

6 Satellite MAS NMR Spectroscopy

6.1 Satellite Spectrum

Satellite signals are part of the first-order quadrupole-broadened NMR spectra of half-integer quadrupolar nuclei. They give rise to satellite MAS sideband if a nonselective (or at least partially selective) excitation is used, and if the MAS frequency is larger than the second-order broadening and smaller than the first-order broadening. Their intensity results mainly from the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions, whereas the predominant intensity of the center band is due to the $-1/2 \leftrightarrow +1/2$ transition. Weak satellite MAS signals are usually not included in the spectroscopy of the second-order quadrupole-broadened central transition of powder samples. However, satellites can be used to increase the resolution of second-order quadrupole-broadened spectra of half-integer quadrupolar nuclei.

The fundamental equation for satellite spectroscopy,

$$\begin{aligned} \nu_{m,m+1} - \nu_L = \nu_{\text{iso}} + \nu(\alpha, \beta, \eta) &= -\frac{\nu_Q^2}{6\nu_L} \left\{ \frac{1}{5} [I(I+1) - 9m(m+1) - 3] \left(1 + \frac{\eta^2}{3}\right) \right. \\ &\quad \left. + \left[I(I+1) - \frac{17}{3}m(m+1) - \frac{13}{6} \right] g(\alpha, \beta, \eta) \right\} \\ &= -\frac{\nu_Q^2}{6\nu_L} \left\{ \frac{1}{5} F^{(0)}(I, m) \left(1 + \frac{\eta^2}{3}\right) + F^{(4)}(I, m) g(\alpha, \beta, \eta) \right\}, \end{aligned} \quad (6.01)$$

was introduced in Section 1 as Eq. (1.68). This equation describes the second-order quadrupole shift under MAS conditions. The function $g(\alpha, \beta, \eta)$ is given in Table 1.2. The first summand in Eq. (6.01) exhibits a rank-0 term and describes the isotropic quadrupole shift. The second summand is a rank-4 term and causes the anisotropic shift or broadening for powder spectra. Table 6.1 gives values for the factors $F^{(0)}$ and $F^{(4)}$ as functions of the nuclear spin I and the magnetic quantum number m . Please note that we use the convention of $m \leftrightarrow m+1$ transitions, and that the mirror satellites give identical values, since we have $F^{(0,4)}(I, m) = F^{(0,4)}(I, -m-1)$; see Eq. (6.01). The values for $F^{(0,4)}(I, m)$ in Table 6.1 depend on the notations in Eq. (6.01), including the notation of the function $g(\alpha, \beta, \eta)$. They can vary by a constant factor in other representations of the equation in the literature. But the ratios with respect to the central transition in Table 6.1 are independent of the notation. The ratio $F^{(0)}(I, m)/F^{(0)}(I, -1/2)$ describes as a factor the relative change of the isotropic quadrupole shifts of a satellite pair with respect to the central transition. The ratio $F^{(4)}(I, m)/F^{(4)}(I, -1/2)$ is the corresponding factor for the spread of the anisotropy. Some authors [1-3] denote these transitions $\pm(q-1) \leftrightarrow \pm q$ and use the term STMAS ratio $R(I, q)$ for the ratio $F^{(4)}(I, m)/F^{(4)}(I, -1/2)$ in our notation. This concept should not be confused with the MQMAS ratio $R(I, p)$; see Eq. (5.02).

An equation similar to Eq. (6.01) and the values in the last two columns of Table 6.1 were used by Samoson [4] in 1985, in order to open a way for "satellite transition high-resolution NMR of quadrupolar nuclei in powders". The proposed procedure [4] is simple: The average resonance shift of the first sidebands of the inner satellites (outside the range of the static spectrum of the central transition) can be experimentally obtained as the center of gravity $\nu_{\text{iso } \pm 1/2, \pm 3/2}$. The center of gravity of the center band of the central transition gives the other experimental value $\nu_{\text{iso } -1/2, +1/2}$. The difference is $\Delta\nu_{\text{iso}} = \nu_{\text{iso } -1/2, +1/2} - \nu_{\text{iso } \pm 1/2, \pm 3/2}$. A theoretical equation for $\Delta\nu_{\text{iso}}$ can be derived from Eq. (6.01):

$$\Delta\nu_{\text{iso}} = \nu_{\text{iso } -1/2, +1/2} - \nu_{\text{iso } \pm 1/2, \pm 3/2} = -\frac{\nu_Q^2}{6\nu_L} \left(1 + \frac{\eta^2}{3}\right) \frac{9}{5}. \quad (6.02)$$

Inserting Eq. (6.02) into Eq. (6.01) we obtain for the central transition ($m = -1/2$),

$$v_{\text{iso } -1/2,+1/2} = \frac{\Delta v_{\text{iso}}}{9} \left[I(I+1) - \frac{3}{4} \right]. \quad (6.03)$$

For spin-5/2 nuclei we have $v_{\text{iso } -1/2,+1/2} = \frac{8}{9} \Delta v_{\text{iso}}$. This value has to be added to the resonance position, in order to obtain the chemical shift. Thus, the determination of Δv_{iso} allows the splitting of the isotropic shift into the quadrupole shift and chemical shift (see Eq. (6.03)) and the determination of the quadrupole parameters (see Eq. (6.02)).

Table 6.1. The factors $F^{(0,4)}(I, m)$ in Eq. (6.01) and the ratios of the satellites with respect to the central transition, $F^{(0,4)}(I, m)/F^{(0,4)}(I, -1/2)$.

I, m	$F^{(0)}(I, m)$	$F^{(4)}(I, m)$	$\frac{F^{(0)}(I, m)}{F^{(0)}(I, -1/2)}$	$\frac{F^{(4)}(I, m)}{F^{(4)}(I, -1/2)}$
3/2, -1/2	3	3	-	-
3/2, -3/2	-6	-8/3	-2	-8/9
5/2, -1/2	8	8	-	-
5/2, -3/2	-1	7/3	-1/8	7/24
5/2, -5/2	-28	-44/3	-7/2	-11/6
7/2, -1/2	15	15	-	-
7/2, -3/2	6	28/3	2/5	28/45
7/2, -5/2	-21	-23/3	-7/5	-23/45
7/2, -7/2	-66	-36	-22/5	-12/5
9/2, -1/2	24	24	-	-
9/2, -3/2	15	55/3	5/8	55/72
9/2, -5/2	-12	4/3	-1/2	1/18
9/2, -7/2	-57	-27	-19/8	-9/8
9/2, -9/2	-120	-200/3	-5	-25/9

Jäger [5] performed MAS satellite studies of various inorganic compounds. He called it SATRAS (satellite-transition spectroscopy) and obtained by the increase of resolution valuable information about the distributions of the interaction parameters in glasses and ceramics [5].

The sideband analysis of satellites that was introduced by Samoson [4] and further developed by Jäger [5] certainly increases the resolution, since the second-order broadening of the inner satellites is reduced, e. g. for $I = 5/2$ nuclei by the factor of 7/24; see Tab. 6.1. But the present satellite MAS spectroscopy, which was introduced by Gan [6], totally removes the second-order quadrupole broadening by a 2D STMAS experiment. STMAS (satellite transition magic-angle spinning) uses the correlation between the satellite and central transitions, in order to refocus the signal decay caused by the second-order quadrupole effect. The resolution of the spectra is similar to the resolution of MQMAS spectra. But the single-quantum nature of the satellite transitions increases the sensitivity of STMAS with respect to MQMAS. Takashi *et al.* [7] performed an ^{27}Al STMAS and MQMAS study of kaolin and glass. They found that STMAS and 3QMAS exhibit comparable resolution for both crystalline and non-crystalline materials whereas STMAS exhibits higher sensitivity than MQMAS for both types of materials [7]. However, a search of articles on NMR spectroscopy of quadrupolar nuclei in the WEB of Science for the time period 2009-2012 yielded 65 and 6 hits for the keywords "MQMAS" and "STMAS", respectively. The disadvantage of STMAS with respect to MQMAS is the fact that STMAS requires an extremely accurate setting of the magic angle, $|\theta - \theta_m| < 0.002^\circ$ [2, 6, 8], to average out the first-order quadrupolar effects. The request is moderated, if a self-compensation for angle misset (SCAM) [2, 9] is used at the expense of sensitivity.

6.2 Experimental Implementation of STMAS

Two reviews were recently published which describe STMAS NMR in detail: one by Gan [8], who introduced STMAS, and another by Ashbrook and Wimperis [2], who refined it. Our comparatively limited presentation of STMAS starts with the description of two pulse sequences in Fig. 6.1.

The maximum possible RF power should be used for the pulses P_1 and P_2 . The length of both pulses can be determined by variation of the pulse durations until the maximum signal is obtained. The maximum RF power is usually insufficient to excite a very broad satellite spectrum by a non-selective 90° pulse. For example, $\nu_{\text{RF}} = 100$ kHz gives a $\pi/2$ -pulse duration of $2.5 \mu\text{s}$ and the first zero-crossings of the excitation at ± 400 kHz; see Section 2. For a satellite spectrum exceeding this range, the optimum flip-angle of the pulse becomes less than 90° [8].

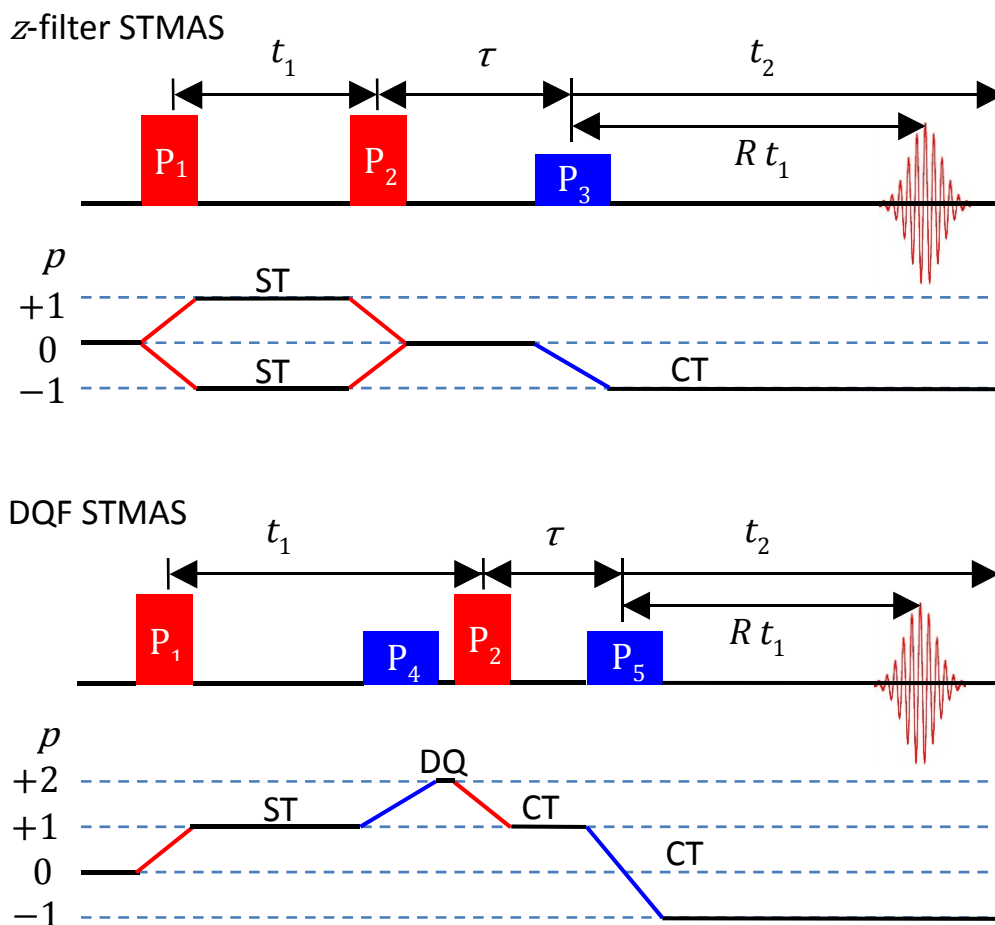


Fig. 6.1. Pulse sequences and coherence transfer pathways for the rotor-synchronized ($t_1 = n \tau_{\text{rot}}$) STMAS experiments. ST and CT denote developments in the satellite transitions and the central transition, respectively. P_1 and P_2 are strong pulses with the maximum possible value of ν_{RF} . Much weaker selective pulses for the central transition are P_3 , flip-angle 90° , and P_4 and P_5 , flip angle 180° . The delay τ lasts a few rotation periods for the z-filter and a few milliseconds for the shifted echo. The amplitude-modulated z-filter pulse sequence and coherence transfer pathways are given on the top, whereas the double-quantum filtered (DQF) phase-modulated shifted-echo STMAS experiment is shown on the bottom.

A three-pulse sequence as shown in the top figure of Fig. 6.1 was originally used by Gan [6]. The z-filter sequence is still in use for STMAS. It has the same phase cycling as the 2D exchange experiments and selects both $p = \pm 1$ coherence orders during the evolution period t_1 [8]. Spectra obtained by this sequence show a strong unresolved diagonal peak due to the unwanted presence of magnetization in the central transition during t_1 . The resolved cross peaks are not perpendicular to the δ_1 scale. The latter can be remediated by a shearing procedure analogous to the shearing of z-filter MQMAS spectra; see Section 5. Likewise, split- t_1 shifted-echo STMAS experiments [2] analogous to those in MQMAS can be performed in order to avoid the necessity of shearing. The

unwanted diagonal peak can be quenched by presaturation of the central transition using a weak, selective and very long pulse prior to the z -filter sequence.

The most promising approach for the removal of a strong unwanted signal is the double-quantum filter (DQF), which was introduced by Kwan and Gan [10]. The shifted-echo DQF STMAS experiment (see Fig 6.1, bottom) includes a weak π -pulse P_4 a few microseconds before the second strong pulse P_2 , which is selective to the central transition. This inversion pulse converts the inner satellite-transition coherences to double-quantum coherences, $p = +2$, because it inverts $|\pm 1/2\rangle$ states while leaving the other spin states undisturbed. 2Q coherences are converted back to single-quantum coherences $p = +1$ by the strong pulse P_2 . Finally, the selective pulse P_5 causes the inversion to $p = -1$, in order to obtain the shifted echo. The unwanted diagonal signal is removed by an appropriate 16-step phase cycling [10].

Finally, some modification should be mentioned that can result in faster performance of STMAS experiments. STARTMAS [2, 11] stands for "satellite transition acquired in real-time MAS" and is based on the DQF STMAS [10] experiment. In the original version [11] it uses repeated π -pulses and repeated acquisition in between like CPMG MAS. Ultrafast STMAS [12] is based on the z -filter STMAS pulse sequence. It provides a two-dimensional STMAS spectrum by detection of multiple isotropically encoded echoes within a one-dimensional scan and subsequent splicing and rearrangement into a 2D matrix [12].

6.3 References

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