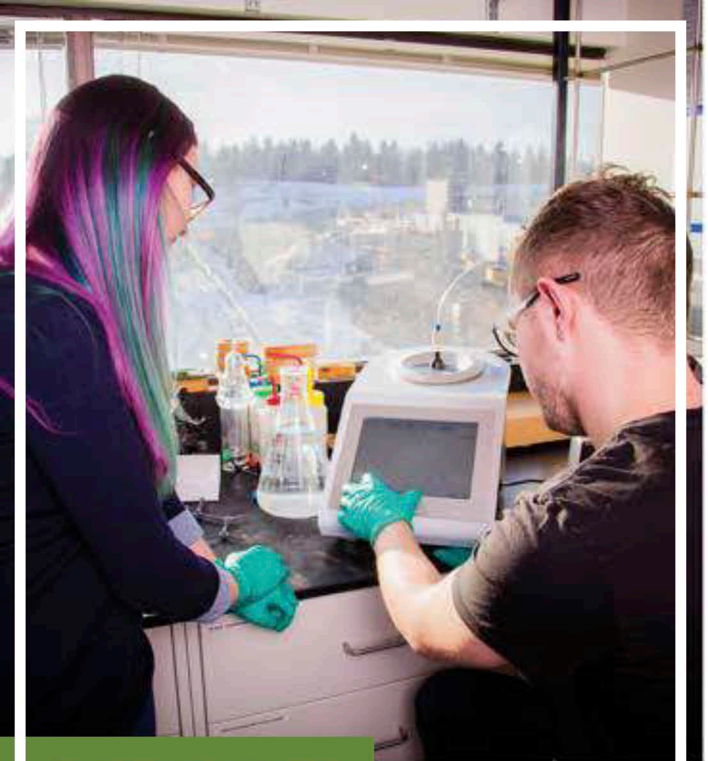


INORGANIC

UNDERGRADUATE EXPERIMENT

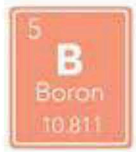
Measuring the Isotopic Ratio of $^{10}B/^{11}B$ by 60 MHz ^{1}H NMR Spectroscopy

QuantAnalitica
Via Guido Rossa 14
23875 Osnago (LC) - Italy
Tel. +39 039 9280061
Fax. +39 039 9289636
info@quantanalitica.com
www.quantanalica.com

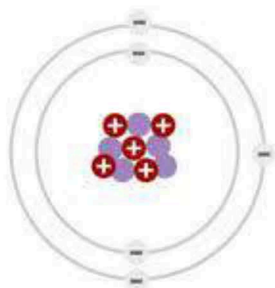
www.nanalysis.com

Introduction

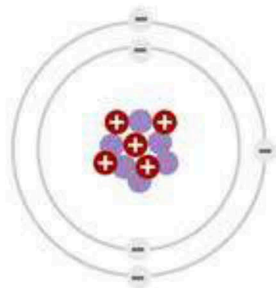
NMR spectroscopy is used widely across all branches of chemistry due to its powerful structure elucidation capabilities and the inherently quantitative nature of this technique. The technique is typically introduced in the organic chemistry curriculum with discussion primarily focused on nuclei with a nuclear spin quantum number, *I*, of ½, *i.e.* ^{1}H and ^{13}C. Typically, quadrupolar nuclei are specialized and require more advanced probes to detect. Therefore, they are often reserved for more advanced inorganic courses.



In this experiment, we employ a simple indirect method for an undergraduate student to accurately measure the distribution of boron isotopes by detecting the hydrogen atoms directly bonded to the boron atoms.[1] While the boron isotopes are NMR active and could be observed at different resonant frequencies (see table 1), it is not possible to record spectra for both isotopes in a single 1D NMR experiment. While both ^{10}B and ^{11}B NMR experiments have been performed and studied separately,[2] it is only through coupling to a common nucleus that both nuclei can be observed indirectly in a single spectrum. Therefore, the ^{1}H NMR spectrum of sodium borohydride is recorded and the effects of the boron nuclei on the resulting spectrum will be used as an indirect observation probe to calculate the isotopic ratio of $^{10}B/^{11}B$.



^{10}B



^{11}B

Background

Crucial to the success of this experiment is the fact that ^{10}B and ^{11}B are both NMR active and have different nuclear spin quantum numbers (table 1). Therefore, each boron isotope will split the ^{1}H nuclei in BH_4^- differently.

The expected splitting pattern can be calculated using the

$$2In+1 \text{ rule}$$

where I = spin quantum number
n = number of nuclei

Students are likely familiar with the n+1 rule used to predict the splitting pattern in a ^{1}H NMR spectrum, which is derived from the 2*I*n+1 rule. Since *I* is ½ for the ^{1}H nucleus, the equation simplifies into n+1.

Table 1. Properties of Selected NMR-Active Nuclei[3]

Isotope	*I*	Gyromagnetic Ratio (γ)[a]	% Natural Abundance	Larmor Frequency[b]
^{1}H	½	26.7522	99.99	400.00
^{13}C	½	6.7282	1.07	100.58
^{10}B	3	2.8747	19.90	42.98
^{11}B	3/2	8.5847	80.10	128.34

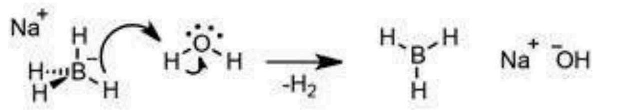
[a] *Gyromagnetic ratios are in units of 10^7 rad s^{-1} T^{-1}.*
[b] *Larmor frequencies in MHz at a magnetic field of 9.4 T.*

For this particular example, n is 1 for both cases as there is only one boron nuclei in the borohydride molecule. Therefore, the ^{10}B isotope, with *I* = 3, will split the coupled ^{1}H nucleus into a heptet (2 x 3 x 1 + 1) while ^{11}B, which has *I* = 3/2, will result in a quartet (2 x 3/2 x 1 + 1). Due to the distinctly different coupling constants between a proton and the two boron isotopes, all 11 peaks are well resolved and integrating the individual signals are straightforward. Comparing the sum of the areas of the heptet (^{10}B) with the combined areas of the quartet (^{11}B) will give the isotopic distribution of the two boron isotopes.

Procedure

Sodium borohydride (50 mg) was weighed into a vial and dissolved in D_2O (1.0 mL). The resultant solution was mixed gently to give a clear solution. Approximately 0.7 mL of this solution was then transferred to an NMR tube.

***Note**: The cap should be vented to prevent pressure build-up due to the slow production of hydrogen gas as the $NaBH_4$ slowly reacts with D_2O.*



The ^{1}H NMR spectrum was then acquired on a NMReady-60 NMR spectrometer using standard 1D acquisition parameters (16 scans). To calculate the isotopic ratio, the signals should be integrated individually and the areas of the quartet are added together as are those of the heptet. From the totals, the relative percentages for each isotope are calculated.

Results

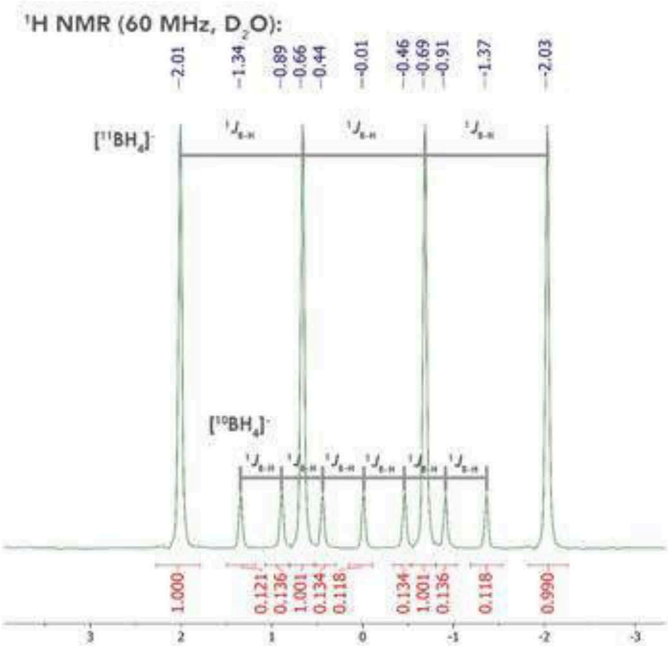


Figure 1. ^{1}H NMR Spectrum of $NaBH_4$ in D_2O.

Discussion

Figure 1 displays the 60 MHz ^{1}H NMR spectrum of $NaBH_4$ in D_2O. The spectrum consists of a large, 1:1:1:1 quartet ($^1J_{BH}$ = 80.6 Hz) and a 1:1:1:1:1:1:1 heptet ($^1J_{BH}$ = 27.0 Hz).

Given the 2*I*n+1 rule:
^{11}B: (2 x (3/2) x 1) + 1 = 4
^{10}B: (2 x 3 x 1) + 1 = 7

Therefore the quartet shows us the number of hydrogens directly bonded to the boron-11 isotope present in the sample of sodium borohydride whereas the heptet indicates the amount of hydrogen atoms bonded to the boron-10 isotope. Additionally, this assignment is consistent with the observed coupling constant. $^1J_{BH}$ are proportional to the gyromagnetic ratio[4], from table 1 $\gamma(^{11}B)/\gamma(^{10}B) \sim 3$, so 80.6/27.0 = 3.

Because the two signals overlap, instead of summing the multiplets traditionally, we integrate each peak individually and sum them.

Total $[^{11}BH_4]^-$ quartet integration = 3.992
Total $[^{10}BH_4]^-$ heptet integraton = 0.897

Total integration = 3.992 + 0.897 = 4.889
$\%^{11}B$ = (3.992/4.889) x 100 = 81.65%
$\%^{10}B$ = (0.897/4.889) x 100 = 18.34%

The experimentally determined ratio of 81.7:18.3 for $^{11}B/^{10}B$ compares very well with the known ratio of 80.1/19.9.[3]

Conclusions

In this experiment the isotopic ratio of $^{10}B/^{11}B$ was measured by ^{1}H NMR spectroscopy. While this is not a universal method that can be applied to any other nuclei, the experiment provides an excellent introduction to quadrupolar nuclei, elements with more than one NMR active nuclei, coupling to quadrupolar nuclei, and a unique application of the NMR experiment beyond structure elucidation.

References

[1]a) Walker, J. M.; Starks, R. J.; Gray, G. A.; Schoolery, J. *N. Appl. Spectrosc.* **1981**, *35*, 607;
b) Zanger, M.; Moyna, G. *J. Chem. Ed.* **2005**, *82*, 1390.

[2]Kennedy, J. Boron. *In Multinuclear NMR*; Mason, J., Ed.; Springer US: New York, **1987**; pp 221-258.

[3]Coursey, J. S.; Schwab, D. J.; Dragoset, R. A. NIST Atomic Weights and Isotopic Compositions Home Page http://physics.nist.gov/Comp (accessed July 2018).

[4]Eaton, G. R. *J. Chem Educ.* **1969**, *46(9)*, 547-556

Data Accessibility

The data can be processed directly on the NMReady-60 and printed and/or exported directly to a USB or networked file where it can be worked up using third party NMR processing software.