SATELLITE TRANSITION HIGH-RESOLUTION NMR OF QUADRUPOLAR NUCLEI IN POWDERS

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Relative shifts of the central and satellite transition lines determine the precise iosotropic chemical shifts of $I = 5/2$ and $9/2$ quadrupolar nuclei in solids. The satellite transition is conveniently measured through the rotation sidebands.

1. Introduction

Determination of the analytically important chemical shifts in polycrystalline or amorphous solids is readily achieved in high-resolution magic-angle spinning (MAS) NMR spectroscopy of spin $I = 1/2$ nuclei [1]. In the case of ^{13}C and ^{29}Si nuclei, it has found wide and effective application.

Apart from spin $I = 1/2$ nuclei, lines of quadrupolar nuclei with half-integer spin have finite width and are shifted from the position of the isotropic chemical shift σ_{CS} under MAS conditions due to interaction with the electric field gradients (EFGs) [2]. If the characteristic lineshapes [2] are obscured by other, mostly ill-defined, interactions, determination of the chemical shifts

$$\sigma_{CS} = \sigma_{CG} - \sigma_{QS} \tag{1}$$

from MAS NMR spectra that yield a value only for the line centre of gravity σ_{CG} is not a trivial matter.

Two methods may be used for the determination of the chemical shifts:

(i) repetition of the measurements at several magnetic fields and

(ii) registration of 2D spectra [3].

Both methods, based on registration of the prominent central transition $(1/2,-1/2)$ signal, may involve experimental difficulties in practice.

In this study we demonstrate an alternative approach to the determination of isotropic chemical shifts, based on the registration of the satellite transition $(m,m-1)$, $m \neq 1/2$ spectra. In order to analyze its feasibility, the positions and intensities of the detectable lines are to be considered.

2. Theoretical

All single-quantum transition lines with the exception of the $(1/2,-1/2)$ transition, in stationary powders consisting of many randomly oriented particles, are broadened due to the first-order quadrupole interaction. This line broadening is in principle reduced to zero by fast magic-angle spinning and the resulting single crystal lines are determined by the second-order quadrupole interaction term, expressed as

$$\omega^{(2)}(m) = \omega_L \sigma_{QS}(m) + \frac{3}{128} \frac{C_Q^2}{\omega_L} \frac{6I(I+1) - 34m(m-1) - 13}{I^2(2I-1)^2} g(\alpha, \beta, \eta) . \tag{2}$$

Here the quadrupole shift of the centre of gravity $\sigma_{QS}(m)$ of the powder pattern $(m,m-1)$ transition lineshape follows from an equivalent expression, presented in ref. [2], by integrating over all possible crystallite orientations:

$$\sigma_{QS}(m) = \frac{1}{\omega_L} \frac{1}{4\pi} \int \omega^{(2)}(m) \, d\mu \, d\alpha = -\frac{3}{40} \frac{C_Q^2}{\omega_L^2} \frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2} (1 + \tfrac{1}{3}\eta^2) . \tag{3}$$

α and β ($\mu = \cos\beta$) determine the orientation of the spinner with respect to the principal axes system of the EFG tensor, characterized by its strongest component C_Q/eQ and asymmetry η. eQ is the nuclear quadrupole moment and ω_L the Larmor frequency.

The orientation-dependent second term of (2), where

$$g(\alpha,\beta,\eta) = \tfrac{1}{10}(-3 + 30\mu^2 - 35\mu^4) + \tfrac{1}{3}\eta(1 - 8\mu^2 + 7\mu^4)\cos 2\alpha + \tfrac{1}{18}\eta^2[(-3 + 10\mu^2 - 7\mu^4)\cos^2 2\alpha - \tfrac{4}{5}] , \quad (4)$$

determines the width of the particular transition.

As evidenced by (2), symmetrical transitions $(m,m-1)$ and $(-m+1,-m)$ overlap and need not be separately considered. The lineshapes of all transitions are similar, but may be mirror images.

Quadrupole shifts of satellite transitions relative to the central transition are shown as the first line of entries in table 1 for any I,m combination.

The effective amplitude of a satellite transition line is determined by three factors, assuming a uniform excitation:

(i) It depends on the inherent quantum intensity, determined by the squared ratio of the matrix elements, corresponding to a satellite and the central transitions,

$$\propto 2\frac{I(I+1) - m(m-1)}{I(I+1) + \frac{1}{4}} . \quad (5)$$

(ii) The second factor is the relative linewidth of the satellite with respect to the central transition, determined by the ratio of the coefficients in (2),

$$\frac{\Delta(m)}{\Delta(1/2)} = \frac{6I(I+1) - 34m(m-1) - 13}{6I(I+1) - \frac{9}{2}} \quad (6)$$

The relative linewidth characterizes the resolution enhancement and is shown in the second line of entries in table 1 (a negative sign means a reversed lineshape).

The total linewidth of the $(m,m-1)$ transition (in Hz) is determined by extremal values of the function (4) and for the central transition is equal to

$$\Delta(1/2) = \frac{9}{56}\frac{C_Q^2}{\omega_L}\frac{I(I+1) - \frac{3}{4}}{I^2(2I-1)^2}(1 + \tfrac{1}{6}\eta)^2 . \quad (7)$$

(iii) The third factor takes into account the actual observable intensity of the satellite transition signal.

First-order quadrupole line broadening may exceed by several orders of magnitude the rotation frequency ω_{rot}. The corresponding ratio is much larger than one,

$$\kappa = \frac{3(2m-1)}{4I(2I-1)}\frac{C_Q}{\omega_{rot}} \gg 1 , \quad (8)$$

and therefore the intensity of the signal is distributed among numerous ($N = 1, 2, ...$) rotation sidebands, situated at $\pm N\omega_{rot}$ from the centreband [4].

The satellite transition rotation centreband is usually obscured by the prominent central transition line. The satellite transition parameters can, however, be conveniently registered on the low-order rotation sidebands ($N = 1$ or 2), if these do not contain any contribution from the central transition. Due to the symmetry of the $(m,m-1)$ and $(-m+1,-m)$ transitions, the $+N$ and $-N$ sidebands are identical and their average position provides the centre of gravity of the satellite transition line $\sigma_{CG}(m)$:

Generally, the satellite transition MAS lineshapes (and quadrupole shifts of the centre of gravity), presented by the rotation sidebands, are dependent on the ratio κ. Exact evaluation of this dependence is not possible analytically and demands time-consuming numerical computations. In this study we rather seek

Table 1
Quadrupole shifts (first line), linewidths (second line) and amplitudes (third line) of the $(m,m-1)$ satillite transition first sidebands in relation to the central transition for different values of I

	$m = 3/2$	$m = 5/2$	$m = 7/2$	$m = 9/2$
$I = 3/2$	−2.000			
	−0.8889			
	0.031			
$I = 5/2$	−0.1250	−3.5000		
	0.2917	−1.8333		
	0.12	0.0056		
$I = 7/2$	0.4000	−1.4000	−4.4000	
	0.6222	−0.5111	−2.4000	
	0.055	0.027	0.0022	
$I = 9/2$	0.6250	−0.5000	−2.3750	−5.0000
	0.7639	0.0556	−1.1250	−2.7778
	0.046	0.28	0.0070	0.0012

for easy-to-use approximate expressions, supported by numerical calculations and experimental data.

Numerical computation of the relative intensity of a single sideband $I_N(\kappa)$ can be done in full analogy with a procedure described in ref. [5] by Herzfeld and Berger for chemical shift anisotropy, if one uses in their formula (30) coefficients that are relevant for the quadrupole interaction:

$$\bar{A}_1 = \kappa(-\tfrac{1}{2}\sqrt{2}\sin 2\beta + \tfrac{1}{6}\sqrt{2}\eta \sin 2\beta \cos 2\alpha)\,,$$
$$\bar{A}_2 = \tfrac{1}{2}\kappa\,[\tfrac{1}{2}\sin^2\beta + \tfrac{1}{6}\eta(1+\cos^2\beta)\cos 2\alpha]\,,$$
$$\bar{B}_1 = \kappa\eta\,\tfrac{1}{3}\sqrt{2}\sin\beta \sin 2\alpha\,,$$
$$\bar{B}_2 = \tfrac{1}{2}\kappa\eta\,\tfrac{1}{3}\cos\beta \sin 2\alpha\,. \tag{9}$$

The calculated normalized intensities of the first rotation sideband $I_1(\kappa)$ are, to a good approximation, inversely proportional to $1/\kappa$, if $\kappa > 10$:

$$I_1(\kappa) \approx k(\eta)/\kappa\,, \quad \text{where} \quad k(\eta) = 0.55\,, \quad \eta = 0\,;$$
$$= 0.63\,, \quad \eta = 0.6\,;$$
$$= 1.0\,, \quad \eta = 1.0\,. \tag{10}$$

An estimate for the amplitude of the satellite transition signal, relative to the amplitude of the central transition, is obtained as a product of (5) and (10), divided by the relative width (6). Representative values for $\kappa = 15$, $\eta = 0$ are shown in the third line of entries in table 1.

Numerical calculations also put a useful limit on the full rotation-dependent change of the quadrupole shift $\sigma_{QS}(m, \kappa)$ of the low-order sidebands if $\kappa > 10$:

$$\sigma_{QS}(m) \lesssim \sigma_{QS}(m,\kappa) \lesssim \sigma_{QS}(m) \pm \tfrac{1}{8}\Delta(m)\,. \tag{11}$$

The sign of the κ-dependent change is positive (upper signs) if the corresponding satellite transition lineshape is reversed in comparison with the central transition lineshape.

3. Results and discussion

The suitability of any transition for high-resolution NMR work is determined by the corresponding linewidth and intensity, if the position of the line is reasonably well defined. From the data presented in table 1 it is evident that the best alternatives are the (3/2,1/2) transition for $I = 5/2$ and (5/2,3/2) transition for $I = 9/2$ nuclei. For moderate quadrupole interaction ($C_Q = 1$ MHz, $I = 5/2$ and $C_Q = 3.6$ MHz, $I = 9/2$; $\eta = 0$, $\omega_{rot} = 5$ kHz) the satellite transition signal, detected as the first rotation sideband, is only about an order of magnitude less in amplitude than the central transition signal. The abovementioned satellite transitions also offer a significant gain in resolution and thus provide a convenient and precise means for the determination of the chemical and quadrupole shifts. The isotropic chemical shift can, to a good approximation, be calculated from the readily observed centres of gravity of the central transition and an average of the low-order rotation sidebands of the satellite transition.

As evidenced by table 1, due to the proximity of the (3/2,1/2) transition line to the chemical shift position for $I = 5/2$ nuclei, limiting values for the latter can be expressed in a convenient η-independent manner from eq. (3) as

$$\sigma_{CG}(3/2) > \sigma_{CS}$$
$$> \sigma_{CG}(3/2) - \tfrac{1}{9}[\sigma_{CG}(3/2) - \sigma_{CG}(1/2)]\,. \tag{12}$$

The expression (12) gives the chemical shift of ^{27}Al nuclei at 11.7 T with a precision equal to

$$\tfrac{1}{18}[\sigma_{CG}(3/2) - \sigma_{CG}(1/2)]$$

$$= \frac{3}{80}\,\frac{1}{I^2(2I-1)^2}\,\frac{C_Q^2}{\omega_L^2}(1+\tfrac{1}{3}\eta^2) < 0.1 \text{ ppm}$$

for $C_Q = 2$ MHz, $\eta = 0.5$.

The (3/2,1/2) satellite transition was observed experimentally in the ^{27}Al NMR spectrum of the mineral albite, see fig. 1. The central transition lineshape at 130.3 MHz is defined mainly by the relatively strong quadrupole interaction ($C_Q = 3.37$ MHz, $\eta = 0.63$ [6]) and the curve fitting provides for the determination of the chemical shift $\sigma_{CS} = 63.2 \pm 0.1$ ppm (relative to 3 M $Al(NO_3)_3$ water solution). From the rotation sidebands $\sigma_{CG}(3/2) = 63.4$ ppm and according to (12) $\sigma_{CS} = 63.2 \pm 0.2$ ppm. For comparison, the central transition centre of gravity is located at 58.7 ppm and the linewidth at half height is 6.8 ppm.

The relative intensity of the satellite transition sideband ($\omega_{rot} = 7.2$ kHz, $\kappa = 70$) follows from (5) and (10) as

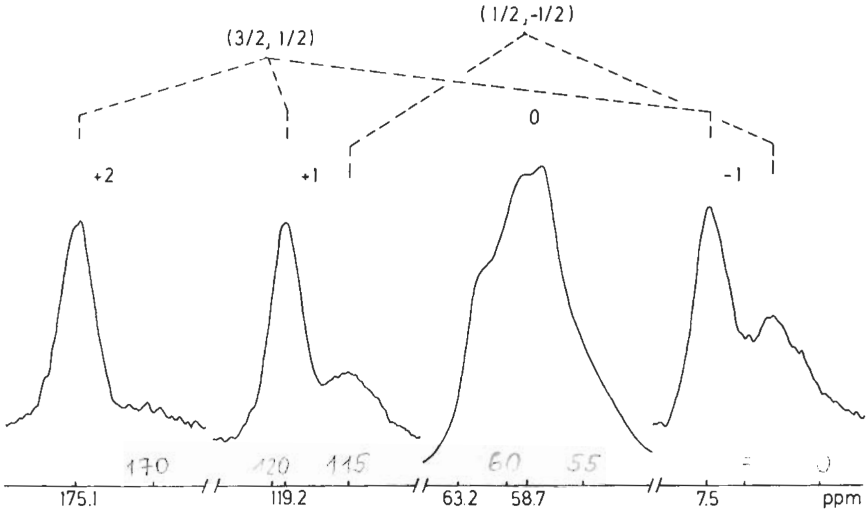

Fig. 1. The ^{27}Al NMR spectrum of the mineral albite. The rotation sidebands N = +2, +1, −1 are shown 15 × magnified. The position of the isotropic chemical shift (63.2 ppm) is shifted by +4.5 ppm from the central transition line centre of gravity, but almost coincides with the average of the rotation sideband positions of the (3/2,1/2) transition.

$$\tfrac{16}{9} I_1(70) \approx 0.016$$

and agrees well with the experimental value of 0.018 for the low-order sidebands. The width of sidebands demonstrates a threefold gain in resolution as compared to the central transition line.

The registration of satellite transition spectra, though of great potential value in solid-state high-resolution NMR, may encounter some difficulties in practical applications. Firstly it demands ultimate precision in the setting of the magic angle in order to reduce to zero the first-order quadrupole line broadening, and secondly, intensity of the signal may be stronly reduced by a fast transition-dependent quadrupole relaxation.

Nevertheless, signal accumulation and an ultra-fast and stable sample spinning using a side-supported cylindrical rotor make registration of the satellite transitions, easily recognized as a large number of almost equal rotation sidebands, a convenient method for the refinement of the chemical shifts of quadrupolar nuclei in solids.

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