

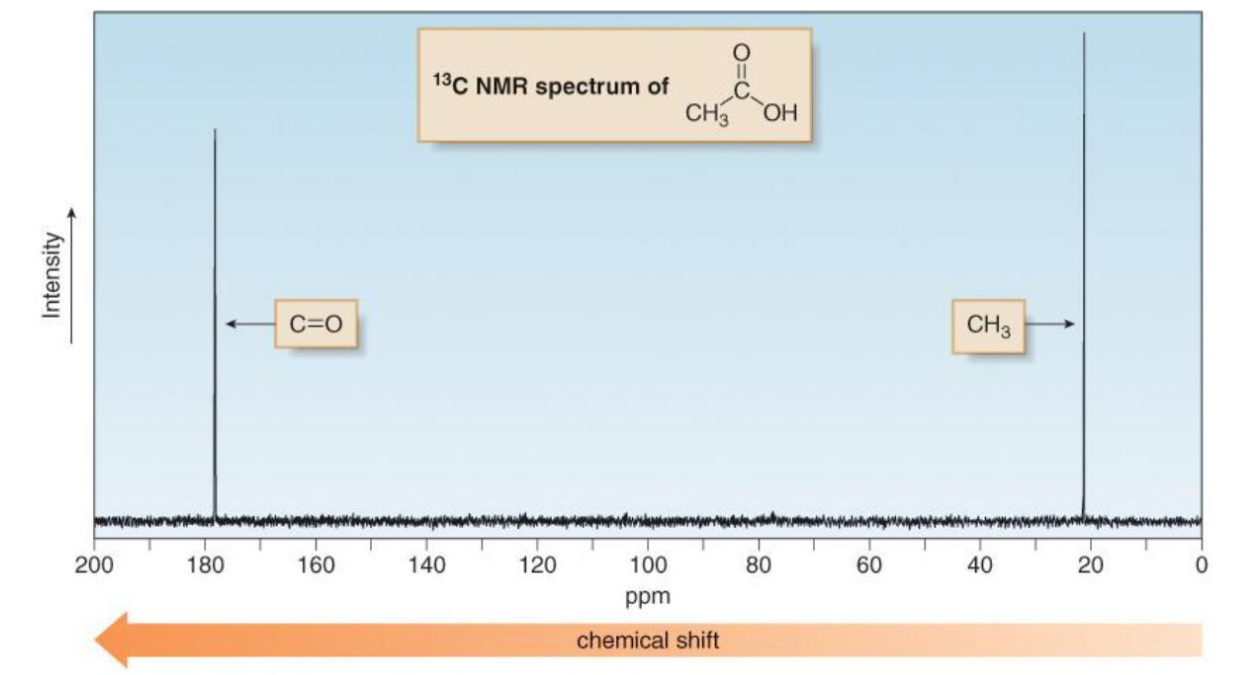
# $^{13}\text{C}$ NMR Spectroscopy

- The number of signals reflects the number of **different kinds of carbons** in a compound.
  - The chemical shift ranges over **220 ppm**.
  - The reference compound is **TMS**.
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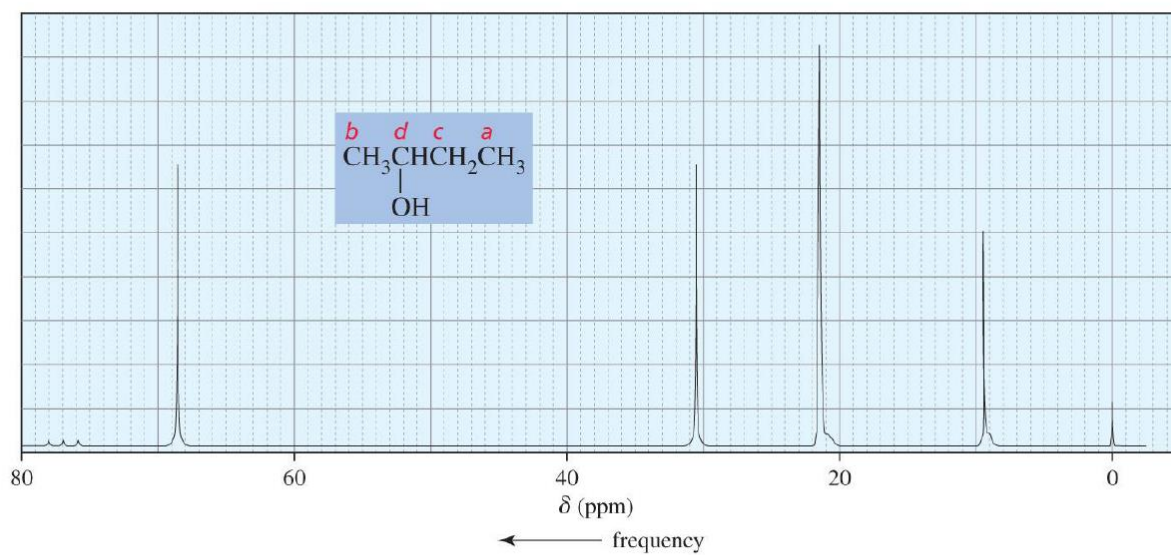
# Nuclear Magnetic Resonance Spectroscopy

## $^{13}\text{C}$ NMR

$^{13}\text{C}$  Spectra are easier to analyze than  $^1\text{H}$  spectra because the signals are not split. Each type of carbon atom appears as a single peak.



# The $^{13}\text{C}$ NMR Spectrum of 2-Butanol



# Nuclear Magnetic Resonance Spectroscopy

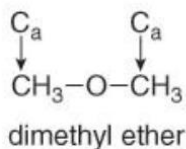
## $^{13}\text{C}$ NMR

- The lack of splitting in a  $^{13}\text{C}$  spectrum is a consequence of the low natural abundance of  $^{13}\text{C}$ .
- Recall that splitting occurs when two NMR active nuclei—like two protons—are close to each other. Because of the low natural abundance of  $^{13}\text{C}$  nuclei (1.1%), the chance of two  $^{13}\text{C}$  nuclei being bonded to each other is very small (0.01%), and so no carbon-carbon splitting is observed.
- A  $^{13}\text{C}$  NMR signal can also be split by nearby protons. This  $^1\text{H}$ - $^{13}\text{C}$  splitting is usually eliminated from the spectrum by using an instrumental technique that decouples the proton-carbon interactions, so that every peak in a  $^{13}\text{C}$  NMR spectrum appears as a singlet.
- The two features of a  $^{13}\text{C}$  NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.

# Nuclear Magnetic Resonance Spectroscopy

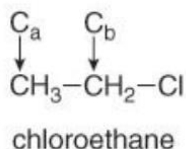
## $^{13}\text{C}$ NMR—Number of Signals

- The number of signals in a  $^{13}\text{C}$  spectrum gives the number of different types of carbon atoms in a molecule.
- Because  $^{13}\text{C}$  NMR signals are not split, the number of signals equals the number of lines in the  $^{13}\text{C}$  spectrum.
- In contrast to the  $^1\text{H}$  NMR situation, peak intensity is not proportional to the number of absorbing carbons, so  $^{13}\text{C}$  NMR signals are not integrated.

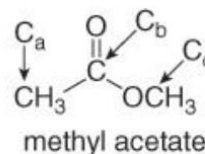


1  $^{13}\text{C}$  NMR signal

Both C's are equivalent.



2  $^{13}\text{C}$  NMR signals



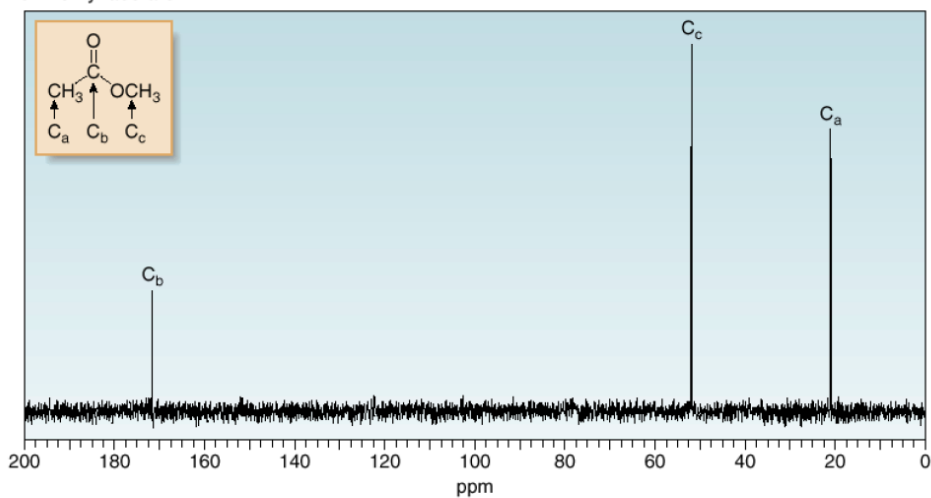
3  $^{13}\text{C}$  NMR signals

# Nuclear Magnetic Resonance Spectroscopy

## $^{13}\text{C}$ NMR—Number of Signals

- The three types of C's in methyl acetate—identified as  $\text{C}_a$ ,  $\text{C}_b$ , and  $\text{C}_c$ —give rise to three  $^{13}\text{C}$  NMR signals.
- The carbonyl carbon ( $\text{C}_b$ ) is highly deshielded, so it absorbs farthest downfield.
- $\text{C}_a$ , an  $sp^3$  hybridized C that is not bonded to an O atom, is the most shielded, and so it absorbs farthest upfield.
- Thus, in order of increasing chemical shift:  $\text{C}_a < \text{C}_c < \text{C}_b$ .

b. Methyl acetate



## DEPT <sup>13</sup> C-NMR Spectra

One of these techniques is known as DEPT (distortionless enhancement of polarisation transfer) which can be used to give similar information to an off-resonance decoupled spectra i.e. the number of attached H. DEPT experiments distinguish carbon nuclei based on the number of protons attached to it. <sup>13</sup>CNMR spectra show all carbons, DEPT-90 shows only CH's (3° carbons) and DEPT-135 shows protonated carbons, with CH and CH<sub>3</sub>'s appearing positive and CH<sub>2</sub>'s (2° carbons) appearing negative. In a DEPT experiment, a sequence of pulses with various delay times are used to create the DEPT spectra where -CH<sub>3</sub> and CH peaks appear as normal and -CH<sub>2</sub>- peaks appear inverted. Quaternary C are not usually seen. This way the number of H attached to C can usually be deduced. An example of a DEPT is shown below for 2-butanol (notice how the peak for the -CH<sub>2</sub>- points down) with the corresponding broadband decoupled spectra. It has to be run three times with different final pulse angles and compared with the regular decoupled <sup>13</sup>C spectrum in order to provide a full analysis. The DEPT experiment requires at least four scans in order to cancel out the quaternary signals although many more scans are usually acquired so this is not a problem. DEPT 45 yields CH, CH<sub>2</sub> and CH<sub>3</sub> signals positive, DEPT 90 yields only CH signals and DEPT 135 yields CH and CH<sub>3</sub> positive while CH<sub>2</sub> is negative. The use of DEPT in <sup>13</sup>C assignment is described in connection with <sup>13</sup>C NMR. See Fig below

**DEPT 135 – yields spectra with CH and CH<sub>3</sub> signals in opposite phase to CH<sub>2</sub> signals. DEPT 90 – yields spectra with only CH signals. DEPT 45 - yields spectra with positive CH, CH<sub>2</sub>, and CH<sub>3</sub> signals (all protonated carbons).**