

# NMR SPECTROSCOPY

SEM-4, CC-8  
PART-6, PPT-18

## Contents (Part-6)

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## Nuclear Magnet Resonance (NMR) Spectroscopy (PART-6, PPT-18)

### Relative Intensities of First-Order Multiplets

In general, *first-order* spectra will only arise if the separation between multiplets (the chemical shift difference between signals, expressed in Hz) is much larger than the coupling constant,  $J$ ; if  $\Delta\nu \geq 8J$ , then fairly unperturbed spectra will arise. In a simple *first-order* multiplet, the number of peaks is determined by the number of coupled neighbouring protons with the same (or very slightly different) coupling constants. The multiplicity then is ' $n + 1$ ' where  $n$  being the number of neighbouring equally coupled protons, and Pascal's triangle hold in this case.

The relative intensities of the peaks of a *first-order* multiplet also depend on  $n$ . The *doublet* peaks ( $n = 1$ ) appear in the ratio 1:1, *triplets* ( $n = 2$ ) are 1:2:1, and *quartets* ( $n = 3$ ) are 1:3:3:1, and so forth.

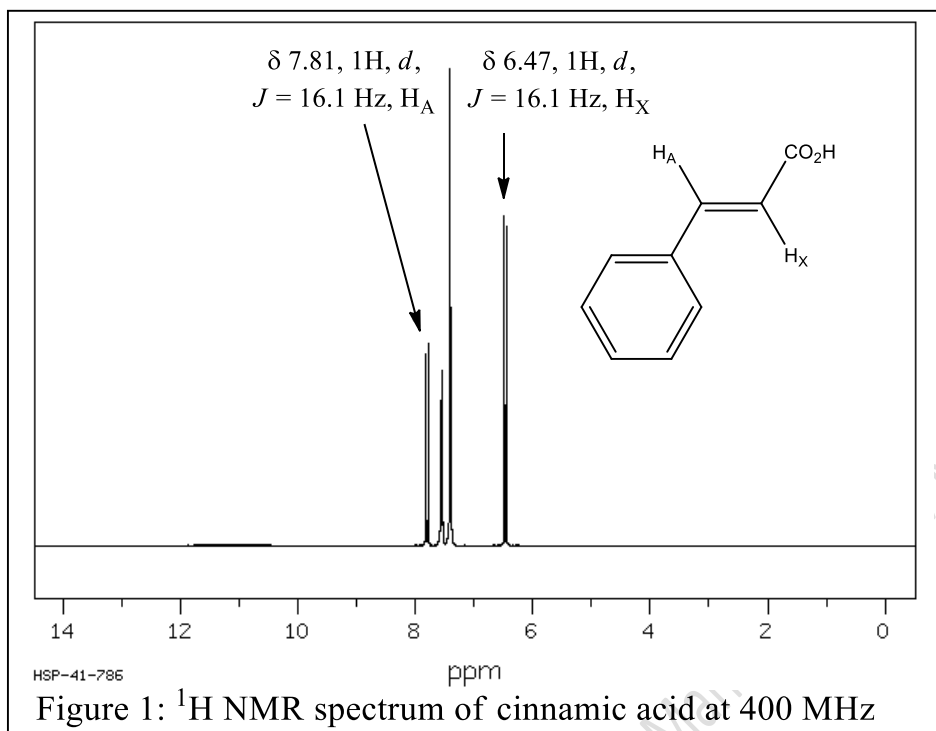
### Requirements for a simple, First-Order Multiplet

1. The ratio  $\Delta\nu/J$  must be larger than about 8;  $\Delta\nu$  is the distance between the midpoints of the coupled multiplets.  $J$  is the coupling constant.
2. The number of peaks in the multiplet is ' $n + 1$ ', where  $n$  is the number of neighbouring protons with the same coupling constant.
3. The distance in Hz between the individual peaks of a simple, *first-order* multiplet represents the coupling constant.
4. The simple *first-order* multiplet is centrosymmetric, with the most intense peak(s) central.

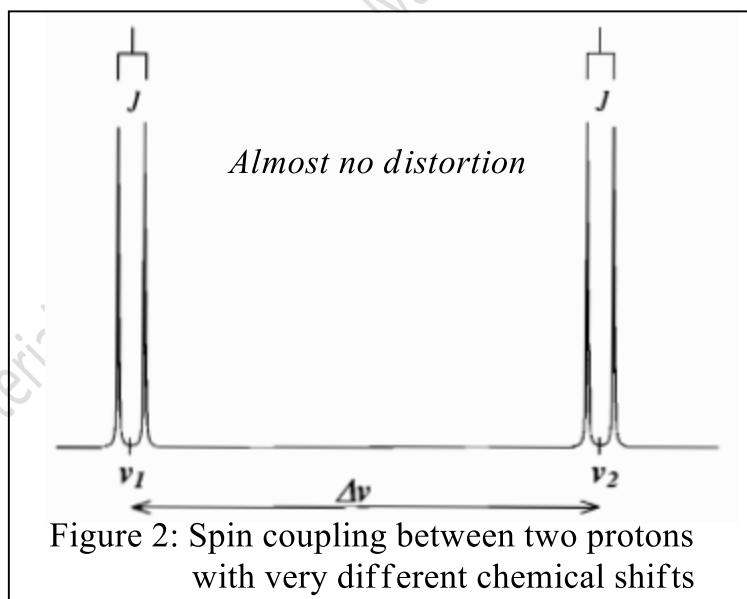
### Relative Intensities of First-Order Multiplets

Figure 1 shows  $^1\text{H}$  NMR spectrum of cinnamic acid, and is considered as a *first-order* with respect to the interacting *trans* doublets. Cinnamic acid contains a pair of interacting doublets with  $J = 16.1$  Hz (*trans* coupling).

Each of the interacting *trans* protons appears as a *doublet* in the spectrum at  $\delta$  7.81 and 6.47 ppm for proton A and proton X, respectively. The difference between the chemical shift ( $\delta$ ) positions of these protons in 400 MHz instrument is 536 Hz [(7.81 – 6.47) x 400]. Therefore,  $\Delta\nu/J$  value in this case is greater than 33. Consequently, this is an ideal example of AX system (A set of two non-equivalent protons separated by a large chemical shift so that  $\Delta\nu/J > \sim 10$ )

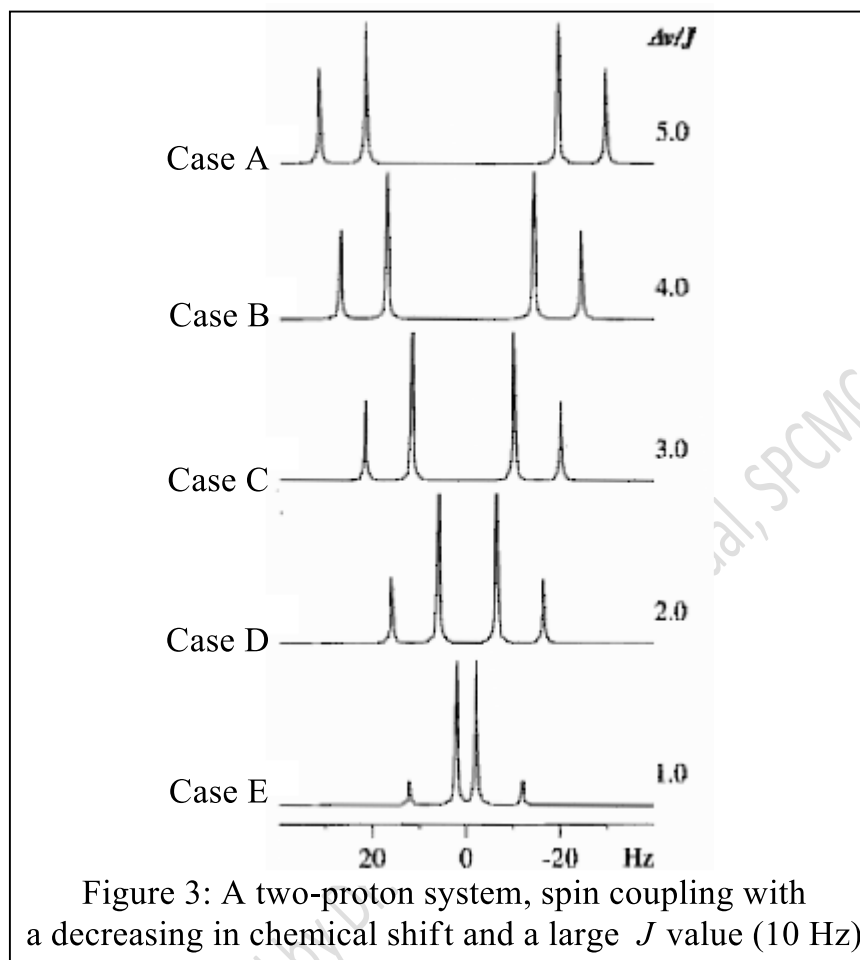


So long as the chemical shift difference in hertz ( $\Delta\nu$ ) is much larger than the coupling constant (arbitrarily  $\Delta\nu/J$  is greater than about 8), the simple pattern of two doublets appear as shown in Figure 2.

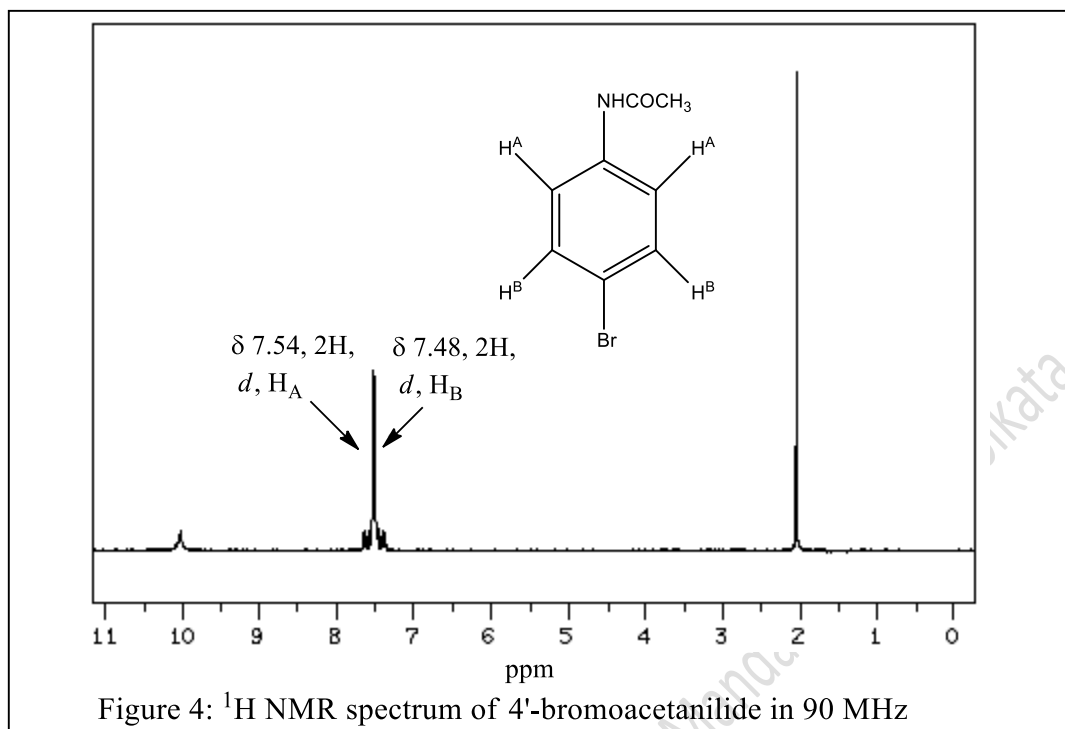


If the signals from coupling protons are closer together on the spectrum, and the chemical shift difference is small, distortion of the signals arises. As  $\Delta\nu/J$  becomes smaller, the doublets approach each other, the inner two peaks increase in intensity, and the outer two peaks decrease as shown in Figure 3. The positions of the lines also change, the origin chemical shift positions are no longer found at the mid-points of the doublets, but lie approximately at the 'centre of gravity' of the doublets. Such spectra are usually called AB spectra indicating that the chemical shift values are closer than in AX cases.

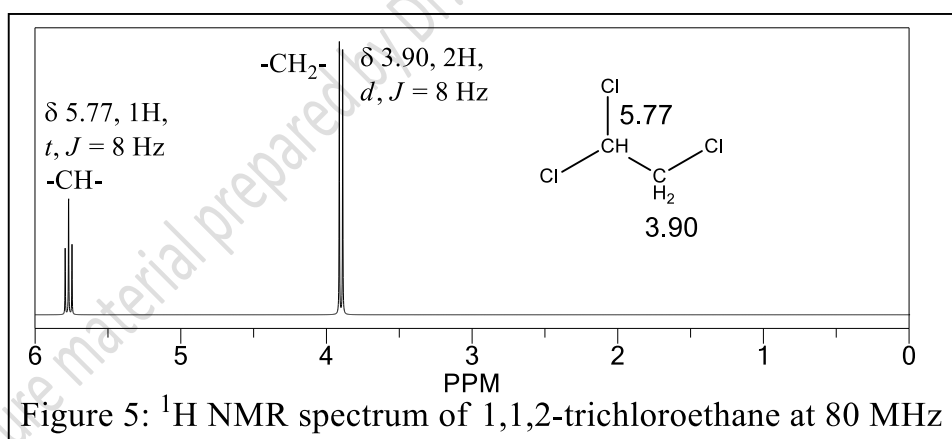
The spectrum which consists of two distorted doublets as shown in Case D of Figure 3 with  $\Delta\nu/J = 2$ , can readily be mistaken for a *quartet*.



When  $\Delta\nu/J$  value reduces as low as 1 or less, the interacting *doublets* look as shown in Case E of Figure 3.  $^1\text{H}$  NMR spectrum of 4'-bromoacetanilide (Figure 4) resembles that situation.



Here,  $\Delta\nu = (7.54 - 7.48) \times 90 \text{ Hz} = 5.4 \text{ Hz}$ ;  $J = 8 \text{ Hz}$  (for *ortho* coupling); hence,  $\Delta\nu/J \approx 0.07$ . In the  $^1\text{H}$  NMR spectrum of 1,1,2-trichloroethane (Figure 5) the coupling constant ( $J$ ) between the two sets of interacting protons is 8 Hz, while the difference between the chemical shift ( $\delta$ ) positions of CH and  $\text{CH}_2$  is 1.87 ppm, which corresponds to  $\sim 150 \text{ Hz}$  on an 80 MHz spectrum. Therefore,  $\Delta\nu/J \approx 19$ .



The two equally coupled methylene protons induce a doublet, and the neighbouring methine proton induces a triplet. The relative line intensities predicted by the spin coupling mechanism are 1:1 in doublets and 1:2:1 in triplets. Real spectra almost always depart from this *first-order* prediction in a characteristic manner: the doublet and triplet are slightly distorted, the inner lines being a little more intense than the outer lines.

In the  $\text{AX}_2$  case of 1,1,2-trichloroethane (Figure 5) only five lines appear, as predicted by *first-order* ( $n + 1$ ) rules. If the chemical shift values of methylene and methine protons are closer together, the spectrum is *non-first-order* (and should be called  $\text{AB}_2$ ); in that case

additional lines may appear due to fine splitting. The precise appearance of the spectrum depends on the ratio  $\Delta\nu/J$ .

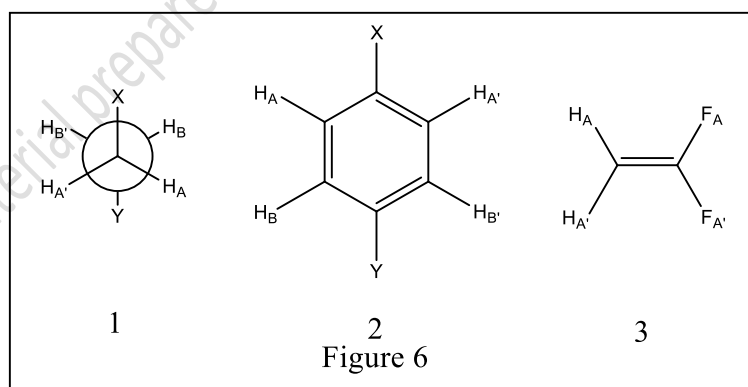
### Chemical and Magnetic Equivalence in NMR

Two or more protons are defined as being chemically equivalent if, by virtue of symmetry within the molecule, their electronic environments are indistinguishable. They experience identical shielding effects, and therefore, they possess the same value of chemical shift.

Two protons are defined as being magnetically equivalent if each couples equally to a third neighbouring proton; otherwise they are magnetically nonequivalent. Chemical equivalence means chemical shift equivalence, and magnetic equivalence means coupling equivalence. Chemically equivalent (isochronous) nuclei comprise a set within a spin system. A spin system consists of sets of nuclei that interact (spin couple) among each other, but do not interact with any nuclei outside the spin system.

Spin systems are insulated from one another, e.g., the ethyl protons in ethyl isopropyl ether  $[\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}(\text{CH}_3)_2]$  constitute one spin system, and the isopropyl protons another. Magnetically equivalent nuclei will not only be chemically equivalent but also have the same coupling constant with every other nucleus in the molecule. Therefore, the test for magnetic equivalence is valid only when the two nuclei are chemically equivalent.

Let us consider that formula I in Figure 6 represents the most stable conformation of the molecule of the type  $\text{X}-\text{CH}_2-\text{CH}_2-\text{Y}$ . As a result of symmetry,  $\text{H}_\text{A}$  and  $\text{H}_\text{A}'$  will have the same chemical shift values, as will  $\text{H}_\text{B}$  and  $\text{H}_\text{B}'$ . Now  $\text{H}_\text{A}$  will undergo spin-spin coupling to  $\text{H}_\text{B}$ , but (assuming no rotation around the C-C bond) this will be different from the coupling of  $\text{H}_\text{A}'$  to  $\text{H}_\text{B}$ .



Therefore, the protons  $\text{H}_\text{A}$  and  $\text{H}_\text{A}'$  are chemically equivalent but are magnetically nonequivalent. The labels A and B are allocated to each separate group of chemically equivalent nuclei; if two  $\text{H}_\text{A}$  protons are magnetically nonequivalent, this is indicated by the use of primes (thus,  $\text{H}_\text{A}$  and  $\text{H}_\text{A}'$ ). Similarly, protons,  $\text{H}_\text{B}$  and  $\text{H}_\text{B}'$ , must be chemically equivalent but magnetically nonequivalent.

Molecules 2 and 3 in Figure 6 contain equivalent and nonequivalent groups of nuclei labelled to show the differences between chemical and magnetic equivalence. All *para*-substituted

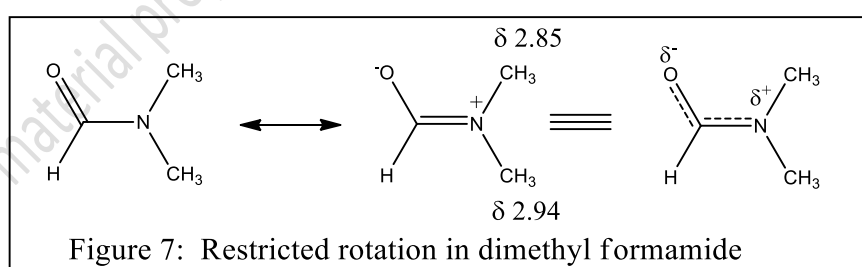
benzene derivatives of this type (molecule 2, where group X is different from group Y) often show *non-first order* NMR spectra. Since  $H_A$  and  $H_{A'}$  couple differently to another specific proton (say  $H_B$ ), they are magnetically nonequivalent, and *first-order* rules do not apply. The system is described as  $AA'XX'$ , and the spectrum is very complex. As the *para* substituents become more similar to each other (in their shielding properties), the system tends toward  $AA'BB'$ .

The two fluorine atoms in molecule 3, as shown in Figure 6, are subject to the same considerations, and are chemically equivalent but magnetically nonequivalent. The protons  $H_A$  and  $H_{A'}$  comprise a set, and two fluorines  $F_A$  and  $F_{A'}$  comprise a set (of chemical shift equivalent nuclei), but the nuclei in each set are not magnetic equivalent and the spectrum is complex.

Therefore, two protons which are chemically nonequivalent must also be magnetically nonequivalent, but that two protons can be magnetically nonequivalent while still being chemically equivalent. Nuclei are chemical shift equivalent if they are interchangeable through any symmetry operation or by a rapid process. Nuclei are interchangeable if the structures before and after the operation are indistinguishable. A rapid process means one that occurs faster than once in about  $10^{-3}$  s.

Protons that are interchangeable through an axis of symmetry ( $C_n$ ) are *homotopic*; that is, they are chemical shift equivalent in any environment whether achiral or chiral. Protons that are interchangeable through any other symmetry operation are called *enantiotopic*, and these are chemical shift equivalent only in an achiral environment. Non-interchangeable *geminal* protons are *diastereotopic* in nature, and they are not chemical shift equivalent in any environment.

At room temperature, a neat sample of dimethylformamide (DMF) shows two  $CH_3$  peaks because the rate of rotation around the hindered “partial double bond” is slow. At  $\sim 123^\circ$ , the rate of exchange of the two  $CH_3$  groups is rapid enough so that the two peaks merge.



DMF is represented by two resonance forms as shown in Figure 7, and the result of conjugation between the carbonyl group and the nitrogen nonbonding pair is to increase the double-bond character of the C-N bond sufficiently to restrict the rotation at room temperature; one methyl group is *cis* to oxygen, the other is *trans*.

## Deceptive Simplicity: Accidental Equivalence in NMR

**Deceptive simplicity:** As a result of chance, it occasionally arises that the chemical shifts of two protons are equal or very nearly so, even though they do not have the same chemical environment. This is called *accidentalequivalence*. If they couple to a third proton, the coupling pattern will be affected and one example is in the molecule of 2,5-dichloronitrobenzene, (4), where the protons,  $H_B$  and  $H_C$ , have near-identical chemical shifts.

The  $^1\text{H}$  NMR spectrum of this molecule (Figure 8) is superficially *first-order*, with a doublet near  $\delta$  7.51 for  $H_B$  and  $H_C$  (because they couple with  $H_A$ ) and a triplet near  $\delta$  7.88 for  $H_A$  (coupling with  $H_B$  and  $H_C$ ). The expected coupling constants are  $J_{AB}$  (*meta*) 2-3 Hz, and near zero for  $J_{AC}$  (*para*). Although in appearance the spectrum is  $\text{AX}_2$  in type, nevertheless it is strictly a special case of an ABX spectrum. Such a spectrum is said to exhibit *deceptive simplicity*. The observed spacings in both the *triplet* and the *doublet* do not correspond to either of these values, but are the *average* of them, at 1.6 Hz.

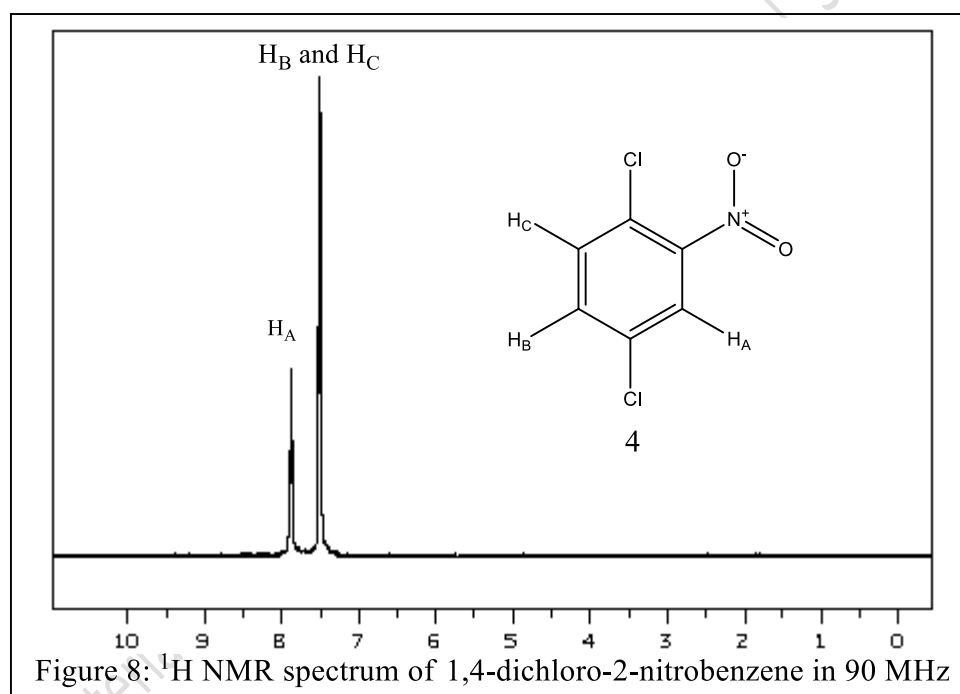
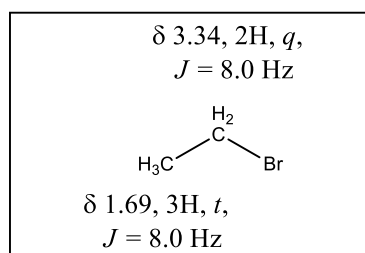


Figure 8:  $^1\text{H}$  NMR spectrum of 1,4-dichloro-2-nitrobenzene in 90 MHz

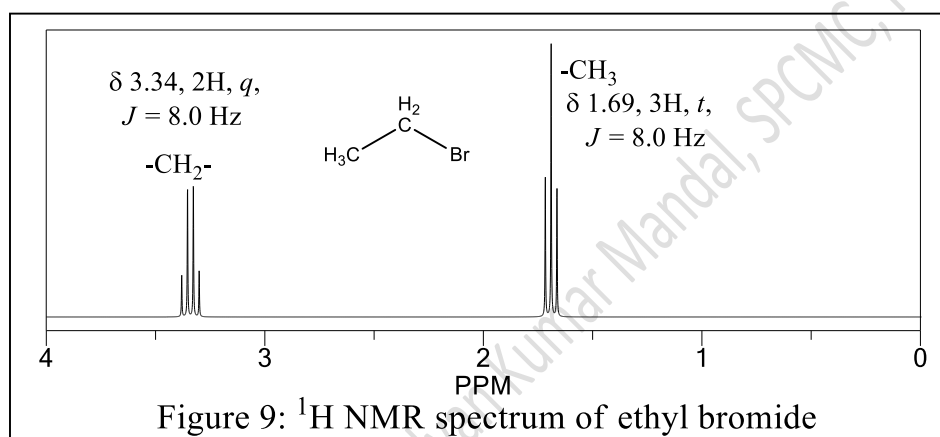
## $^1\text{H}$ NMR Spectral Analysis of Ethyl Bromide

Ethyl bromide contains two sets of protons. The protons present in the methylene ( $-\text{CH}_2-$ ) group are equivalent. Similarly, the protons present in the methyl ( $-\text{CH}_3$ ) group are equivalent, but the two sets of protons are nonequivalent. Therefore, these two sets give rise to different signals with different  $\delta$  values as shown in Figure 9.





The electron density around the methylene protons is lower than that of the methyl protons as the electronegative bromine atom is closer to the former. Consequently, methylene protons resonated at higher frequency than that of the methyl protons. Therefore, methylene protons appeared at higher  $\delta$  value compared to the protons of methyl group.



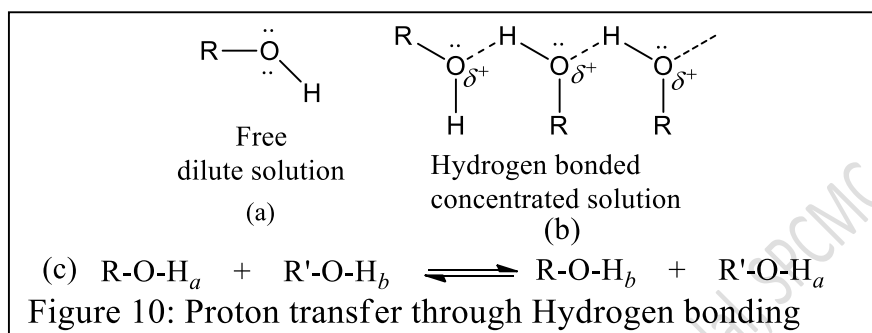
Methylene protons appeared as a *quartet* because of interaction with the neighbouring equally coupled methyl protons ( $n + 1 = 3 + 1 = 4$  lines with intensity 1:3:3:1). Methyl protons, on the other hand, appeared as a *triplet* because of interaction with the neighbouring equally coupled methylene protons ( $n + 1 = 2 + 1 = 3$  lines with intensity 1:2:1).

In the  $^1\text{H}$  NMR spectrum (Figure 9), the area under each peak is proportional to the number of hydrogens generating that peak. Hence, in ethyl bromide, the area ratio of the *quartet* and the *triplet* as appeared in the spectrum is 2:3, the same as the ratio of the numbers of the two types of hydrogens. The *triplet* and *quartet* observed in the  $^1\text{H}$  NMR spectrum of ethyl bromide is an  $\text{A}_2\text{X}_3$  system. All isolated ethyl groups produce a similar spectrum, and the chemical shift positions of the  $\text{CH}_2$  protons depend on the nature of the substituent present.

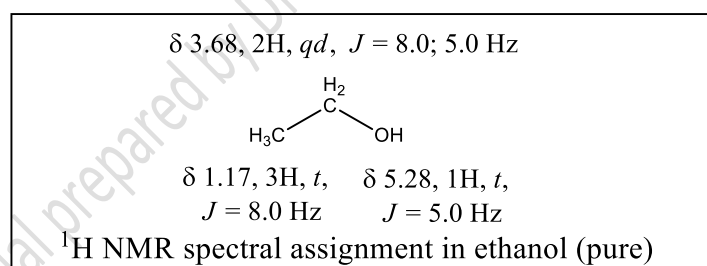
### $^1\text{H}$ NMR Spectral Analysis of Ethyl Alcohol

The protons present in the methyl ( $-\text{CH}_3$ ) group of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) are equivalent, and that in the methylene ( $-\text{CH}_2-$ ) group are also equivalent. On the contrary, the  $\text{CH}_3$ -protons,  $\text{CH}_2$ -protons, and  $-\text{OH}$  proton are nonequivalent. So, three signals will be observed in the  $^1\text{H}$  NMR spectrum of ethyl alcohol whether it is pure or not. The signal positions of  $\text{CH}_3$ -protons,  $\text{CH}_2$ -protons are independent on the purity of the sample. Only the signal position of hydroxyl proton shifted upfield on dilution due to decreased intermolecular hydrogen bonding.

The absorption frequencies, and hence the chemical shifts of these three types of nonequivalent protons depend on the electron density around the protons. Hydrogen of –OH group in ethanol is most deshielded ( $\delta$  5.28) due to (i) shift of electron cloud towards the electronegative oxygen atom, and (ii) hydrogen bonding (electron cloud is further transferred to more electronegative oxygen atom) as shown in Figure 10 (case b). Signal of hydroxyl hydrogen depends on concentration of the solution, and in pure liquid (neat) generally appears in the region  $\delta$  5.10 - 5.30.



Two hydrogens of CH<sub>2</sub> group also deshielded due to adjacent oxygen atom, signal for CH<sub>2</sub> protons appears at  $\delta$  3.68. Hydrogens of CH<sub>3</sub> (mostly shielded) appear near  $\delta$  1.17. The appearance of the ethanol spectrum as a function of concentration in carbon tetrachloride is shown in Figure 11. The positions of the CH<sub>3</sub> and CH<sub>2</sub> resonances are little affected by dilution. The OH peak, in contrast, moves from 5.28 ppm in pure ethanol at 40° to ~1 ppm in 0.5% solution. This increased shielding is due to the breaking up of hydrogen bonded complexes, mainly dimers.



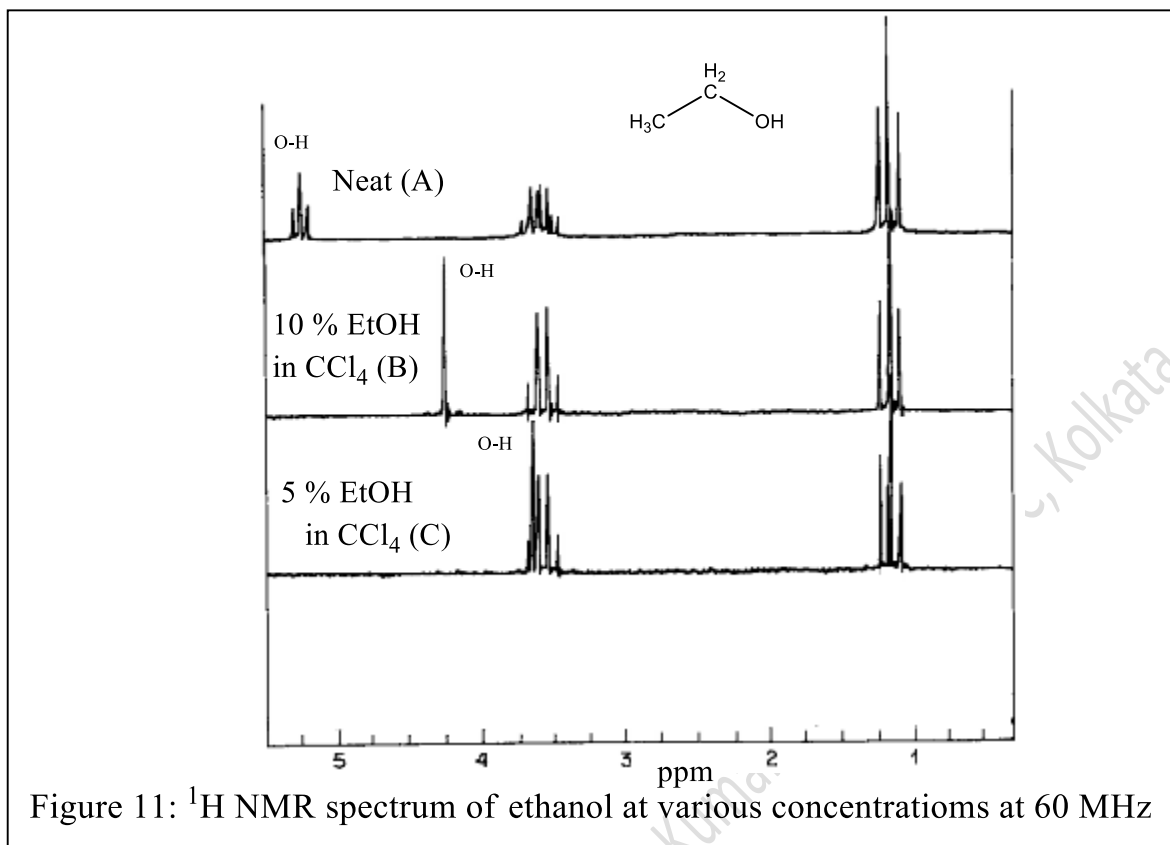


Figure 11:  $^1\text{H}$  NMR spectrum of ethanol at various concentrations at 60 MHz

### Splitting pattern in pure Ethanol sample

For pure, dry ethanol, coupling between OH and  $\text{CH}_2$  protons becomes evident (Case-A, Figure 11), the OH resonance being now a *triplet* and the  $\text{CH}_2$  resonance more complex than a *quartet*. This is a consequence of slower intermolecular proton exchange in the pure alcohol. The OH and  $\text{CH}_2$  protons experience each other in an NMR time scale.

The  $\text{CH}_3$ -protons appear as a *triplet* ( $J = 8.0$  Hz) because of coupling to neighbouring  $\text{CH}_2$ -protons. The hydroxyl proton signal appears as a *triplet* ( $J = 5.0$  Hz) because of coupling to  $\text{CH}_2$ -protons. The  $\text{CH}_2$ -proton signal is split into a *quartet* by  $\text{CH}_3$ -protons and each line is further split into two lines by the OH-proton, thus appears as *quartet of doublets* (*qd*,  $J = 8.0$  and  $5.0$  Hz; 8 lines).

### Rapid-Proton Exchange in Ordinary Ethanol

In carbon tetrachloride solution, proton exchange (case c, Figure 10) is rapid enough to abolish this coupling, probably because of traces of water or acidic impurities. Rapid exchangeability explains why the hydroxyl proton signal of ethanol is usually seen as a *singlet* (Case-B, Figure 11). Due to rapid proton exchange, the proton is not on the oxygen atom of an individual molecule long enough for it to be affected by the methylene protons; therefore there is no coupling. The OH proton shows a *singlet*, the  $\text{CH}_2$  a *quartet* and the  $\text{CH}_3$  a *triplet*.

With moderately concentrated solution alcohol hydroxyl proton appears at around  $\delta$  4.0-5.5 but on dilution the signal shifted upfield (lower  $\delta$  value) and at infinite dilution it appears at  $\delta$  0.5.

### **Moderate-rate of Proton Exchange**

The appearance of the hydroxyl proton as a *broad singlet* in ordinary ethanol containing traces of acidic or basic impurities is due to moderate to rapid rate of proton exchange/chemical exchange. Due to this a particular hydroxyl proton, within the NMR time scale is not attached to a particular ethanol molecule, but is attached to a number of different ethanol molecules so that a hydroxyl proton experiences an average of the spin orientations of the methylene protons. As a result, the signal for the hydroxyl proton is not split by the methylene protons and vice-versa.

As hydroxyl proton feels an average of the spin orientations of the neighbouring methylene protons, it appears as a *broad singlet*. Therefore, nature of hydroxyl proton signal depends on the dilution as well as on the purity of the sample.

Lecture material prepared by Dr. Kalyan Kumar Mandal, SPCL, IIT Kharagpur