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Communication

Homogeneous broadenings in 2D solid-state NMR of half-integer quadrupolar nuclei

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Abstract

The question of the homogeneous broadening that occurs in 2D solid-state NMR experiments is examined. This homogeneous broadening is mathematically introduced in a simple way, versus the irreversible decay rates related to the coherences that are involved during t_1 and t_2. We give the pulse sequences and coherence transfer pathways that are used to measure these decay rates. On $AlPO_4$ berlinite, we have measured the ^{27}Al echo-type relaxation times of the central and satellite transitions on 1Q levels, so that of coherences that are situated on 2Q, 3Q, and 5Q levels. We compare the broadenings that can be deduced from these relaxation times to those directly observed on the isotropic projection of berlinite with multiple-quantum magic-angle spinning (MAS), or satellite-transition MAS. We show that the choice of the high-resolution method, should be done according to the spin value and the corresponding homogeneous broadening.

Keywords: Magic-angle spinning NMR; Quadrupolar nuclei; Multiple-quantum MAS; Satellite-transition MAS; High-resolution; Homogeneous broadening

High resolution solid-state NMR of polycrystalline powders faces various anisotropic interactions [1] that have to be removed for high-resolution purposes. Until late 1980s, for nuclei with spin value $S > 1/2$, submitted to large electric quadrupole interactions, the second-order quadrupolar line broadening was the ultimate broadening not reduced by magic-angle spinning (MAS). MAS averages all first-order broadenings, but scales the central transition (CT: $1/2 \leftrightarrow -1/2$) linewidth of half-integer quadrupolar nuclei by a factor of only roughly three. A better resolution for such cases is obtained by more complex motions of the sample. Complete spatial averaging requires either mechanical rotation around two axes, as in double rotation (DOR) [2], or correlation of signals acquired at two different angles in a two-dimensional (2D) experiment as in dynamic angle spinning (DAS) [3]. However, both methods present many technical shortcomings. Frydman and Harwood [4] have demonstrated that line narrowing of the CT can be obtained without changing the orientation of the spinning axis. The 2D method thus derived, called multiple quantum MAS (MQMAS), correlates both second-order patterns of multiple quantum (MQ) and CT coherences and allows of extraction of isotropic information. More recently, a new class of 2D experiments, called Satellite Transition MAS (STMAS), has been introduced [5], which correlates second-order patterns of STs during t_1 with those of CT during t_2. The most recently proposed STMAS methods remove all unwanted signals by using a double-quantum filter (DQF), which is a CT-selective π pulse [6]. This pulse has been used in three different versions of STMAS: the DQF-STMAS and the double-quantum (DQ) STMAS experiments, which only differ by the fact the selective π pulse is at the end (DQF-STMAS) or at the beginning (DQ-STMAS) of the t_1 period [6], and the t_1-split STMAS for spin 3/2 nuclei [7]. In 1D experiments, the same filtration principle can also be used, simultaneously with a rotor-synchronized acquisition, to enhance by a factor 24/7 the resolution that can be observed

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for spin $S = 5/2$ nuclei, leading to the DQF-SATRAS experiment [8]. The comparison of all MQMAS (3QMAS, 5QMAS [9], etc.) and STMAS (DQF, DQ, t_1-split, etc.) results has been facilitated recently by the introduction of a unified representation for all 2D methods [10]. In this representation, that we will use in the following, resonances are always located at the same places in the 2D spectra, which means that they always have the same isotropic (δ_{iso}) and anisotropic (δ_2) projections. However, differences in resolutions between the various techniques have been observed, but these differences remained poorly understood for several years. Recently, this issue has been addressed for the first time for MQMAS methods [11], and it has been shown that these differences of resolutions are mainly related to homogeneous irreversible decays that occur on the coherences that are involved from the excitation pulse until the refocusing of the second-order quadrupole interaction occurring at $t_{2e} = Rt_1$.

In this communication, we extend the theory to all MQ/ST-MAS 2D experiments in the frame of unified representation. Moreover, we propose sequences that allow quantifying these extra-broadenings. On a test sample, $AlPO_4$ berlinite, we have measured the ^{27}Al transverse spin–echo decay time constants of the CT and ST$_1$ ($\pm 3/2 \leftrightarrow \pm 1/2$) on 1Q levels, and of coherences that are situated on 2Q ($\pm 3/2 \leftrightarrow \mp 1/2$), 3Q ($\pm 3/2 \leftrightarrow \mp 3/2$), and 5Q ($\pm 5/2 \leftrightarrow \mp 5/2$) levels. We compare the broadenings that can be deduced from these relaxation times to those that are directly observed on the isotropic projection of berlinite with 3QMAS and 5QMAS, or with DQF-STMAS and DQ-STMAS.

In the following, we will only consider the echo pathway of 2D experiments, as the anti-echo signal is either not recorded, or only used to cancel the dispersive parts in amplitude-modulated experiments [12]. The coherence transfer pathway of the echo-signal of all MQ/ST-MAS amplitude-modulated experiments can always be described in the same way: 0Q → pQ (t_1) → −1Q (CT, t_2). Let us call T_{CT} and $T_p = \alpha T_{CT}$ the transverse homogeneous relaxation times of the CT (−1Q, t_2) and pQ (t_1) coherences, respectively. The 2D signal can be written:

$$s(t_1, t_2) = \exp\left(\mathrm{i}(\omega_p t_1 + \omega_{CT} t_2) - \frac{t_1}{\alpha T_{CT}} - \frac{t_2}{T_{CT}}\right). \quad (1)$$

The isotropic signal corresponds to the top of the echo ($t_{2e} = Rt_1$, with $R > 0$), which means that all anisotropic terms disappear:

$$s(t_1, Rt_1) = \exp\left(\left\{\mathrm{i}(p-R)\cdot \nu_0 \left[\delta_{CS} + \frac{(\delta_{QIS}^{p} + R\delta_{QIS}^{CT})}{p-R}\right] - \frac{1}{\alpha T_{CT}} - \frac{R}{T_{CT}}\right\}\cdot t_1\right), \quad (2)$$

where ν_0 is the Larmor frequency, and δ_{CS} and δ_{QIS} are the actual-chemical and quadrupolar-induced shifts, respectively. It has been shown that this equation can be simplified [10,13]:

$$s(t_1, Rt_1) = \exp\left(\left\{-\mathrm{i}\nu_0^{app}\delta_{iso} - \frac{1}{T_{tot}}\right\}.t_1\right), \quad (3)$$

with

$$\nu_0^{app} = (R-p)\nu_0; \quad \delta_{iso} = \delta_{CS} - 10\delta_{QIS}^{CT}/17 + 10^6 m_I J/\nu_0;$$
$$T_{tot} = \alpha T_{CT}/(1+\alpha R). \quad (4)$$

The unified ppm scaling consists in using ν_0^{app} instead of ν_0 [10,13]. J is the scalar coupling constant between spin S and another spin I with magnetic number m_I. After Fourier and shearing transforms, isotropic projections are thus independent on the 2D high-resolution method, when unified ppm scaling is used, and when only inhomogeneous interactions are taken into account (Eq. (3), without the relaxation term) [10,13]. These interactions may be of different types, such as chemical and quadrupolar-induced shifts, scalar couplings, hetero-nuclear dipolar interactions, and quadrupolar-dipolar cross-terms [14]. In the case of distributed surroundings, such as amorphous samples, these interactions lead to broad resonances. This may be also the case of inhomogeneous static magnetic fields. One possible explanation for the variation of isotropic resolution in 3QMAS and 5QMAS experiments has been proposed, based on the difference of excitation versus the quadrupolar tensor orientation with respect to the RF-field [13]. However, this explanation does not apply when using strong RF-field amplitudes. Therefore, the only remaining explanation for the changes of isotropic resolutions, may thus arise from the homogeneous relaxation term [11]. This term leads, in unified ppm scaling, to a broadening (full-width at half-maximum: FWHM) equal to

$$B\ (\mathrm{ppm}) = \frac{10^6\cdot(1+\alpha R)}{\alpha\pi\nu_0\cdot|R-p|\cdot T_{CT}}. \quad (5)$$

Most of the time, T_p and T_{CT} relaxation time values are close, and hence $\alpha \approx 1$. The broadenings described in Table 1 correspond to 3QMAS, 5QMAS, DQF-STMAS, and DQ-STMAS experiments, in the case of $\alpha = 1$.

It is important to note that homogeneous broadenings largely increase with the spin value. Indeed, they are multiplied by a factor of ca. 16, 7.5, and 20, in 3QMAS, DQF-STMAS, and DQ-STMAS, respectively, when increasing the spin value from 3/2 to 9/2 (Table 1).

In the case of all STMAS-based experiments, ST coherences are submitted to first-order quadrupole interactions during t_1. When the nuclei undergo molecular motions with a frequency approximately equal to the quadrupole interaction, the homogeneous transverse relaxation times of the ST coherences decrease largely [15]. This is not the case for the CT and MQ coherences involved in MQMAS, which are only submitted to second-order quadrupole interactions. In STMAS-based experiments, these motions result in a large decrease of the α ratio, and hence to a large increase of the broadening, especially for high-spin value, leading to the disappearing of the signal: