PURE ISOTROPIC PROTON SOLID STATE NMR

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Coherent averaging methods are at the heart of modern NMR spectroscopy ranging from simple spin echoes to remove heteronuclear *J*-couplings in solution, to rotor-synchronized symmetry-based pulse sequences to modulate dipolar couplings under MAS in solids. However, coherent averaging schemes are never perfect, and residuals are always present.

In solids, the workhorse of coherent averaging is magic-angle-spinning. Physically spinning the sample around an axis tilted at 54.74° with respect to the main magnetic field direction averages the interactions that have a second rank spatial dependence (such as dipolar couplings), while preserving the isotropic interactions (such as chemical shifts). However, for abundant spins, such as protons, imperfect averaging leads to residual dipolar broadening. Even after careful calibration of the magic angle and at the fastest MAS rates (around 100 - 150 kHz) possible today, the spectra obtained are hundreds of Hertz broader than their isotropic linewidths.

Here, instead of optimizing an averaging scheme, we introduce a new approach which parametrically maps the residual terms deriving from the imperfect averaging of MAS and removes them in a k-space representation, allowing the extraction of the pure isotropic signal. For example, by recording a series of MAS spectra at different spinning rates, we can model the parametric behaviour of the intrinsic pure isotropic shift terms in comparison to the residual broadening terms.

We illustrate the method on a series of eight organic solids using either a parametric fitting approach[1] or a machine-learning based model. In both cases we are able to produce pure isotropic spectra that are significantly narrower (by a factor of 7 on average) than the fastest MAS spectrum we can record (at 100 kHz). We also illustrate how we can expand this approach to produce high resolution two-dimensional NMR spectra.

REFERENCES

[1]   P. Moutzouri, B. Simões de Almeida, D. Torodii, L. Emsley, *J. Am. Chem. Soc.* **2021**, *143*, 9834–9841.