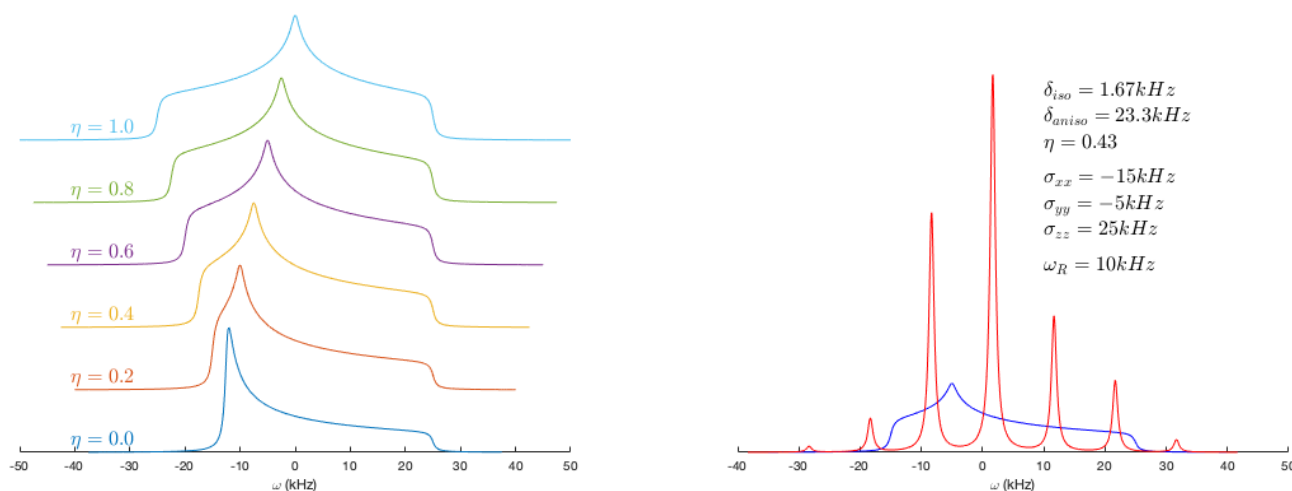


# September 2022 NMR Topic of the Month: To Spin or Not to Spin Solids



That is the question... What do powder NMR spectra look like?

The lineshapes arrayed on the left are simulations of signals for the indicated asymmetry ( $\eta$ ) values. Lineshapes such as these are produced in experiments on static powder samples with a single type of spin- $\frac{1}{2}$  nuclei (eg: lead in  $\text{Pb}(\text{NO}_3)_2$ ), often with decoupling. Quadrupolar nuclei produce similar spectra that are composed of more than one of these lineshapes. Couplings also produce spectra composed of multiple lineshapes that are determined by the sum and difference tensors between all total lineshape's contributions. Static signals are broad and have features produced by the full tensor as it is sampled in all possible orientations.

What happens when you spin a powder sample?

The broad answer is that the spinning does some averaging to the signal components that are orthogonal to the spinning axis. In a liquid sample, the spinning is done about the axis parallel to the magnetic field (conventionally called the z-axis). This is why your shims that go strictly as polynomials of z (z, z<sup>2</sup>, z<sup>3</sup>, etc.) are still sensitive, and the other shims are not. In solid samples there is a different axis about which samples are (most commonly) spun, one that is the magic angle ( $54.74^\circ$ ) off from the magnetic field. The magic angle is the null of Wigner  $D_{00}^2(\alpha, \beta, \gamma)$  when  $\beta=54.74^\circ$ , which means all the other spherical tensor components (apart from the isotropic  $D_{00}^0(\alpha, \beta, \gamma)$ ) will see some averaging. In the spectroscopy this spinning/averaging manifests as the signal being **concentrated** into a manifold of lines that are separated by the spinning speed. In the figure on the right the area under the static blue curve is equal to the area under the spinning red curve. In other words, spinning solid samples at the magic angle improves the resolution and sensitivity of the experiment, but may sacrifice some of the information content. If the sample is spun at a rate at least twice the frequency of  $\delta_{aniso}$  then a single line at the isotropic value will be observed, and the individual principle axis components and the structural information they convey are lost. But if the spinning is (significantly) slower than  $\delta_{aniso}$  the tensor information may still be recovered by analyzing the spinning sideband pattern.

## References

1. N. Bloembergen and T. J. Rowland, *Acta Metall.* **1**(6), 731-746 (1953).
2. K. W. Zilm and D. M. Grant, *J. Am. Chem. Soc.* **103**(11), 2913-2120 (1981).
3. U. Haeberlen, *High Resolution NMR in Solids Selective Averaging*, Academic Press, New York (1976).
4. M. E. Rose, *Elementary Theory of Angular Momentum*, John Wiley, New York (1967).
5. M. M. Mariq and J. S. Waugh, *J. Chem. Phys.* **70**(7), 3300-3316 (1979).
6. J. Herzfeld and A. E. Berger, *J. Chem. Phys.* **73**(12), 6021-6030 (1980).
7. M. Mehring, *Principles of High Resolution NMR in Solids - 2nd Ed.*, Springer-Verlag, New York (1983).