How solid-state NMR works

In NMR spectroscopy, the resonance frequencies of nuclei are measured in the existence of an applied magnetic field (usually represented as B0). Solid-state NMR is similar to solution-state NMR but the sample is solid instead of solution. For solution state NMR, chemical shift and J-coupling (spin-spin splitting) are the interactions basically influence the resulting spectra. Two other interactions, the 1H-13C dipole-dipole couplings and chemical shift anisotropy (CSA), are averaged in solution-state NMR due to the rapid tumbling of the molecules in solution. In other words, both interactions were related to the orientation of molecules. However, molecules in solids don't tumble a lot and the direction matters. So both of the interactions have significant effect in the solid-state NMR, which results in much more broad peaks instead of narrow peaks in solution-state NMR.

To gain solid-state NMR spectra with higher resolution, additional hardwares needs to be used, such as magic-angle spinning (MAS) which spins the sample rapidly at an angle of 54.7° with respect to the external magnetic field and averages the chemical shifts to their isotropic value (Figure 1 a compared to c). The rate of MSA needs to be greater than (or equal to) the magnitude of the anisotropic interaction to average it to zero. As well as it enhances the resolution of solid-state NMR, the MAS may lead to the presence of spinning sidebands as shown in Figure 1 b, e and f. These are spurious signals (i.e. peaks) that result from the modulation of the magnetic field at the spinning frequency. The peaks always appear on either side of any large genuine peak at a separation of integer multiples to the spinning rate. The intensity of these sidebands will be proportional to the intensity of the genuine peak. Thus if the spin rate is 20 revolutions/second (= 20 Hz), you would look for spinning sidebands at frequencies 20n Hz (n is an integer) above and below the resonance frequencies of genuine signals.

Figure 1 link: https://pubs.acs.org/doi/10.1021/ac504288u

How do you interpret a solid-state NMR spectrum?

The principles behind solid-state NMR are similar to those of liquid-state, and it is a useful method of characterization when a sample cannot be dissolved in solution. The peaks tell us about the chemical environment that a specific type of proton exists in. Similar to liquid-state NMR where the instrument can identify 1H, 13C, 31P, etc., solid-state NMR is capable of looking at the same types of nuclei, however the 1H NMR generally displays a broad, featureless peak, that is challenging to interpret (Western Science). The methods used in analyzing liquid-state NMR can also be applied to solid-state. If multiple nuclei are present in a compound in equivalent chemical environments, they will appear as one peak in the spectrum. Multiple peaks will be seen when the nuclei exists in more than one environment. The ideas of multiplicity and integration can also be applied. Solid-state NMR is valuable because it can also provide information beyond that of liquid-state. For example, dipole-dipole couplings can show the spatial arrangements of atoms. Relaxation times can tell us about system dynamics, like if the compound is in a porous media (Pines Lab Berkeley). The shape of the peak relates to the environment the nuclei exist in. The following image shows an example of how the peak shape changes in 13C-NMR from three different symmetries:

(Rossum 2011)
What are good literature examples?

Link to the paper: https://pubs.acs.org/doi/10.1021/cm900129u

Figure 5. 7Li NMR MAS (10 kHz) spectra of LLTO powder after synthesis (a), after exchange in water at 25 °C for 24 h (b), and after exchange in water at 70 °C for 24 h (c). Spectra have been normalized to the powder weight. The insert shows the reconstruction of curve (a). * is for impurity (1% of lithium total). 2

The goal of this paper was to perform ion exchange of H+ for Li+ in lithium lanthanum titanate Li0.30La0.57TiO3 (LLTO) in water with different temperatures. The figure shows the comparison of normalized 7Li NMR spectra between the as-synthesized LLTO powder (Figure 5a), the powder exchanged in water at 25°C for 24 h (Figure 5b) and the powder exchanged in water at 70°C for 24 h (Figure 5c). Since the intensity of peaks in 7Li NMR spectra is proportional to the number of 7Li nuclei and the intensity of the peak decreases with increasing exchange temperature, the number of 7Li nuclei after exchange decreases with increasing exchange temperature. In other words, the rate of exchange increases with increasing exchange temperature. 2

What are useful resources for in-depth reading?

Some potentially useful books on solid state NMR include:


https://en.wikipedia.org/wiki/Solid-state_nuclear_magnetic_resonance

http://www.emory.edu/NMR/web_swu/SSNMR_redor/ssnrmr_schurko
Bibliography


(2) Boulant, A.; Maury, P.; Emery, J.; Buzare, J.-Y.; Bohnke, O. Efficient Ion Exchange of h+ for Li+ in (Li0.30 La0.57 T0.13 )Tio3 Perovskite in Water: Protons as a Probe for Li Location. *Chem. Mater.* **2009**, *21* (11), 2209–2217.