Dynamics of Cross Polarization in Solid State Nuclear Magnetic Resonance Experiments of Amorphous and Heterogeneous Natural Organic Substances

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Nuclear magnetic resonance (NMR) experiments on carbon-13 in the solid state were done with cross polarization (CP) and magic angle spinning (MAS) in order to overcome the low NMR sensitivity of ¹³C and the chemical shift anisotropy, respectively. In the present research, CPMAS ¹³C-NMR spectra were collected by modulating the contact time needed for cross polarization (variable contact times experiments, VCT) on two different humic acids (a soil-HA and a coal-HA). VCT data were fitted by a model containing either a monotonic or a non-monotonic cross polarization term. The non-monotonic model, which fitted the experimental results better than the monotonic one, provided two cross-polarization rates, thereby suggesting that two different mechanisms for the energy transfer from protons to carbons arise in amorphous and heterogeneous humic substances. The first mechanism was a fast proton-to-carbon energy transfer due to protons directly bound to carbons. The second mechanism was related to a slow transfer mediated by local segmental motions. Different domains in the humic acids were identified. Soil-HA was made of rigid domains, containing mainly aromatic and carboxylic moieties, and fast moving domains, containing alkyl, C-O and C-N groups. Coal-HA showed a rigid aromatic domain that was differentiated from a very mobile domain made of alkyl and COOH groups.

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Introduction

Cross polarization magic angle spinning (CPMAS) ¹³C NMR spectroscopy is a very powerful tool for analyzing organic materials that are insoluble or poorly soluble in the deuterated solvents commonly used in liquid state NMR. The technique is widely used in the environmental field¹ to study natural organic matter (NOM)² for a better comprehension of its environmental role either in bulk soils or in sediments³ or when it is isolated from environmental matrices.^{4,5}

One of the main goals in applying CPMAS ¹³C NMR spectroscopy on NOM is to obtain quantitative information on its chemical composition,⁵⁻⁸ although some papers have shown the quantitative inefficiency of this technique.⁹⁻¹² Moreover, a number of CPMAS ¹³C NMR experiments were also performed to assess molecular dynamics in the solid state with the aim of gaining knowledge of the environmental behavior of NOM.^{7,12-16}

The model generally used to describe the CP phenomenon and to obtain both quantitative information and information on the dynamics of NOM is a thermodynamic model based on the idea that nuclear spins are in thermal equilibrium. The perturbation of the thermal equilibrium produces the ¹³C NMR magnetization which evolves first under the effect of the dipolar coupling between carbons and protons, then under the influence of the

relaxation of the protons.³ In this view, only a monotonic cross polarization mechanism is displayed.³ However, it has been shown that the monotonic CP model fails when it is applied for studying cross polarization either in polycrystalline materials¹⁷ or in amorphous natural organic matter.^{18,19} In fact, Taylor *et al.*¹⁷ reported that the best fit for variable contact time (VCT) experiments done on crystalline organic systems is a non-monotonic model, in which two different cross polarization mechanisms are introduced. The faster CP mechanism is governed by the H-C internuclear distance, whereas the slower one is mediated by fast local segmental motions.¹⁷ Proton-to-carbon distances and local segmental motions were also used by Abelman *et al.*¹⁹ to interpret the CP behavior of humic substances from two different coals. Conversely, Dria *et al.*¹⁸ attributed the non-monotonic CP behavior of heterogeneous and amorphous NOM extracted from different sources only to different local dynamics experienced by the molecular groups resonating at the same chemical shift values.

The model proposed by Müller *et al.*²⁰ for the interpretation of the CP dynamics in crystalline materials was modified by Taylor *et al.*¹⁷ by considering the longitudinal proton relaxation time term averaged over all the possible crystallite orientations in the applied magnetic field. In addition, two other different mathematical models were applied by Dria *et al.*¹⁸ and Abelman *et al.*¹⁹ to study the CP dynamics of NOM. Dria *et al.*¹⁸ used a model which was empirically modified from the classical monoexponential one in order to account for the poor data fitting obtained by the application of the classical model.

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Table 1 Elemental content of the humic acids (HAs) used in the present study

Sample	C, %	H, %	N, %	O, % ^a
Soil-HA	54.0 ± 0.9	5.0 ± 0.9	5.0 ± 0.9	36 ± 3
Coal-HA	63.5 ± 0.5	3.8 ± 0.1	1.0 ± 0.1	32 ± 1

a. The oxygen amount was obtained as a complement of 100.

Their modification consisted in the introduction of the terms P and (1-P) into the classical monotonic CP model.¹⁸ These two terms were related to the percent of each NMR peak experiencing fast and slow cross polarization transfer, respectively. On the other hand, Abelman *et al.*¹⁹ modified the model proposed by Mehring²¹ simply by adding two different Mehring terms.

The aims of the present paper are: 1) to study the CP dynamics of two humic substances (from a soil sample and a coal sample) by applying the model proposed by Taylor *et al.*¹⁷ modified in order to account for the natural heterogeneity and amorphism of NOM; 2) to suggest a possible conformation in the solid state of the two humic substances.

Experimental

Humic substances

Two humic acids (HAs) were extracted and purified with a traditional procedure²² from 1) the surface horizon of a Planosol at the field site in Krauthausen (North Rhine-Westphalia, Germany) (soil-HA) and 2) a Rhenish brown coal sample from an opencast mine at Bergheim (Rheinbraun AG, Frechen, North-Rhine Westphalia, Germany) (coal-HA). Briefly, the original materials were shaken overnight in 0.5 M NaOH and 0.1 M Na₂P₂O₇ under N₂ atmosphere. The HAs were then precipitated from the alkaline extract with 6 M HCl. Ashes were removed by re-dissolving the HAs in 0.5 M NaOH and flocculating again in 6 M HCl. This procedure was repeated three times. The HAs were then shaken twice in a 0.25 M HF/HCl solution for 24 h, dialyzed until they were chloride-free and freeze-dried.

The HAs were analyzed to determine their elemental composition (C, H, N) in a Fisons Interscience EA1108 elemental analyzer. The elemental composition was corrected for the ash content measured by burning few milligrams of each sample at 650°C overnight. Ash content < 3% resulted for all samples. Table 1 shows the C, H, N contents for the two HAs used in the present study.

The humic samples were also analyzed by atomic-absorption spectrometry (AAS) in order to verify the presence of potentially paramagnetic species (Fe, Mn, Cu) in the ash content. No traces of those paramagnetic metals were found. The AAS analyses were performed on a Perkin-Elmer Analyst 700 with an instrumental sensitivity of 0.1 mg kg⁻¹. The samples (50 mg of each HA) were boiled in a nitric/perchloric acid solution until complete mineralization of the organic matter and dissolution of the inorganic ashes were obtained. Each solution was transferred to a 20 mL volumetric flask and each sample was analyzed by AAS.

Solid state NMR spectroscopy

A 7.05 T Varian UNITY INOVA™ (Varian Inc., Palo Alto, CA), equipped with a wide bore probe operating at a ¹³C frequency of 75.4 MHz, was used to acquire the CPMAS ¹³C-NMR spectra of HAs. The samples were packed in 6 mm

Fig. 1 CPMAS ¹³C-NMR spectra of the humic acids with the indication of the areas used for the integration. The spinning side bands (SSB) were recognized and are indicated by one (SSB from COOH groups) and two (SSB from aromatic carbons) stars.

zirconium rotors with Teflon® bottom and top spacers and Vespel® drive tips. The temperature was kept constant at 25.0 ± 0.1°C. Magic angle spinning was carried out at 5000 ± 1 Hz. A ¹H RAMP sequence was applied to account for possible inhomogeneities of the Hartmann-Hahn condition.² Variable contact time experiments were performed by arraying 50 different contact times from 0.1 to 7 ms. An acquisition time of 30 ms, a ¹H 90° pulse of 4 μs with a power level of 60 dB at the maximum decoupler power modulation, 4k data points, a recycle delay of 2 s and 2000 transients were used to acquire all the spectra.

VNMRJ software (Version 1.1 RevisionD, Varian Inc., Palo Alto, CA) was used to acquire all the free induction decays (FID). Spectra elaboration was conducted by Mestre-C software (Version 4.9.9.9, Mestrelab Research, Santiago de Compostela, Spain). All the FIDs were transformed by applying first a 4k zero filling and then an exponential filter function with a line broadening (LB) of 100 Hz. Fully automatic baseline correction using a Bernstein algorithm was applied for baseline corrections.²³ Integration was done peak by peak by identifying the start point and end point of each peak (Fig. 1) as reported in the literature.^{2,3,5,6,22} The spectral regions of soil-HA were 0 – 45 ppm (alkyls), 45 – 63 ppm (C-N moieties), 63 – 90 ppm (C-O systems), 90 – 112 ppm (anomeric C), 112 – 160 ppm (aromatic C) and 160 – 185 ppm (COOH groups) (Fig. 1). The spectral regions in the spectrum of coal-HA were: 0 – 65 ppm (alkyls), 65 – 90 ppm (C-O), 90 – 160 ppm (aromatic C) and 160 – 180 ppm (COOH groups) (Fig. 1). Signal attribution was done according to the literature.³ All the spinning side bands (SSB) were recognized and accounted for by using the mathematical procedure described in Conte *et al.*² The fitting procedures described in Results and Discussion were achieved by importing the areas of each integrated spectral region in OriginPro 7.5 SR6 (Version 7.5885, OriginLab Corporation, Northampton, MA). All the errors reported in Table 2 were obtained from the fitting procedure.

Table 2 NMR parameters (see text for their meaning) as measured by using the classical monotonic and the non-monotonic thermodynamic approaches

	Classical thermodynamic approach				Non-monotonic approach			
	T_{CH}/ms	$T_{ip}(H)/ms$	Carbon content, %	b	T_{CH1}/ms	T_{CH2}/ms	$T_{ip}(H)/ms$	Carbon content, %
Soil-HA								
0 – 45 ppm	0.09 ± 0.01	5.0 ± 0.6	30 ± 3	2 ± 1	0.033 ± 0.006	1.4 ± 0.3	3.9 ± 0.3	32 ± 2
45 – 63 ppm	0.10 ± 0.01	5.5 ± 0.8	13 ± 1	-2.4 ± 0.9	0.038 ± 0.007	1.1 ± 0.3	4.2 ± 0.4	14 ± 2
63 – 90 ppm	0.11 ± 0.01	4.4 ± 0.7	17 ± 2	-3.3 ± 0.9	0.034 ± 0.007	1.0 ± 0.2	3.5 ± 0.3	18 ± 3
90 – 112 ppm	0.15 ± 0.03	6 ± 1	7 ± 1	2.3 ± 0.7	0.06 ± 0.01	0.6 ± 0.1	4.3 ± 0.6	7 ± 1
112 – 160 ppm	0.34 ± 0.08	15 ± 7	15 ± 3	2.0 ± 0.2	0.08 ± 0.02	0.22 ± 0.07	12 ± 3	14 ± 2
160 – 185 ppm	0.9 ± 0.1	4.6 ± 0.8	18 ± 3	-1.7 ± 0.2	0.34 ± 0.06	0.18 ± 0.04	6.1 ± 0.9	15 ± 3
Coal-HA								
0 – 65 ppm	0.11 ± 0.02	8 ± 1	46 ± 5	2.3 ± 0.8	0.037 ± 0.005	1.1 ± 0.2	6.1 ± 0.4	55 ± 6
65 – 90 ppm	0.51 ± 0.08	14 ± 5	8 ± 2	-0.0020 ± 0.0001	1.7 ± 0.6	2.1 ± 0.9	10 ± 3	1.0 ± 0.6
90 – 160 ppm	0.31 ± 0.06	105 ± 240	45 ± 5	-1.7 ± 0.3	0.09 ± 0.01	0.32 ± 0.07	31 ± 10	39 ± 4
160 – 180 ppm	0.91 ± 0.07	11 ± 2	6 ± 2	0.0008 ± 0.0001	3 ± 1	1.1 ± 0.1	8 ± 2	5 ± 2

Results and Discussion

The classical thermodynamic picture describing the cross polarization (CP) dynamics of humic substances (HAs) is reported in Eq. (1).³ In this equation, $I^i(t_{CP})$ is the experimental signal area at the assigned contact time (t_{CP}), I_0^i is the total nuclear magnetization of ^{13}C nuclei in thermal equilibrium, T_{CH}^i is the cross polarization time of a chemical group generating the i -th NMR signal, $T_{ip}^i(H)$ is the proton longitudinal relaxation time in the rotating frame associated to each group resonating in

the i -th spectral region, and $\alpha = 1 - \frac{T_{CH}^i}{T_{ip}^i(H)}$.

$$I^i(t_{CP}) = I_0^i \alpha^{-1} \left[1 - \exp\left(-\alpha \frac{t_{CP}}{T_{CH}^i}\right) \right] \times \exp\left(-\frac{t_{CP}}{T_{ip}^i(H)}\right) \quad (1)$$

Equation (1) combines the exponential signal increase due to proton-to-carbon cross polarization with the exponential signal decrease associated with the proton spin lattice relaxation in the rotating frame. The main limit in the application of this equation is the mismatch of the basic NMR condition which is $T_{CH}^i < T_{ip}^i(H)$.³ In fact, if the proton spin lattice relaxation starts before the full $H \rightarrow C$ cross polarization is achieved (slow CP regime), Eq. (1) cannot be used to study the molecular CP dynamics of humic substances and the CPMAS ^{13}C -NMR spectra are not representative of the chemical composition of HAs.²

Equation (1) was applied for the interpolation of the variable contact time (VCT) data from the CPMAS ^{13}C -NMR experiments on two different humic acids (Table 2 and dashed lines in Figs. 2 and 3, respectively). T_{CH}^i and $T_{ip}^i(H)$ values were obtained for all the integrated regions. In all cases the condition $T_{CH}^i < T_{ip}^i(H)$ was fulfilled (Table 2), thereby indicating that the CPMAS ^{13}C -NMR spectra (Fig. 1) are representative of the chemical composition of soil-HA and coal-HA, and that Eq. (1) is suitable for the interpretation of the cross polarization dynamics of the two humic acids.³ The values measured for each spectral area according to Eq. (1) were used to calculate the relative amounts of each chemical group (Group _{i} (%)) in soil-HA and coal-HA through Eq. (2):²⁴

$$\text{Group}_i(\%) = \frac{I_0^i}{\sum I_0^i} \times 100 \quad (2)$$

Due to its origin, soil-HA revealed, as expected,²² larger relative intensities in the C-N (45 – 63 ppm), C-O (63 – 90 ppm), anomeric (90 – 112 ppm) and COOH (160 – 185 ppm) regions (Fig. 1 and the fourth column in Table 2), whereas coal-HA appeared richer in alkyl (0 – 65 ppm) and aromatic (90 – 160 ppm) carbons (Fig. 1 and the fourth column in Table 2). The greater oxygenated and nitrogenated nature of soil-HA as compared to coal-HA was also confirmed by elemental analysis (Table 1). In fact, N and O contents in soil-HA were 5.0 ± 0.9 and $36 \pm 3\%$ respectively, whereas they were 1.0 ± 0.1 and $32 \pm 1\%$ in coal-HA.

The T_{CH}^i values of soil-HA (second column in Table 2) were similar for the alkylic (0 – 45 ppm), C-N (45 – 63 ppm), C-O (63 – 90 ppm) and anomeric (90 – 112 ppm) systems. The cross polarization time increased to 0.34 ± 0.08 ms for the aromatic carbons (112 – 160 ppm) and to 0.9 ± 0.1 ms for the carboxylic groups (160 – 185 ppm) (Table 2). The similarities between the T_{CH}^i values for the signals in the regions from 0 to 112 ppm were ascribed to the larger numbers of protons directly bound to the carbons resonating in that chemical shift range. In fact, the shorter the proton-carbon distance, the stronger the H-C dipolar interaction is; such a situation provides faster cross polarization rate and shorter T_{CH}^i value.²⁵ On the other hand, the average H-C distances in the aromatic systems of soil-HA can be longer than those in the previously analyzed molecular moieties due to the possible presence of aromatic quaternary carbons.³ For this reason, a less efficient average cross polarization with longer T_{CH}^i values can result. Carboxyl groups do not have directly bonded protons, so that the ^{13}C nuclei can only cross polarize *via* a slow intermolecular spin diffusion. According to the literature,³ COOH systems always reveal the lowest CP efficiency and the longest T_{CH}^i values. Similar signs can be found for the differences in T_{CH}^i values of coal-HA (Table 2). In coal-HA, the proton-rich alkylic moieties at 0 – 65 ppm showed the shortest cross polarization time. Conversely, the aromatic (90 – 160 ppm) and carboxylic (160 – 180 ppm) systems which are poorly protonated revealed a more inefficient cross polarization. The region between 65 and 90 ppm also showed a very long cross polarization time (Table 2), probably due either to rapid local movements or poor protonation.

The limit of the previous data interpretation is the poor fitting of the experimental VCT data (dashed lines in Figs. 2 and 3). In fact, the coefficients of determination (R^2) in Figs. 2 and 3 were above 0.90 only for the alkylic and carboxylic regions of soil-HA

Fig. 2 Fitting curves of the VCT data of soil-HA. The curves were obtained by interpolating the experimental data (black dots) with the classical thermodynamic model (dashed lines) and with the non-monotonic thermodynamic model (solid lines). A, Curves interpolating the VCT areas of the region 0 – 45 ppm; B, curves interpolating the VCT areas of the chemical shift region 45 – 63 ppm; C, curves interpolating the VCT areas of the chemical shift region 63 – 90 ppm; D, curves interpolating the VCT areas from the region 90 – 112 ppm; E, curves interpolating the VCT areas in the region 112 – 160 ppm; F, curves interpolating the VCT areas of the region 160 – 185 ppm. The R^2 values for each interpolation were also reported.

(Figs. 2A and 2F, respectively) and for the C–O and carboxylic intervals of coal-HA (Figs. 3B and 3D, respectively). The remaining intervals were not well fitted by Eq. (1) since R^2 ranged from 0.75 (Fig. 2E) to 0.87 (Figs. 2B, 2C and 3C).

Recently, Taylor *et al.*¹⁷ reported that the classical thermodynamic approach depicted in Eq. (1) cannot be applied to study the cross polarization dynamics of many polycrystalline materials due to a poor fitting of the variable contact time curves. For a better data fitting, the authors modified the original CP model from Müller *et al.*²⁰ in order to account for the proton spin lattice relaxation time and for all the possible crystallite orientations relative to the applied magnetic field. With this new approach, Taylor *et al.*¹⁷ showed that a non-monotonic cross polarization can explain better the CP dynamics in polycrystalline molecules.

On the basis of the work prepared by Taylor *et al.*,¹⁷ we multiplied the original Müller *et al.*²⁰ model by the exponential $T_{\rho}(H)$ containing a term in order to account not only for the CP increasing part of the variable contact time curve (*i.e.* Müller *et al.*²⁰ model), but also for the descending portion that is related to the proton longitudinal relaxation in the rotating frame. Equation (3) was obtained:

$$I^i(t_{CP}) = I_0^i \times \left(1 - \frac{1}{2} \exp\left(-\frac{t_{CP}}{T_{CH1}^i}\right) - \frac{1}{2} \exp\left(-\frac{3t_{CP}}{2T_{CH2}^i}\right) \times \cos\left(\frac{bt_{CP}}{2}\right) \right) \times \exp\left(-\frac{t_{CP}}{T_{\rho}^i(H)}\right) \quad (3)$$

All the terms in Eq. (3) have the same meaning as in Eq. (1). T_{CH1}^i and T_{CH2}^i are cross polarization times of each chemical

group generating the i -th NMR signal and $b = \frac{\gamma_H \gamma_C \hbar}{2r_{C-H}^3} \times (3\cos^2 \vartheta - 1)$.

$\vartheta - 1$).²⁰ b is the C–H dipolar coupling parameter containing 1) the proton and carbon magnetogyric ratios (γ_H and γ_C , respectively), 2) the chemical shift anisotropy term ($3\cos^2 \vartheta - 1$) and 3) the proton-to-carbon distance (r_{C-H}).

The solid lines in Figs. 2 and 3 show the fit of the VCT data for soil-HA and coal-HA when Eq. (3) is applied. All the coefficients of determination were above 0.90, the lowest one being 0.93 for the fit reported in Fig. 2E (aromatic C in soil-HA). Only for the carboxylic groups in coal-HA (Fig. 3D) was the R^2 value similar to that obtained with Eq. (1). In all the other cases, Eq. (3) fitted the VCT data obtained for soil-HA and coal-HA better than Eq. (1) (Figs. 2 and 3).

Fig. 3 Fitting curves of the VCT data of coal-HA. The curves were obtained by interpolating the experimental data (black dots) with the classical thermodynamic model (dashed lines) and with the non-monotonic thermodynamic model (solid lines). A, Curves interpolating the VCT areas of the region 0 – 65 ppm; B, curves interpolating the VCT areas of the interval 65 – 90 ppm; C, curves interpolating the VCT areas of the chemical shift region 90 – 160 ppm; D, curves interpolating the VCT areas from the region 160 – 180 ppm. The R^2 values for each interpolation were also reported.

The comparison between T_{CH1}^i , T_{CH2}^i and T_{lp}^i (Table 2) revealed that the basic NMR condition for CPMAS ^{13}C -NMR spectroscopy was still valid. For this reason, the I_0^i values obtained from Eq. (3) were used in Eq. (2) for a quantitative evaluation of the NMR spectra of soil-HA and coal-HA. The last column in Table 2 shows that no substantial differences were observed between the quantitative carbon contents obtained by the classic thermodynamic approach (Eq. (1)) and those obtained by the non-monotonic modified Müller *et al.*²⁰ model (Eq. (3)). However, more detailed and precise information was obtained on the cross polarization dynamics in humic substances. In fact, Eq. (3) provided two different values of the cross polarization time (Table 2), which can be associated with the two different spin diffusion mechanisms affecting the magnetization transfer from protons to carbons in HAs. The first CP mechanism is a very fast polarization obtained when proton and carbons are directly bound.¹⁷ The rate of this mechanism is measured by T_{CH1}^i , whose values for the carboxylic carbons resonating at 160 – 185 ppm in soil-HA and 160 – 180 ppm in coal-HA (Table 2) were the longest. The absence of protons directly bound to carbons only allows carboxylic carbons to be excited by protons that are distant more than one C-H bond-length. The nature of the two humic substances may explain why T_{CH1} associated to COOH groups in soil-HA was ten times shorter than that measured for the carboxyl groups in coal-HA (Table 2). In fact, the number of protons in soil-HA was larger than in coal-HA (Table 1), thereby enhancing the cross-polarization efficiency in soil-HA as compared to coal-HA. Moreover, the 65 – 90 ppm region in coal-HA revealed a long T_{CH1}^i which is in the same range as T_{CH2}^i . As reported below, this similarity can be associated with a predominance of one CP mechanism over the other. The second CP mechanism, whose rate is governed by T_{CH2}^i , is related to the segmental motions inside the solid amorphous humic substances.¹⁷ The larger the local molecular motions, the

weaker are the H-C dipolar interactions and the longer is the time needed for cross polarization. The alkyl (0 – 45 ppm), C-N (45 – 63 ppm) and C-O (63 – 90 ppm) groups in soil-HA revealed the longest T_{CH2}^i values due to possible fast segmental movements. Conversely, the remaining molecular soil-HA systems (*i.e.*, the anomeric C at 90 – 112 ppm, the aromatic C at 112 – 163 ppm and the COOH groups between 160 and 185 ppm) showed shorter T_{CH2}^i values that, in turn, decreased from the anomeric to the carboxylic groups (Table 2). Decreasing molecular mobilities due to either formation of H-bonds (such as in anomeric and COOH moieties) or to the stacking of aromatic rings²⁶ can explain the measured T_{CH2}^i values for the carbon nuclei resonating in the intervals going from 90 to 180 ppm.

The T_{CH2}^i values for coal-HA were the largest for the alkyl (0 – 65 ppm), C-O (65 – 90 ppm) and carboxylic (160 – 180 ppm) groups, whereas the aromatic moieties (90 – 160 ppm) revealed the shortest T_{CH2}^i values (Table 2). The similarity between the T_{CH1}^i and T_{CH2}^i values for the molecular systems resonating in the 65 – 90 ppm region in the coal-HA spectrum can be attributed to a structure with a high local mobility which also lacks protons. For this reason, the CP is mainly dominated by the segmental mobility. The structural conformation of the coal-HA can then be thought of as motionless, highly condensed or strongly associated aromatic systems³ surrounded by largely moving alkyl tails with polar terminations (COOH and C-O groups).²⁶

Equation (3), as well as Eq. (1), cannot be used to gain information on the proton relaxation dynamics due to the overestimation of the $T_{\text{lp}}^i(H)$ values obtained when thermodynamic approaches are used to describe the CPMAS phenomenon.²⁷ However, the non-monotonic model applied for humic substances provided a new parameter, b , that is the dipolar coupling between protons and carbons.²⁰ Since b depends on the angle between the direction of the vector connecting protons to carbons and that of the applied magnetic field (ϑ), we should have expected it to be null at the magic

angle used to perform our CP experiments. On the contrary, non-null values were obtained (Table 2). Non-null b values can be explained by the fact that the non-crystalline humic substances do not provide the classical powder-pattern CP spectra, thereby making the dipolar coupling parameter both time and θ -dependent.²⁷ A residual chemical shift anisotropy is, then, still measured due to the non-ordered distribution of the C $\rightarrow$ H vectors along the magic angle.

Conclusions

The present paper confirmed findings from Dria *et al.*¹⁸ and Abelman *et al.*¹⁹ which revealed that the natural organic matter from sediments, waters, peat, wood,¹⁸ a highly volatile bituminous coal and a lignite coal¹⁹ are subjected to complex cross polarization dynamics. In our work we found that also the cross polarization dynamics of two humic acids (from a soil and a coal that was different from those investigated by Abelman *et al.*)¹⁹ were differentiated into two different mechanisms. The first mechanism was a fast carbon excitation through the directly bound protons, whereas the second one was a spin-diffusion-based mechanism mediated by local molecular movements. Based on these two different mechanisms, different domains were hypothesized in the solid state conformation of the two humic acids. Highly condensed or strongly associated rigid aromatic systems interact with carboxyl groups, involved in hydrogen-bondings formation, and mobile C-O/C-N systems that, in turn, should be mainly displaced, as well as the mobile alkyl moieties, on the surface of the solid state HAs.

We propose the use of the non-monotonic model (Eq. (3)) for the interpretation of the VCT data of humic substances when the classical thermodynamic model (Eq. (1)) does not provide a good fit. However, more extensive studies are still needed in order to understand the role of the dipolar coupling parameter b in the cross polarization dynamics of HAs, and to correct Eq. (3) to account for the different proton relaxation mechanisms in complex mixtures.²⁷

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