Towards accurate diffusion measurements of slowly diffusing species

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NMR-based diffusion measurements are now extremely common place and are generally seen as the method of choice for measuring self-diffusion due to their non-invasive nature and general applicability including no specific concentration requirements, minimal sample preparation and speed. Further, as motion is measured over a specific timescale the NMR diffusion measurements can also report on geometries within which diffusion is occurring [1-3].

Most contemporary NMR spectrometers are now able to generate modest pulsed magnetic field gradients (e.g., gradient amplitudes ≤ 0.5 T m^{-1}) suitable for performing measurements on low viscosity/rapidly diffusing samples (e.g., $D > 1 \times 10^{-11}$ m^2s^{-1}) using predominantly ^{1}H as the probe nucleus with reasonably long relaxation times. The nature of the diffusion to be measured is normally a priori clear cut (e.g., isotropic or anisotropic, Gaussian or restricted). Such measurements are generally straightforward and typically make only modest demands on spectrometer performance and the gradient generation hardware. However, many samples of interest are by nature more viscous or even solid samples (e.g., solid phase electrolytes) with less initial certainty regarding the nature of the diffusion to be measured. Further, the probe nucleus may be a less favourable isotope than ^{1}H with an inherently much shorter relaxation time. Such measurements require special high current amplifiers and special NMR probes capable of generating high gradient pulses. Some commercial equipment is now capable of generating pulses in excess of 20 T m^{-1}. Performing measurements with such pulses can push a spectrometer to its performance limits such that it becomes difficult to separate artefact from reality and some aspects have long been recognised (e.g., ref. [4]). In fact, even the calibration of such equipment is not straightforward [5, 6].

This presentation details the complications of high gradient diffusion measurements, methods for obviating the problems and our progress in developing a protocol that will allow definition of a usable range of measurement variables (e.g., maximum gradient strength that allows reproducible results). Such a protocol would facilitate the comparison of results between different machines.

References

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