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Second-order quadrupole interaction based detection of ultra-slow motions: Tensor operator framework for central-transition spectroscopy and the dynamics in hexagonal ice as an experimental example

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ABSTRACT

The second-order quadrupolar broadening of the central transition of nuclear probes with half-integer spins I is demonstrated to be useful to detect ultraslow molecular motions. On the basis of density matrix calculations explicit expressions are derived for quadrupolarly modulated sin–sin and cos–cos signals of selectively excited nuclei with $I = 3/2$, 5/2, 7/2, and 9/2. These correlation functions are suitable for implementation in two-dimensional exchange spectroscopy as well as for stimulated-echo experiments. As an application, ^{17}O measurements of the reorientational correlation function of water molecules in hexagonal ice are presented.

1. Introduction

Detection of molecular and ionic motions in the milliseconds to seconds range is often accomplished using two-dimensional exchange spectroscopy and stimulated-echo time-domain techniques. These methods are applicable to spin-1/2 nuclei that allow for an excitation of their entire NMR spectra which are typically broadened by chemical shift interactions. If the broadening is predominantly quadrupolar in nature, there are only a few but very important nuclear probes such as deuterons ^{2}H [1] and the lithium isotope ^{6}Li [2] with spin $I = 1$ as well as the spin-3/2 species ^{7}Li [3] and ^{9}Be [4] that are typically suitable for the direct detection of ultra-slow motions. For ^{6}Li it is often possible to spin out the anisotropic part of the interactions so that an exchange spectroscopy based on isotropic shifts can be implemented [5–7]. Under favorable circumstances this type of spectroscopy can be implemented for other nuclei as well [8,9].

Like for ^{2}H, the spectral width of the spin-3/2 probes ^{7}Li and ^{9}Be is governed by the first-order quadrupolar interaction which does usually not exceed a few 100 kHz. Such lines thus can be excited non-selectively by suitable radio-frequency irradiation. But for most quadrupolar nuclei with half-integer spin, e.g., ^{23}Na ($I = 3/2$) and ^{17}O ($I = 5/2$) representing important examples, the spectra are typically several MHz broad. Hence, only the region of the central transition, which in powder samples then is broadened by second-order quadrupolar effects, is easily amenable to radio-frequency excitation.

The tensor algebra on which multidimensional spectroscopy relies is fully worked out for spin-1 [10–12] and spin-3/2 nuclei [4,13,14] for which consideration of the first-order quadrupolar broadening is usually sufficient. However, a theoretical treatment for second-order quadrupolar perturbation based multidimensional exchange spectroscopy at high field is not available, so far.

In the present work, we develop the conceptual basis for such a technique focusing on the excitation of and detection in the central-line transition region of half-integer quadrupolar spins in non-rotating solids. In addition to our theoretical treatment we also provide ^{17}O stimulated-echo experiments on hexagonal ice as an example to demonstrate the feasibility of our approach. The time scales accessible with the present technique generally range from sub-milliseconds to the limit set by the longitudinal relaxation which in solids is often beyond seconds. This kind of stimulated-echo measurements can thus complement analyses of central transition line shapes that are broadened by second-order quadrupolar interactions [15–20].

2. Theory

Most of our calculations will be in terms of normalized irreducible spherical tensor operators T_{lm} with rank l and order m which are related to the standard irreducible spherical tensor operators $\hat{T}_{lm} = \lambda_{l,I}^{-1} T_{lm}$ [21] using the normalization factors [22]

$$\lambda_{l,I} = \left[\frac{(2I+1)2^l(2l)!(2I-l)!}{(l!)^2(2I+l+1)!}\right]^{\frac{1}{2}}. \quad (1)$$

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If convenient we use the operators $T^{(\alpha)}_{lm} = (T_{lm} \pm T_{l-m})/\sqrt{2}$ where α denotes symmetric (s) or anti- symmetric (a) combinations. All calculations will be performed in the rotating frame. In the present treatment spin relaxation is not taken into account.

2.1. Quadrupolar interactions

The secular part of the first-order quadrupolar interaction for a given spin I can be written as [1]

$$H^{(1)}_{\mathrm{Q}} = \omega_{20} T_{20} = \omega_{20} \frac{\lambda_{2,I}}{\sqrt{6}} \left[3I_z^2 - I(I+1)\right], \tag{2}$$

with T_{20} as defined in Eq. (2) and the quadrupolar precession frequency

$$\omega_{20} = \sqrt{\frac{3}{2}} \frac{\Omega_{\mathrm{Q}}}{\lambda_{2,I}} \frac{1}{2} (3\cos^2\theta - 1 - \eta \sin^2\theta \cos 2\phi). \tag{3}$$

For the coupling frequency Ω_{Q} different definitions exist in the literature [23,24]. Here the definition $\Omega_{\mathrm{Q}} = 2\pi C_{\mathrm{Q}}/[2I(2I-1)]$ in units of rad/s is adopted [24]. The use of normalized spherical tensor operators requires to keep the normalization factor $\lambda_{l,I}$ if the standard definition [23,25] of the quadrupole coupling constant $C_{\mathrm{Q}} = e^2qQ/h$ (in units of Hertz) is to be retained. η identifies the asymmetry parameter. The polar angle θ and the azimuthal angle ϕ describe the orientation of the electrical field gradient (EFG) tensor in the laboratory frame in the usual fashion.

In the laboratory frame the secular part of the second-order quadrupolar interaction can be written as [26]

$$H^{(2)}_{\mathrm{Q}} = \omega_{10} T_{10} + \omega_{30} T_{30}, \tag{4}$$

with the precession frequencies ω_{10} and ω_{30} for which explicit expressions are provided in Appendix A. Different representations of $H^{(2)}_{\mathrm{Q}}$ are given in [23,24,27–29]. The third-order quadrupolar interaction, $H^{(3)}_{\mathrm{Q}}$, leaves the central transition unaffected and needs not be taken into account [30]. The second-order quadrupolar contribution to the Zeeman spin levels m_I with $m_I \in \{I, I-1, \ldots, -I\}$ is [26]

$$\omega^{(2)}_{\mathrm{Q},m_I} = \frac{\Omega_{\mathrm{Q}}^2}{2\omega_{\mathrm{L}}} m_I \Big\{ \left[3m_I^2 - I(I+1)\right] V^{\mathrm{Q}}_{00} + \left[12m_I^2 + 3 - 8I(I+1)\right] V^{\mathrm{Q}}_{20} + \left[34m_I^2 + 5 - 18I(I+1)\right] V^{\mathrm{Q}}_{40} \Big\}.$$

Here ω_{L} denotes the Larmor frequency. The parameters V^{Q}_{k0} with $k = 0, 2, 4$ are called new spherical harmonics and can be calculated from [26,31]

$$V^{\mathrm{Q}}_{k0} = \sum_n D^k_{n0}(\theta, \phi, \gamma) A_{kn}. \tag{5}$$

The Wigner rotation matrix elements D^k_{n0} depend on the Euler angles θ, ϕ, and γ and on the coefficients A_{kn} which are provided in Appendix A.

The central transition frequency can be written as [26]

$$\omega_{\mathrm{c},I} = \omega^{(2)}_{\mathrm{Q},1/2} - \omega^{(2)}_{\mathrm{Q},-1/2} = \frac{\Omega_{\mathrm{Q}}^2}{4\omega_{\mathrm{L}}} [4I(I+1) - 3] \left(\frac{1}{2} V^{\mathrm{Q}}_{00} + 4V^{\mathrm{Q}}_{20} + 9V^{\mathrm{Q}}_{40} \right), \tag{6}$$

and can be described also in terms of ω_{10} and ω_{30} as

$$\omega_{\mathrm{c},I} = \lambda_{1,I} \left[\left(\frac{1}{2} \middle| \widehat{T}_{10} \middle| \frac{1}{2} \right) - \left(-\frac{1}{2} \middle| \widehat{T}_{10} \middle| -\frac{1}{2} \right) \right] \omega_{10} + \lambda_{3,I} \left[\left(\frac{1}{2} \middle| \widehat{T}_{30} \middle| \frac{1}{2} \right) - \left(-\frac{1}{2} \middle| \widehat{T}_{30} \middle| -\frac{1}{2} \right) \right] \omega_{30}, \tag{7}$$

with the matrix elements $(m'_I \mid \widehat{T}_{lm} \mid m_I)$. Exploiting the Wigner–Eckart theorem [21], the relevant matrix elements are $\left(\pm\frac{1}{2} \middle| \widehat{T}_{10} \middle| \pm\frac{1}{2} \right) = \pm\frac{1}{2}$ and $\left(\pm\frac{1}{2} \middle| \widehat{T}_{30} \middle| \pm\frac{1}{2} \right) = \mp\frac{3}{8\sqrt{10}}(2I+3)(2I-1)$. This simplifies the equation for $\omega_{\mathrm{c},I}$ to

$$\omega_{\mathrm{c},I} = \lambda_{1,I}\omega_{10} - \frac{3}{4}\frac{1}{\sqrt{10}}(2I+3)(2I-1)\lambda_{3,I}\omega_{30}. \tag{8}$$

For an explicit expression of $\omega_{\mathrm{c},I}$ see Appendix A. For instance for $I = 3/2$ one gets $\omega_{\mathrm{c},\frac{3}{2}} = (\omega_{10} - 3\omega_{30})/\sqrt{5}$.

Using the arrow notation we define matrix elements $q_{lm\alpha,l'm'\alpha'}(\omega_{10}, \omega_{30}, t)$ that describe the transition

$$T^{(\alpha)}_{lm} \xrightarrow{(\omega_{10}T_{10} + \omega_{30}T_{30})t} q_{lm\alpha,l'm'\alpha'}(\omega_{10}, \omega_{30}, t) T^{(\alpha')}_{l'm'}, \tag{9}$$

under the action of $H^{(2)}_{\mathrm{Q}}$ from a state $T^{(\alpha)}_{lm}$ to another state $T^{(\alpha')}_{l'm'}$. The coherence transfer amplitudes q arising under the second-order quadrupolar interaction, Eq. (4), can be computed in a straightforward manner and the results are shown in Table 1.

2.2. Selective excitation of the central line

For a hard pulse, i.e., when the radio-frequency ω_{RF} dominates the internal interactions within the sample, the magnetization is rotated by a certain flip angle

$$\beta = \omega_{\mathrm{RF}} t, \tag{10}$$

during the pulse duration t about an axis φ. The corresponding Hamiltonian is

$$H^{\varphi}_{\mathrm{RF}} = \omega_{\mathrm{RF}} I_{\varphi}, \tag{11}$$

with $I_{\varphi} = I_y \cos\varphi + I_x \sin\varphi$. The operators I_x and I_y are related to the spherical tensor operators through the relations $I_x = -\lambda^{-1}_{1,I} T^{(\mathrm{a})}_{11}$ and $I_y = \mathrm{i}\lambda^{-1}_{1,I} T^{(\mathrm{s})}_{11}$.

If the quadrupolar interaction is sizeable, i.e., if Ω_{Q} is not much smaller than ω_{RF}, then it has to be considered during a finite pulse length. In this case the Hamilton operator for a soft pulse, i.e., when the internal interaction is comparable to or larger than ω_{RF}, can be written as

$$H^{\varphi,\mathrm{soft}}_{\mathrm{RF}} = H^{(1)}_{\mathrm{Q}} + H^{\varphi}_{\mathrm{RF}} = \omega_{20} T_{20} + \omega_{\mathrm{RF}} I_{\varphi}. \tag{12}$$

To obtain the matrix elements $x^{(I,\mathrm{soft})}_{lm\alpha,l'm'\alpha'}(\omega_{\mathrm{RF}}, \omega_{20}, t)$ that describe the transition

$$T^{(\alpha)}_{lm} \xrightarrow{(\omega_{20}T_{20} + \omega_{\mathrm{RF}}I_x)t} x^{(I,\mathrm{soft})}_{lm\alpha,l'm'\alpha'}(\omega_{\mathrm{RF}}, \omega_{20}, t) T^{(\alpha')}_{l'm'}, \tag{13}$$

under a soft x-pulse from a state $T^{(\alpha)}_{lm}$ to another state $T^{(\alpha')}_{l'm'}$ one needs to diagonalize the Hamilton operator $H^{x,\mathrm{soft}}_{\mathrm{RF}} = \omega_{20}T_{20} + \omega_{\mathrm{RF}}I_x$, see, e.g., [3,32–36]. The transition matrix elements for a soft y-pulse can be gained from those for a soft x-pulse by simply rotating the former about the z-axis by an angle of $\pi/2$.

If the quadrupolar precession frequency ω_{20} of Eq. (3) fulfills the condition $\omega_{20} \gg \omega_{\mathrm{RF}}$ and if the excitation width arising from the finite pulse duration does not exceed the strength of the internal interactions, the system can be treated as a fictitious spin-1/2 system [23,37]. Focusing on the central line of powdered samples [23,38], i.e., for the important case $\omega_{20} \gg \omega_{\mathrm{RF}}$, Eqs. (12) and (13) can be replaced by a simpler description. This is because in the limit of large Ω_{Q} the selective excitation of the central line can be described by choosing the appropriate 2×2 submatrix out of a suitable representation of the operators I_x and I_y. This leads one to the definition of the central line operators I_{xc} and I_{yc}. The matrix elements of I_{xc} and I_{yc} can be calculated according to

$$(m'_I|I_{\mathrm{xc}}|m_I) = (m'_I| \pm \mathrm{i}I_{\mathrm{yc}}|m_I) = \begin{cases} (m'_I|I_x|m_I) & \text{for } m'_I, m_I \in \{-1/2, 1/2\} \\ 0 & \text{otherwise} \end{cases},$$