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Feasibility of the overtone NMR for half-integer quadrupolar nuclei

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Abstract

We present a theoretical description and computer simulations for the overtone NMR of half-integer quadrupolar nuclei in solids. It is shown that the overtone NMR has the ability to produce high-resolution solid NMR spectra for the quadrupolar nuclei under magic angle spinning conditions. We demonstrate that when polycrystalline $^{23}Na_2MoO_4$ is placed in the static magnetic field of 7.05 T, the direct detection of the overtone NMR is possible. It becomes, however, apparent that indirect detection schemes are required to obtain the usual NMR spectra that have separated resonance lines corresponding to chemically non-equivalent sites.
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1. Introduction

Quadrupolar nuclei with half-integer spins are present in many important engineering materials such as ceramic materials, clay minerals, and functional zeolites. Most of these materials exhibit their useful functions in the solid state. Hence, it is useful to obtain solid-state high-resolution NMR spectra of half-integer quadrupolar nuclei for finding out the origin of the functionalities.

Magic angle sample spinning (MAS) yields high-resolution NMR spectra for rare spin-1/2 nuclei in solids. However, for quadrupolar nuclei having half-integer spins, it cannot completely remove the effects of anisotropic interactions on the central transitions (CTs). In the MAS spectra, frequency distributions arising from the second-order quadrupolar interactions still remain. In order to solve this problem, sample double-rotation (DOR) [1–3], dynamic-angle sample spinning (DAS) [1,4,5], and multiple-quantum magic angle spinning (MQ-MAS) [6–8] have already been developed. They all succeeded in averaging out the second-order broadening in the CT resonance lines.

DOR experiments perform complicated rotations of polycrystalline samples. DAS experiments are accompanied by rapid switching of a sample spinning axis. Special NMR probeheads are required in these experiments; it is rare for us to find such probeheads in most NMR laboratories.

On the other hand, special equipments are not necessary for MQ-MAS experiments. These experiments may be performed using MAS NMR probeheads. In addition, the pulse sequences generally comprises two or three radio-frequency (rf) pulses [6–8]. Thus the MQ-MAS experiments have found widespread acceptance in the field of solid-state NMR. However, we must not forget that they also have a serious problem: the sensitivities are generally poor. One reason for this problem is that they are two-dimensional experiments. Furthermore, an accumulation of more than ten free induction decay (FID) signals is needed in order to obtain pure absorption mode spectra [8]; the signal produced by the accumulation is as large as that for a single scan. This is another important reason.

In this Letter, we investigate whether or not the overtone (OT) NMR [9] for half-integer quadrupolar nuclei can be an alternative to DOR, DAS, or MQ-MAS. In order to elucidate the resolution and sensitivity of the OT NMR, we derive its theoretical description. Furthermore, computer simulations are performed to depict the complete motions of the OT magnetizations subjected to a static magnetic field and an OT rf pulse. More extensive discussion about the detection schemes will be described on the basis of the simulation results.

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2. Theory

For the CTs and satellite transitions of half-integer quadrupolar nuclei, the rf responses have been presented in several papers [10–14]. However, the theories given in [10–14] are not suited for studies of the OT NMR. In this section, we introduce the total Hamiltonian of half-integer quadrupolar nuclei according to the procedure given in [15,16]. After the total Hamiltonian is obtained, the rf responses and FID signals of the quadrupolar nuclei can be calculated using the Liouville–von Neumann equation, $\mathrm{d}\rho(t)/\mathrm{d}t = -\mathrm{i}[\mathscr{H}, \rho(t)]$. In addition, we limit the discussion to spin-3/2 nuclei in this Letter; but the procedure that will be shown in this section also applies to quadrupolar nuclei having half-integer spins other than spin-3/2 (spin-5/2, spin-7/2, etc.).

The total laboratory frame Hamiltonian for a half-integer quadrupolar nucleus in a polycrystalline solid is written as

$$\begin{aligned}\mathscr{H}^{\mathrm{T}} &= \mathscr{H}^{\mathrm{LAB}}_{\mathrm{int}} + \mathscr{H}^{\mathrm{LAB}}_{\mathrm{rf}}(t) \\ &= \mathscr{H}_{\mathrm{Z}} + \mathscr{H}_{\mathrm{cs}} + \mathscr{H}_{\mathrm{Q}} + \mathscr{H}^{\mathrm{LAB}}_{\mathrm{rf}}(t),\end{aligned} \tag{1}$$

with

$$\mathscr{H}_{\mathrm{Z}} = -\gamma B_0 I_z = -\omega_0 I_z. \tag{2}$$

Here, $\mathscr{H}_{\mathrm{Z}}$ is the Zeeman interaction for the quadrupolar spin in a static magnetic field B_0, and $\mathscr{H}_{\mathrm{cs}}$ is the full chemical-shielding Hamiltonian. $\mathscr{H}_{\mathrm{Q}}$ is the untruncated quadrupolar interaction characterized by the quadrupole frequency $\omega_{\mathrm{Q}} = (e^2qQ/\hbar)/[4I(2I-1)]$ and the asymmetric factor η; it can be written in the principal axis frame as

$$\mathscr{H}_{\mathrm{Q}} = \omega_{\mathrm{Q}}\left\{\sqrt{6}T^{\mathrm{PAS}}_{20}(\mathbf{I}) + \eta\left(T^{\mathrm{PAS}}_{22}(\mathbf{I}) + T^{\mathrm{PAS}}_{2-2}(\mathbf{I})\right)\right\}, \tag{3}$$

with the irreducible spherical tensor operators $\{T^{\mathrm{PAS}}_{2m}(\mathbf{I})\}_{-2\leqslant m\leqslant 2}$. $\mathscr{H}^{\mathrm{LAB}}_{\mathrm{rf}}(t)$ denotes the coupling between the quadrupolar spin and a linearly polarized oscillating field:

$$\mathscr{H}^{\mathrm{LAB}}_{\mathrm{rf}}(t) = 2\omega_1(I_x\sin\chi + I_y\cos\chi)\cos(\omega_{\mathrm{irr}}t + \phi), \tag{4}$$

where ω_1 is the amplitude of two rotating components that constitute $\mathscr{H}^{\mathrm{LAB}}_{\mathrm{rf}}(t)$, ω_{irr} is the oscillation frequency, and χ is the orientation of the NMR coil with respect to the static Zeeman field [15,16].

In order to handle the Hamiltonian without difficulty, the following operations are needed: (i) the diagonalization of $\mathscr{H}_{\mathrm{Z}} + \mathscr{H}_{\mathrm{Q}}$ and (ii) the rotation of all the spin operators about the z axis of the new frame (where $\mathscr{H}_{\mathrm{Z}} + \mathscr{H}_{\mathrm{Q}}$ is diagonalized) [16]. After these transformations, with the assumption that $\omega_{\mathrm{irr}} \approx 2\omega_0$, we obtain the following expressions:

$$\mathscr{H}^{\mathrm{R}} = \mathscr{H}^{\mathrm{R}}_{\mathrm{int}} + \mathscr{H}^{\mathrm{R}}_{\mathrm{rf}}(t), \tag{5}$$

with

$$\mathscr{H}^{\mathrm{R}}_{\mathrm{int}} = \begin{bmatrix} 3\omega^{(1)} - 3/2\omega^{(2a)} + 3/2\omega_{\mathrm{cs}} & 0 & 0 & 0 \\ 0 & -3\omega^{(1)} + 3/2\omega^{(2b)} + 1/2\omega_{\mathrm{cs}} & 0 & 0 \\ 0 & 0 & -3\omega^{(1)} - 3/2\omega^{(2b)} - 1/2\omega_{\mathrm{cs}} & 0 \\ 0 & 0 & 0 & 3\omega^{(1)} + 3/2\omega^{(2a)} - 3/2\omega_{\mathrm{cs}} \end{bmatrix}, \tag{6}$$

$$\mathscr{H}^{\mathrm{R}}_{\mathrm{rf}}(t) = \begin{bmatrix} 3\omega_{\mathrm{off}}/2 & 0 & \sqrt{3}\omega_1\varepsilon(f\sin\chi + g\cos\chi)\mathrm{e}^{\mathrm{i}\phi} & 0 \\ 0 & \omega_{\mathrm{off}}/2 & 0 & \sqrt{3}\omega_1\varepsilon(f\sin\chi + g\cos\chi)\mathrm{e}^{\mathrm{i}\phi} \\ \sqrt{3}\omega_1\varepsilon(f^*\sin\chi + g^*\cos\chi)\mathrm{e}^{-\mathrm{i}\phi} & 0 & -\omega_{\mathrm{off}}/2 & 0 \\ 0 & \sqrt{3}\omega_1\varepsilon(f^*\sin\chi + g^*\cos\chi)\mathrm{e}^{-\mathrm{i}\phi} & 0 & -3\omega_{\mathrm{off}}/2 \end{bmatrix}. \tag{7}$$

In these equations, $\omega^{(1)}$ is the first-order quadrupolar shift and $\varepsilon = \omega_{\mathrm{Q}}/\omega_0$. Two quantities, f and g, depend on the Euler angles between the laboratory frame and the principal axis frame for the quadrupolar interaction. The explicit forms are presented in [9,15]. ω_{off} is the offset frequency of the OT irradiation pulse; it is given by $\omega_{\mathrm{off}} = \omega_{\mathrm{irr}} - 2\omega_0$. $\omega^{(2a)}$ and $\omega^{(2b)}$ are both the second-order quadrupolar shifts; they are given by $\omega^{(2a)} = (\omega^2_{\mathrm{Q}}/\omega_0)(2|f|^2 + |g|^2)$ and $\omega^{(2b)} = (\omega^2_{\mathrm{Q}}/\omega_0)(2|f|^2 - |g|^2)$, respectively. Note that Eqs. (6) and (7) are expressed in term of the quadrupole-perturbed eigenstates $\{|\psi_{3/2}\rangle, |\psi_{1/2}\rangle, |\psi_{-1/2}\rangle, |\psi_{-3/2}\rangle\}$ of the spin-3/2 nucleus [15,16]. In what follows, they are represented as $|1\rangle = |\psi_{3/2}\rangle$, $|2\rangle = |\psi_{1/2}\rangle$, $|3\rangle = |\psi_{-1/2}\rangle$, and $|4\rangle = |\psi_{-3/2}\rangle$.

In this study, we employed the following reference frames to perform the computer simulations: the principal axis frame of the quadrupolar interaction P, an arbitrarily chosen spinner fixed frame S, and the laboratory frame L. The Euler angles relating these frames are as follows:

$$P \overset{(\alpha,\beta,\gamma)}{\rightarrow} S \overset{(\omega_{\mathrm{r}}t,\theta_{\mathrm{m}},0)}{\rightarrow} L,$$

where ω_{r} is the sample spinning speed and θ_{m} is the magic angle. (In the case of the stationary-state calculations, ω_{r} and θ_{m} were set to zero.) The computer simulations were carried out using a multiple-time-step method [17] on the basis of Eqs. (5)–(7). The chemical shift anisotropy was omitted for simplicity and the static magnetic field was assumed to be 7.05 T.

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