Off-Resonance Nutation NQR Spectroscopy of Powders

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Z. Naturforsch. 50a, 957–960 (1995); received April 12, 1994

The peculiarities of nutation NQR spectra of nuclei with spin \( I = 3/2 \) in powders are considered in the case of a resonance offset. An equation, which takes into account the offset is given for the determination of the asymmetry \( \eta \). It is shown that structural of monocrystals by means of nutation spectroscopy are possible.

Introduction

Nuclear quadrupole resonance is one of the most informative methods for the investigation of solids. The possibilities of nutation spectroscopy, however, are little known yet, although such investigations on crystals allow to obtain new information.

As a result of the offset, the experimental nutation frequency deviation always takes place in experiments. In fact such a frequency, i.e. the resonance offset, arises in the nutation spectrum. This leads to strict requirements for the stability of the power supply the transmitter. In order to excite the spectrum, the offset \( \Delta v \) and the r.f. pulse duration must meet the condition \( \Delta t_w \ll 1 \).

A theoretical analysis for spin systems \( I = 1 \) and \( 3/2 \) was performed in order to investigate peculiarities of two-dimensional nutation NQR spectra of nitrogen, chlorine and other nuclei in powder and monocrystalline samples. The calculation of the response of the nuclear spin system with electric quadrupole interactions to r.f. pulses with a frequency deviation from resonance is achieved by means of nonstationary perturbation theory with the assumption that the nuclear spin system has no time for the establishment of a new equilibrium in the rotating frame and that, beside, the spin system is insulated from the lattice.

Theory and Methods

In order to obtain undistorted nutation spectra, the variable duration of the r.f. pulse must remain smaller than the relaxation times of the sample, i.e. \( t_w \ll T_1^*, T_2, T_1 \). This demands a high power of the transmitter. The field amplitude \( B_1 \) must be constant during the \( t_w \) pulse duration, otherwise a false signal arises in the nutation spectrum. This leads to strict requirements for the stability of the power supply the transmitter. In order to excite the spectrum, the offset \( \Delta v \) and the r.f. pulse duration must meet the condition \( \Delta t_w \ll 1 \).

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The intensity of the free induction signals for $I = 3/2$ after an r.f. pulse with width $t_w$ was obtained in [3] in the form

$$
G(t, t_w) = \frac{\gamma}{\xi} R^2(\theta, \phi) \sqrt{4 \xi^2 \cos^2 \xi t_w + \Delta \omega^2 \sin^2 \xi t_w} 
\cdot \sin \xi t_w [\omega_0 (t - t_w) + \beta],
$$

where

$$
\alpha = \frac{\gamma B_1}{4}, \quad \xi = \frac{1}{2} \sqrt{4 m^2 + \Delta \omega^2}, \quad m = \frac{\alpha R(\theta, \phi)}{\sqrt{3 + \eta^2}},
$$

$$
R(\theta, \phi) = \sqrt{4 \eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6 \eta \cos 2 \phi)},
$$

$$
\beta = \arccos \left( \frac{U}{\sqrt{U^2 + V^2}} \right),
$$

$$
U = \cos \xi t_w \cos \Delta \omega t_w + \frac{\Delta \omega}{2 \xi} \sin \xi t_w \sin \Delta \omega t_w,
$$

$$
V = - \cos \xi t_w \sin \Delta \omega t_w + \frac{\Delta \omega}{2 \xi} \sin \xi t_w \cos \Delta \omega t_w.
$$

$\theta$ and $\phi$ represent the orientation of the r.f. field in the principal axis system (PAS) of the EFG tensor.

If a frequency offset is present (as it usually is) the phase of the free induction decay (FID) changes when the r.f. pulse duration $t_w$ is increased. In order to overcome this problem, all spectra obtained after the first Fourier transformation of $G(t, t_w)$ (i.e., with respect to $t$) must be phase corrected before the second Fourier transformation, i.e., with respect to $t_w$.

The nutation frequency $2 \xi$ depends on the angles $\theta$ and $\phi$. Therefore, in the case of a powder, the powder average must be calculated for these frequencies. The result will be given for the various relative frequency deviations for $I = 1$ and $I = 3/2$ [4].

**Results and Discussion**

If $S(t) = S_0 \sin \omega_0 t$ is the NQR signal at the input of the phase sensitive detector (PSD), and $A(t) = A_0 \sin (\omega t + \psi)$ is the reference signal, then at the output of the PSD we have the signal $S_{PSD} \propto S_0 \cos (\Delta \omega t + \psi)$, where $\Delta \omega = \omega - \omega_0$ is the offset frequency, $\omega_0$ is the Larmor frequency, and $\omega$ denotes the ratio frequency of the spectrometer. For the signal (1) at the output of the phase sensitive detector we have

$$
G_{PSD}(t, t_w) \propto \frac{\alpha}{\xi} R^2(\theta, \phi) \sin \xi t_w \sqrt{4 \xi^2 \cos^2 \xi t_w + \Delta \omega^2 \sin^2 \xi t_w} \cos [\Delta \omega (t - t_w) - \beta + \psi],
$$

With

$$
\cos \beta = \frac{U}{\sqrt{U^2 + V^2}}, \quad U^2 + V^2 = \frac{1}{4} \xi^2 (4 \xi^2 \cos^2 \xi t_w + \Delta \omega^2 \sin^2 \xi t_w) \quad \text{and}
$$

$$
\cos [\Delta \omega (t - t_w) - \beta + \psi] = \cos [\Delta \omega (t - t_w) + \psi] U + \sin [\Delta \omega (t - t_w) + \psi] V,
$$

(2) can be rewritten as

$$
G_{PSD}(t, t_w) \propto \frac{\alpha}{\xi} R^2(\theta, \phi) \sin \xi t_w \cdot \{ U \cos [\Delta \omega (t - t_w) + \psi] + V \sin [\Delta \omega (t - t_w) + \psi] \},
$$

and then we have

$$
G_{PSD}(t, t_w) \propto \frac{\alpha}{\xi} R^2(\theta, \phi) \sin \xi t_w \{ U \sin \Delta \omega t_w
+ V \cos \Delta \omega t_w \sin (\Delta \omega t + \psi) + (U \cos \Delta \omega t_w
+ V \sin \Delta \omega t_w) \cos (\Delta \omega t + \psi) \}. \quad (3)
$$

With

$$
\sin \xi t_w (U \sin \Delta \omega t_w + V \cos \Delta \omega t_w) = \frac{\Delta \omega}{4 \xi} (1 - \cos 2 \xi t_w)
$$

and

$$
\sin \xi t_w (U \cos \Delta \omega t_w - V \sin \Delta \omega t_w) = \frac{1}{2} \sin 2 \xi t_w
$$

(5) it follows

$$
G_{PSD}(t, t_w) \propto \frac{\alpha}{\xi} R^2(\theta, \phi) \{ 2 \xi \sin 2 \xi t_w \cos (\Delta \omega t + \psi)
- \Delta \omega \cos 2 \xi t_w \sin (\Delta \omega t + \psi) + \Delta \omega \sin (\Delta \omega t + \psi) \}. \quad (6)
$$

The spectrum of a monocrystal contains one nutation frequency $2 \xi$.

Equation (6) shows that the offset $\Delta \omega$ leads to the appearance of a zero frequency component in the nutation spectrum. This requires a correction of the constant part in the signal $G_{PSD}(t, t_w)$.

We simulated the nutation NQR spectra for $I = 1$ and $3/2$ by means of the histogram-method. The form of the 2D nutation NQR spectrum for a powder ($I = 3/2, \eta \neq 0$) with the frequency offset $\Delta \omega/\gamma B_1 = 0.3$ is shown in Figure 1.

Obviously, a 2D nutation NQR spectrum, which consists of several lines, allows to determine, which lines are causes by inequivalent positions of the EFG tensor axes relative to the radiofrequency field direc-
Fig. 1. The simulated off-resonance 2D-nutation NQR spectrum for powder \( I = 3/2; \Delta \omega / \gamma B_1 = 0.3; \eta = 0.5 \)

tion, and which lines are caused by various quadrupole interactions. The projection of the 2D nutation spectrum to one of the two axes can be used for the discussion.

The nutation frequency for a monocrystal \( I = 3/2 \) is

\[
2 \xi = \sqrt{\frac{4 \eta^2}{3 + \eta^2} [4 \eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6 \eta \cos 2 \varphi)] + \Delta \omega^2}.
\]

We transform (7):

\[
\sin^2 \theta = 1 - \frac{(2 \xi^2 - \Delta \omega^2)}{(4 \alpha^2)}.
\]

Equation (8) presents a cone with the symmetry axis \( z \). The nutation frequency for the monocrystal remains constant if the axis of the radio-frequency coils is directed along the conic surface, the parameter of the conic surface depending on the deviation and the asymmetry parameter \( \eta \) of EFG tensor. The equation of the conic surface for spin \( I = 3/2 \) has the form of (8). For spin \( I = 1 \) the cones for the second-order frequencies \( \omega_+ \) and \( \omega_- \) are imaginary, but it is real for the forbidden transition \( \omega_A = \omega_+ - \omega_- : \)

\[
\sin^2 \theta = 1 - \frac{(2 \xi^2 - \Delta \omega^2)}{(4 \alpha^2)}. \tag{9}
\]

An analogous situation for monocrystals in the case of NQR in a constant magnetic field arises when the field is directed along the “zero splitting conic surface” [5, 6]. Then for \( I = 3/2 \) in monocrystals instead of four NQR lines only three can be observed [5].

The measurement of the conic surface parameters from the nutation spectrum of a monocrystal allows to determine the asymmetry parameter \( \eta \). If the radiofrequency field \( B_1 \) is directed along the symmetry axis \( z \) of the cone (that is, \( \theta = 0 \)), then

\[
\eta = \frac{3(4 \xi^2 - \Delta \omega^2)}{\sqrt{16 \alpha^2 - 4 \xi^2 + \Delta \omega^2}}. \tag{10}
\]

Since the number of “conic surfaces” in the crystal is defined by the symmetry class of the crystal [6], the...
present method can be used for structure determinations.

The formulas for the NQR-frequencies in the rotating reference frame (RF) for monocrystals and half-integer spins were obtained in [7, 8]. These frequencies are equal to the nutation frequencies. For \( I = \frac{3}{2} \) we have

\[
\Omega_{RF} = 2 \xi = \sqrt{\frac{\Delta \omega^2 + \frac{4 \chi^2}{3 + \eta^2}}{\left[4 \eta^2 \cos^2 \theta + \sin^2 \theta(9 + \eta^2 + 6 \eta \cos 2 \varphi)\right]}}
\]  

For spin \( I = 1 \) and for the NQR frequency \( \omega_+ \), we obtain

\[
\Omega_{RF} = \frac{\sqrt{\Delta \omega^2 + (4 \chi)^2 \sin^2 \theta \cos^2 \varphi}}{\gamma / B_1}.
\]

The frequency singularities \( \omega_1, \omega_2 \) and \( \omega_3 \) [1] are obtained as functions of the offset \( \Delta \omega \) in the form

\[
\begin{align*}
\omega_1 &= \sqrt{\frac{4 \chi^2 \eta^2}{3 + \eta^2} + \Delta \omega^2}, \\
\omega_{2,3} &= \frac{4 \chi^2 (3 + \eta^2)}{3 + \eta^2} + \Delta \omega^2.
\end{align*}
\]

The formula for the experimental determination of the asymmetry parameter from nutation spectra has the form

\[
\eta = \frac{3 (\sqrt{\omega_3^2 - \Delta \omega^2} - \sqrt{\omega_2^2 - \Delta \omega^2})}{\sqrt{\omega_3^2 - \Delta \omega^2} + \sqrt{\omega_2^2 - \Delta \omega^2}}.
\]

In the case of a small frequency deviation \( \Delta \omega \ll 4 \chi \), instead of (14) a simplified formula is obtained:

\[
\eta \approx \frac{3 (\omega_3 - \omega_2)}{\omega_3 + \omega_2} \left(1 + \frac{\Delta \omega^2}{\omega_2 \omega_3}\right).
\]

The off-resonance simulated one-dimensional nutation spectrum for powder (\( I = 3/2, \eta = 0.5 \)) without the zero frequency component is present in Figure 2. The nutation frequency is given in relative units (2%/\( B_1 \)).

The knowledge of nutation NQR frequencies allows a unique solution of the problem of a simultaneous determination of the asymmetry parameter and the quadrupole coupling constant \( e^2 Qq \) not only for \( I = 3/2 \), but for any other spin (\( I > 1 \)), even if the measurement is carried out only for one quadrupole transition.

In conclusion, the nutation NQR-spectra of powder samples of \( I = 3/2 \), nuclei which are measured off-resonance, were interpreted in this work. This is essential for the experimental determination of the parameters \( e^2 Qq \) and \( \eta \) from “pure” NQR data for \( I = 3/2 \).

**Acknowledgements**

The authors thanks Professor Dr. U. Haeberlen of the Max-Planck-Institut für Medizinische Forschung, Heidelberg, for his hospitality and useful discussions. Financial support from the Gottlieb Daimler and Karl Benz Foundation is gratefully acknowledged.

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