Indirect detection of nuclei subject to large anisotropic interactions via protons using T-HMQC sequences

Racha Bayzou*[1], Julien Trebosc[1], Ivan Hung[2], Zhehong Gan[2], Olivier Lafon[1,3], and Jean-Paul Amoureux[1,4,5]

[1]Unité de Catalyse et Chimie du Solide - UMR 8181 (UCCS) – Université de Lille : UMR8181, Centre National de la Recherche Scientifique : UMR8181, Ecole Nationale Supérieure de Chimie de Lille : UMR8181, Ecole Centrale de Lille : UMR8181, Université d'Artois : UMR8181 – Cité Scientifique - Bâtiment C3 - 59655 Villeneuve dÁscq Cedex, France

[2]National High Magnetic Field Laboratory (NHMFL) – 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, États-Unis

[3]Institut Universitaire de France (IUF) – Ministère de l'éducation nationale, de l'enseignement supéreur et de la recherche – Maison des Universités 103 Boulevard Saint-Michel 75005 Paris, France

[4]Bruker Biospin, Wissembourg, France – Bruker Daltonics, Wissembourg – 34 Rue de l'Industrie, 67160 Wissembourg, France

[5]Riken NMR Science and Development Division – Yokohama, 230-0045 Kanagawa, Japan, Japon

Résumé

Solid-state NMR spectroscopy is a unique technique for the characterization of the atomic-level structure and dynamics of materials. However, this technique can often prove challenging to detect nuclei S subject to large anisotropic NMR interactions, such as chemical shift anisotropy (CSA) or quadrupolar coupling for $S \geq 1$. It has been shown recently that such spectra can be detected indirectly *via* protons using the 1H-$\{S\}$T-HMQC scheme.[1,2] This simple sequence is made of only four rectangular pulses: a pi/2 and pi pulses forming a spin echo on the 1H channel and two symmetrical long pulses applied to the S spin, which reintroduces the 1H-S dipolar coupling through the TRAPDOR (TRAnsfer of Populations in DOuble-Resonance) effect. Because of the lack of any recoupling scheme on the 1H channel, the T-HMQC sequence is robust to spinning speed fluctuations and thus free of $t1$-noise. Moreover, its sensitivity is higher than the conventional D-HMQC sequence.

In the present work, we analyze using simulations of spin dynamics and solid-state NMR experiments at 18.8 T under fast magic-angle spinning the efficiency and robustness of the T-HMQC sequence for the indirect detection of spin-1/2 (195Pt), spin-1 (14N) and spin-3/2 (35Cl) isotopes.[3] We show that maximum sensitivity is achieved for offsets multiple of MAS frequency and moderate radiofrequency fields, accessible with common MAS NMR probes. For 195Pt, the transfer efficiency increases with larger CSA and still significant for CSA values of 3 MHz. For 14N, single- (1Q) or double-quantum (2Q) coherences can be selected during the indirect evolution period, $t1$. We show that the 2Q version is less efficient than the 1Q one, but yields higher spectral resolution. In the case of 35Cl, the T-HMQC method allows to scale up the resolution either by a factor of 18 or 3.9 with respect to the D-HMQC

*Intervenant

by selecting 2Q or triple-quantum (3Q) coherences, respectively, during $t1$ period.

I. Hung, P. Gor'kov, Z. Gan, *J. Chem. Phys*, 151 (**2019**) 154202.

I. Hung, Z. Gan, *J. Phys. Chem. Lett*, 11 (**2020**) 4734-4740.

R. Bayzou, J. Trébosc, I. Hung, Z. Gan, O. Lafon, J.-P. Amoureux, in preparation.