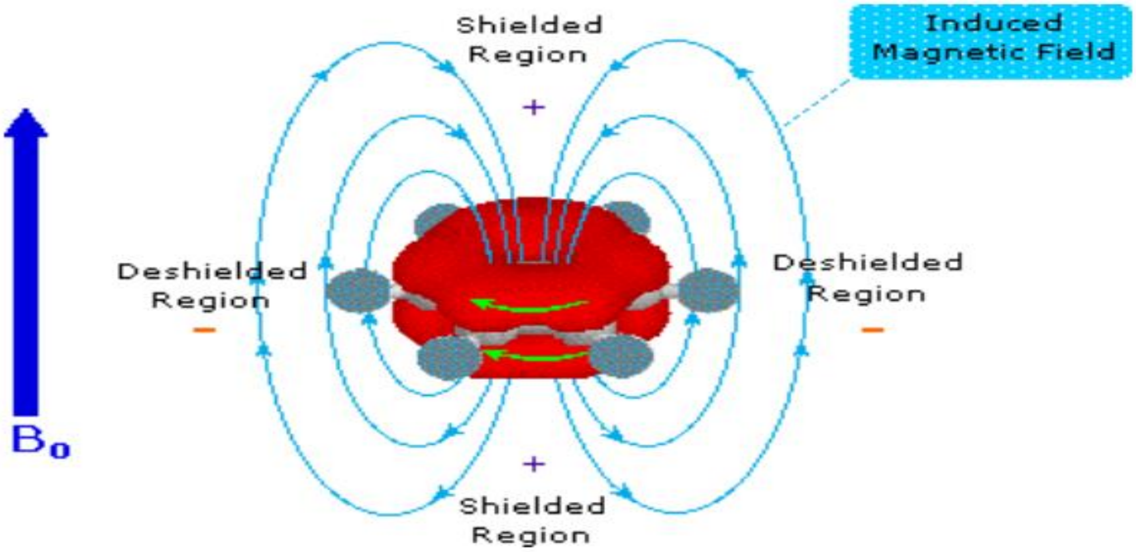
π-Electron Functions

An examination of the proton chemical shift chart (above) makes it clear that the inductive effect of substituents cannot account for all the differences in proton signals. In particular the low field resonance of hydrogens bonded to double bond or aromatic ring carbons is puzzling, as is the very low field signal from aldehyde hydrogens. The hydrogen atom of a terminal alkyne, in contrast, appears at a relatively higher field. All these anomalous cases seem to involve hydrogens bonded to pi-electron systems, and an explanation may be found in the way these pi-electrons interact with the applied magnetic field.

Pi-electrons are more polarizable than are sigma-bond electrons, as addition reactions of electrophilic reagents to alkenes testify. Therefore, we should not be surprised to find that field induced pi-electron movement produces strong secondary fields that perturb nearby nuclei. The pi-electrons associated with a benzene ring provide a striking example of this phenomenon, as shown below. The electron cloud above and below the plane of the ring circulates in reaction to the external field so as to generate an opposing field at the center of the ring and a supporting field at the edge of the ring. This kind of spatial variation is called **anisotropy**, and it is common to nonspherical distributions of electrons, as are found in all the functions mentioned above. Regions in which the induced field supports or adds to the external field are said to be **deshielded**, because a slightly weaker external field will bring about resonance for nuclei in such areas. However, regions in which the induced field opposes the external field are termed **shielded** because an increase in the applied field is needed for resonance. Shielded regions are designated by a **plus sign**, and deshielded regions by a **negative sign**. The anisotropy of some important unsaturated functions will be displayed by clicking on the benzene diagram below. Note that the anisotropy about the triple bond nicely accounts for the relatively high field chemical shift of ethynyl hydrogens. The shielding & deshielding regions about the carbonyl group have been described in two ways, which alternate in the display.



Sigma bonding electrons also have a less pronounced, but observable, anisotropic influence on nearby nuclei. This is seen in the small deshielding shift that occurs in the series CH_3–R, R–CH_2–R, R_3CH; as well as the deshielding of equatorial versus axial protons on a fixed cyclohexane ring.

Solvent Effects

Chloroform-d ($CDCl_3$) is the most common solvent for nmr measurements, thanks to its good solubilizing character and relative unreactive nature (except for 1º and 2º-amines). As noted earlier, other deuterium labeled compounds, such as deuterium oxide (D_2O), benzene-d6 (C_6D_6), acetone-d6 (CD_3COCD_3) and DMSO-d6 (CD_3SOCD_3) are also available for use as nmr solvents. Because some of these solvents have π-electron functions and/or may serve as hydrogen bonding partners, the chemical shifts of different groups of protons may change depending on the solvent being used. The following table gives a few examples, obtained with dilute solutions at 300 MHz.

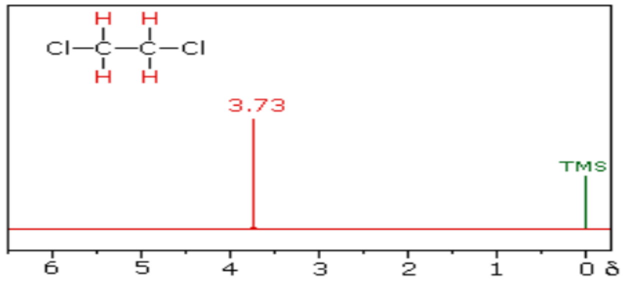
Some Typical ^{1}H Chemical Shifts (δ values) in Selected Solvents

Solvent **Compound**	**$CDCl_3$**	**C_6D_6**	**CD_3COCD_3**	**CD_3SOCD_3**	**$CD_3C{\equiv}N$**	**D_2O**
$(CH_3)_3C–O–CH_3$						
C–CH_3	1.19	1.07	1.13	1.11	1.14	1.21
O–CH_3	3.22	3.04	3.13	3.03	3.13	3.22
$(CH_3)_3C–O–H$	1.26	1.05	1.18	1.11	1.16	---
C–CH_3	1.65	1.55	3.10	4.19	2.18	---
O–H						
$C_6H_5CH_3$						
CH_3	2.36	2.11	2.32	2.30	2.33	---
C_6H_5	7.15-7.20	7.00-7.10	7.10-7.20	7.10-7.15	7.15-7.30	---
$(CH_3)_2C=O$	2.17	1.55	2.09	2.09	2.08	2.22

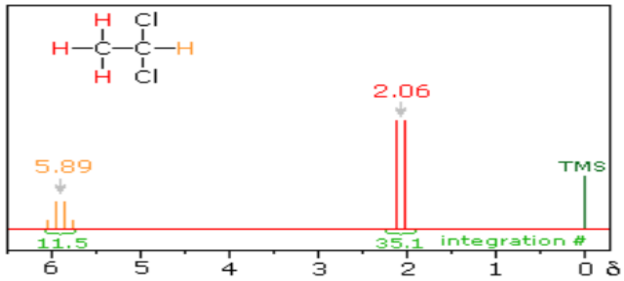
For most of the above resonance signals and solvents the changes are minor, being on the order of ±0.1 ppm. However, two cases result in more extreme changes and these have provided useful applications in structure determination. First, spectra taken in benzene-d_6 generally show small upfield shifts of most C–H signals, but in the case of acetone this shift is about five times larger than normal. Further study has shown that carbonyl groups form weak π–π collision complexes with benzene rings, that persist long enough to exert a significant shielding influence on nearby groups. In the case of substituted cyclohexanones, axial α-methyl groups are shifted upfield by 0.2 to 0.3 ppm; whereas equatorial methyls are slightly deshielded (shift downfield by about 0.05 ppm). These changes are all relative to the corresponding chloroform spectra. The second noteworthy change is seen in the spectrum of tert-butanol in DMSO, where the hydroxyl proton is shifted 2.5 ppm down-field from where it is found in dilute chloroform solution. This is due to strong hydrogen bonding of the alcohol O–H to the sulfoxide oxygen, which not only de-shields the hydroxyl proton, but secures it from very rapid exchange reactions that prevent the display of spin-spin splitting. Similar but weaker hydrogen bonds are formed to the carbonyl oxygen of acetone and the nitrogen of acetonitrile. A useful application of this phenomenon is described elsewhere in this text.

Spin-Spin Interactions

The nmr spectrum of 1,1-dichloroethane (below right) is more complicated than we might have expected from the previous examples. Unlike its 1,2-dichloro-isomer (below left), which displays a single resonance signal from the four structurally equivalent hydrogens, the two signals from the different hydrogens are split into close groupings of two or more resonances. This is a common feature in the spectra of compounds having different sets of hydrogen atoms bonded to adjacent carbon atoms. The signal splitting in proton spectra is usually small, ranging from fractions of a Hz to as much as 18 Hz, and is designated as **J** (referred to as the coupling constant). In the 1,1-dichloroethane example all the coupling constants are 6.0 Hz, as illustrated

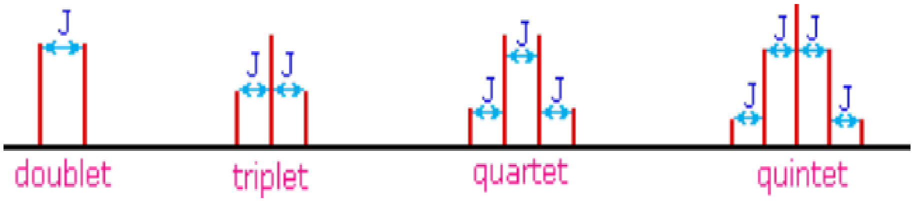


1,2-dichloroethane



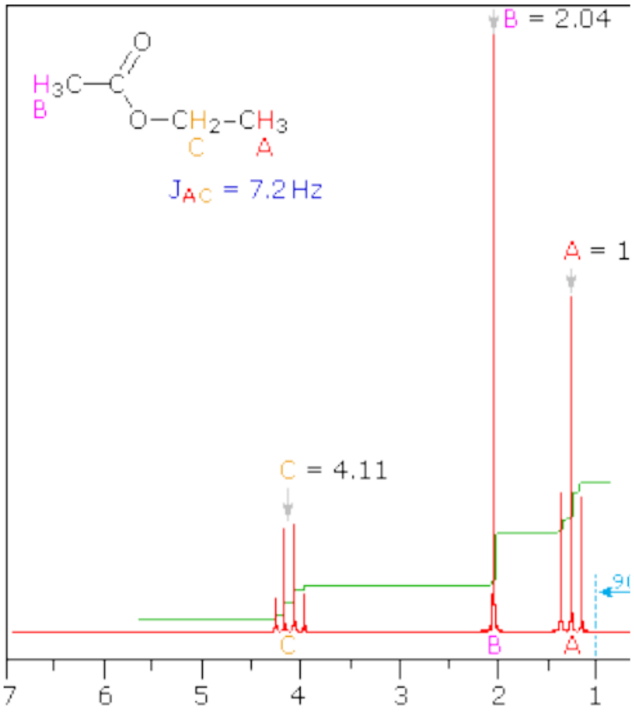
1,1-dichloroethane

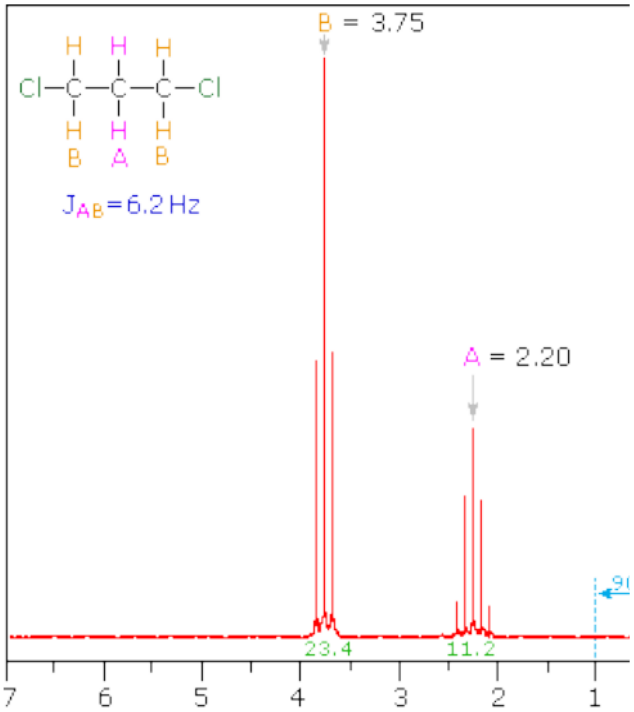
The splitting patterns found in various spectra are easily recognized, provided the chemical shifts of the different sets of hydrogen that generate the signals differ by two or more ppm. The patterns are symmetrically distributed on both sides of the proton chemical shift, and the central lines are always stronger than the outer lines. The most commonly observed patterns have been given descriptive names, such as **doublet** (two equal intensity signals), **triplet** (three signals with an intensity ratio of 1:2:1) and **quartet** (a set of four signals with intensities of 1:3:3:1). Four such patterns are displayed in the following illustration. The line separation is always constant within a given multiplet, and is called the **coupling constant (J)**. The magnitude of J, usually given in units of Hz, is magnetic field independent.



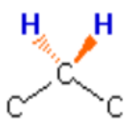
The splitting patterns shown above display the ideal or "**First-Order**" arrangement of lines. This is usually observed if the spin-coupled nuclei have very different chemical shifts (i.e. Δν is large compared to J). If the coupled nuclei have similar chemical shifts, the splitting patterns are distorted (second order behavior). In fact, signal splitting disappears if the chemical shifts are the same. Two examples that exhibit minor 2nd order distortion are shown below (both are taken at a frequency of 90 MHz). The ethyl acetate spectrum on the left displays the typical quartet and triplet of a substituted ethyl group. The spectrum of 1,3-dichloropropane on the right demonstrates that equivalent sets of hydrogens may combine their influence on a second, symmetrically located set.

Even though the chemical shift difference between the A and B protons in the 1,3-dichloroethane spectrum is fairly large (140 Hz) compared with the coupling constant (6.2 Hz), some distortion of the splitting patterns is evident. The line intensities closest to the chemical shift of the coupled partner are enhanced. Thus the B set triplet lines closest to A are increased, and the A quintet lines nearest B are likewise stronger. A smaller distortion of this kind is visible for the A and C couplings in the ethyl acetate spectrum.

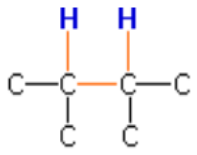




What causes this signal splitting, and what useful information can be obtained from it ?
If an atom under examination is perturbed or influenced by a nearby nuclear spin (or set of spins), the observed nucleus responds to such influences, and its response is manifested in its resonance signal. This spin-coupling is transmitted through the connecting bonds, and it functions in both directions. Thus, when the perturbing nucleus becomes the observed nucleus, it also exhibits signal splitting with the same J. For spin-coupling to be observed, the sets of interacting nuclei must be bonded in relatively close proximity (e.g. vicinal and geminal locations), or be oriented in certain optimal and rigid configurations. Some spectroscopists place a number before the symbol J to designate the number of bonds linking the coupled nuclei (colored orange below). Using this terminology, a vicinal coupling constant is ^3J and a geminal constant is ^2J.



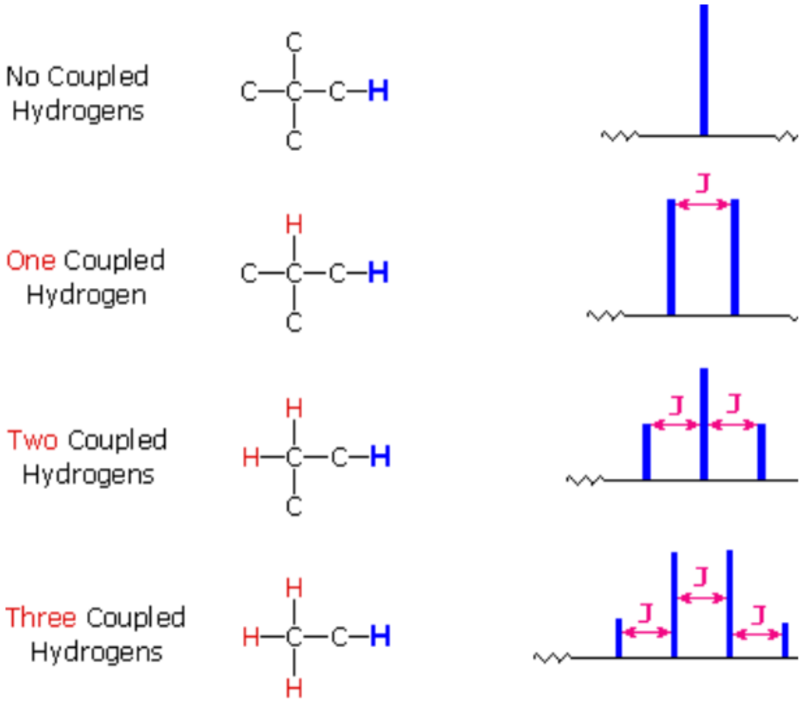
Geminal Hydrogens

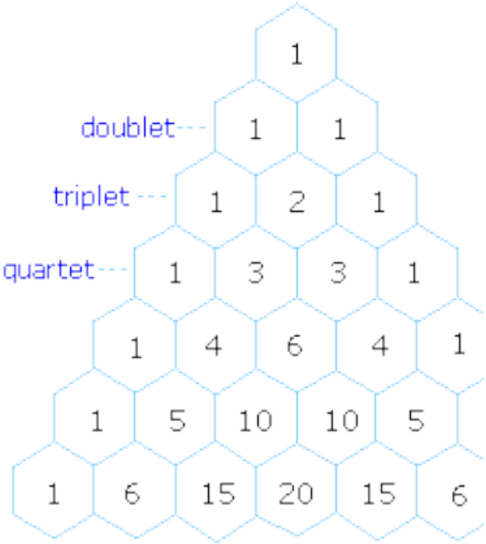


Vicinal Hydrogens

The following general rules summarize important requirements and characteristics for spin 1/2 nuclei :

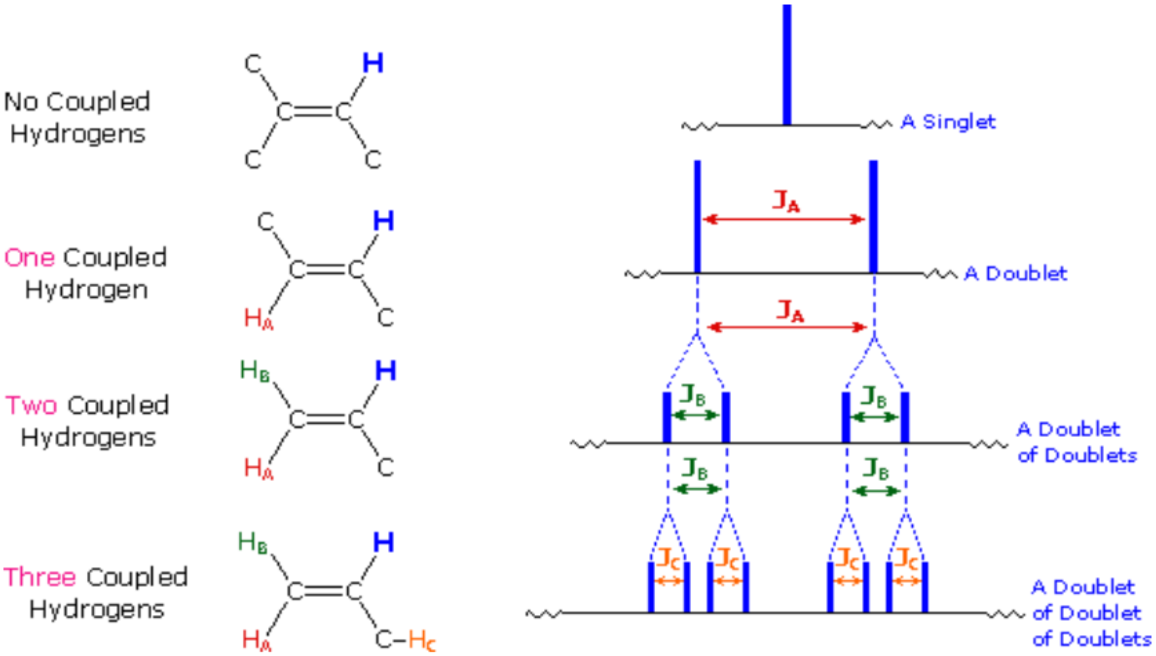
1) Nuclei having the same chemical shift (called **isochronous**) do not exhibit spin-splitting. They may actually be spin-coupled, but the splitting cannot be observed directly.
2) Nuclei separated by three or fewer bonds (e.g. vicinal and geminal nuclei) will usually be spin-coupled and will show mutual spin-splitting of the resonance signals (same J's), provided they have different chemical shifts. Longer-range coupling may be observed in molecules having rigid configurations of atoms.
3) The magnitude of the observed spin-splitting depends on many factors and is given by the coupling constant **J** (units of Hz). J is the same for both partners in a spin-splitting interaction and is independent of the external magnetic field strength.
4) The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the **n+1 rule**, where n is the number of neighboring spin-coupled nuclei with the same (or very similar) Js. If there are 2 neighboring, spin-coupled, nuclei the observed signal is a triplet (2+1=3); if there are three spin-coupled neighbors the signal is a quartet (3+1=4). In all cases the central line(s) of the splitting pattern are stronger than those on the periphery. The intensity ratio of these lines is given by the numbers in Pascal's triangle. Thus a doublet has 1:1 or equal intensities, a triplet has an intensity ratio of 1:2:1, a quartet 1:3:3:1 etc. To see how the numbers in Pascal's triangle are related to the Fibonacci series click on the diagram.



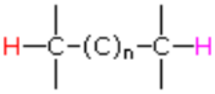
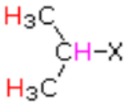
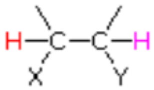
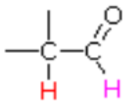
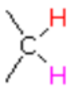


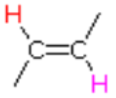
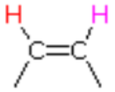
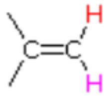
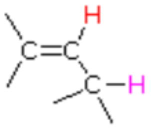
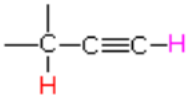
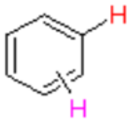
Pascal's Triangle

If a given nucleus is spin-coupled to two or more sets of neighboring nuclei by different J values, the n+1 rule does not predict the entire splitting pattern. Instead, the splitting due to one J set is added to that expected from the other J sets. Bear in mind that there may be fortuitous coincidence of some lines if a smaller J is a factor of a larger J.



Magnitude of Some Typical Coupling Constants

Structural Type	**J** (Hz)
	0 (unless in a rigid ideal orientation)
H_3C-CH_2-X	6 to 8
	5 to 7
	2 to 12 (depends on dihedral angle and the nature of X and Y)
	0.5 to 3
	12 to 15 (must be diastereotopic)

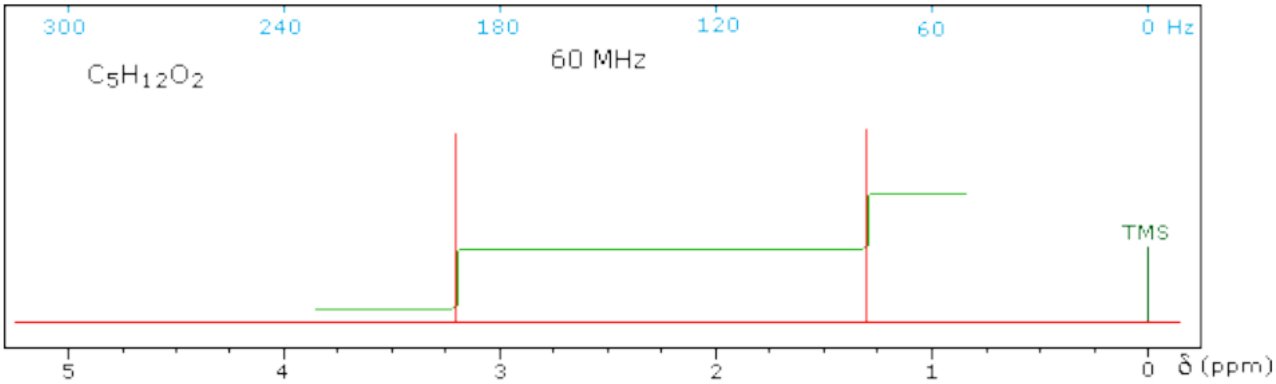
Structural Type	**J** (Hz)
	12 to 18
	7 to 12
	0.5 to 3
	3 to 11 (depends on dihedral angle)
	2 to 3
	o 6 to 9 m 1 to 3 p 0 to 1

Spin 1/2 nuclei include ^{1}H, ^{13}C, ^{19}F & ^{31}P. The spin-coupling interactions described above may occur between similar or dissimilar nuclei. If, for example, a ^{19}F is spin-coupled to a ^{1}H, both nuclei will appear as doublets having the same J constant. Spin coupling with nuclei having spin other than 1/2 is more complex and will not be discussed here.

To make use of a calculator that predicts first order splitting patterns Click Here. This application was developed at Colby College.

Some Examples

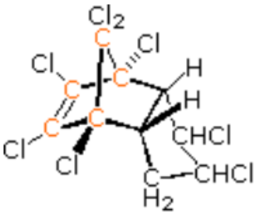
Test your ability to interpret ^{1}H nmr spectra by analyzing the seven examples presented below. The seven spectra may be examined in turn by clicking the "Toggle Spectra" button. Try to associate each spectrum with a plausible structural formula. Although the first four cases are relatively simple, keep in mind that the integration values provide ratios, not absolute numbers. In two cases additional information from infrared spectroscopy is provided. When you have made an assignment you may check your answer by clicking on the spectrum itself. In the sixth example, a similar constitutional isomer cannot be ruled out by the data given.



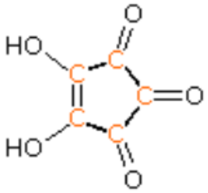
For a challenging problem having many spin couplings Click Here.

3. Carbon NMR Spectroscopy

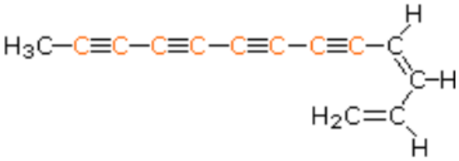
The power and usefulness of ^{1}H nmr spectroscopy as a tool for structural analysis should be evident from the past discussion. Unfortunately, when significant portions of a molecule lack C-H bonds, no information is forthcoming. Examples include polychlorinated compounds such as chlordane, polycarbonyl compounds such as croconic acid, and compounds incorporating triple bonds (structures below, orange colored carbons).



chlordane

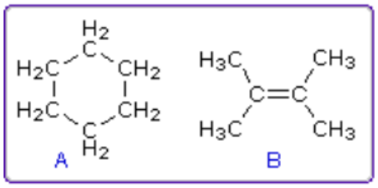


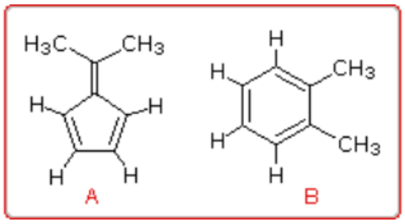
croconic acid

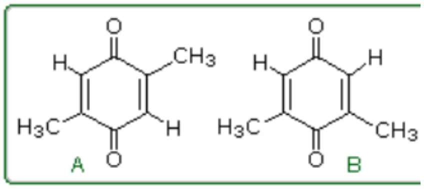


a polyacetylene from *Dahlia*

Even when numerous C-H groups are present, an unambiguous interpretation of a proton nmr spectrum may not be possible. The following diagram depicts three pairs of isomers (A & B) which display similar proton nmr spectra. Although a careful determination of chemical shifts should permit the first pair of compounds (blue box) to be distinguished, the second and third cases (red & green boxes) might be difficult to identify by proton nmr alone.







These difficulties would be largely resolved if the carbon atoms of a molecule could be probed by nmr in the same fashion as the hydrogen atoms. Since the major isotope of carbon (^{12}C) has no spin, this option seems unrealistic. Fortunately, 1.1% of elemental carbon is the ^{13}C isotope, which has a spin I = 1/2, so in principle it should be possible to conduct a carbon nmr experiment. It is worth noting here, that if much higher abundances of ^{13}C were naturally present in all carbon compounds, proton nmr would become much more complicated due to large one-bond coupling of ^{13}C and ^{1}H.

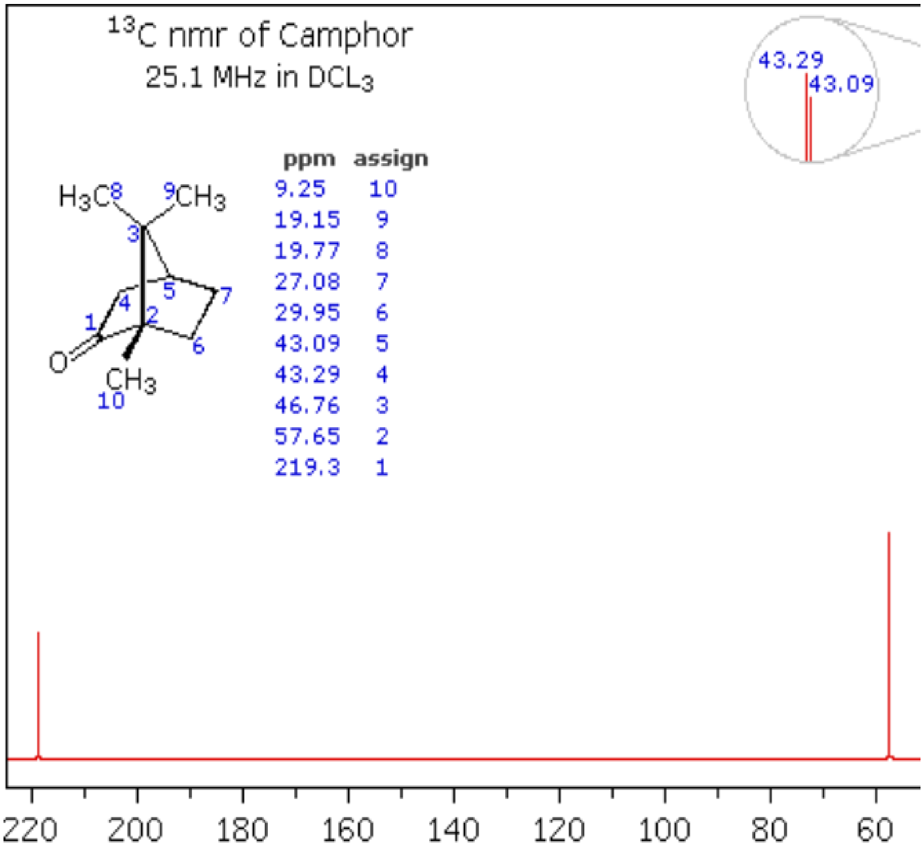
Many obstacles needed to be overcome before carbon nmr emerged as a routine tool :

i) As noted, the abundance of ^{13}C in a sample is very low (1.1%), so higher sample concentrations are needed.

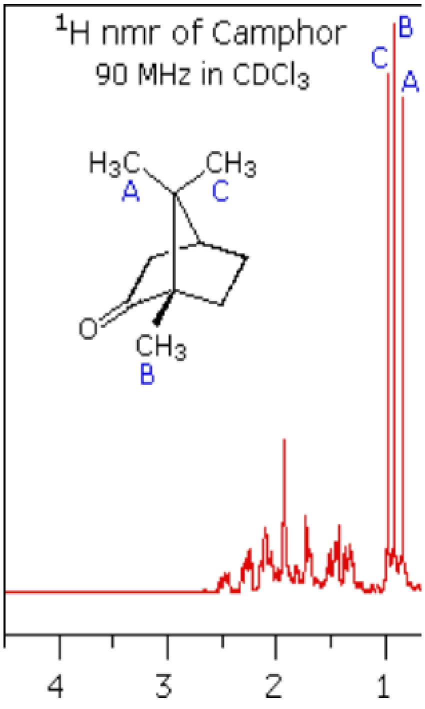
ii) The ^{13}C nucleus is over fifty times less sensitive than a proton in the nmr experiment, adding to the previous difficulty.

iii) Hydrogen atoms bonded to a ^{13}C atom split its nmr signal by 130 to 270 Hz, further complicating the nmr spectrum.

The most important operational technique that has led to successful and routine ^{13}C nmr spectroscopy is the use of high-field pulse technology coupled with broad-band heteronuclear decoupling of all protons. The results of repeated pulse sequences are accumulated to provide improved signal strength. Also, for reasons that go beyond the present treatment, the decoupling irradiation enhances the sensitivity of carbon nuclei bonded to hydrogen. When acquired in this manner, the carbon nmr spectrum of a compound displays a single sharp signal for each structurally distinct carbon atom in a molecule (remember, the proton couplings have been removed). The spectrum of camphor, shown on the left below, is typical. Furthermore, a comparison with the ^{1}H nmr spectrum on the right illustrates some of the advantageous characteristics of carbon nmr. The dispersion of ^{13}C chemical shifts is nearly twenty times greater than that for protons, and this together with the lack of signal splitting makes it more likely that every structurally distinct carbon atom will produce a separate signal. The only clearly identifiable signals in the proton spectrum are those from the methyl groups. The remaining protons have resonance signals between 1.0 and 2.8 ppm from TMS, and they overlap badly thanks to spin-spin splitting.

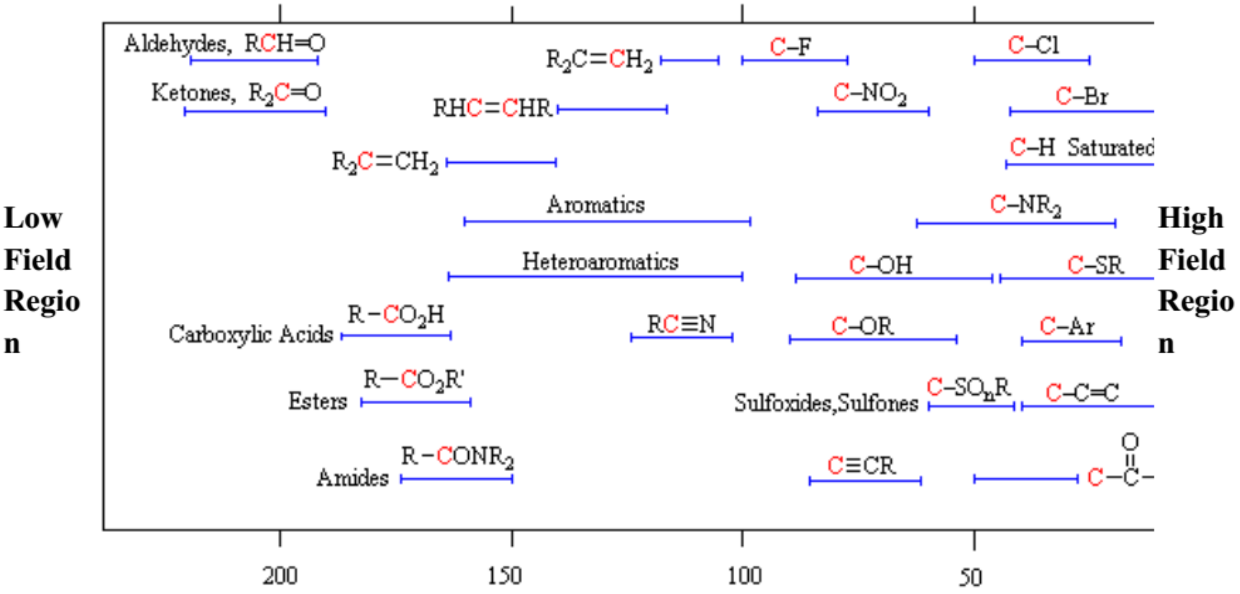


ppm	assign
9.25	10
19.15	9
19.77	8
27.08	7
29.95	6
43.09	5
43.29	4
46.76	3
57.65	2
219.3	1



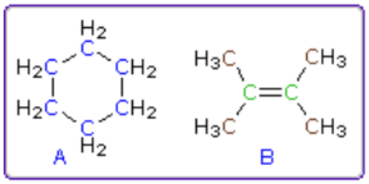
Unlike proton nmr spectroscopy, **the relative strength of carbon nmr signals are not normally proportional to the number of atoms generating each one**. Because of this, the number of discrete signals and their chemical shifts are the most important pieces of evidence delivered by a carbon spectrum. The general distribution of carbon chemical shifts associated with different functional groups is summarized in the following chart. Bear in mind that these ranges are approximate, and may not encompass all compounds of a given class. Note also that the over 200 ppm range of chemical shifts shown here is much greater than that observed for proton chemical shifts.

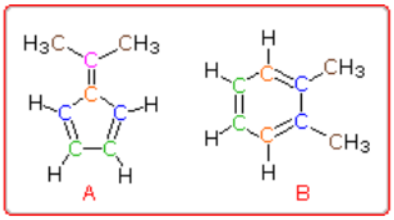
^{13}C Chemical Shift Ranges*

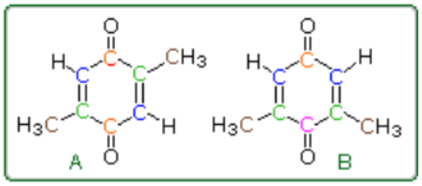


* For samples in $CDCl_3$ solution. The δ scale is relative to TMS at δ=0.

The isomeric pairs previously cited as giving very similar proton nmr spectra are now seen to be distinguished by carbon nmr. In the example on the left below (blue box), cyclohexane and 2,3-dimethyl-2-butene both give a single sharp resonance signal in the proton nmr spectrum (the former at δ 1.43 ppm and the latter at 1.64 ppm). However, in its carbon nmr spectrum cyclohexane displays a single signal at δ 27.1 ppm, generated by the equivalent ring carbon atoms (colored blue); whereas the isomeric alkene shows two signals, one at δ 20.4 ppm from the methyl carbons (colored brown), and the other at 123.5 ppm (typical of the green colored sp^2 hybrid carbon atoms).







The C_8H_{10} isomers in the center (red) box have pairs of homotopic carbons and hydrogens, so symmetry should simplify their nmr spectra. The fulvene (isomer A) has five structurally different groups of carbon atoms (colored brown, magenta, orange, blue and green respectively) and should display five ^{13}C nmr signals (one near 20 ppm and the other four greater than 100 ppm). Although ortho-xylene (isomer B) will have a proton nmr very similar to isomer A, it should only display four ^{13}C nmr signals, originating from the four different groups of carbon atoms (colored brown, blue, orange and green). The methyl carbon signal will appear at high field (near 20 ppm), and the aromatic ring carbons will all give signals having δ > 100 ppm.

Finally, the last isomeric pair, quinones A & B in the green box, are easily distinguished by carbon nmr. Isomer A displays only four carbon nmr signals (δ 15.4, 133.4, 145.8 & 187.9 ppm); whereas, isomer B displays five signals (δ 15.9, 133.3, 145.8, 187.5 & 188.1 ppm), the additional signal coming from the non-identity of the two carbonyl carbon atoms (one colored orange and the other magenta).

ELECTRON SPIN RESONANCE (ESR)

Electron Spin Resonance (ESR), often called Electron Paramagnetic Resonance (EPR), is similar to Nuclear Magnetic Resonance (NMR), the fundamental difference being that ESR is concerned with the magnetically induced splitting of electronic spin states, while NMR describes the splitting of nuclear spin states. In both ESR and NMR, the sample material is immersed in a strong static magnetic field and exposed to an orthogonal low- amplitude high-frequency field. ESR usually requires microwave-frequency radiation (GHz), while NMR is observed at lower radio frequencies (MHz). With ESR, energy is absorbed by the sample when the frequency of the radiation is appropriate to the energy difference between two states of the electrons in the sample, but only if the transition satisfies the appropriate selection rules. Splitting can occur only when the electron is in a state with non-zero total angular momentum, i.e. electrons in atoms with closed atomic shells cannot show this behavior. The term ESR refers specifically to the case in which the spins of the electrons absorbing the radiation are only weakly interacting ("weakly coupled") with each other. In NMR the static magnetic field splits the quantum states of a nucleus which has non-zero nuclear spin. The observation of NMR requires that the total electronic spin be zero. Why? (Read Feynman's discussion of NMR, Vol. 2, 35-6.)

Our experiment makes use of a bulk sample (as contrasted to Rabi's molecular beam resonance method discussed in Feynman), and is limited to those materials that have electrons with non-zero total angular momentum (or a "dipole moment"). Because of chemical binding, most materials in bulk form do not have net electronic angular momentum, and thus are not suitable for this experiment. Some materials which are suitable are:

1. Atoms or ions of the transition elements which contain unpaired 3d electrons inside the completed 4s shell. This experiment will allow you to examine the elements Mn++ and either Cr+++ or Fe+++ as dilute impurities in a MgO host crystal.
2. A small number of organic molecules are called free radicals because they contain a single unpaired electron, *aa-Di-phenyl-b-picryl-hydrazyl (DPPH)* being the one that will be used as a calibration source for this experiment. All but one of the electrons of this molecule are paired so there is only the orbital and spin motion of one electron present per molecule. In fact the orbital motion of that electron is quenched. (Refer to C. P. Slichter, *Principles of Magnetic Resonance* - page 65ff). The spin motion of this single unpaired electron gives to this molecule a g-factor that very nearly equals that of a free electron; $g = 2.0038$ instead of 2.00232.

THEORY

1. ENERGY LEVEL STRUCTURE:

If a paramagnetic atom or molecule is placed in a solid there will be interactions between it and its surroundings. In the case we will examine, the result of these interactions will be to leave the single paramagnetic electron in a state which appears similar to that of an s - state electron, which has zero orbital angular momentum and therefore allows us to examine the effect of a magnetic field on the spin motion.

The paramagnetic atom or molecule has a quantum state determined by the Hamiltonian, which contains several terms. The dominant potential term is the Coulomb interaction between the paramagnetic electron and the electrons of its own atom, the neighboring atoms, and the positive charges of its own nucleus. This large Coulomb interaction defines the basic ground state for the electron. The remaining terms can be considered as perturbations.

Assuming that the effect of the Coulomb terms has been to leave this electron in an L=0 (quenched orbital motion) state, the magnetic perturbation Hamiltonian can be written:

$$\begin{aligned} H &= a\, I \bullet J - g\beta\, J \bullet H_0 + g_N \beta_N I \bullet H_N \quad , \quad \text{or} \\ H &= a\, I \bullet J - g\beta\, M_J H_0 + g_N \beta_N m_I H_N \quad . \end{aligned} \qquad (1)$$

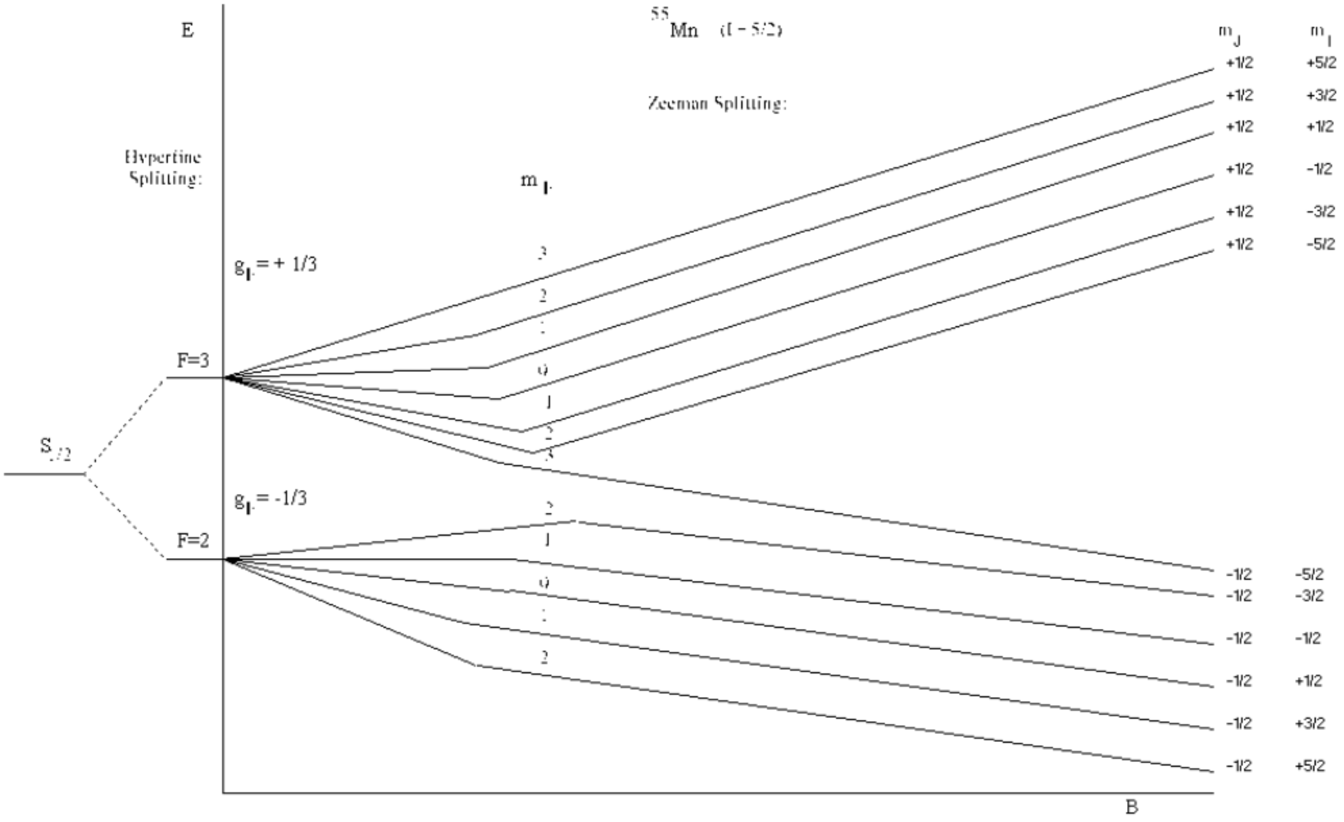
The total electron angular momentum quantum number J is just the spin quantum number, S, in this case. The nuclear angular momentum quantum number I is determined by the net spin of the nucleus. The first term is the hyperfine interaction, and in this case (L = 0) is the "Fermi Contact" term. The second term is the electronic Zeeman term due to the effect of the applied magnetic field H0 on the electron spin. The third term is the nuclear Zeeman term due to the effect of the magnetic field on the nuclear spin. Since beta_N is much smaller than beta, this last term is small. The magnetic field H_N seen by the nucleus may be modified by the electron system. Beta and beta_N are the electron and nuclear "magnetons" beta = e h / (4 pi mc).

The electron's 'g' factor is given by the Lande rule for the vector model of the atom. The nuclear 'g' factor, g_N, is obtained from a knowledge of the structure of the nucleus.

With fields of the magnitude used in this experiment (several kiloGauss), F = I + J is not a good quantum number. Energy splittings due to the applied field are comparable to, or larger than, the energy splittings between different F states. Put another way, the states of total F are "mixed" by the applied field, and thus F is not a good description of the state of the system. However, J = L + S is a good quantum number, for even at fields of the magnitude used here, the spin-orbit splitting is much greater than the splitting due to the applied field.

Thus the good quantum numbers for use in this experiment are J and I, and their projections along the field axis. The energy levels of a paramagnetic ion in a magnetic field of the magnitude available to this experiment will be dependent on the values of M_J and M_I, as illustrated for Mn++ in Figure 1.

Mn++ is the manganese atom with two 'd' electrons missing from the 3d shell. This leaves 5 electrons in the 3d shell (half filled). The ground state for this case is that in which all 5 electron spins are parallel, i.e.,6S_5/2. Since the nuclear spin I = 5/2, the total quantum number F = I + S (since L = 0), ranges from 0 to 5. Figure 1 shows the splitting of just the S = 1/2 component. The other spin components will split more rapidly with magnetic field than does the S = 1/2 component, but the allowed transitions will be degenerate with those for S = 1/2, so only 6 lines will be seen in the spectrum.



S=1/2. L=0, J=1/2, I=5/2

Lande Formula: $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

Zeeman and Hyperfine Splitting Hamiltonian:

$$H = aI \cdot J - g\beta J \cdot H_0 + g_N \beta_N I \cdot H_N$$

Hyperfine

Field "seen" by an electron

Field "seen" by the nucleus

Figure 1. Hyperfine splitting.

2. WIDTH OF ABSORPTION PEAKS:

The width of the absorption peak in ESR is very much greater than in NMR. This width arises from the spin-spin interaction between neighboring atoms. In a sample containing N spins per cm^3 (e.g., N DPPH molecules per cm^3 with one unpaired electron per molecule), each acting as a dipole of strength m, the field H at any spin is the sum of the applied field plus that due to neighboring spins:

$$\mathrm{H} = \mathrm{H}_{app} \pm \mu / d^3 = H_{app} \pm \mu \times N. \qquad (2)$$

Spins throughout the sample see a field varying between H_0 + mu N and H_0 - mu N, giving rise to a "line width", just as if the external field were non-uniform. For nuclear spins we find that:

$$\mu N = (10^{-23}\mathrm{ergs/Gauss})(10^{23}\mathrm{nuclei/cm}^3) = 1\ \mathrm{Gauss}; \qquad (3)$$

while for electronic spins;

$$\mu N = (10^{-20}\mathrm{ergs/Gauss})(10^{23}\mathrm{nuclei/cm}^3) = 1000\ \mathrm{Gauss}. \qquad (4)$$

The breadth of the ESR lines makes them difficult to observe unless the applied field is quite large. (Why not reduce N?)

In some materials, DPPH for one, the line will not be this broad. In DPPH, the single unpaired electron wave function extends over the entire volume of the molecule, which is about 10^-7cm in diameter. Furthermore, in a solid material, the exchange integral between neighboring molecules is large, and the electron is shared between neighboring molecules, as in the hydrogen bond. This gives rise to "exchange narrowing", a quantum phenomenon first described by Van Vleck (*Phys. Rev.*, **74**, 1168 (1948)). This "exchange narrowing" might also be called "migration narrowing", and can be pictured classically by supposing that the electron is smeared over a large region of many molecules. It sees an average H field, averaged over many molecules, with fluctuations averaged to zero, leaving only the applied field. Support for this explanation will be found in the fact that, in a dilute solution of DPPH, the resonance line becomes broader, presumably because the exchange integral is reduced due to increased inter-molecular spacing. In DPPH crystals, such as you will use, the line width is about 2.7 Gauss.

EXPERIMENTAL APPARATUS

This consists of an electromagnet with power supplies to generate and modulate a uniform magnetic field of several thousand Gauss, as well as the components that generate and detect microwaves.

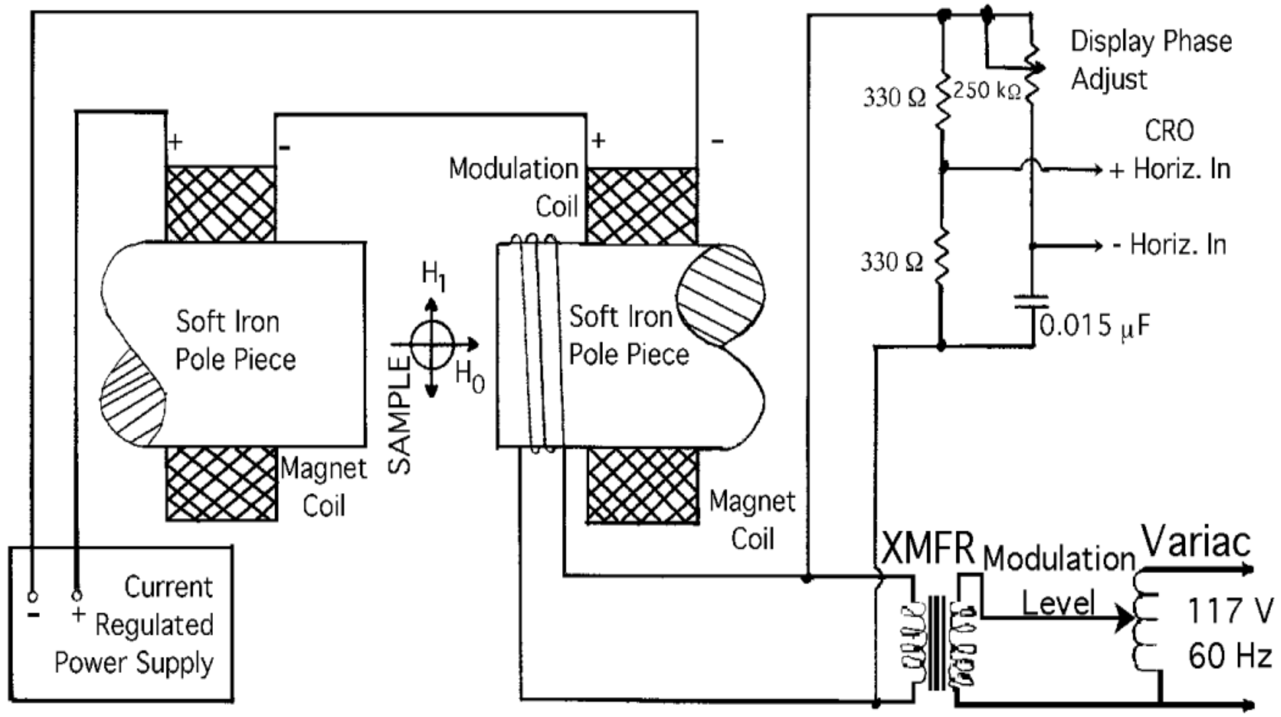


Figure 2. An ESR Spectrometer showing the sample, magnetic fields applied to it, and the sources of these fields.

MAGNET:

A static magnetic field is provided by a 10 cm diam. electromagnet with a current- regulated power supply (15 A Maximum). A 60 Hz AC component is added to this field by an adjustable current through a winding on one pole piece of the electromagnet. A voltage that is proportional to the amplitude of this modulation provides the horizontal display for the CRO, with provision for shifting the phase between the signal delivered to the CRO and the modulation applied to the main magnetic field. As with an NMR experiment, a homogeneous field is required for best results.

HALL MAGNETOMETER:

A Hall device, driven from a stable constant-current power system, with a digital multimeter (DMM) reading the Hall voltage, is used to measure the average value of the magnetic field applied to the ESR samples. The drive current has been set to make the device direct-reading with an error of < ± 3%, providing that the temperature of the Hall device does not deviate significantly from normal (19-25 oC). The DMM must be set to its 200 mV range (1 microV least significant digit) and carefully "zeroed". Ignore the decimal point. The change in the least significant figure will then be 1 Gauss. When making a measurement place the probe as close to the microwave cavity wall as possible and away from the warm magnet pole face.

MICROWAVE OSCILLATOR/DETECTOR SYSTEM:

The microwave system is contained entirely within the gap of the electromagnet. See Figure 3. It consists of a short length of Ku (RG-53) rectangular waveguide (12 GHz), short circuited at both ends to provide a relatively high-Q resonant cavity. The samples to be investigated are mounted slightly off center on a rotatable cylindrical plug whose end surface is flush with one end of the cavity. This allows the samples to project slightly into the microwave field of the cavity and their positions to be optimized for best signal-to-noise ratio. A microwave Gunn diode is mounted along the center of the long axis of the cavity, approximately 1/3 of the cavity length from the end opposite the samples. The diode spans the short dimension of the rectangular waveguide, efficiently coupling to the E vector of the microwave field, resulting in maximum efficiency both in generating microwaves and in simultaneously detecting the influence on that field by samples at resonance.

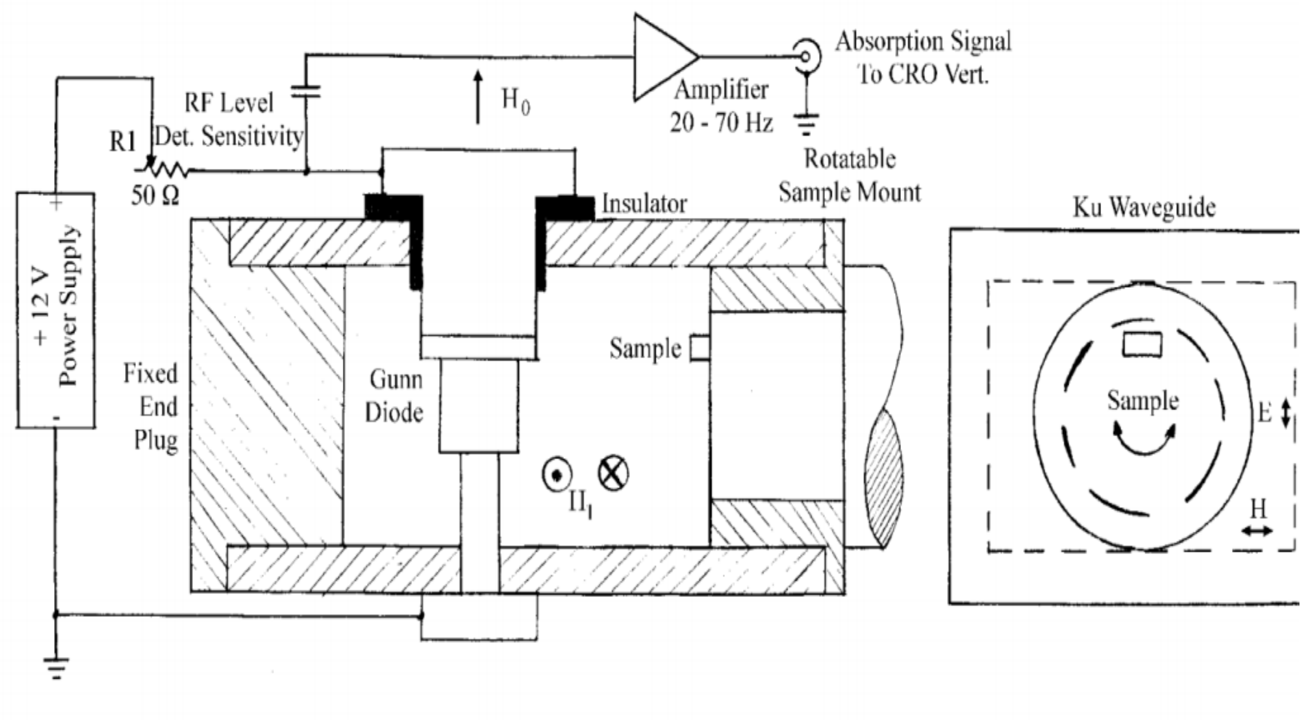


Figure 3. The Microwave Generator/Detector components.

GUNN DIODE:

A Gunn diode displays conductivity that is non-linear with applied voltage; i.e., it has a negative-resistance V/I characteristic.

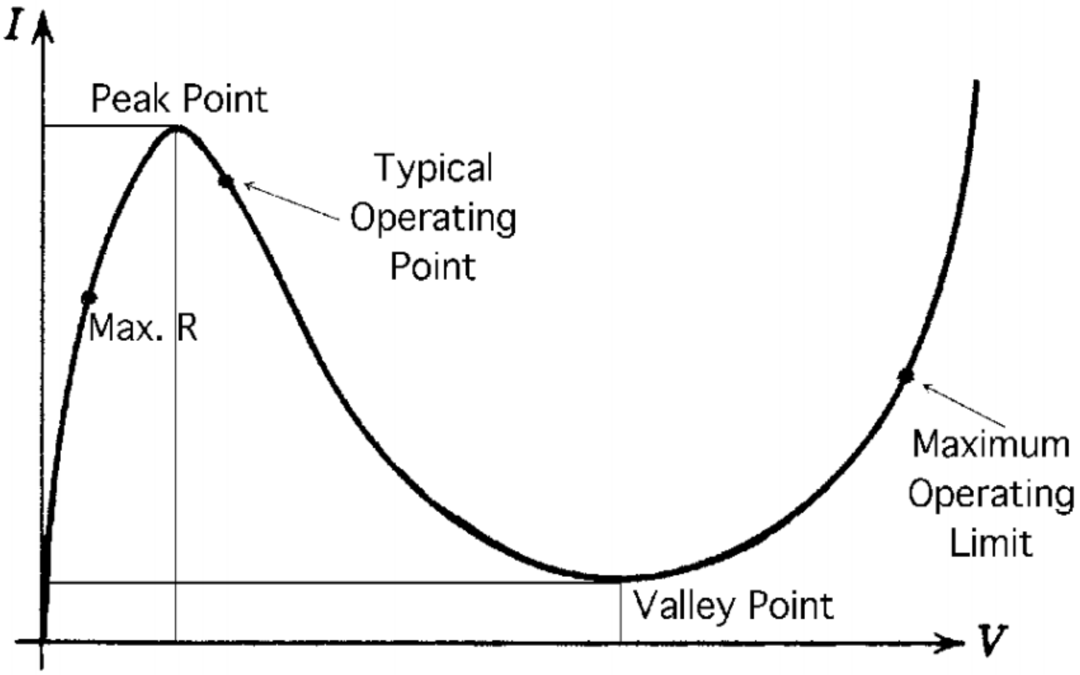


Figure 4. Characteristic V/I curve for a negative-resistance device (Gunn diode).

The diode contains an extremely thin P-N junction diffused into a heavily doped GaAs (Gallium Arsenide) substrate. The frequency of oscillation is determined by the very high mobility of the electron/hole carriers in GaAs, and the thickness of the junction. A benefit of the very thin junction (10^-3cm) is that the conduction electrons are minimally affected by large magnetic fields (4-5 kG).

The diode is powered by a stable regulated power supply and R1, a series ten-turn variable 50 Ohm resistor. When Rl is set to its maximum (cw), the operating point is to the left of the Peak Point. As this resistance is reduced, the operating point moves to the right of the Peak Point into the negative-resistance region where a microwave frequency of extreme spectral purity is generated. Further reduction in series resistance increases the power.

Because the Gunn diode acts simultaneously as both source and detector of microwaves, optimization of the Signal-to-Noise Ratio is an interdependent exercise. Both the level of microwave fields generated and the detection sensitivity are affected by Rl. A 60 Hz signal, produced by the reduction of the cavity Q when a sample absorbs energy at resonance (a reduction in the microwave field level), is detected by the diode, and amplified by a low-noise amplifier used to drive the vertical display of the CRO. Detection sensitivity will be greatest when the operating point is "marginal", just to the right of the Peak Point. The optimum requires operation a bit farther into the negative-resistance region.

Samples in the cavity are DPPH plus trace quantities of several ions of the 3d series (Mn++ and either Cr+++ or Fe+++) diffused into a carrier lattice of crystalline MgO (Magnesium Oxide).

The field for one of the resonances depends slightly upon the orientation of the crystal of MgO with respect to the magnetic field. Can you suggest a reason for this?

EXPERIMENTAL TASKS

1. First set the 60 Hz modulation at maximum, and preset Rl to its CLOCKWISE stop (maximum value of 50 Ohm). Force the diode to oscillate by slowly rotating Rl COUNTER CLOCKWISE, i.e., reduce the value of Rl. The onset of oscillations will be indicated by an abrupt jump of the trace on the CRO. *Sometimes* the narrow trace will suddenly be replaced by a broad vertical band of low-frequency waveforms ("squegging"). If the latter are seen, you have set the operating point almost exactly on the peak point. Increase the level of oscillations slightly to restore a thin trace with a bit of "grass" growing on it (thermal noise), then slowly raise the magnet current until you locate the large DPPH peak and then readjust the diode bias to get the best S/N. Note the effect of varying the modulation amplitude and phase. Why are two peaks seen?

2. Use the Hall probe to measure H_0 with the DPPH peak centered on the trace, then calculate the frequency of the microwaves by using the g-factor for DPPH (2.0038). Measure and explain the width of the signal. (The Hall probe operating current has been set to make the system direct reading, with an absolute accuracy of (< 3%. When the DMM is set to its 200 mV range, the least significant digit will equal 1 Gauss (ignore the decimal point). The Hall device has a substantial temperature coefficient (~ -0.1%/Co), and should be exposed to the warm magnet pole caps for the shortest practical time, and then removed to allow it to return to "room temperature".

3. Measure the magnetic fields required to center all other peaks on the CRO. Six are due to Mn++ while the others are due to either Cr+++ or Fe+++. Try to determine which of the peaks are due to Cr+++ or Fe+++. You will require a knowledge of the electron configuration of both ions in order to do this (the 'g' factor for Cr+++ in MgO is 1.9800 ± 0.0063; and for Fe+++, 'g' = 2.0037 ± 0.0007).