B.Sc. Semester-VI
Paper CC-XIV
Organic Chemistry-V

III. Nuclear Magnetic Resonance Spectroscopy

Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

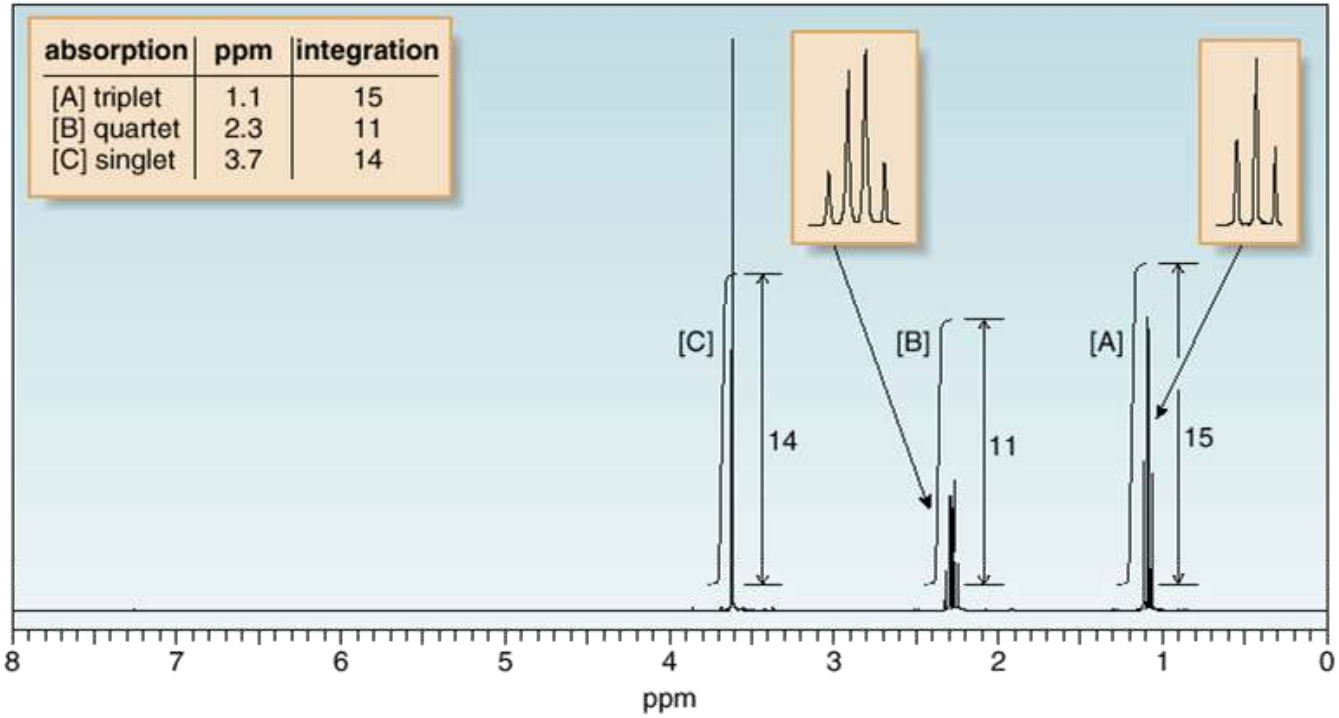
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

How To **Use ^{1}H NMR Data to Determine a Structure**

Example Using its ^{1}H NMR spectrum, determine the structure of an unknown compound **X** that has molecular formula $C_4H_8O_2$ and contains a C=O absorption in its IR spectrum.

absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14



Step [1] Determine the number of different kinds of protons.

- The number of NMR signals equals the number of different types of protons.
- This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H_a, H_b, and H_c).

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

How To, continued . . .

Step [2] Use the integration data to determine the number of H atoms giving rise to each signal (Section 14.5).

- Total number of integration units: 14 + 11 + 15 = 40 units
- Total number of protons = 8
- Divide: 40 units/8 protons = **5 units per proton**
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.

$\frac{15}{5}$ = 3 H_a protons (signal [A]) → Three equivalent H's usually means a CH_3 group.

$\frac{11}{5}$ = 2.2 ≈ 2 H_b protons (signal [B]) → Two equivalent H's usually means a CH_2 group.

$\frac{14}{5}$ = 2.8 ≈ 3 H_c protons (signal [C]) → Three equivalent H's usually means a CH_3 group.

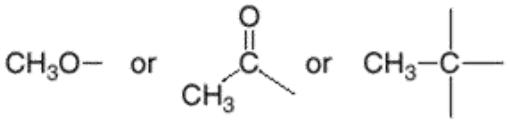
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

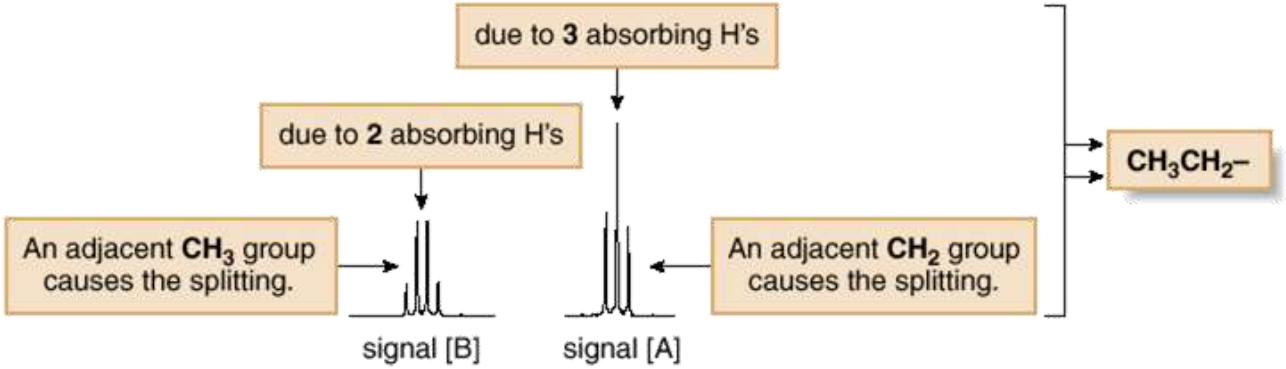
How To, continued . . .

Step [3] **Use individual splitting patterns to determine what carbon atoms are bonded to each other.**

- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:



- Because signal [A] is a **triplet,** there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet,** there must be **3 H's** (CH_3 group) on the adjacent carbon.
- This information suggests that **X** has an **ethyl** group ----→ CH_3CH_2-.



To summarize, **X** contains CH_3-, CH_3CH_2-, and C=O (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a ^{1}H NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.

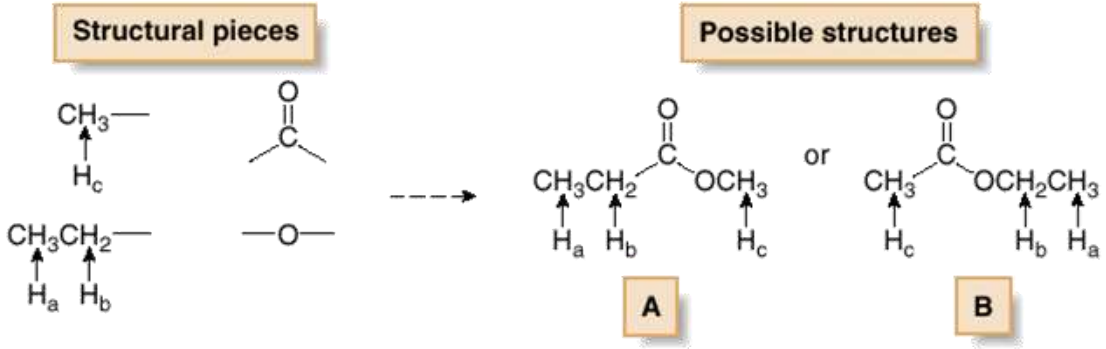
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Structure Determination

How To, continued . . .

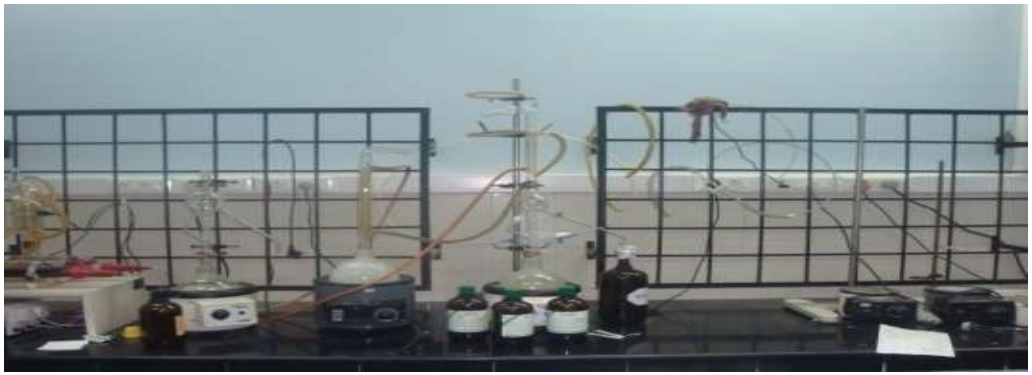
Step [4] **Use chemical shift data to complete the structure.**

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (**A** and **B**) are possible for **X** considering the splitting data only:



- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If **A** is the correct structure, the singlet due to the CH_3 group (H_c) should occur downfield, whereas if **B** is the correct structure, the quartet due to the CH_2 group (H_b) should occur downfield.
- Because the NMR of **X** has a singlet (not a quartet) at 3.7, **A is the correct structure.**

Thank You



Dr. Rajeev Ranjan

University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi