

# Introduction to NMR:

## Principles

NMR is one of the most popular techniques in chemical analysis. A considerable number of Nobel prizes have been awarded to scientists due to their contribution to the development of NMR-related discoveries. Nowadays it has extensive applications in inorganic chemistry, organic chemistry, biochemistry, and medical sciences. Talking in general, NMR is based on the interaction of the magnetic properties of nuclei with an external magnetic field.

Nuclei are positively charged and for some elements that it spins, a magnetic dipole is generated. The quantum spin number of the nucleus,  $I$ , is used to demonstrate the angular momentum of the charge that is spinning. If the atomic mass of an element is odd,  $I$  will be half-integer and the element can be studied using 1D NMR.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are two famous examples of this type of elements. If the atomic number and the atomic mass are both even,  $I$  will be zero and that element cannot be studied using NMR as it does not have any magnetic dipole. A good example for this category is  $^{12}\text{C}$ , which is NMR inactive. If the atomic mass is even and the atomic number is odd,  $I$  will be integer and the element will have a poor resolution in NMR due to the asymmetrical charge distribution in the nuclei.

In the absence of an external magnetic field, nuclei situate in such a way that the magnetic dipoles orient randomly. However, in the presence of an external magnetic field,  $2I + 1$  different orientations exist for the magnetic dipole of a nucleus, each of which will have its own energy state. In the cases of  $^1\text{H}$  and  $^{13}\text{C}$ ,  $I$  is  $1/2$ , and there will be two states (Figure 1), which are energetically split by an energy difference of  $\Delta E$ , which is governed by the following equation:

$$\Delta E = \left(\frac{h\gamma}{2\pi}\right) B_0$$

where  $\gamma$  is the *gyromagnetic ratio*,  $h$  is the *Planck's constant*, and  $B_0$  is the strength of the external magnetic field.  $\Delta E$  can be provided using an alternating magnetic field with proper frequency. Since  $\Delta E$  is related to frequency, the following equation can simply be derived:

$$\nu = \left(\frac{\gamma}{2\pi}\right) B_0$$

where  $\nu$  is frequency. As it is shown in the above equation,  $\nu$  is related to the strength of the magnetic field. For a 100 MHz  $^1\text{H}$  NMR instrument as an example,  $B_0$  is 2.35 Tesla. For such instrument,  $\Delta E$  is  $1.3 \times 10^{-25}$  J. Using *Boltzmann distribution* equations; there will be a difference of  $4.8 \times 10^9$  atoms ( $8.1 \times 10^{-15}$  mole atom) in the populations of the ground state and the excited state for 1.0 ml of a  $1.0 \mu\text{M}$  solution ( $1.0 \times 10^{-9}$  mole atom). Excitation can happen until the population difference decreases to zero. It means that only half of the population difference can interact with light, which for this sample is about  $4.0 \times 10^{-4}$  percent of all atoms (figure 1). This small population difference between the ground state and the excited state causes NMR to be hardly able to analyze diluted

samples. To increase the population difference (i.e. increasing the sensitivity),  $\Delta E$  can be increased by increasing the strength of the applied magnetic field.

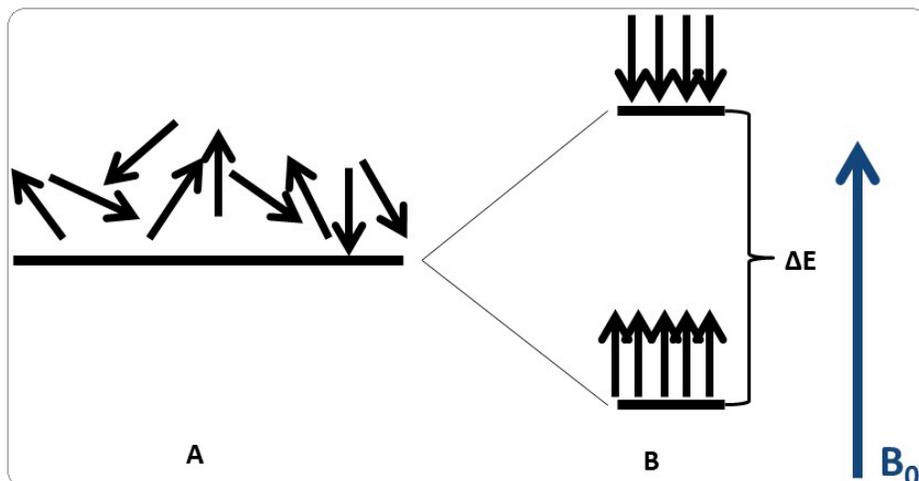


Figure 1. General representation of spins of hydrogen atoms under A) no magnetic field, B) an external magnetic field ( $B_0$ ). Note the population difference between the two states.

It is not only the nucleus that interacts with the magnetic field. Electrons also spin, and they have magnetic dipoles. The interaction of the applied magnetic field with electrons results in getting the electrons to move in such a way that they produce their own magnetic field. What a nuclei feels will be the sum of the two magnetic fields: applied magnetic field and the magnetic field by the surrounding electrons. Since the electron cloud is not uniformly distributed in a molecule, the magnetic field that a nucleus feels depends on the environment that it is experiencing. Equation 2 is rewritten in the following way to include the effects of the electron cloud in a molecule:

$$\nu_i = \left(\gamma/2\pi\right)B_0(1 - \sigma_i)$$

where  $\sigma_i$  is the shielding constant for the nucleus  $i$  and it depends on the level of shielding the nucleus  $i$  by the electron cloud.  $\sigma_i$  is not the same for different types of the same element. This is how NMR differentiates different types of a certain element in a molecule.

In the presence of an external magnetic field, nuclei precess as it is shown in figure 2. The frequency of this precession depends on the strength of the magnetic field that the nucleus feels, and as the overall magnetic field is not the same for different types of a certain element, they will each have their own precession frequency. The precession frequency is the same as that of the applied alternating magnetic field that interacts with the nucleus.

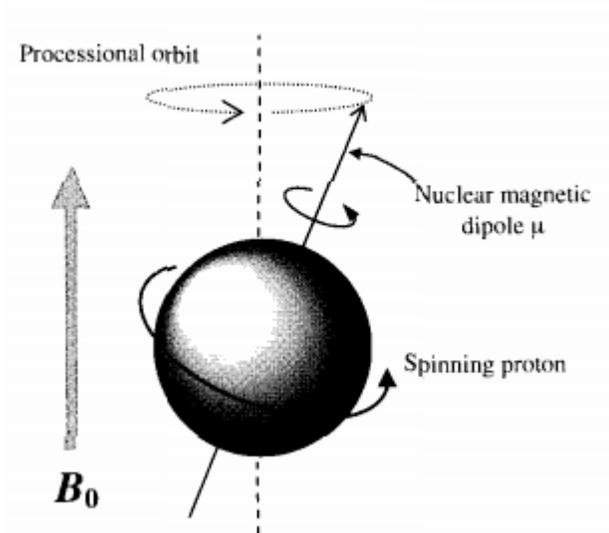


Figure 2. Precessing of a proton in an external magnetic field ( $B_0$ ). Picture from “Textbook: Robert M. Silverstein, Francis X. Webster, and David Kiemle, Spectrometric Identification of Organic Compounds - 7th edition, John Wiley & Sons, Inc., 2005.”

### ***Instrument Set up.***

Because of the population difference, there will be an overall magnetization for all nuclei. Since the precession does not occur in the same phase for the nuclei, the direction of the magnetization will be the same as the direction of the applied magnetic field. Figure 3 shows how the vectors of different magnetic dipoles create the overall *magnetization*.

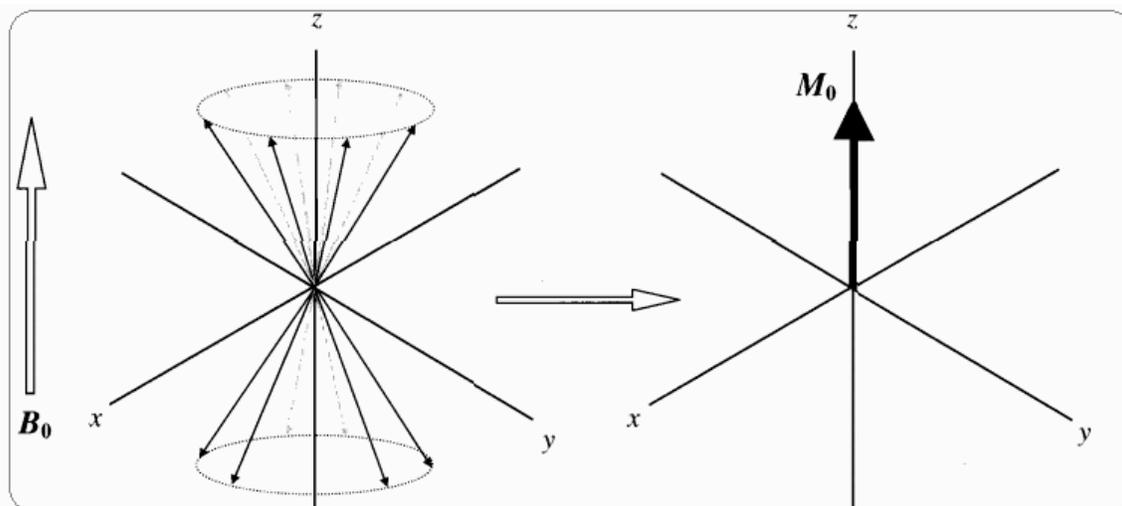
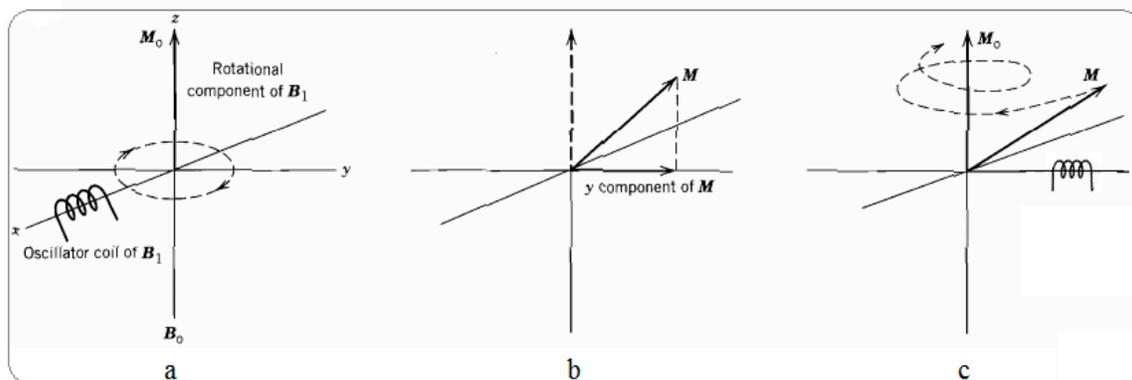


Figure 3. Concept of the net magnetization ( $M_0$ ). Picture from “Textbook: Robert M. Silverstein, Francis X. Webster, and David Kiemle, Spectrometric Identification of Organic Compounds - 7th edition, John Wiley & Sons, Inc., 2005.”

Practically a coil is situated perpendicular to the access of the magnetization ( $x$  access), through which an alternating magnetic field will be applied on the magnetization vector. If the frequency of the magnetic field matches with the precession frequency, the magnetization vector will be forced to rotate in accordance with the right hand rule. The rotated magnetization vector will be forced by the applied magnetic field of the instrument to get oriented toward the  $z$  access in a process called *relaxation*. During the relaxation process, the magnetization vector will induce a current in a coil that is designated in the  $y$  access (Figure 4). This current is the detected signal in NMR which contains the frequency information of all nuclei present in the magnetization vector.



**Figure 4. Applying a pulse to rotate the net magnetization.**

Picture adopted from "Textbook: Robert M. Silverstein, Francis X. Webster, and David Kiemle, *Spectrometric Identification of Organic Compounds* - 7th edition, John Wiley & Sons, Inc., 2005."

There are two ways to do NMR spectroscopy: *Continuous Wave NMR* (CW-NMR) and *Fourier Transform NMR* (FT-NMR). In the CW-NMR instrument, one frequency is scanned at a time and the signal for that certain frequency will be detected. In FT-NMR instruments, a pulse containing a wide range of frequencies is applied and one signal for all nuclei is detected. This one signal contains information about all nuclei present in the magnetization vector. *Fourier Transform* will be applied in the next step to deconvolute all frequencies. FT-NMR instrument perform the analysis faster, and are highly preferred. For a particular sample, several spectra could be recorded and averaged in order to increase the signal to noise ration. Figure 5 represents a typical CW-NMR instrument. An FT-NMR instrument is somehow similar to a CW-NMR instrument. Please notice the direction of the coils with respect to the applied magnetic field of the instrument.

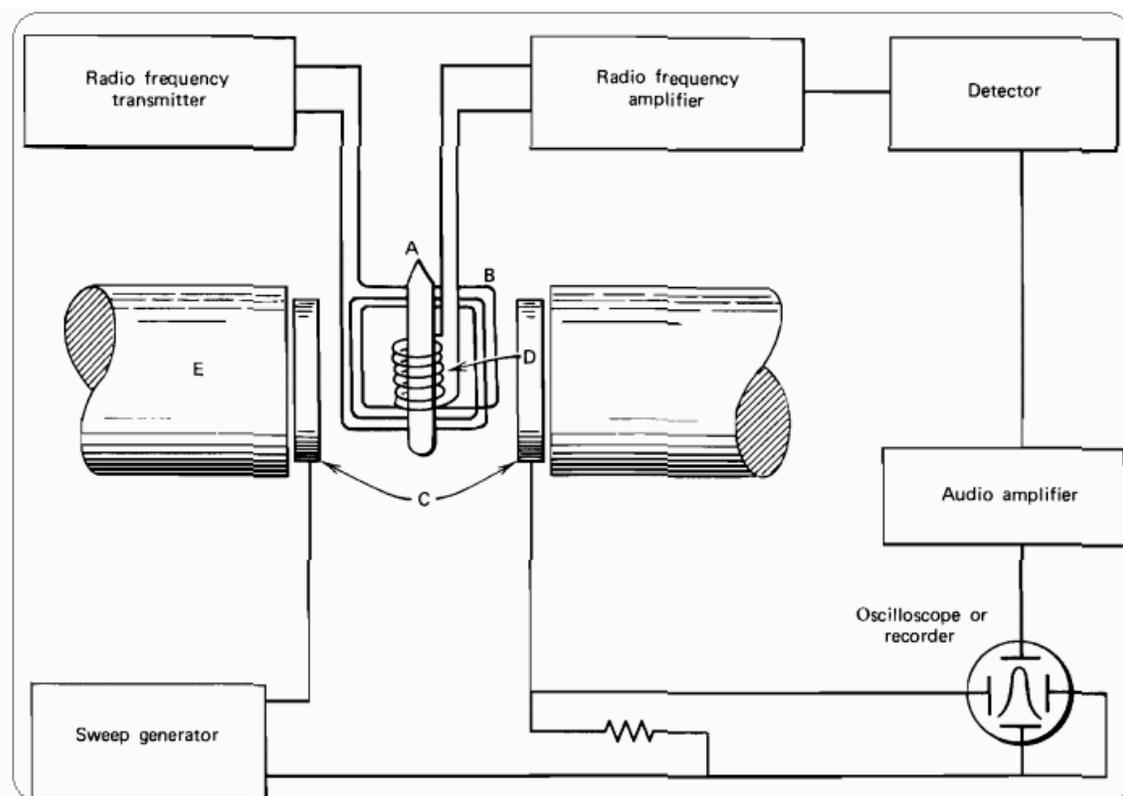


Figure 5. A typical CW-NMR instrument.

Picture from "Textbook: Robert M. Silverstein, Francis X. Webster, and David Kiemle, Spectrometric Identification of Organic Compounds - 7th edition, John Wiley & Sons, Inc., 2005."

### <sup>13</sup>C-NMR vs. <sup>1</sup>H-NMR

Carbon is the element that is found in any organic molecule. Therefore, C-NMR could be very helpful, but unfortunately <sup>12</sup>C is not NMR active as it was mentioned. Fortunately enough, <sup>13</sup>C with a natural abundance of 1.1% is NMR active. This low natural abundance along with lower gyromagnetic ratio for <sup>13</sup>C causes the sensitivity to decrease. Because of this lower sensitivity, getting a <sup>13</sup>C-NMR spectrum with a certain signal to noise ratio requires averaging more spectra than the number of spectra that would be required to average in order to get the same signal to noise ratio for a <sup>1</sup>H-NMR spectrum. Although it has a lower sensitivity, it is still highly used as it discloses valuable information.

Peaks in a <sup>1</sup>H-NMR spectrum are split to  $n + 1$  peak, where  $n$  is the number of hydrogen atoms on the adjacent carbon atom. Splitting pattern in <sup>13</sup>C-NMR is different. First of all, C-C splitting is not observed, because the probability of having two adjacent <sup>13</sup>C is about 0.01%. Observed splitting pattern, which is due to the hydrogen atoms on the same carbon atom not on the adjacent carbon atom, is governed by the same  $n + 1$ .

In  $^1\text{H}$ -NMR, the integral of the peaks are used for quantitative analysis, while this is an issue in  $^{13}\text{C}$ -NMR. The long relaxation process for carbon atoms takes longer comparing to that of hydrogen atoms, which also depends on the order of carbon (i.e. 1°, 2°, etc.). This causes the peak heights not to be related to the quantity of the corresponding carbon atoms.

## Using $^{13}\text{C}$ -NMR to study carbon nanomaterials

In a 1D  $^1\text{H}$ -NMR, information is mostly related to individual atoms. The *correlation* information that we achieve is limited to splitting patterns. In a 2D NMR experiment, it is tried to observe the interaction of different atoms with each other. There is no doubt that a 2D NMR experiment would release considerable amount of valuable information. In a 2D NMR experiment, a *pule sequence*, instead of a single pulse, is applied to the sample. By manipulating the pulse sequence, different type of correlation between atoms can be observed.

NMR spectrum could also be recorded for solid samples. The peaks for solid samples are very broad because the sample being solid cannot have all anisotropic (or orientation-dependent) interactions canceled due to *rapid random tumbling*. However, it is still possible to do high resolution solid state NMR by spinning the sample at  $54.74^\circ$  with respect to the applied magnetic field, which is called the *magic angle*. In other words, we can spin the sample to artificially cancel the orientation-dependent interaction due to averaging. In general, the spinning frequency has a considerable effect on the spectrum.

As an example for application of  $^{13}\text{C}$ -NMR in studying nanomaterial, this paper will be discussed: “Leah B. Casabianca, Medhat A. Shaibat, Weiwei W. Cai, Sungjin Park, Richard Piner, Rodney S. Ruoff, and Yoshitaka Ishii, *J. AM. CHEM. SOC.*, **2010**, 132, 5672.”

In this paper, structure of GO (Graphite Oxide) was studied using multidimensional  $^{13}\text{C}$ -NMR. GO can be used as the precursor for the production of normal and chemically modified graphene. The two candidates that were more likely to be correct were studied: Lerf-Klinowski model (molde A, figure 6.d), and Dékány model (model B, figure 6.e). In model A, the structure is mostly flat and 50% of carbon atoms are oxidized. In model A, there is 1,2-epoxides whereas model B exhibits 1,3-epoxides. Model B is not completely flat and areas with chair configuration are found. In model A, alternating oxidized and conjugated carbons are observed, while in model B we mostly find highly oxidized areas.

$^{13}\text{C}$  enriched GO was analyzed to find out which one of the candidates is the correct structure. Figure 6.a is an experimental Single Quantum/Double Quantum (SQ/DQ) 2D Solid State NMR spectrum from the  $^{13}\text{C}$  enriched sample. The diagonal peaks are eliminated. In figure 1.a, peaks connected by the red, orange, pink, and purple lines are for the correlations between COH and epoxide carbons, epoxide and  $\text{sp}^2$  carbons, COH and  $\text{sp}^2$  carbons, and two  $\text{sp}^2$  carbons respectively. Figures 6.b and 6.c are predicted spectra for models A and B respectively using ab initio calculations. Although the peak assignments are done, it can easily be recognized with a simple “finger print” comparison

that model A is the correct proposed structure. They have done some other experiments and calculations to further support their claim.

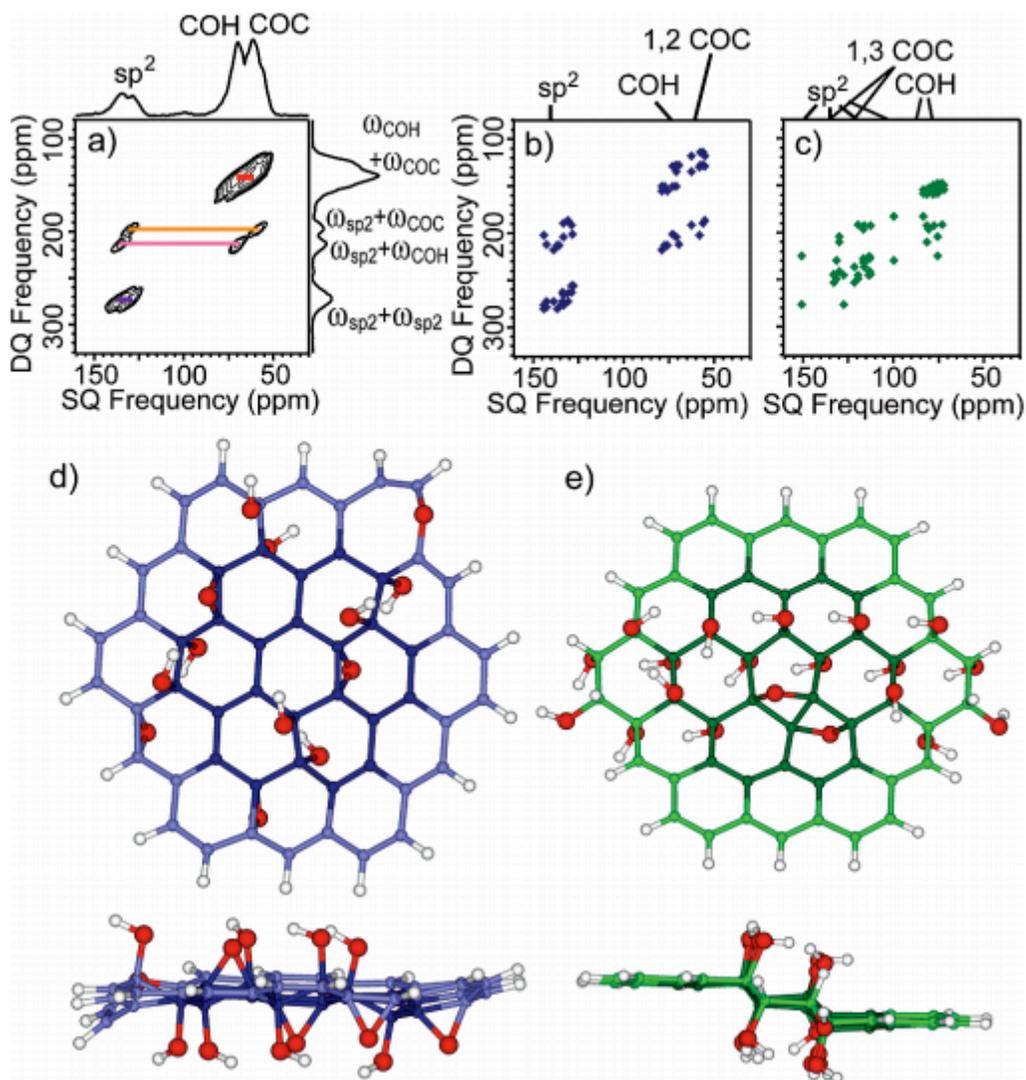


Figure 6. a) Experimental SQ/DQ 2D SSNMR spectrum. b, c) Predicted spectrum for b) model A and c) model B. d) Structure for model A. e) Structure for model B.  
 Picture from "Leah B. Casabianca, Medhat A. Shaibat, Weiwei W. Cai, Sungjin Park, Richard Piner, Rodney S. Ruoff, and Yoshitaka Ishii, *J. AM. CHEM. SOC.*, 2010, 132, 5672."