

## Solid-State NMR Facility for Solids

### Introduction

Solid-state NMR (SSNMR) services at the University of Alberta are provided by the research groups of Profs. Vladimir Michaelis and Roderick Wasylshen in the Department of Chemistry. As the only solid-state NMR facility in the region, we try to help groups within and outside the university community who may require SSNMR services as well as Canadian industry. It is important that potential clients understand that our priority is advancing our own research program. In addition, our budget precludes the hiring of a technician, so acquiring NMR spectra depends not only on the availability of an instrument, but also on the availability of a qualified person to obtain these spectra. Because most people requesting SSNMR services are unfamiliar with the technique, this brief summary was prepared to help potential clients decide whether or not this is the most suitable approach for them. Frequently asked questions are presented first, followed by a more detailed explanation of the common SSNMR techniques.

### FAQ: Frequently Asked Questions

#### ***Q: How much will this cost?***

*A:* Operating an NMR facility is a costly endeavour, and budget constraints require us to request payment of user fees from people requesting NMR services. Obtaining NMR spectra of solid samples invariably requires much more time than for the corresponding solution spectra. The actual time required will of course depend on the information desired. A rough preliminary estimate will be provided upon request by Drs. Ryan McKay and Guy Bernard, but it is important to understand that once we start acquiring spectra, we may find that we were overoptimistic about the time required, or about the quality of the spectra we can provide. If we find that it will require much more time than estimated, the client will be contacted to determine whether she/he wishes to proceed.

It is often helpful if you can provide us with NMR papers on related compounds to assist in the estimate.

#### ***Q: Should I obtain Solution NMR Spectra Instead?***

*A:* If solution NMR can answer your questions, then the answer is yes. Such spectra can be acquired in a fraction of the time required for the corresponding SSNMR spectra and the resolution almost certainly will be better. The three most compelling reasons to obtain SSNMR spectra to characterize samples are (i) the sample is insoluble (*e.g.*, *Hard and Soft Materials*,

Minerals, Oxides, Inorganics, etc.), (ii) the sample decomposes/changes in solution or (iii) it requires you to change the chemical environment to become soluble (e.g., surfactants, etc.).

***Q: Will my spectra be quantitative?***

*A:* This can be done but usually involves longer acquisition times. Please see the discussion on the direct polarization technique below.

***Q: Can you obtain  $^1\text{H}$  SSNMR spectra for us?***

*A:* Yes we are able to obtain such spectra, they typically are broad and featureless in many solids, the characterization utility depends heavily on the particular sample of interest. It is often helpful if you can provide us with NMR papers on related compounds.

***Q: What kind of signal-to-noise ratios can I expect?***

*A:* As for solution NMR, the S/N depends on the number of scans acquired for a given spectrum. Because one usually obtains broader peaks with SSNMR compared to solution NMR, the S/N will probably not be what solution NMR spectroscopists expect. Improvements can be achieved if more sample is provided (to a maximum of approximately 400 mg), and advanced techniques are applied. Please see the cross-polarization section below for further details.

***Q: Can I operate the spectrometer?***

*A:* We are not a “walk-up” facility. Members of our groups have received extensive training in the use of the instrument and hence one of them will acquire the spectra.

***Q: What we can and cannot do.***

*A:* Currently, we can obtain spectra for samples in the  $^{15}\text{N}$  to  $^{31}\text{P}$  range, with  $^1\text{H}$  decoupling. However, obtaining spectra for quadrupolar nuclei is often time consuming. With further discussions of the need and feasibility with Profs. Michaelis and Wasylishen, SSNMR of low-gamma nuclei (*i.e.*, those below  $^{15}\text{N}$ ) may be possible.

There are of course hundreds of SSNMR techniques; a thorough description of these is beyond the scope of this summary. Most people requesting SSNMR services require one-dimensional SSNMR spectra to characterize their compounds; this usually can be accomplished either by direct polarization (DP), sometimes called Bloch decay, or by cross polarization (CP). These two techniques are discussed in more detail below. More advanced techniques can be undertaken, however may entail substantial operator time which will add to the final total cost.

## Samples

Samples should be provided in clearly marked vials and labeled with the appropriate handling and safety documentation as per EHS. Spectra are usually acquired with the magic-angle spinning technique (see below). To achieve stable spinning and to obtain better resolution, the sample should be a fine powder. If not already a fine powder, the sample would ideally be crushed with an agate mortar and pestle. Please advise if this is not acceptable, and note that if the material is too uneven, we will not be able to spin the sample. Air-sensitive samples can be handled, though these must be packed in a glove box, increasing the time required to obtain the spectra. Of course, we should be able to advise you of any special handling techniques during consultation.

Samples should be stable, non-radioactive, non-explosive and non-magnetic. Note that in most cases, samples will be spun at a relatively high frequency during data acquisition. This can lead to significant sample heating, up to 30 °C above ambient temperatures at the highest spinning frequencies. Please keep this in mind when requesting NMR spectra of your samples, as variable temperature control or alternative probe options exist.

Generally, samples are returned after the data has been acquired (apart from minor losses during handling). However, in some cases, rotor “crashes” occur, leading to extensive damage to the probe and costly repairs. Fortunately this is a rare occurrence but it is important to understand that in such cases, the sample would not be recovered. To minimize the chances of crashes, we are unable to acquire spectra unless the sample distributes evenly within the rotor. In addition, we are unable to handle dangerous samples (*i.e.*, ones that will preclude safe decontamination of the probe in the event of a rotor crash). Non-spinning experiments may also be valuable or needed, these can be placed in rotors or modified glass sample holders.

The sample fill volumes range between 10 and 400 microliters, this equates to sample masses ranging from 10 to 400 mgs, heavily dependent on density, and composition. During consultation we can assist in identifying the proper probe and sample holder (rotor) for your experiment and address the sample volumes / masses required. Isotopic enrichment can also be essential depending on the particular problem needed to be addressed.

Since we most frequently receive requests for  $^{13}\text{C}$  SSNMR spectra, the acquisition of such spectra is discussed, but the same concepts apply to other spin- $\frac{1}{2}$  nuclei, such as  $^{29}\text{Si}$  and  $^{31}\text{P}$ . In some cases, useful spectra of quadrupolar nuclei (e.g.,  $^{11}\text{B}$ ,  $^{27}\text{Al}$  and  $^{23}\text{Na}$ ) can be obtained using DP combined with magic angle spinning and  $^1\text{H}$  decoupling.

### *Magic Angle Spinning*

In most cases, solid-state NMR spectra are obtained with the magic-angle spinning (MAS) technique (combined with CP or DP). By spinning a sample rapidly at the “magic angle”,  $54.74^\circ$  relative to the applied magnetic field, “solution-like” spectra are obtained, although the actual resolution will probably not be as high as what is generally obtained for samples in solution. The actual resolution obtained depends on numerous factors; for example, crystalline samples will yield sharper NMR peaks, while an amorphous sample will yield broad peaks. Other factors that can lead to line broadening, even with magic angle spinning, are neighbouring spin-active nuclei such as  $^{31}\text{P}$  or  $^{19}\text{F}$  that we are unable to decouple, or quadrupolar broadening.

### *Direct Polarization (DP)*

DP is the basic SSNMR technique. It entails directly irradiating the observe frequency and acquiring the NMR signal, usually with  $^1\text{H}$  decoupling. The benefit of this technique is that one may acquire quantitative spectra. However, in most cases, the process is very time consuming, because the relaxation times for most nuclei are very long. For example, for  $^{13}\text{C}$ , recycle delays of over 100 s per scan, with hundreds or thousands of scans required, are not uncommon. In addition, if the relaxation times of the nuclei are not known, additional experiments are required to ascertain that integrations are reliable. For example, if one obtained a  $^{13}\text{C}$  DP NMR spectrum with a 100 s recycle delay and observed an aromatic/aliphatic ratio of 2:1, we could not confidently assert that there are twice as many aromatic carbons unless we verified that the carbon nuclei at both sites are fully relaxed; typically this is accomplished by acquiring another spectrum with a different recycle delay.

### *Cross Polarization*

The CP experiment entails the transfer of magnetization from (usually)  $^1\text{H}$  to  $^{13}\text{C}$ , then acquiring the NMR signal from the latter. There are two large benefits of the technique: the first is that one obtains an enhanced NMR signal equal to the ratio of the Larmor frequencies for the nuclei (a factor of  $\sim 4$  for  $^{13}\text{C}$ ), and, usually an even greater benefit, the recycle delay for CP is limited by the  $^1\text{H}$  relaxation time, which typically is much shorter than that for  $^{13}\text{C}$ . Hence, one can obtain useful  $^{13}\text{C}$  NMR spectra much more quickly. In addition,  $^{13}\text{C}$  from the background are not detected if CP is from  $^1\text{H}$ . However, the magnetization transfer from  $^1\text{H}$  to  $^{13}\text{C}$  depends on factors which vary from nucleus to nucleus. **Thus, the technique is *not* quantitative**, although reliable chemical shift values are usually obtained. Experimental techniques have been

developed to render such spectra quantitative, but these are only practical if one is doing a series of closely related samples. Although not quantitative, qualitative information about related samples can be obtained with CP. For example, if one obtains two SSNMR spectra with CP, one with a 2:1 aromatic/aliphatic peak intensity ratio and a second with a 1:1 ratio, we could confidently assert that the second sample has  $\frac{1}{2}$  the aromatic carbons, relative to the aliphatic carbons, when compared to the former sample, although we would not know the actual ratio. Note that this is only valid if the spectra being compared are for closely related samples.

## Hardware

Besides the NMR technique to be used, the other important decision when requesting NMR services is the hardware, discussed below.

### *NMR System*

Currently, there are three SSNMR spectrometers, operating at 11.75, 9.4 and 7.05 T ( $^1\text{H}$  frequencies of 500, 400 and 300 MHz, respectively). Higher magnetic fields provide greater sensitivity and resolution, although depending on the dominating anisotropic interaction one may benefit from lower or multiple magnetic fields. This can be discussed further during consultation.

### *Probes*

Another important factor affecting the quality of the spectra and the time required to acquire these is the choice of NMR probe. Currently, the practical options for the 11.75 and 7.05 T systems are probes capable of spinning 4.0 or 7.0 mm rotors (*i.e.*, the sample holders—the dimensions refer to the outside diameters of these rotors), while only the former is available for the 400 MHz system. The benefits of the 4.0 mm rotors are: samples can be spun faster (up to 14 kHz), yielding improved resolution and minimizing problems with spinning sidebands; spectra can be acquired with higher-power  $^1\text{H}$  decoupling, also improving the resolution; and the smaller diameter improves the sensitivity. However, the latter factor is offset by the fact that samples are restricted to approximately 100 mg. The 7.0 mm rotors hold approximately 400 mg of sample, thus allowing for improved sensitivity if sufficient sample is available. However, the maximum spinning is restricted to 5.0 kHz (7.05 T system) or 7 kHz (11.75 T system), resulting in reduced resolution and complications arising from spinning sidebands. Unfortunately, another problem with the 7.0 mm rotors is that they usually are difficult to spin, so acquiring such spectra may require more operator time. Because of the difficult spinning, it is impractical to acquire spectra unless sufficient sample is provided to fill the rotor (note that if it is acceptable, the rotor can be “filled out” with a sample that does not contain the nucleus of interest, such as KCl added to a sample submitted for  $^{13}\text{C}$  NMR analysis; please tell us if the sample is hydrated!). Finally, we also have a probe capable of high-frequency (35 kHz) spinning for the 11.75 T instrument, but

the rotors for this probe (2.5 mm) only hold approximately 10 mg of sample so they are only used for specialized applications.

### **Would you like to set-up a consultation or have further questions?**

Please send an email to

Dr. Guy Bernard for questions about the experimental details, [guy.bernard@ualberta.ca](mailto:guy.bernard@ualberta.ca) &

Dr. Ryan McKay for questions regarding service rates, [rmckay@ualberta.ca](mailto:rmckay@ualberta.ca).

If an industrial partnership is needed such as initiating an Engage or CRD grant to study polymorphs, minerals, experimental design, etc. please contact [Guy Bernard](#).

### **Previously Successful Solids Analysis:**

- 1.) Porous Materials ( $^{29}\text{Si}$  and  $^{27}\text{Al}$ )
- 2.) Polymorph/Phase Identification ( $^{13}\text{C}$ ,  $^{31}\text{P}$ , etc.)
- 3.) Minerals/Clays ( $^{113}\text{Cd}$ ,  $^{11}\text{B}$ ,  $^9\text{Be}$ ,  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ , etc.)
- 4.) Soil and Food Analysis (e.g.,  $^{31}\text{P}$ ,  $^{13}\text{C}$ , etc.)
- 5.) Amorphous or Disordered Materials
- 6.) Guest-Host Complexes
- 7.) Inorganic and Organometallic complexes, etc.

### **A Few Useful Resources:**

*Practical Aspects of Modern Routine Solid-State Multinuclear Magnetic Resonance Spectroscopy: One Dimensional Experiments.* D.L. Bryce, G.M. Bernard, M. Gee, M.D. Lumsden, K. Eichele and R.E. Wasylshen, *Can. J. Analyt. Sci. Spectrosc.* **2001**, *46*, 46-82. This journal is no longer in print but you may request a copy from [guy.bernard@ualberta.ca](mailto:guy.bernard@ualberta.ca).

*Solid State Nuclear Magnetic Resonance. A Practical Introduction.* David E. Axelson, CreateSpace, 2012 (472 pages).

*Solid State NMR. Basic Principles and Practice.* David C. Apperley, R.K. Harris and P. Hodgkinson. Momentum Press, 2012.