



## **<sup>1</sup>H to <sup>13</sup>C Energy Transfer in Solid State NMR Spectroscopy of Natural Organic Systems**

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Cross polarization (CP) magic angle spinning (MAS) <sup>13</sup>C-NMR spectroscopy is a solid state NMR technique widely used to study chemical composition of organic materials with low or no solubility in the common deuterated solvents used to run liquid state NMR experiments. Based on the magnetization transfer from abundant nuclei (with spin of 1/2) having a high gyromagnetic ratio ( $\gamma$ ), such as protons, to the less abundant <sup>13</sup>C nuclei with low  $\gamma$  values, <sup>13</sup>C-CPMAS NMR spectroscopy is often applied in environmental chemistry to obtain quantitative information on the chemical composition of natural organic matter (NOM) (Conte et al., 2004), although its quantitative assessment is still matter of heavy debates. Many authors (Baldock et al., 1997; Conte et al., 1997, 2002; Dria et al., 2002; Kiem et al., 2000; Kögel-Knabner, 2000; Preston, 2001), reported that the application of appropriate instrument setup as well as the use of special pulse sequences and correct spectra elaboration may provide signal intensities that are directly proportional to the amount of nuclei creating a NMR signal. However, many other papers dealt with the quantitative unsuitability of <sup>13</sup>C-CPMAS NMR spectroscopy. Among those, Mao et al. (2000), Smernik and Oades (2000 a,b), and Preston (2001) reported that cross-polarized NMR techniques may fail in a complete excitation of the <sup>13</sup>C nuclei. In fact, the amount of observable carbons via <sup>13</sup>C-CPMAS NMR spectroscopy appeared, in many cases, lower than that measured by a direct observation of the <sup>13</sup>C nuclei. As a consequence, cross-polarized NMR techniques may provide spectra where signal distribution may not be representative of the quantitative distribution of the different natural organic matter components.

Cross-polarization is obtained after application of an initial  $90^\circ_x$  pulse on protons and a further spin lock pulse (along the y axis) having a fixed length (contact time) for both nuclei (<sup>1</sup>H and <sup>13</sup>C) once the Hartmann-Hahn condition is matched. The Hartmann-Hahn condition can be expressed as  $\gamma_H B_1^H = \gamma_C B_1^C$ , where  $\gamma_H$  and  $\gamma_C$  are the gyromagnetic ratios of protons and carbons, whereas  $B_1^H$  and  $B_1^C$  are the <sup>1</sup>H and <sup>13</sup>C radio-frequency (r.f.) fields applied to the nuclei. The Hartmann-Hahn condition is affected by the H-C dipolar interaction strength (Stejskal & Memory, 1994). All the factors affecting dipolar interactions may mismatch the Hartmann-Hahn condition and prevent a quantitative representation of the NOM chemical composition (Conte et al., 2004). It has been reported that under low speed MAS conditions, broad matching profiles are centered around the Hartmann-Hahn condition..... With increasing spinning speed the Hartmann-Hahn matching profiles break down in a series of narrow matching bands separated by the rotor frequency (Stejskal & Memory, 1994). In order to account for the instability of the Hartmann-Hahn condition at higher rotor spin rates (>10 kHz), variable amplitude cross-polarization techniques (RAMP-CP) have been developed (Metz et al., 1996).

So far, to our knowledge, the prevailing way used to obtain quantitative <sup>13</sup>C-CPMAS NMR results was to optimize the <sup>1</sup>H and <sup>13</sup>C spin lock r.f. fields on simple standard systems such as glycine and to use those r.f. field values to run experiments on unknown organic samples.

The aim of the present study was to experimentally evidence that the stability of the Hartmann-Hahn condition was different for different samples with a known structure. Moreover, Hartmann-Hahn profiles of four different humic acids (HAs) were also provided in order to show that the <sup>1</sup>H/<sup>13</sup>C r.f. spin lock field strength must also be tested on the HAs prior to a quantitative evaluation of their <sup>13</sup>C-CPMAS NMR spectra.

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