

Introduction to NMR Spectroscopy - CH114

Measurement of the Isotopic Ratio of $^{10}\text{B}/^{11}\text{B}$ in NaBH_4

Background

Nuclear Magnetic Resonance (NMR) is one of the most powerful and useful analytical techniques that chemists employ daily in the study of molecular structure and dynamics. As ultra-violet (UV) or infra-red (IR) spectroscopies, NMR is an absorption/emission spectroscopy: It can detect the absorption or emission of electromagnetic radiation at characteristic frequencies by certain nuclei in a molecule under certain conditions.

As you learned in lecture, only nuclei with *nuclear spin number* (I) different from 0 are NMR-active. This somewhat limits the atoms we can study by NMR. Fortunately, most interesting nuclei from a biological standpoint (H, C, N, P) have one or more isotopes which have $I \neq 0$. All hydrogen isotopes are NMR-active ($I = 1/2$ for ^1H , $I = 1$ for ^2H , $I = 1/2$ for ^3H); for carbon, the isotope 13 (^{13}C), with a 1% natural abundance, has an $I = 1/2$, and so forth. Due to the nuclear charge, the geometric distribution of neutrons and protons in the nucleus, and the fact that these subatomic particles *spin* around the nuclear axis, nuclei with $I \neq 0$ behave as small magnets, which we call *nuclear magnetic dipoles*.

The NMR phenomenon manifests when nuclei with $I \neq 0$ are placed in a strong external magnetic field, which is usually given the name \mathbf{B}_0 . Under the action of this external magnetic field, the nuclear magnetic dipoles will adopt different orientations with respect to the direction of \mathbf{B}_0 , which will have different energies. One can make a macroscopic analogy with a small bar magnet in a large magnetic field (i.e., a compass under the action of Earth's magnetic field): The small bar magnet will in this case align with the large magnetic field to lower its energy. At the microscopic, quantum mechanical level, the picture is not so simple: Instead of having only two, the number of possible orientations, or energy levels, will depend on the *magnetic quantum number* (m) of the nucleus, which is related to nuclear spin number I through the following relationship:

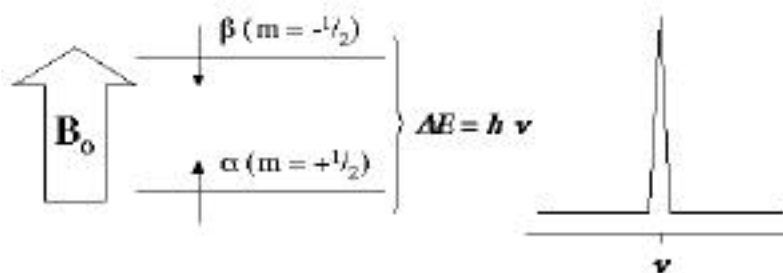
$$m = I, I - 1, I - 2, I - 3, \dots, -I$$

Therefore, the ^1H isotope of hydrogen, or *proton*, can have $m = +1/2$ or $m = -1/2$, which means that it can have two orientations with respect to an external magnetic field \mathbf{B}_0 : In favor or against the direction of \mathbf{B}_0 . These two orientations are related to two different energies, or *states*, of the proton in the magnetic field \mathbf{B}_0 ; one which corresponds to $m = +1/2$, is in favor of \mathbf{B}_0 and therefore less energetic, and one which corresponds with $m = -1/2$, is against \mathbf{B}_0 , and more energetic. These two states are called α and β respectively. The difference in energy (ΔE)

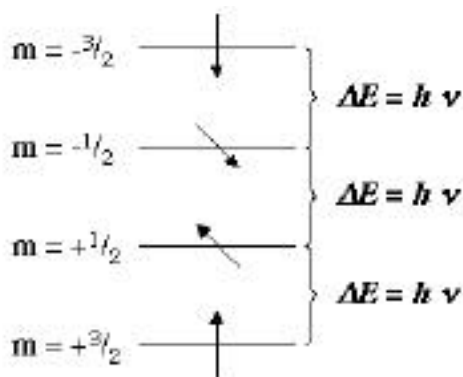
between the two levels is directly proportional to \mathbf{B}_0 and the type of nuclei (γ , see below). Furthermore, from quantum mechanics we know that ΔE is proportional to a frequency:

$$\mathbf{E}_\beta - \mathbf{E}_\alpha = \Delta E = \gamma \mathbf{B}_0 = h \nu$$

h is the Planck constant, and γ is the *gyromagnetic ratio*, which depends on the type of nuclei. This equation also tells us that for a particular nucleus and magnetic field, there will be a characteristic energy associated with the α to β transition. If we irradiate the nucleus with a radiowave of frequency ν , we will give the system the right amount of energy to promote the transition of that nuclei's spin from the α to the β state: We 'flip' the nuclear magnet. This absorption of energy can be recorded, in what becomes known as a *peak in the spectrum*:

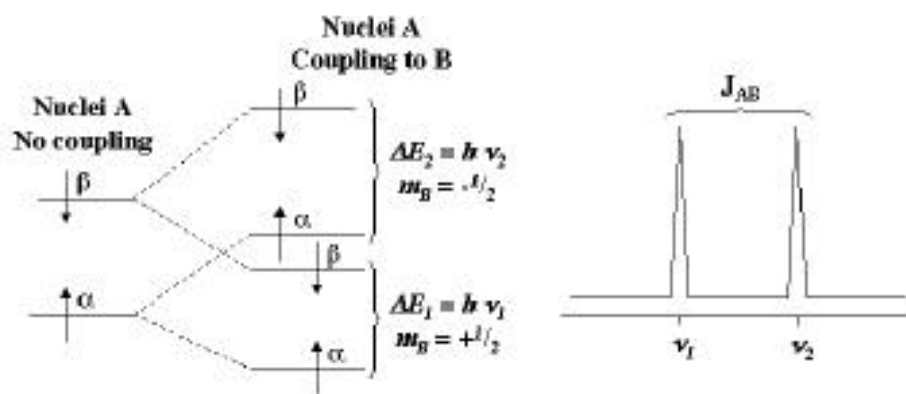


For nuclei with $I = 3/2$, for example boron 11 (^{11}B), there will be 4 different states ($m = 3/2$, $m = 1/2$, $m = -1/2$, and $m = -3/2$). This means that a ^{11}B nucleus will be able to adopt 4 different orientations in a magnetic field! Again, this a consequence of quantum mechanics. In any case, we will have 4 possible states, and the energy involved in hopping from one state to the other will also be related to a characteristic frequency, which is equal for every transition:



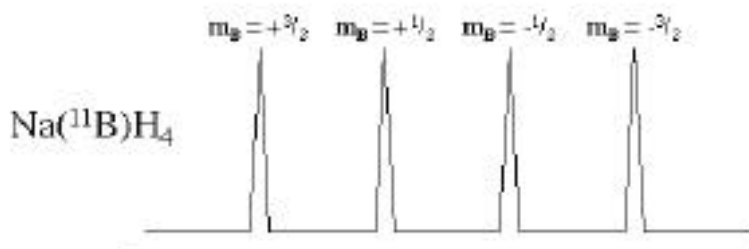
Since ^{11}B and ^1H have different gyromagnetic ratios, the energy, and therefore the frequency, involved in the transitions will be very different. The bottom line is that we can decide which type of nuclei to observe by selecting different frequencies in our instrument.

When two NMR-active nuclei with $I = 1/2$, **A** and **B**, are connected with each other through bonds, the **A** nuclei will 'feel' the state of the **B** nuclei due to the interaction of both nuclei through the molecular orbitals formed. In very simple terms, the energy of the α to β transition of the **A** nuclei will be slightly higher if the **B** nuclei is in the β state than if it is in the α state. Since the α to β transitions of the **B** nuclei are a statistical average of what is happening to all **B** nuclei in a macroscopic sample, the spectrum peak of the **A** nuclei will not appear as a single peak anymore, but as a *doublet* peak: one of the peaks of the doublet corresponds to the **A** nuclei's α to β transition associated with the **B** nuclei in the α state, and the other peak corresponds to the **A** nuclei's α to β transition associated with the **B** nuclei in the β state. The separation of the two peaks is called the *coupling constant*, J_{AB} , and is measured in *Hertz (Hz)*:

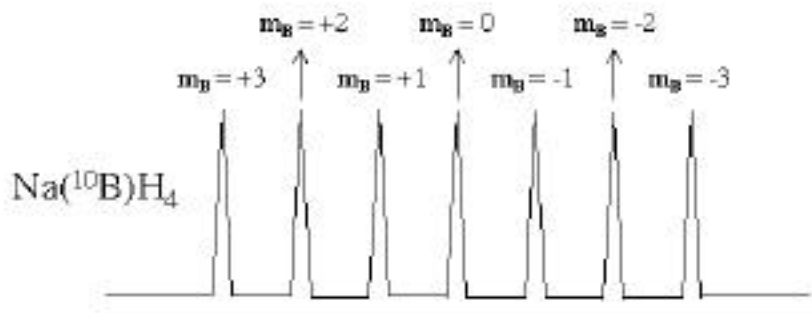


If we reverse the roles of the **A** and **B** nuclei, the same principles apply, and the peak for **B** will also be split into a doublet due to the different states of nuclei **A**.

In the previous example we considered two nuclei with $I = 1/2$. We can extend concept of coupling to interacting nuclei with any value of I . For example, in sodium borohydride (NaBH_4), we have 4 equivalent ^1H nuclei connected to a boron nuclei. Boron has two NMR-active naturally existing isotopes, ^{10}B and ^{11}B , with $I = 3$ and $I = 3/2$, respectively. If we consider first how the ^1H signals will be split by ^{11}B , the energy corresponding to the ^1H α to β transition will depend on the state of the ^{11}B nuclei. Since we have 4 possible states for ^{11}B , our ^1H signal will be split into four equal lines in the spectrum, or a *quartet*:



The $J_{11\text{BH}}$ is approximately 80 Hz. Similarly, ^1H nuclei connected to ^{10}B isotopes will be split into 7 lines, because ^{10}B can adopt 7 different orientations in the magnetic field:



This is called an *heptet* or *septet*., and will have a $J_{10\text{BH}}$ of approximately 30 Hz. If we generalize, we will see that the number of lines into which the peak of nuclei **A** will be split, or *multiplet*, will depend on the **I** of nuclei **B**, I_B :

$$\text{Number of lines in multiplet of nuclei A} = 2I_B + 1$$

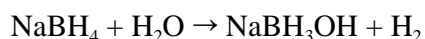
These coupling patterns are of crucial importance in the analysis of samples by NMR, because they tell us about the structure of our molecule. It is this particular phenomenon that we will exploit in our experiment...

The Experiment

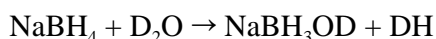
In today's experiment, you will record a ^1H spectrum of NaBH_4 , a very important reducing agent used by organic chemists, and by analyzing the pattern of the signals obtained you will be able to determine the abundances of the two naturally occurring boron isotopes, ^{10}B and ^{11}B . Both are magnetically active and have nuclear spin numbers (**I**) of 3 and $3/2$ respectively. Their natural abundances are 19.58% for ^{10}B and 80.42% for ^{11}B . As mentioned above, the different boron isotopes will split the proton signal into multiplets of $2I + 1$ peaks: 7 for ^{10}B and 4 for ^{11}B . Since we have both ^{10}B and ^{11}B in the sample, you will see the splitting of ^1H by both nuclei at the same time as overlapping multiplets. However, the J_{HB} coupling constants for the two isotopes are very large and of different magnitudes, and the two multiplets can be easily identified. Since the area beneath each of the multiplets is proportional to the number of nuclei associated with the transition, integration of the multiplet area, a procedure easily done with the NMR data processing software NUTS, will give a ratio of signals belonging to ^{10}B and ^{11}B . This

ratio will be equal to the ratio of ^{10}B to ^{11}B in nature, and with the data you will collect today it should be within $\pm 5\%$ of the value reported in the literature.

You will work in groups of 4 or 5 students. Each group will pick a vial which contains a measured amount of solid NaBH_4 and an 5 mm NMR tube. A solution in deuterated water, $^2\text{H}_2\text{O}$ or D_2O , of NaBH_4 should be prepared to carry out the experiment. However, NaBH_4 is very reactive, and in water, the following reaction takes place:



or



Here H_2 is hydrogen gas, and DH is hydrogen gas in which one of the ^1H atoms is replaced by a ^2H atom. As you know H_2 is a very dangerous gas, and despite that we will use very small amounts of NaBH_4 for this lab, you will prepare the sample immediately before taking the measurements.

To prepare the solution, measure 0.7 ml of D_2O , add them to the vial containing the NaBH_4 , and make sure all the solid is dissolved. The solution may be slightly cloudy at first, but it will clear up quickly. After you dissolve the NaBH_4 , transfer the solution to the 5 mm NMR tube. **BE VERY CAREFUL WITH THIS TUBE**, as it is quite expensive. Once the solution is in the NMR tube, observe the tiny bubbles of H_2 gas coming out of the bottom of the vial. Cap the tube with one of the NMR tube caps supplied by the TA. These caps have a little hole bored through to allow H_2 gas escape from the solution safely.

After your sample is ready, all the members of the group should go to room GH-351 (third floor). Dr. Moyna will assist you with the operation of the NMR instrument. The data will be saved in a floppy disk, and you will analyze the data using NUTS with the computers in the cluster in room GH-230A.

In your group report you should include an introduction which explains briefly how the NMR experiment works, and which experimental parameters were used to calculate the ^{10}B to ^{11}B isotopic ratio. You should also include how this ratio was calculated, and compare it to the reported literature values. Include any references used at the end of your report.