

SOLID-STATE NMR

1. Why one might need to use Solid-State NMR?

- a) Sample is not soluble or not stable in the solution;
- b) very large molecules (>100 kDa);
- c) temperature at which sample should be studied is outside of solvent's liquid phase range;
- d) study of the physics of the solid state.

2. Line Broadness.

A typical solid-state NMR spectrum as compared to a liquid-state NMR spectrum seems to consist of broad and featureless lines. This is due to many concurrent strong interactions of a nuclear spins that are dependent on spins' mutual orientation and their orientation with respect to the external magnetic field such as: direct dipole-dipole interactions (both homo- and heteronuclear), chemical shift anisotropy and quadrupolar coupling. In fact, these anisotropic orientation-dependent interactions are also present in liquid-state spectra but in a typical solution or a melt they are averaged due to rapid random molecular motions and reorientations that lead to narrow well-defined lines. However, when these molecular motions slow down (when viscosity of a solution grows or temperature lowers or sample molecules are large and heavy) one can notice that lines in a spectrum become broader.

In the Fig. 1 are depicted two ^{13}C NMR spectra of the same substance (adamantane): one dissolved in CDCl_3 when molecules reorient fast and another in solid state at room temperature when molecular motion is significantly reduced, not entirely however. Due to their shape adamantane molecules in solid state at room temperature still exhibit isotropic motion (another example is fullerene). In rigid solids molecules are almost motionless and spectrum lines are much broader.

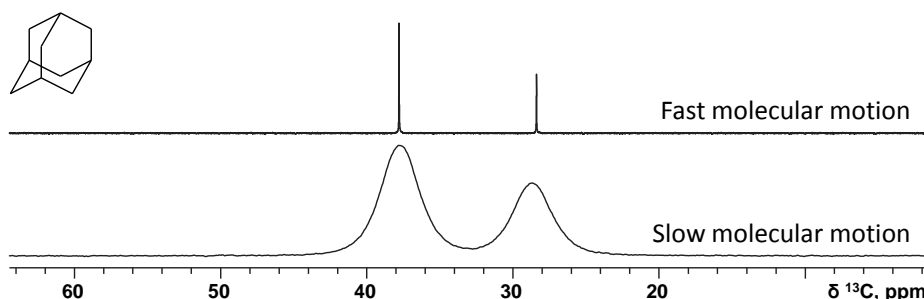


Fig. 1. ^{13}C NMR spectra of adamantane.

3. Cross Polarization

In the case of heavy nuclei they not only often exhibit low natural abundance of isotopes with spin quantum number 1/2, such as ^{29}Si , ^{15}N and ^{13}C , but also have small gyromagnetic ratio compared to that of the proton, which leads to small Zeeman splitting of the energy levels. Thus the signal-to-noise ratio in their spectra is often far from satisfactory. Moreover, the spin-lattice (T_1) relaxation time in solids can be very long, reaching dozens of minutes and even longer.

In order to enhance the signals from rare nuclei a Cross Polarization (CP) pulse sequence is used. It utilizes the effect of "flow" of the magnetization from highly polarized nuclei (most commonly, ^1H) to lower polarized ones via the dipolar coupling between them when they are brought into contact, which results in more intensive NMR signal and better signal-to-noise ratio.

Another advantage of CP technique is that the sampling rate depends on the relaxation time of nuclei from which the magnetization is transferred, which helps in case of ^1H nuclei, because they typically relax much faster than other 1/2 spin nuclei, allowing more scans to be acquired over the same time, as compared to simple single-pulse experiment that detects rare nuclei directly.

4. Magic Angle Spinning

It appeared that certain anisotropic interactions could be suppressed to some extent by introducing an artificial motion of the sample – by rotating the sample around an axis oriented at $54^\circ 44'$ by respect to the external magnetic field (Fig. 2, left). This technique is known as Magic Angle Spinning (MAS). However it works effectively only when the spinning frequency is equal or greater than the line width, which can be in

order of tens and even hundreds of kHz. Nowadays modern commercially-available MAS NMR probeheads can spin the sample up to ca. 40 kHz.

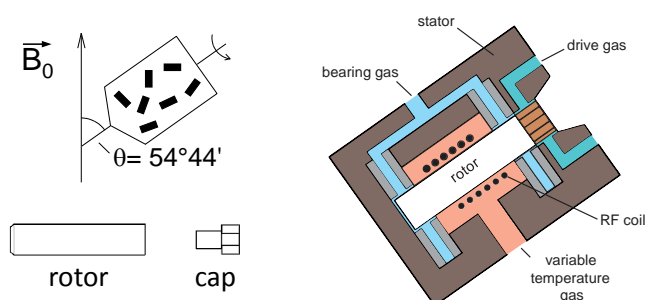


Fig. 2. Schematic representation of MAS rotor and stator.

In order to spin the sample, it should be packed in special rotor which is usually made of zirconia and closed tightly with a cap (Fig. 2, right). Rotors have different diameters that vary from 1.3 to 7 mm in modern spectrometers. The smaller the diameter, the higher MAS speed is achievable. The typical volume for regular 4 mm rotor is 80 μL . In special cases or when there is not enough sample available, reduced volume rotors with different inserts are used which allow to pack 50 or even 12 μL of sample being certain that it is located in the center of the RF coil. That is essential the sample to be packed so that the spinner is well balanced, because an unbalanced spinner can crash suddenly, causing severe damage to the coil, stator and other probehead parts.

In the case when spinning rate is less than the magnitude of the anisotropic interaction, additional artifactual lines appear in the spectrum which are separated by the rate of spinning in Hz and are called spinning sidebands (SSB) (Fig. 3). In publications they usually are marked with asterisks to distinguish them from the “real” lines. There exist a number of methods to get rid of these artifacts (Fig. 4), though in some studies they are useful or even essential. Cross polarization is often used in combination with the magic angle spinning (CP MAS).

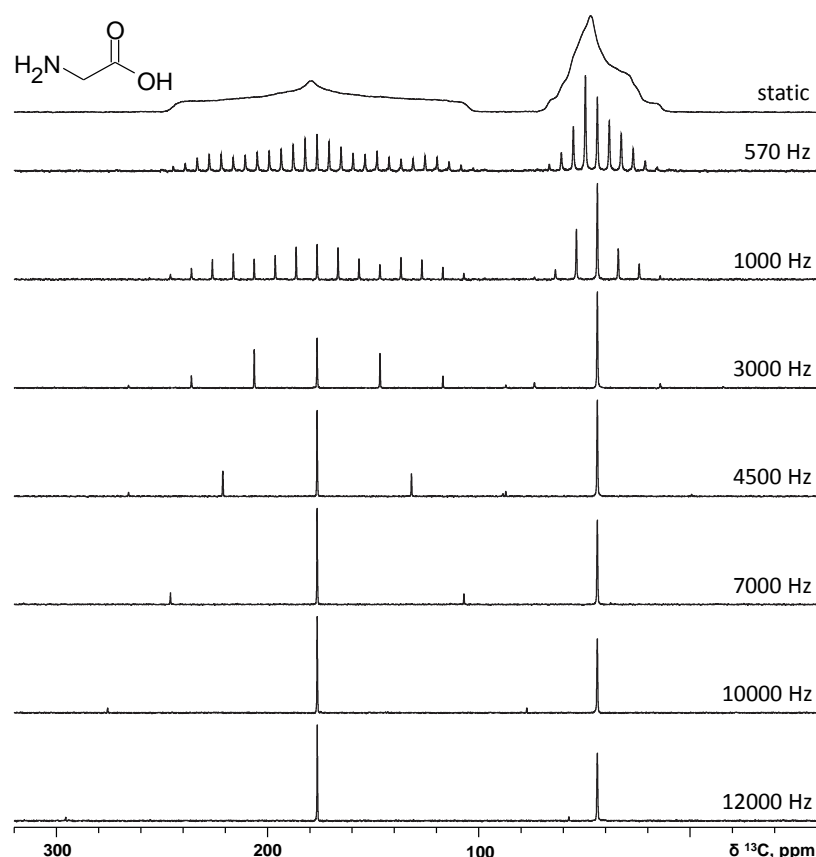


Fig. 3. ^{13}C NMR spectra of glycine at different MAS speeds. Even at 12 kHz MAS rate small SSB are still present. Note that isotropic line is not necessarily the most intensive one and its chemical shift doesn't depend on the spinning rate.

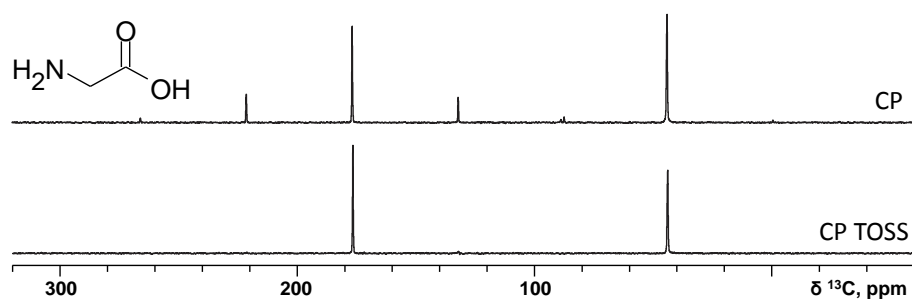


Fig. 4. ^{13}C NMR spectra of glycine (MAS 4.5 kHz): normal CP and CP TOSS (Total Sideband Supression).

5. High Power Decoupling

In the case of the most common ^{13}C NMR spectra the ^1H - ^{13}C dipolar coupling is typically the dominant interaction experienced by the ^{13}C spin. Its typical value is usually in order of tens of kHz. This interaction can also be reduced to some extent by MAS, however it is often not enough (Fig. 5). In order to obtain narrow lines in ^{13}C spectra, the solid-state dipolar version of spin decoupling, which is used in solution NMR spectroscopy is needed. Unlike the latter it requires much more powerful RF fields. Note, that spectra shown in Figs. 3 and 4 were also recorded with ^1H decoupling.

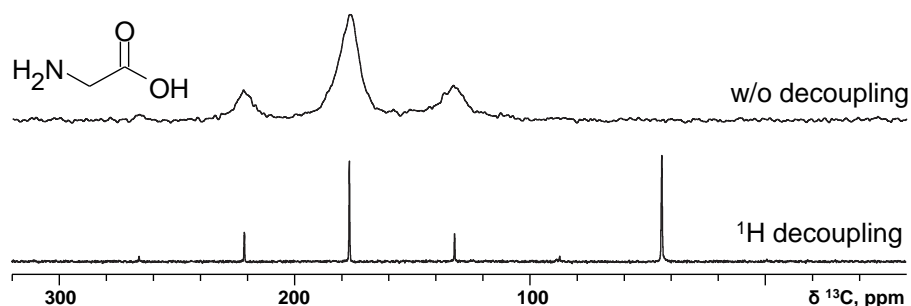


Fig. 5. ^{13}C NMR spectra of glycine (MAS 4.5 kHz): with and without decoupling.