Ultrafast 2H QUOSY 2D-NMR in Weakly Aligning Media: Concepts and Analytical Potential

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Résumé

NMR spectroscopy in weakly aligning media enables the measurement of residual anisotropic interactions while maintaining high-resolution conditions. This provides valuable molecular information that has led to numerous analytical applications, in particular for the elucidation of relative configuration/conformation of chiral/prochiral compounds as well as in the measurement of enantiopurity of scalemic mixtures [1].
Among the anisotropic observables, the residual quadrupolar couplings (RQC) – from nuclei with a weak quadrupolar moment such as 2H ($I = 1$) – leads to the best spectral enantiodiscriminations due to its high sensitivity to local order differences.

The doubling of quadrupolar doublets for each unequal C-2H direction in perdeuterated chiral molecules (or in natural abundance 2H) in chiral aligning solvents often yields very informative but complex spectra from which the extraction of RQC values for each 2H site of the molecule can be tedious. The use of 2D QUadrupole-Ordered SpectroscopY (QUOSY) experiments dramatically eases such measurements [1].

However, the time-constraint associated with conventional QUOSY 2D-NMR is not suitable in applications where the time-resolution is of paramount importance as in the case of the real-time enzymatic reaction monitoring by 2H NMR of enriched analytes in chiral aligning solvents [2]. While 2H 1D-NMR is sufficient for simple systems, this tool may become insufficient whenever multiple species and/or cascade reactions are involved, making ultrafast 2H 2D-NMR experiments an appealing alternative tool.

The proof of concept of anisotropic Ultrafast (UF) 2H 2D-NMR yielding a whole 2H 2D spectra in a single transient has been first reported in 2016, [3]. Since several new UF QUOSY 2D experiments have been recently designed based on Q-COSY, Q-resolved and Q-DQ pulse schemes [4].

In this work, we present the main theoretical and practical features of this methodology along with illustrative 2H UF QUOSY 2D spectra of model deuterated prochiral/chiral dissolved in polymeric chiral liquid crystals. The analytical performance of this approach in terms of resolution, sensitivity and quantitativity is examined as well as its potential for future applications [4].

*Intervenant

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