nm range form the basis of UV-VIS spectroscopy. The absorption peaks tend to be broad but are often useful in indicating the presence of particular *p electron* systems within a molecule.

### ***Mass Spectrometry***

Section 13.22 Mass spectrometry exploits the information obtained when a molecule is ionized by electron impact and then dissociates to smaller fragments. Positive ions are separated and detected according to their mass-to-charge ( $m/z$ ) ratio. By examining the fragments and by knowing how classes of molecules dissociate on electron impact, one can deduce the structure of a compound. Mass spectrometry is quite sensitive; as little as  $10^{29}$  g of compound is sufficient for analysis.

Section 13.23 A compound's molecular formula gives information about the number of double bonds and rings it contains and is a useful complement to spectroscopic methods of structure determination.