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Probing structural and motional features of organic and inorganic solids through extended family of cross-polarization experiments

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ABSTRACT

Combined use of cross-polarization and magic-angle spinning in the middle of the seventies has opened a new era of high-resolution solid-state NMR spectroscopy. Cross-polarization procedure is commonly used to obtain a shorter measuring time and to investigate or exploit one nucleous by means of the other nucleous involved in the polarization transfer. An extended family of cross-polarization experiments including constant time cross-polarization approach, cross-polarization inversion and indirect observation of proton spin system is reviewed and illustrated with applications to a large range of solids.

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1. Introduction

Cross-polarization (CP) transfer of magnetization [1] between two spin systems I and S is routinely used in magic-angle spinning (MAS) NMR [2] to reduce the measuring time. This reduction is due to a gain of sensitivity through signal enhancement of low gamma S spins by abundant I spins and a potentially shorter spin-lattice relaxation of I spins (usually protons). The commonly used CP method [1] is based on the spin-locking procedure of I spin magnetization along the radio-frequency field B_1. When employed to probe the CP dynamics during the variable contact time, the recorded build up curves may suffer from a simultaneous decay with a time constant $T_{1\rho}^I$, usually much shorter than $T_{1\rho}^S$. This may complicate the access to subtle details of cross-polarization dynamics containing structural and motional fingerprints of molecular systems and lead to a false structural and dynamic image of investigated materials when the cross-polarization transfer time T^{IS} is longer than the relaxation time in the rotating frame of protons, as frequently encountered in inorganic solids. This drawback can be circumvented by using constant time CP experiment which will be described in the second part along with its applications in inorganic materials.

Part 3 will review the potential of cross-polarization inversion in probing the molecular geometry and motional features of organic and inorganic systems through one- and two-dimensional

experiments.

The last part will focus on the experiments devoted to indirect observation of proton system via cross-polarization and their applications in a large range of organic solids.

This review was written from the perspective of author's research group studies. All relevant contributions from other groups which are not included in the references were quoted in the original papers.

2. Constant time cross-polarization experiment

2.1. TORQUE pulse sequence

The CP transfer of magnetization between the abundant I and the rare S spins can be described by the simplified thermodynamic model [3] when the average I–I homonuclear dipolar interaction is larger than the I–S heteronuclear dipolar interaction. Assuming negligible rotating-frame relaxation of the S spins, the dependence of their NMR signal as a function of contact time t_{CP}, can be described by the well-known relationship [1]

$$M_S(t_{CP}) = M_S^\infty \alpha \frac{\gamma_I}{\gamma_S} \frac{1}{1 - \frac{T^{IS}}{T_{1\rho}^I}} \left(\exp\left(-\frac{t_{CP}}{T_{1\rho}^I}\right) - \exp\left(-\frac{t_{CP}}{T^{IS}}\right) \right) \tag{1}$$

where M_S^∞ is the equilibrium magnetization of spins S; $\alpha = \omega_{1I}/\omega_{1S} = (\gamma_I H_{1I})/(\gamma_S H_{1S})$ is the ratio of the radio-frequency fields at the I and S frequencies (the Hartman–Hahn mismatch

parameter); $\frac{1}{T^{IS}}$ is the cross-polarization rate, which not only relies on the strength of the heteronuclear I–S dipolar interaction but also depends in a complex way on the strength of the homonuclear I–I dipolar interaction, on the correlation time and amplitude of molecular motions and the experimental parameters; $T^I_{1\rho}$ is the relaxation time in the rotating frame of the I spins. According to Eq. (1), the CP build up curves are inherently sensitive to internuclear distances via T^{IS} and the presence of mid-kHz motions via $T^I_{1\rho}$.

It is important to realize that the Eq. (1) is valid not only when $T^{IS} < T^I_{1\rho}$, the usual condition (fast CP regime), but also holds whatever the ratio $T^{IS}/T^I_{1\rho}$. NMR cross-polarization measurements are usually analyzed assuming that the cross-polarization time T^{IS} of magnetization transfer is shorter than the relaxation time $T^I_{1\rho}$. However, the reverse situation (i.e. $T^{IS} > T^I_{1\rho}$, slow CP regime) can be frequently encountered (*vide infra*), especially in inorganic solids where protons are more remote from rare nuclei than in organic systems. In this case, the S spin magnetization will as well begin to rise but this increase cannot proceed further when the I spin system is rapidly depleted by the $T^I_{1\rho}$ relaxation. Consequently, the transfer of magnetization is stopped at a time close to $T^I_{1\rho}$ and there is a reverse flow from the S to I spin system which remains depleted by the faster $T^I_{1\rho}$ relaxation. This reverse flow from the S to I reservoir occurs, as does the forward one, at the cross-polarization rate $1/T^{IS}$. In such a situation, when analyzing the experimental data under the usual fast CP assumption, an interpretation of both dynamic parameters will be strongly in error. In fact, it is impossible to know from the cross-polarization curve alone, whether $T^{IS} < T^I_{1\rho}$, or $T^{IS} > T^I_{1\rho}$. This is the consequence of the fact, that apart from the intensity factor, Eq. (1) is fully symmetrical with respect to the interchange of T^{IS} and $T^I_{1\rho}$.

Contrary to the standard variable-contact CP experiment, a direct visualization of the ratio $T^{IS}/T^I_{1\rho}$ is easily accessible by using the TORQUE pulse sequence [4]. This experiment has been originally designed with the aim of quenching the I spin $T^I_{1\rho}$ dependence (**T O**ne **R**ho **QUE**nching) when studying polarization transfer in organic solids with $T^{IS} < T^I_{1\rho}$. It uses a spin lock period on spin I of duration t_{SL} followed by the cross polarization of variable duration t_{CP}, the total time $t_{const} = t_{CP} + t_{SL}$ being kept constant (see Fig. 1 left). The TORQUE signal grows as a function of t_{CP} according to

$$M_S^{TORQUE}(t_{CP}) = \exp(-T_{TORQUE}/T^I_{1\rho}) \left(\frac{1 - \exp(-(1-\lambda)(t_{CP}/T^{IS}))}{(1-\lambda)} \right) \quad (2)$$

with $\lambda = T^{IS}/T^I_{1\rho}$. Fig. 1 (right) shows the temporal evolution of S spin magnetization calculated for a standard CP experiment and

the TORQUE experiment, both in two different scenarios: (i) $T^{IS} < T^I_{1\rho}$; (ii) $T^{IS} > T^I_{1\rho}$.

As expected, in the standard CP experiment, apart from the differences in the absolute intensity, which is not known *a priori*, identical temporal evolution of magnetization is observed in each case. In contrast, the difference in outwards and inwards curving of the TORQUE temporal evolution is immediately visible. This allows, as exemplified below, unambiguous determination of the $T^{IS}/T^I_{1\rho}$ ratio and assures proper interpretation of dynamic CP parameters in terms of structural and/or motional features.

2.2. Pitfalls of ^1H–^{29}Si cross-polarization dynamics

High-resolution solid state ^{29}Si NMR spectroscopy is frequently used in structural studies of inorganic materials including zeolites, minerals, glasses, and cement-based systems. Its important place in structure determination of these materials relies on the fact that ^{29}Si NMR spectra permit a precise determination of the ^{29}Si isotropic chemical shift in different silicon environments of powdered samples. Although the easiest way to record the quantitative ^{29}Si NMR spectrum is a direct excitation by a single pulse, this cannot be reasonably applied in most cases due to extremely long ^{29}Si longitudinal relaxation times. To avoid this inconvenience, one can take advantage of magnetization transfer from protons to ^{29}Si spins. Although when using cross-polarization procedure, the quantitative proportions of chemically or crystallographically inequivalent sites cannot be reached as with single pulse excitation, an extremely valuable structural and dynamic information can be obtained in this manner. For this, some basic precautions have to be taken. Commonly encountered complication arises indeed from the fact, that the cross-polarization transfer time may be quite long and is frequently longer than the relaxation time in the rotating frame of protons. This fact must be clearly recognized to avoid a false structural and dynamic image of investigated materials. This is illustrated below in two classes of inorganic materials.

2.2.1. Silica gels

Silica gels are highly porous materials which play an important role in numerous applications such as catalysis or chromatographic separation and have been the subject of much NMR investigations for several years. The high-resolution solid state ^{29}Si CP/MAS NMR spectra of silica gel show three peaks at –91.5 ppm, –101 ppm and –110 ppm assigned respectively to three $Q^{(2)}$, $Q^{(3)}$ and $Q^{(4)}$ types of silicon environments. The results from the CP and TORQUE experiments on a Fisher S-157 silica gel sample are presented in Fig. 2.
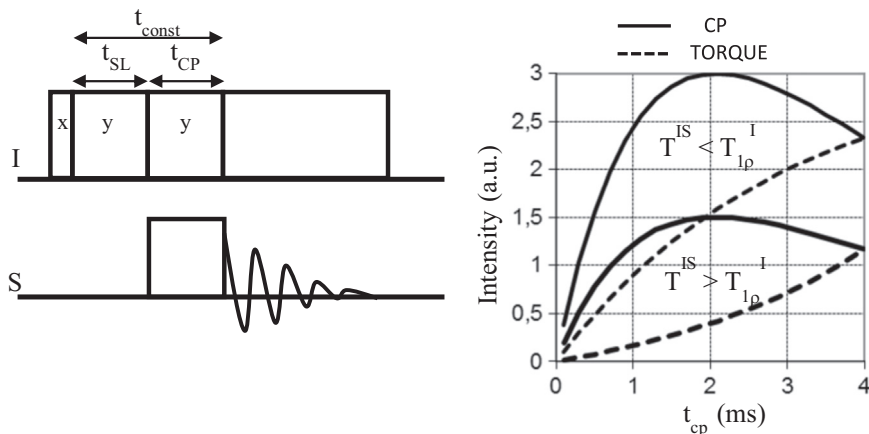

Fig. 1. (left) Scheme of TORQUE pulse sequence [4]. (right) Magnetization transfer time dependence in standard CP and TORQUE experiments. Top: $T^{IS} = 1.5$ ms, $T^I_{1\rho} = 3.0$ ms. Bottom: $T^{IS} = 3.0$ ms, $T^I_{1\rho} = 1.5$ ms. Note the change in the curvature of TORQUE graphs.