Two-dimensional NQR using ultra-broadband electronics

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A B S T R A C T

We have recently developed an ultra-broadband instrument that can effectively excite and detect NMR and NQR signals over a wide frequency range. Our current system operates between 100 kHz and 3.2 MHz using an un-tuned sample coil. The major benefits of this instrument compared to conventional NQR/NMR systems include increased robustness, ease of use (in particular for multi-frequency experiments), and elimination of the need for tuning adjustments in the hardware. Here we describe its use for performing two-dimensional (2D) scans, which allow improved interpretation of complex NQR spectra by detecting the connected resonances. Our method relies on population transfers between the three energy levels of spin-1 nuclei (such as $^{14}$N) by using multi-frequency excitation and a single RF coil. Experimental results on pure samples and mixtures are also presented.

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1. Introduction

NQR is a valuable spectroscopic technique for non-invasive identification of chemicals, particularly hazardous ones such as explosives and drugs [1,2]. It is also used to investigate the symmetry and structure of crystals, the extent of ordering in macromolecules, and the nature of chemical bonds [3]. In addition, measuring the width of NQR lines makes it possible to investigate internal stresses, the presence of impurities, and ordering in crystals. Finally, many NQR transition frequencies depend strongly upon temperature, and sensitive thermometers have been built that exploit this effect.

Several research groups around the world are currently working on methods that use pulsed $^{14}$N NQR to detect explosives and illegal drugs, both of which almost always contain significant amounts of nitrogen [4,2,5]. In addition, companies are actively developing NQR-based field equipment designed to detect land mines and explosives concealed in luggage or on the human body. The technique is popular because the $^{14}$N nucleus ($I = 1$) is strongly quadrupolar, has almost 100% natural abundance, and produces NQR lines at reasonable frequencies (hundreds of kHz to several MHz), as shown in Fig. 1. Unfortunately, the figure also shows that this frequency range coincides with the popular medium-wave and shortwave bands (widely used for AM broadcasting and amateur radio transmissions), which makes external RF interference (RFI) a serious problem.

The electronics used for NQR is similar to that in NMR spectrometers [6]. It consists of an RF power source (transmitter), a coil to excite the spins and a detector circuit (receiver) which monitors the NQR signal produced by the sample. However, because every compound possesses a unique spectrum of NQR resonances, traditional NQR spectrometers have to be re-tuned to handle different spectral lines or different compounds. This issue limits the usefulness of NQR in many practical situations. In this paper we remove this restriction by using ultra-broadband transmitter and receiver electronics and an un-tuned sample coil [7,8]. The operating frequency of such an ultra-broadband system can be freely set over a wide range (0.1–3 MHz in our current system) entirely by software, while the sensitivity is comparable to narrow band (tuned) systems over the entire range. The absence of hardware re-tuning also allows this frequency to be rapidly switched, which simplifies multi-frequency measurements. For example, wait times for longitudinal relaxation can be utilized to acquire signals at other frequencies, thus decreasing the overall measurement time.

We have taken advantage of the ultra-broadband nature of our system to develop two-dimensional NQR techniques to simplify the analysis of complex molecules or mixtures. This development was inspired by multi-dimensional NMR, which is widely used in numerous applications including spectroscopy, relaxometry, and diffusometry. We use population transfers between the coupled energy levels of a single $^{14}$N site in a molecule as the basis of our two-dimensional experiments [9]. The relevant resonance frequencies can span a wide range both for a single site and between different sites and molecules. As a result, the use of an ultra-broadband system is extremely convenient, and perhaps even necessary.

This paper is organized as follows. Section 2 describes the theory of NQR population transfers using a single RF coil, and introduces two-dimensional NQR techniques based on such transfers.

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The lengths of the first and second pulses are denoted by \( t_{p1} \) and \( t_{p2} \), respectively. The signal-to-noise ratio is increased by repeating the detection pulses at an echo spacing of \( T_E \) and adding up the resultant train of spin echoes. This part of the sequence is the spin-locked spin echo (SLSE) pulse train that is commonly used in pulsed NQR [15–17].

The \(^{14}\text{N}\) atom has spin \( I = 1 \), so each nitrogen site in a molecule has three NQR frequencies that are either denoted by \( \omega_{x} \), \( \omega_{y} \), and \( \omega_{z} \) or by \( \omega_{x0} \), \( \omega_{y0} \), and \( \omega_{z0} \). We will use the latter convention. Assume that \( \omega_{RF,1} \) and \( \omega_{RF,2} \) are picked to match two of these frequencies for a single site, while the delay \( \tau \ll T_E \) to avoid relaxation. As a result of coupled population levels in the three-level system, saturating or inverting the second transition with the first pulse will change its NQR signal amplitude. Simple models can be used to calculate the expected amplitude changes [9]. In this way we can indirectly detect the presence of one NQR transition (at \( \omega_{RF,1} \)) by observing signals produced by another transition (at \( \omega_{RF,2} \)). Detection of multiple transitions makes identification of chemicals more reliable by greatly reducing the probability of false positives, such as those caused by RFI, ringing, and other artifacts. In certain cases this pulse sequence can also be used to increase the amplitude and SNR of the NQR signal at \( \omega_{RF,2} \).

Most prior work on multi-frequency NQR has used two or three transmit and receive coils that are oriented along orthogonal axes [11,12,14]. Each coil is typically tuned and impedance matched to one of the NQR frequencies of interest. However, we will show that our broadband system allows certain multi-frequency experiments to be performed on powder samples with a single RF coil, which significantly simplifies the experimental setup. The main limitation imposed by our current hardware on such experiments is that only a single RF frequency can be transmitted at any given time, so simultaneous multi-frequency excitation is not possible. However, the frequency can be changed very quickly (typically, within a microsecond), so in practice the excitation can be nearly simultaneous, or interleaved.

We assume that each RF pulse in the two-frequency sequence shown in Fig. 1 is selective, i.e., excites a single NQR transition. This assumption is valid when the separation between any two resonant frequencies greatly exceeds the excitation bandwidth. A detailed derivation of the resultant NQR signal amplitudes (denoted by \( s(p,q) \)) detected by a single RF coil has been provided in the Appendix. The results for a single crystallite in the sample are summarized in the matrix below, with the perturbation frequency (denoted by \( p \)) varying along the rows, and the detection frequency (denoted by \( q \)) varying along the columns. All amplitudes have been normalized to the case, denoted by \( s_0(p,q) \), when the initial pulse is absent (\( t_{p1} = 0 \)).

\[
\frac{s(p,q)}{s_0(p,q)} = \begin{bmatrix}
\cos(h_1q) & \cos(h_1b) & \cos(h_1c) \\
\frac{1}{3} \cos(h_1q) & \frac{1}{3} \cos(h_1b) & \frac{1}{3} \cos(h_1c) \\
\frac{1}{3} \cos(h_1q) & \frac{1}{3} \cos(h_1b) & \frac{1}{3} \cos(h_1c)
\end{bmatrix}.
\]

Here \( 0 < \eta < 1 \) is the asymmetry parameter of the electric field gradient (EFG) tensor fixed on the nuclear site, \( h_1 \equiv t_{p1} \omega_{RF,1} \) and \( b_1 \equiv t_{p2} \omega_{RF,2} \) are the nominal flip angles of the pulses, and \( \omega_{RF,1} \) and \( \omega_{RF,2} \) are the nutation frequencies of the first and second pulses, respectively. The special cases \( \eta = 0 \) and \( \eta = 1 \) have been excluded since some of the resonant frequencies become degenerate under these conditions, which violates our original assumption of selective RF pulses. In addition, \( a, b, \) and \( c \) are projection functions of the Euler angles \( \alpha \) and \( \beta \) that define the orientation of the RF coil with respect to the principal axis system of the EFG tensor (details are provided in the Appendix). These projection functions are also known as receptivity factors, since the received NQR signal amplitudes are proportional to them. They vary randomly from crystallite to crystallite in a powder sample.

We now consider the special case when the perturbation pulse saturates the corresponding transition. In this case \( \cos(h_1r) = 0 \) where \( r = a, b, \) or \( c \). Ignoring the diagonal terms, which correspond to the cases when the perturbation and detection pulses are at the same frequency, the normalized signal amplitudes are then given by

\[
\frac{s(p,q)}{s_0(p,q)} = \begin{bmatrix}
\frac{2}{3} & \frac{1}{3} \left( 1+\eta \right) & \frac{1}{3} \left( 1+\eta \right) \\
\frac{1}{3} \left( 1-\eta \right) & \frac{2}{3} & \frac{1}{3} \left( 1-\eta \right) \\
\frac{1}{3} \left( 1-\eta \right) & \frac{1}{3} \left( 1-\eta \right) & \frac{2}{3}
\end{bmatrix}.
\]

These expressions match those in [9]. In another special case, the perturbation pulse inverts the corresponding transition, thus...
producing the largest possible changes in signal amplitude. In this case \(\cos(\theta_1 q) = -1\) where \(r = a, b,\) or \(c\). Again ignoring the diagonal terms, the normalized signal amplitudes are now given by

\[
\frac{s(p, q)}{s_0(p, q)} = \left[ \frac{2\eta}{(3/\eta)} \times -\frac{2\eta}{(3/\eta)} \times -\frac{2\eta}{(3/\eta)} \times \right].
\]

The expressions derived so far are only valid for particular values of azimuthal angle \(\alpha\) and polar angle \(\beta\), i.e., for a particular crystallite. We have to average over all possible values of these angles to estimate the signal produced by a powder sample. The Jacobian in spherical coordinates is given by \(\sin(\beta)d\beta/d\alpha\), so the averaged signal is

\[
s_{av}(t) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi s(\alpha, \beta, t) \sin(\beta)d\beta d\alpha.
\]

2.2. Simulations

We have simulated the NQR signal expected from a powder sample using the expressions derived in the previous section. The signal has been estimated as a function of both \(\theta_2\) (the nominal flip angle of the detection pulse) and \(\theta_1\) (the nominal flip angle of the perturbation pulse).

If we assume that \(\eta = 0\) and plot the signal amplitude as a function of \(\theta_2\) in the absence of the perturbation pulse \((\theta_1 = 0)\) we obtain the usual NQR nutation curve for powder samples, which is given by

\[
s_{av}(\theta_2) = \sqrt{\frac{\pi}{2\eta}} J_{3/2}(\theta_2). \tag{5}
\]

Here \(J_{3/2}\) is the Bessel function of the first kind and order 3/2, and the maximum signal amplitude is obtained for a flip angle of \(\theta_2 \approx 120^\circ\). A slightly different function is obtained in the special case when \(\eta = 0\) [2]. The perturbation pulse changes the shape of this curve in a way that depends upon both the perturbation and detection frequencies. The effect can be shown more directly by plotting the normalized signal amplitude \(s/s_0\) as a function of the perturbation flip angle \(\theta_1\) (while keeping the value of \(\theta_2\) fixed).

Fig. 3 shows the simulated signal amplitudes for two of the six possible cases in which \(p \neq q\). We assumed \(\eta = 0.50\) in this example. In the first case \((p, q) = (x, y)\). In this case the perturbation pulse decreases the signal amplitude by up to 80%. The maximum decrease in signal amplitude occurs for \(\theta_1 \approx 305^\circ\). In the second case \((p, q) = (z, y)\). In this case the perturbation pulse increases the signal amplitude by up to 23%. The maximum increase in signal amplitude in this case also occurs for \(\theta_1 \approx 305^\circ\). In either case, long perturbation pulses saturate the corresponding transition.

2.3. Two-dimensional NQR experiment

We have used the two-frequency experiment shown in Fig. 2 as the basis of a two-dimensional (2D) NQR experiment. Eq. (1) shows that changes in the detected NQR signal amplitude at some frequency will be produced if and only if the perturbation frequency matches one of the other resonant frequencies of the same \(^{14}\text{N}\) site. This change constitutes unambiguous evidence that the two frequencies arise from the same site in the molecule. Furthermore,
the sign and magnitude of the change can be used to distinguish between the six possible pairs of perturbation and detection frequencies. The information contained in such off-diagonal signals may therefore be useful for simplifying complex NQR spectra even in the presence of external RFI.

The procedure for carrying out the 2D NQR experiment is summarized below:

1. Vary perturbation and detection frequencies \( \omega_{RF1} \) and \( \omega_{RF2} \) of the two-frequency sequence, detect signal amplitudes \( S(\omega_{RF1}, \omega_{RF2}) \) using SLESE.
2. Repeat step (1) after turning off the perturbation pulse to get reference amplitudes \( S_0(\omega_{RF1}, \omega_{RF2}) \).
3. Calculate the normalized difference spectrum \( \frac{S(\omega_{RF1}, \omega_{RF2})}{S_0(\omega_{RF1}, \omega_{RF2})} - 1 \).
4. Threshold the difference spectrum at an appropriate level to highlight coupling between NQR lines.

One useful feature of this experiment is that the difference operation cancels out static errors such as fixed RF interference, and receiver offsets. However, the range of NQR frequencies is typically much larger than the excitation bandwidth, which is approximately \( \pm \omega_1 \) for rectangular RF pulses. As a result, we need to step through both \( \omega_{RF1} \) and \( \omega_{RF2} \) to acquire the 2D spectrum, which makes it similar to a typical three-dimensional NMR experiment.

The frequency resolution along the perturbation axis \( \omega_{RF1} \) is determined by the excitation bandwidth of the perturbation pulse, which is approximately \( \pm \omega_1 \). On the other hand, resolution along the detection axis \( \omega_{RF2} \) is determined by the length of the signal acquisition window, and scales as \( 1/T_2 \) where \( T_2 \) is the SLESE echo spacing. Finally, the number of steps required to build up a 2D spectrum that covers a range of frequencies \( \Delta \omega \) along both axes scales as \( (\Delta \omega/\omega_1)^2 \).

2.4. Faster two-dimensional experiment

The number of steps required to generate a complete 2D NQR spectrum may take a prohibitively long time for many field applications, such as screening packages for explosives or verifying the authenticity of medicines. In such cases we can run a faster version of the 2D experiment to simplify complex NQR spectra, as summarized below:

1. Run the normal (single-frequency) SLE sequence while scanning the detection frequency \( \omega_{RF2} \) over the range of interest.
2. Identify \( M \) lines in the resulting one-dimensional (1D) NQR spectrum for further analysis.
3. Run the two-frequency experiment for each pair of lines identified in the previous step, resulting in a total of \( M(M - 1) \) experiments.
4. Compare the resultant signal amplitudes with the unperturbed values obtained in step (1). Changes in amplitude indicate the two lines originate from the same site in the molecule.

The number of steps required for this experiment scales as \( \Delta \omega/\omega_1 + M(M - 1) \). It is therefore much faster than the full 2D experiment if the 1D spectrum exhibits only a few lines of interest, i.e. if \( M \ll \Delta \omega/\omega_1 \).

3. Experiments

3.1. Setup

We have performed two-frequency \(^{14}\)N NQR experiments on various powder samples at room temperature using a single untuned sample coil and ultra-broadband transmitter and receiver electronics. One feature of this system is that pulse amplitudes are inversely proportional to the RF frequency, i.e., \( \omega_1 \propto 1/\omega_{RF} \). Pulse lengths were automatically adjusted during broadband frequency sweeps in order to compensate for this effect and maintain a constant flip angle. A commercial spectrometer (Kea 2, Magnetek) with a software interface was used to generate low-power RF signals and digitize the data. Most of the experiments described in this paper used a solenoidal sample coil that had ID = 2.8 cm and length = 8.4 cm. This coil consisted of 42 turns of AWG 18 magnet wire wound with a pitch of 0.2 cm, and had a measured self-inductance of 14.5 \( \mu H \) when assembled inside an aluminum shield box. A few experiments were performed with a larger solenoidal coil that had ID = 5.5 cm, length = 8.8 cm, and approximately the same inductance.

3.2. Two-frequency experiments

One of our samples was glycine, which has a single nitrogen site with quadrupolar coupling constant \( \omega_{o2} = 1193 \) kHz and asymmetry parameter \( \eta = 0.528 \), resulting in \( \omega_{o2}/(2\pi) \sim 1052 \) kHz, \( \omega_{o2}/(2\pi) \sim 737 \) kHz, and \( \omega_{o2}/(2\pi) \sim 315 \) kHz. The matrices below show the normalized signal amplitudes obtained from the two-frequency experiment for glycine when \( \theta_1 \approx 320^\circ, \theta_2 \approx 120^\circ \), and the delay between the first and second pulses was \( \tau = 100 \) \( \mu s \). The matrix on the left shows our theoretical predictions based on Eq. (1), while the one on the right shows our experimental results.

\[
\begin{bmatrix}
S/S_0^{\text{theory}} & 0.28 & 0.20 & 0.90 \\
0.60 & 0.28 & 2.33 & \\
0.83 & 1.24 & 0.28
\end{bmatrix}
,\quad
\begin{bmatrix}
S/S_0^{\text{exp}} & 0.21 & 0.57 & x \\
0.74 & 0.26 & 1.70 & x \\
0.87 & 1.12 & x
\end{bmatrix}
\]

There is good overall agreement between the theoretical and experimental results. In each case the theory correctly predicts the sign of the amplitude change, i.e., whether the signal amplitude increases \( (S/S_0 > 1 \text{ shown in bold}) \) or decreases \( (S/S_0 < 1 \text{ due to the perturbation pulse}) \). There is also reasonable quantitative agreement between the predicted and measured values of these ampli- tude changes. However, most of the measured changes are somewhat smaller than the theoretical values. This result may be due to pulse length calibration errors or the fact that the perturbation pulses, being longer, have narrower bandwidths than the detection pulses.

The fact that the amplitude of the \( \omega_{o2} \) transition can be increased by pumping at either of the other transitions can be used simply to increase signal-to-noise ratio (SNR), as shown in Fig. 4. This increase is particularly significant for the \( \omega_{o1} \) transition, since it is at the lowest frequency and hence has the smallest intrinsic SNR. In the case shown in the figure, pumping at the \( \omega_{o1} \) transition of glycine increased the signal amplitude detected at \( \omega_{o2} = 2\pi \times 315 \) kHz by about 70%, thus decreasing the required averaging time by a factor of almost 3.

The dependence of population transfer on the perturbation frequency can be visualized by scanning \( \omega_{RF1} \) around a resonance, while keeping the detection frequency \( \omega_{RF2} \) fixed at another resonance. The left-hand plot in Fig. 5 shows the results when \( \omega_{RF1} \) is scanned around \( \omega_{o2} \) while \( \omega_{RF2} \) is fixed at \( \omega_{o1} \), and the reverse. In both cases the signal amplitude detected at \( \omega_{RF2} \) decreases when \( \omega_{RF1} \) matches the resonance frequency of the indirectly-detected transition, as predicted by Eq. (1). However, when \( \omega_{RF1} \) is scanned around \( \omega_{o2} \) while keeping \( \omega_{RF2} \) fixed at \( \omega_{o1} \), the signal amplitude increases in one case and decreases in the other (see the right-hand plot in Fig. 5) again matching predictions. The observation of such patterns indicates that these three transitions arise from a single molecule, and thus reduces detection uncertainty.
100
0
40
20
20
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¼
10
80
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transitions are
−5
10
−5
60
over the
5
section. This experiment begins by identifying lines of interest in
the faster two-dimensional experiment described in the previous
of glycine (11.6 g) and sodium nitrite (9.5 g). In particular, we used
in a systematic fashion by scanning both
parameters include SLSE pulse length = 120
x
s and
l
x
s, respectively for
x
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s, and
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s, 160
μs and 800 μs, respectively for
l
s, These values correspond to nominal flip
angles of 120° in either case. In addition, we used an initial delay
τ = 100 μs, Nt = 90 echoes, and 512 scans (left-hand plot) or 2048 scans (right-hand plot).

Our broadband system can perform two-frequency experiments
in a systematic fashion by scanning both
l
s and
l
s over the
relevant frequency ranges in order to locate the pairs of frequen-
cies where signal reductions or enhancements occur, as described
in the previous section. Such behavior indicates unambiguously
that the corresponding frequencies are from the same site in the
molecule, thus allowing identification of molecules within an un-
known mixture. An example of such an experiment was performed
on glycine, and the resultant 2D NQR spectrum is shown in Fig. 6.
The cross-peaks corresponding to the
l
s and
l
s transitions are
clearly visible. The detailed shapes of these peaks are also shown
in Fig. 6. The latter plots show that the width of both cross-peaks
is significantly wider along the perturbation frequency axis than
along the detection frequency axis, as expected. In the former case
the width is approximately equal to the RF excitation bandwidth
l
s ≈ 2.8 kHz, while in the latter it is approximately equal to
1/T
acq = 1.95 kHz, where T
acq = 512 μs was the length of the signal
acquisition window within the SLSE detection sequence.

3.3. Experiments on mixtures

We performed two-frequency experiments on a binary mixture
of glycine (11.6 g) and sodium nitrite (9.5 g). In particular, we used
the faster two-dimensional experiment described in the previous
section. This experiment begins by identifying lines of interest in
the broadband 1D NQR spectrum of the sample. The measured
spectrum of this particular mixture from 700 kHz to 1100 kHz is
shown in Fig. 7. We have identified 3 lines of interest, which have
been labeled in the figure. The other lines were identified as exter-
nal RFI, since they persisted even when the sample was removed.

We then ran two-dimensional NQR experiments (see Fig. 2)
with the perturbation and detection frequencies set to each possi-
ble pair of lines. With three lines, there are a total of 6 experiments.
The resultant signal amplitudes were compared with the un-per-
turbed amplitudes at the same detection frequencies (shown in
Fig. 7). The measured fractional amplitude changes (in percent) after
256 scans (first and third rows) or 128 scans (second row) are
shown in Table 1. The uncertainty numbers correspond to ±1σ,
where σ is the standard deviation due to noise. Measured changes
that are significant at the 2.5σ level are highlighted in bold.

The fact that significant amplitude changes are only observed
between lines 1 and 3 indicates that lines 1 and 3 are coupled to
each other, but not to line 2. In addition, the fact that both changes
are negative suggests that line 1 corresponds to
l
s, and line 3 to
l
s, of a single 14N site. These findings match what we expect: lines
1 and 3 belong to glycine, while line 2 belongs to sodium nitrite.
However, there is also a significant decrease in signal amplitude
when we perturb line 1 with an initial pulse at line 2. This is not
due to coupling between lines 1 and 2, but because lines 2 and 3
are only separated by 15 kHz. As a result, the initial pulse at line
2 also partially saturates line 3. The RF amplitude can be decreased
to remove this effect at the cost of a longer experiment (reduced
Δω, so more frequency steps) and lower SNR (increased echo spac-
ing, so fewer echoes).
Conclusion

We have introduced the use of an ultra-broadband system for pulsed \(^{14}\)N NQR. Our system is robust, extremely easy to use, and capable of rapid RF frequency switching. This makes it simple to implement two-dimensional experiments that are useful for simplifying complex NQR spectra by separating the signals from different \(^{14}\)N sites. In addition, the broadband nature of our system allows it to easily detect multiple transitions from a single site, which makes chemical identification more reliable by greatly reducing the probability of false positives such as those caused by external RFI. It also allows wait times for longitudinal relaxation to be used to acquire signals at other frequencies, thus decreasing the overall measurement time.

We have also described the theoretical basis of such two-dimensional measurements. In particular, we have shown that a single RF coil can be used to implement simple two-frequency population transfer experiments on powder samples. Such population transfers change the detected signal amplitude only if the input frequencies match two of the three possible NQR frequencies of a single site, which allows us to unambiguously identify NQR lines that arise from a single site. These theoretical results have been confirmed with experiments on pure samples and a binary mixture.

Our work may be useful for laboratory applications of NQR, such as structural and chemical studies of a variety of compounds. It also has the potential for reducing the size and weight of portable NQR equipment by simplifying the required hardware. Such miniaturized systems may prove useful for field applications such as detection of explosives and authentication of medicines.

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Table 1

<table>
<thead>
<tr>
<th>Perturbation frequency</th>
<th>Detection frequency</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.5 ± 4</td>
<td>-25 ± 9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>-24 ± 8</td>
<td>-5 ± 9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>-50 ± 7</td>
<td>-5 ± 4</td>
<td></td>
</tr>
</tbody>
</table>
Appendix A. Derivation of Eq. (1)

The basic population transfer pulse sequence is shown in Fig. 2. It consists of an initial “perturbation” pulse of length \( t_{p1} \) at a frequency \( \omega_{0g1} \), followed by a spin-locked spin echo (SLSE) “detection” sequence at a frequency \( \omega_{0g2} \). The latter consists of a series of \( N_{s} \) pulses, each of length \( t_{p2} \), that are separated by the echo spacing \( T_{e} \). The delay \( T_{d} \) is assumed to be shorter than \( T_{s} \), so longitudinal relaxation between the perturbation and detection segments of the sequence can be neglected. We will calculate the amplitude of the NQR signal generated by spin-1 nuclei after the second RF pulse. The latter is equal to the initial amplitude of the exponential decay (with time constant \( T_{2g} \)) generated by the SLSE segment. We will denote the duration, phase, nutation frequency, and nominal flip angle of the first and second pulse by \( t_{p1}, \phi_{1}, \omega_{1g}, \) and \( \theta_{1} \equiv \omega_{1g} t_{p1} \) respectively, where \( i = 1 \) or \( 2 \). As an example, \( \omega_{1g} \) denotes the nutation frequency of the second pulse.

We will ignore all relaxation processes in our analysis, which will be performed in the principal axis system (PAS) frame of the electric field gradient (EFG) tensor fixed on the nuclear site. By definition, the EFG tensor is diagonal in this frame, which is denoted by \( \{x, y, z\} \). The latter is related to the laboratory frame \( \{x', y', z'\} \) by the Euler angles \( x, \beta, \) and \( \gamma \). We will also use a Cartesian basis \( \{|x,y,z\}\) to describe the state of the system. This choice makes the nuclear quadrupolar (NQ) Hamiltonian \( H_{0} \) diagonal for spin-1, which simplifies further analysis. In this basis we can write

\[
H_{0} = \frac{\omega_{0}}{3} \begin{bmatrix} 1 - \eta & 0 & 0 \\ 0 & 1 + \eta & 0 \\ 0 & 0 & -2 \end{bmatrix} = \begin{bmatrix} E_{x} & 0 & 0 \\ 0 & E_{y} & 0 \\ 0 & 0 & E_{z} \end{bmatrix}. \tag{A.1}
\]

Here \( 0 \leq \eta \leq 1 \) is the asymmetry parameter of the EFG tensor, and \( E_{x}, E_{y}, \) and \( E_{z} \) are the stationary nuclear energy levels. The latter define the three possible NQR transition frequencies \( \omega_{x} = E_{y} - E_{z} = \omega_{0}(1 + \eta/3), \omega_{y} = E_{x} - E_{z} = -\omega_{0}(1 - \eta/3), \) and \( \omega_{z} = E_{x} - E_{y} = -\omega_{0}(2\eta/3) \). These frequencies are also known as \( \omega_{1g}, \omega_{2g}, \) and \( \omega_{3g} \) respectively.

NQR transitions are excited by a single RF coil, which is assumed to generate an oscillating magnetic field with frequency \( \omega \) and phase \( \phi \) along the \( z \) axis of the laboratory frame. We also assume that the same coil is used during reception. The orientation of the RF magnetic field in the PAS coordinate system is then defined by the azimuthal and polar angles \( x \) and \( \beta \), respectively. As a result, its components along the principal axes are given by \( B_{z} = (B_{1}a)x, B_{y} = (B_{2}b)y, \) and \( B_{z} = (B_{1}c)z, \) where \( B_{1} \) is the magnitude of the field, and the quantities \( a, \) \( b, \) and \( c \) are projection parameters that are defined in terms of \( x \) and \( \beta \) as \( a = \cos(x) \sin(\beta), \) \( b = \sin(x) \sin(\beta), \) and \( c = \cos(\beta) \). In addition, \( x, y, \) and \( z \) denote the unit vectors along \( x, y, \) and \( z \), respectively.

Effective time-averaged Hamiltonians for single-frequency (selective) RF excitation can now be found using the interaction representation, which removes the dominant quadrupolar term [18]. To lowest-order, these quantities are given by

\[
\begin{align*}
\overline{H} &= \omega \frac{a_{0}a}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & ie^{-i\phi} \\ 0 & ie^{i\phi} & 0 \end{bmatrix}, \quad \omega = \omega_{x}, \\
\overline{H} &= \omega \frac{a_{0}b}{2} \begin{bmatrix} 0 & 0 & ie^{i\phi} \\ 0 & 0 & 0 \\ ie^{-i\phi} & 0 & 0 \end{bmatrix}, \quad \omega = \omega_{y}, \\
\overline{H} &= \omega \frac{a_{0}c}{2} \begin{bmatrix} 0 & ie^{-i\phi} & 0 \\ ie^{i\phi} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \omega = \omega_{z}.
\end{align*}
\tag{A.2}
\]

Here we have defined \( \omega_{1g} = -\beta_{1}, \) with the understanding that in general it may vary as a function of the RF frequency \( \omega \). It is important to note that such selective excitation is only possible when \( |\omega_{x}|, |\omega_{y}|, \) and \( |\omega_{z}| \) are distinct, which excludes the special cases \( \eta = 0 \) (for which \( |\omega_{x}| = |\omega_{y} \) and \( \omega_{z} = 0 \)) and \( \eta = 1 \) (for which \( \omega_{x} = \omega_{y} \)).

A simple physical interpretation can now be applied to the NQR excitation process. Firstly, the NQ Hamiltonian \( H_{0} \) is diagonal in the Cartesian basis \( \{|x,y,z\}\) of the EFG PAS frame, so its eigenvector basis identically overlaps the coordinate axes \( \{x,y,z\} \) of this frame. Furthermore, the structure of the effective Hamiltonians in this basis shows that an RF field applied to one of the co-ordinate axes in the PAS frame drives transitions between only one pair of energy eigenstates, while leaving the other unchanged. Thus we can selectively excite each NQR transition by applying an RF field (at the correct resonance frequency) along the appropriate axis in the PAS frame: \( x \) for \( \omega_{x}, y \) for \( \omega_{y}, \) and \( z \) for \( \omega_{z} \). For example, resonant radiation along the \( z \) axis excites the state \( |z\rangle \) to \( |2\rangle \) state, while leaving the population of the \( |2\rangle \) state unaffected. In a classical picture, this corresponds to rotation of the spin-1 vector about the \( z \) axis. In general, only the component of \( B_{1} \) along the excitation axis, which is perpendicular to the plane created by the resonant eigenvector directions, can drive state transitions.

As a result, the effective nutation frequency is determined by the relative orientation between \( B_{1} \) and the excitation axis in the EFG PAS frame. We denote the effective nutation frequency induced by the coil by \( \omega_{p1x} \), where \( \omega_{p1y} = \omega_{p1x} \) when \( \omega = \omega_{x}, \omega_{p1y} = \omega_{p1b} \) when \( \omega = \omega_{y}, \) and \( \omega_{p1z} = \omega_{p1c} \) when \( \omega = \omega_{z} \). The orientation parameters \( a, b, \) and \( c \) are functions of the Euler angles \( x \) and \( \beta \), i.e., depend on the orientation of the coil with respect to the crystal structure. Hence the effective nutation frequency will vary from crystallite to crystallite within a powder sample.

The density matrix at thermal equilibrium is given by

\[
\rho_{eq} \propto \exp \left[ -\frac{H_{0}}{kT} \right],
\tag{A.3}
\]

Only the second term in this expression changes with time. Hence we can perform spin dynamics calculations with an initial density operator that is defined as

\[
\rho(0) = H_{0} \frac{\omega_{0}}{3} \begin{bmatrix} 1 - \eta & 0 & 0 \\ 0 & 1 + \eta & 0 \\ 0 & 0 & -2 \end{bmatrix}.
\tag{A.4}
\]

By solving the von Neumann equation we find that the density matrices at the end of the first (perturbation) and second (detection) RF pulses are given by

\[
\begin{align*}
\rho(t_{p1}) &= e^{-iH_{0}t_{p1}} \rho(0) e^{iH_{0}t_{p1}}, \\
\rho(t_{p1} + t_{p2}) &= e^{-iH_{0}t_{p2}} \rho(t_{p1}) e^{iH_{0}t_{p2}},
\end{align*}
\tag{A.5}
\]

Here \( t_{p1} \) and \( t_{p2} \) are the durations of the first and second RF pulses, respectively. Finally, the detected signal is given by

\[
S(t_{p1} + t_{p2}) = \omega_{p1} \text{Tr}[\rho(t_{p1} + t_{p2})(p_{1} - iH_{0})]
\tag{A.6}
\]

Here \( \omega_{p1} \) is the effective nutation frequency for the second (detection) pulse, and \( p = x, y, \) or \( z \) for detection frequencies of \( \omega_{x}, \omega_{y}, \) or \( \omega_{z}, \) respectively. In addition \( t_{p1} \) and \( t_{p2} \) are fictitious spin-1/2 operators suitable for describing experiments in spin-1 systems [18]. In the Cartesian basis, which is also the eigenbasis of the NQ Hamiltonian, these operators are given by...
\[
I_{1 \lambda} = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ -i & 0 & 0 \end{bmatrix}, \quad I_{2 \lambda} = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}.
\]

\[
I_{1 y} = \frac{1}{2} \begin{bmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{bmatrix}, \quad I_{2 y} = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}.
\]

(A.7)

We can now analytically calculate the detected NQR signal \( s(p, q) \) after both pulses, where \( p \) and \( q \) are equal to \( x, y, \) or \( z \) for pulse frequencies of \( \omega_1, \omega_2, \) or \( \omega_3, \) respectively. Here the first index refers to the frequency of the first (perturbation) pulse, and the second to that of the second (detection) pulse. The results are listed below:

\[
s(x, x) = i \omega_3 \sin \left( (\theta_1 + \theta_2) a_{1b} a_{2b} (3 + \eta) / 6 \right)
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

\[
s(x, y) = -i \omega_3 \sin \left( (\theta_1 + \theta_2) a_{1b} a_{2b} (3 + \eta) / 6 \right)
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

\[
s(z, x) = i \omega_3 \sin \left( (\theta_1 + \theta_2) a_{1b} a_{2b} (3 + \eta) / 6 \right)
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

\[
s(z, y) = -i \omega_3 \sin \left( (\theta_1 + \theta_2) a_{1b} a_{2b} (3 + \eta) / 6 \right)
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

\[
s(z, z) = -i \omega_3 \sin \left( (\theta_1 + \theta_2) a_{1b} a_{2b} (3 + \eta) / 6 \right)
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

(A.9)

These expressions show that in these cases the two pulses are simply equivalent to a single pulse of flip angle \( (\theta_1 + \theta_2) \) (if they have the same phase) or \( (\theta_1 - \theta_2) \) (if they have opposing phases), as one might expect. The detected signal after the phase cycle is the difference between these expressions, which is given by

\[
s(x, x) = i \omega_3 \cos(\theta_3 a) \sin(\theta_3 a) a_{1b} a_{2b} (3 + \eta) / 3
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

\[
s(z, z) = -2i \omega_3 \cos(\theta_3 a) \sin(\theta_3 a) a_{1b} a_{2b} (3 + \eta) / 3
- e^{-2i\phi_3} \left( 1 - \cos(\theta_2 a_3) \right) + 2 \cos(\theta_1) e^{-i\phi_3} \sin(\theta_2 a_3) / 12
\]

(A.10)

We can find the signal amplitudes \( s_0(p, q) \) in the absence of the perturbation pulse by setting \( t_1 = 0 \) in the expressions listed above. We have normalized the perturbed signal amplitudes \( s(p, q) \) by these unperturbed amplitudes. The results are then displayed as a matrix, with the perturbation frequency varying along the rows, and the detection frequency varying along the columns, leading to Eq. (1).

References


