Multi-quantum Quadrupole Relaxation Enhancement effects in $^{209}$Bi compounds

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ABSTRACT

$^1$H spin-lattice Nuclear Magnetic Resonance (NMR) relaxation experiments have been performed for triphenylbismuth dichloride ($\text{C}_{18}\text{H}_{15}\text{BiCl}_2$) and phenylbismuth dichloride ($\text{C}_6\text{H}_5\text{BiCl}_2$) in powder. The frequency range of 20MHz-128MHz has been covered. Due to $^1$H-$^{209}$Bi dipole-dipole interactions a rich set of pronounced Quadrupole Relaxation Enhancement (QRE) peaks (quadrupole peaks) has been observed. The QRE patterns for both compounds have been explained in terms of single – and double-quantum transitions of the participating nuclei. The analysis has revealed a complex, quantum-mechanical mechanism of the QRE effects. The mechanism goes far beyond the simple explanation of the existence of three quadrupole peaks for $^{14}$N reported in literature. The analysis has been supported by Nuclear Quadrupole Resonance (NQR) results that independently provided the $^{209}$Bi quadrupole parameters (amplitude of the quadrupole coupling constant and asymmetry parameter).
I. INTRODUCTION

Nuclear Magnetic Resonance (NMR) relaxometry is one of the most powerful methods providing information about molecular dynamics.\textsuperscript{1-5} Moreover, as NMR and spin relaxation are quantum effects, relaxation data collected in a broad frequency range reflect interplays between spin interactions.\textsuperscript{2,5-12} A special case is here Quadrupole Relaxation Enhancement (QRE) that can be observed for systems containing nuclei possessing quadrupole moments (quadrupole nuclei).\textsuperscript{6-20} The quantum-mechanical scenario of QRE is as follows. There are two contributions to the energy level structure of the quadrupole nucleus: its Zeeman coupling (with an external magnetic field applied in the relaxation experiments) and quadrupole coupling. This statement is correct as long as the orientation of the principal axis system of the electric field gradient at the position of the quadrupole nucleus is fixed (does not fluctuate in time) with respect to the direction of the magnetic field. This can take place in two cases: when the dynamics of the system is slow or/and when the dynamics is anisotropic that implies a non-zero average of the quadrupole coupling referred to as a residual quadrupole interaction; both effects are typical of solids. The energy level structure of the quadrupole nucleus should be compared with the energy level structure of a neighbouring spin-1/2 nucleus (typically $^1$H or $^{19}$F); the two nuclei are coupled by a magnetic dipole – dipole interaction. At some magnetic fields the Zeeman energy level splitting of the spin-1/2 nucleus (\textit{i.e.} its resonance frequency) matches one of the transition frequencies between the energy levels of the quadrupole nucleus. As the transitions of both spins are coupled (via the mutual dipole-dipole interaction), at such magnetic fields the spin-1/2 magnetization can be taken over by the quadrupole nucleus. The loss of the spin-1/2 magnetization manifests itself as an enhancement of its spin-lattice relaxation. This frequency specific effect is referred to as QRE, while the maxima of the spin-1/2 spin-lattice relaxation rate are called quadrupole peaks. For the spin quantum number $S=1$ of the quadrupole nucleus (for instance $^{14}$N) one observes three quadrupole peaks at the frequencies of $\frac{3}{4}a_q\left(1+\frac{\eta}{3}\right)$, $\frac{3}{4}a_q\left(1-\frac{\eta}{3}\right)$ and $\frac{\eta a_q}{2}$, where $a_q$ and $\eta$ denote the amplitude of the quadrupole interaction and its asymmetry parameter, respectively.\textsuperscript{8-14} $^1$H quadrupole peaks associated with $^{14}$N have been observed for solids,\textsuperscript{11,12,20} tissues,\textsuperscript{21,22} and liquid crystals.\textsuperscript{23} The QRE effect is a very sensitive probe of slight changes in the molecular environment leading to alteration of the electric field gradient (the positions of the QRE peaks are fully determined by the electric field gradient tensor). Most of the experimental studies concern $^{14}$N (\textit{i.e.} S=1). The high sensitivity of the QRE to the electric field gradient tensor has given us the idea of exploiting this effect as a possible contrast mechanism in Magnetic Resonance Imaging, which
can be switched on and off in response to a slight alteration of the electronic (molecular) surrounding.\textsuperscript{6,7} We have chosen $^{209}\text{Bi}$ as a promising candidate for this purpose because of its large quadrupole moment leading to QRE appearing at magnetic fields being close to the field at which clinical scanners operate (3T).\textsuperscript{24} Large spin ($S=9/2$) and gyromagnetic factor, both ensuring a relatively strong dipole-dipole coupling, rich chemistry that allows tuning the QRE frequencies, and relatively low toxicity. The high spin quantum number of $^{209}\text{Bi}$ leads to a complex energy level structure and hence several transition frequencies.\textsuperscript{7} At the same time one can expect that the QRE effect involves more (not only one) mutually coupled (by dipole – dipole interactions) $^1\text{H}$ (spin – 1/2) nuclei. In such cases the QRE effects lead to several quadrupole peaks. To fully profit from the “switching mechanism” of QRE based contrast agents, one has to understand in detail the underlying quantum – mechanical scenario of the QRE effects to become aware of the origin of possible quadrupole peaks. The same applies to the situation when the QRE effect is exploited to inquire into structural properties of compounds and materials – otherwise one can easily misinterpret the relaxation data, for instance by treating quadrupole peaks associated with single- and double – quantum coherences as a proof of the existence of different lattice sites although this is not true.

The concept of multi – quantum coherences leading to QRE effects is essential for this paper. QRE involves dipole – dipole and quadrupole interactions; both of them are rank-two spin interactions (in terms of their tensor representation). This implies that the joint spin transitions leading to QRE undergo well – defined rules. The magnetic quantum number of the quadrupole nucleus can change by 1 or by 2: $|\Delta m_j|=1$ or $|\Delta m_j|=2$ upon its transition. The same applies to the coupled pair of spin-1/2 nuclei – they total magnetic quantum number can also change by 1 or by 2: $|\Delta m_i|=|\Delta(m_i+m_j)|=1$ or $|\Delta m_i|=2$, while the total magnetic quantum number of the spin system can change by 0, 1 or 2: $|\Delta n|=|\Delta(m_i+m_j)|=0, 1$ or 2. In consequence, one can see quadrupole peaks originating from multi-quantum transitions of the participating spins.\textsuperscript{6,7,23} In this paper the effect has been demonstrated for two $^{209}\text{Bi}$ solids: triphenylbismuth dichloride and phenylbismuth dichloride and thoroughly analysed in a quantitative way. Revealing the underlying quantum – mechanical effects leading to the complex QRE patterns considerably deepens the current understanding of QRE effects for the profit of material science and biomedical studies with special focus on the potential use of QRE as a contrast mechanism.
II. SPIN INTERACTIONS RELEVANT FOR QRE

As explained in Introduction, the energy level structure of the quadrupole nucleus is determined by a superposition of its quadrupole and Zeeman interactions. Hamiltonians of both interactions have to be expressed in the same reference frame – let us chose the laboratory frame (determined by the direction of the external magnetic field). By applying transformation rules for tensor operators, one obtains the following form of the total Hamiltonian, $H(S)$, of the quadrupole nucleus (of spin $S$):6,25-28

$$H(S) = H_\Omega(S) + H_Q(S),$$

where 

$$H_\Omega(S) = \omega_S S_z + \frac{1}{2} \sqrt{\frac{3}{2}} \frac{a_0}{S(2S-1)} \sum_{m=-2}^{2} (-1)^m \left[ D^2_{0,m}(\Omega) + \frac{\eta}{\sqrt{6}} \left( D^2_{2,m}(\Omega) + D^2_{2,-m}(\Omega) \right) \right] T^2_m(S),$$

and

$$H_Q(S) = \frac{1}{\sqrt{6}} \left( 3 S_z^2 - S(S+1) \right).$$

The tensor operators in Eq. (1) have the form: $T^{\pm}_n(S) = \frac{1}{\sqrt{6}} \left[ S_n S_n \pm S_S S_S \right]$ and $T^z_n(S) = \frac{1}{2} S_n S_n$; the quadrupolar coupling constant is defined as:

$$a_Q = e^2 q Q / \hbar,$$

where $Q$ denotes the quadrupolar moment of the nucleus of spin $S$, $q$ is the value of the $zz$ component of the electric field gradient tensor and $\eta$ is referred to as asymmetry parameter, while $\omega_S$ is the resonance frequency of spin $S$. The Wigner rotation matrices $D^j_{0,q}(\Omega)$ depend on the orientation of the principal axis system of the electric field gradient tensor with respect to the laboratory frame, described by the $\Omega$ angle. As a consequence of the orientation dependence of the Hamiltonian, the energy level structure of the quadrupole nucleus becomes orientation dependent.

The energy level structure of the quadrupole spin at zero magnetic field is solely determined by the quadrupole Hamiltonian which in this case can be considered in a molecule-fixed frame:

$$H_Q(S) = \frac{1}{2} \sqrt{\frac{3}{2}} \frac{a_0}{S(2S-1)} \left[ T^z_0(S) + \frac{\eta}{\sqrt{6}} (T^2_2(S) + T^2_{-2}(S)) \right],$$

(2)

The transitions are caused by $^1H$-$^{209}$Bi magnetic dipole-dipole interactions giving rise to the $^1H$ relaxation.

III. EXPERIMENTAL DETAILS

$^1H$ spin-lattice relaxation rates for powder triphenylbismuth dichloride ($C_{18}H_{15}BiCl_2$) and phenylbismuth dichloride ($C_6H_3BiCl_2$) have been measured at 295 K in the frequency range of 20MHz-128MHz. For this purpose HTC-110 3T superconducting magnet compatible with
STELAR NMR relaxometer has been used. The inversion recovery pulse sequence has been used with the 90° pulse lengths of 3μs - 5μs depending on the 1H resonance frequency.

Zero-field NQR spectroscopy was carried out for both compounds with two pulse-type NQR spectrometers working with two complementary frequency sweep methods both using a variety of transmit/receive coils. The self-built “Graz-NQRS-MK1”36 was used for fast wide band sweeps up to over tens of MHz with specially designed wideband-cryo-probeheads whereas the commercially available “Scout” (Tecmag, Inc., USA) allows for advanced pulse sequence programming. The probe coil is driven during transmit by a 500 W amplifier and enables π/2 pulses down to 300ns. In combination, the two systems cover a frequency range of 20MHz up to 180MHz and can be thermostatized from 77K up to 323K. Experiments for the two compounds were carried out at 77K (immersed in liquid nitrogen), 300K and 310K, respectively.

The structure of triphenylbismuth dichloride (C18H15BiCl2) and phenylbismuth dichloride (C6H5BiCl2) is shown in Fig. 1.

IV. RESULTS AND ANALYSIS

The 1H spin lattice relaxation data for triphenylbismuth dichloride and phenylbismuth dichloride are much different as one can see in Fig. 2.

We begin the analysis of the QRE pattern with triphenylbismuth dichloride as for this compound extensive NQR measurements have been performed.7 In triphenylbismuth dichloride two crystal sites A and B can be found.29 For each of the temperatures: 77K, 300K and 310K, two transitions frequencies have been measured. At 77K and room temperature (300K) the NQR experiment has been restricted to the frequency range below 100MHz. For both temperatures two NQR lines have been detected at the frequencies of 45.51MHz and 87.50MHz (77K) and 44.14MHz and 86.47MHz (300K) for site A and of 45.80MHz and 91.24MHz (77K) and 44.81 MHz and 89.34MHz (300K) for site B. The positions of NQR lines detected at 310K are 86.40MHz and 129.91 MHz for site A, and 89.20MHz and 133.86 MHz for site B. Diagonalising matrix representation of the quadrupole Hamiltonian for 209Bi (Eq. (2)) in the basis \{S,m\}, as described in Section II, one can obtain energy levels of 209Bi as a function of the quadrupole parameters \((Q_a, \eta)\). Comparison of the theoretical results and the experimental positions of the NQR lines give \(Q_a=1039.7MHz, \eta=0.046\) (310K), \(Q_a=1040.3MHz, \eta=0.045\) (300K) and \(Q_a=1055.3MHz, \eta=0.063\) (77K) for site A. The
frequencies of NQR transitions for site B has provided: \( a_q = 1071.0 \text{MHz}, \quad \eta = 0.02 \) (310K), \( a_q = 1072.6 \text{MHz}, \quad \eta = 0.017 \) (300K) and \( a_q = 1095.4 \text{MHz}, \quad \eta = 0.02 \) (77K).

The \(^1\text{H}\) spin-lattice relaxation for triphenylbismuth dichloride shows three distinct quadrupole peaks labelled as I, II and III. Knowing the quadrupolar parameters one can determine the energy level structure of \(^{209}\text{Bi}\) in triphenylbismuth dichloride depending on the magnetic field and the molecular orientation by diagonalising the full Hamiltonian of Eq. (1). The energy level structure for \( \Omega = 0 \) (parallel orientation of the magnetic field and the principal axis system of the electric field gradient) is shown in Appendix (Fig.8) as an example. The energy level structure has been calculated for the parameters characterising site B: \( a_q = 1071.0 \text{MHz} \) and \( \eta = 0.02 \). The results of analogous calculations for site A are added to Fig.8 for comparison.

As explained in Section II, the eigenvectors for the \(^{209}\text{Bi}\) spin are given as linear combinations of the Zeeman functions, \( \{|S,m\rangle\} \). For each eigenvector one can identify the \( |S,m\rangle \) term to which the eigenvector will converge at high magnetic field (when the Zeeman coupling dominates the quadrupole interaction). From now on, labelling the spin transitions we shall refer to the \( m \) value of this term. Following this line one can calculate frequencies of the single-quantum \(^{209}\text{Bi}\) spin transitions for different molecular orientations and plot them versus the magnetic field (converted to \(^1\text{H}\) resonance frequency) as shown in Fig. 3 (top).

Let us again stress at this point that for \(^{209}\text{Bi}\) the term “single-quantum” (“double-quantum”) is used only as a high field labelling. As already explained, beyond the high field limit one cannot characterise the eigenstate by a magnetic quantum number, \( m \), as the corresponding eigenvector includes \( |S,m\rangle \) vectors for different \( m \) values. Coming back to the point - by drawing lines corresponding to \(^1\text{H}\) single- and double-quantum transitions (for the second case one needs two mutually coupled \(^1\text{H}\) nuclei), \textit{i.e.} the frequencies of \( \omega_f \) and \( 2\omega_q \), one can identify the ranges in which these frequencies match one of the single-quantum \(^{209}\text{Bi}\) transition frequencies. By projecting the ranges onto the \(^1\text{H}\) spin-lattice data (Fig. 3, bottom), one can see that the positions of the peaks I and III cannot be attributed neither to the single- nor double-quantum \(^1\text{H}\) transitions (the last represented by the “small”, horizontal bars in Fig.3). Actually, peak II requires more comments. For triphenylbismuth dichloride we have two sites (A and B). The analysis has been performed for the quadrupole parameters of site B. Nevertheless, a closer inspection of Fig.3 shows that peak II is split into two lines (peaks). The splitting can be attributed to the two sites (A and B) as shown in Fig. 4.
One could state then that peak II can be explained by the combination of $^1\text{H}$ and $^{209}\text{Bi}$ single-quantum transitions. This does not apply to peaks I and III- their positions cannot be explained with the help of the site A contribution.

Analogous analysis performed for double-quantum $^{209}\text{Bi}$ spin transitions (Fig.5) shows that the QRE effects can be associated with the joint double-quantum $^1\text{H}$ and $^{209}\text{Bi}$ spin transitions:

$$|\frac{3}{2}\rangle \rightarrow |\frac{1}{2}\rangle$$ (peak I), $$|\frac{5}{2}\rangle \rightarrow |\frac{1}{2}\rangle$$ (peak II) and $$|\frac{7}{2}\rangle \rightarrow |\frac{3}{2}\rangle$$ (peak III).

NQR experiments for phenylbismuth dichloride have turned out to be difficult (due to fast spin-spin relaxation time) and only one transition frequency at 75.5MHz (77K) has been detected. At room temperature no signal could be detected throughout the whole range from 20MHz to 180MHz. From the knowledge of usual temperature coefficients of the NQR transition frequencies of related compounds we expect a downshift by 1MHz – 2MHz at 300K. Knowing only one transition frequency at a temperature different from that of the NMR relaxation measurements, we have decided to rely on some similarities between the $^1\text{H}$ spin-lattice relaxation data for both compounds. Closer inspection of the data suggests that the QRE peaks for triphenylbismuth dichloride labelled as I, II and III can correspond to the peaks for phenylbismuth dichloride denoted as I’, II’ and III’ (Fig. 2) and have the same origin (double-quantum $^1\text{H}$ and $^{209}\text{Bi}$ spin transitions). Treating this as a “working hypothesis” we have found out that somewhat reducing the $a_Q$ value and increasing the asymmetry parameter one can match both: the detected NQR frequency (attributing it to the $$|\frac{2}{2}\rangle \rightarrow |\frac{3}{2}\rangle$$ transition and the observed shift of the I’, II’ and III’ peaks towards lower frequencies (compared to their counterparts, I, II and III, respectively). After systematic simulations it has been found that $a_Q = 915.4\text{MHz}$ and $\eta = 0.09$ is the best choice. For this set of parameters the calculated NQR transition frequencies yield: 40.83MHz, 75.51MHz, 114.25MHz and 152.47MHz. Figure A1(b) (Appendix) shows the energy levels structure obtained for this set of parameters (and $\Omega = 0$). Following the concept applied to triphenylbismuth dichloride, in Fig. 6 the ranges in which the frequency of double-quantum $^1\text{H}$ transitions match one of the frequencies of double-quantum $^{209}\text{Bi}$ spin transitions (top) have been projected onto the $^1\text{H}$ spin-lattice relaxation profile of phenylbismuth dichloride. According to the assumption, the quadrupole peaks I’, II’ and III’ can be associated with the combined $^1\text{H}$ and $^{209}\text{Bi}$ double-quantum transitions ($$|\frac{3}{2}\rangle \rightarrow |\frac{1}{2}\rangle$$, $$|\frac{5}{2}\rangle \rightarrow |\frac{1}{2}\rangle$$ and $$|\frac{7}{2}\rangle \rightarrow |\frac{3}{2}\rangle$$, respectively). Peaks I’ and II’ are, however, not completely
covered. One could get a better agreement with the positions of the peak by changing the quadrupole parameters, but for the price of more significant deviations from the experimental NQR transition frequency.

To reveal the origin of the peaks labelled as 2, 3 and 4, single-quantum $^{209}$Bi spin transitions have been considered (Fig. 7). The peaks 2, 3 and 4 can be attributed to the combination of single – quantum $^1$H spin transition (of the frequency $\omega_i$) with single – quantum $^{209}$Bi transitions: \[ \frac{3}{2} \rightarrow \frac{1}{2} \] and \[ \frac{5}{2} \rightarrow \frac{3}{2} \] for peak 2 and 3, respectively, while peak 4 originates from the combination with the \[ \frac{7}{2} \rightarrow \frac{5}{2} \] $^{209}$Bi transition. The joint $^1$H and $^{209}$Bi single-quantum, \[ \frac{5}{2} \rightarrow \frac{3}{2} \] transition corresponds to the position of peak II’, which has already been associated with the double quantum transitions of $^1$H and $^{209}$Bi \[ \frac{5}{2} \rightarrow \frac{1}{2} \]. One can consider whether, in this situation, the single-quantum transition indeed contributes to the formation of peak II’, but taking into account that peaks 2 and 4 originate from the single-quantum transitions, \[ \frac{3}{2} \rightarrow \frac{1}{2} \] and \[ \frac{7}{2} \rightarrow \frac{5}{2} \], respectively, there is no reason to doubt that the \[ \frac{5}{2} \rightarrow \frac{3}{2} \] transition also leads to QRE effects. The broad \[ \frac{5}{2} \rightarrow \frac{3}{2} \] $^{209}$Bi transition also covers the position of the peak labelled as peak 3. Analysing, in the next step, the effects of $^{209}$Bi single-quantum coherences matched by the frequency of $2 \omega_i$, one can see from Fig.7 that peak 1 and peak I’ can be associated with the \[ \frac{5}{2} \rightarrow \frac{3}{2} \] and \[ \frac{3}{2} \rightarrow \frac{1}{2} \] $^{209}$Bi transition, respectively.

As a result of this discussion one can state that to explain the QRE effects observed for triphenylbismuth dichloride one has to involve double-quantum $^{209}$Bi spin transitions combined with the frequency $2 \omega_i$. This finding can be explained by fast spin-spin (single-quantum) $^{209}$Bi relaxation in triphenylbismuth dichloride. The spin-spin relaxation times (single-quantum coherences) associated with the transitions \[ \frac{3}{2} \rightarrow \frac{1}{2} \], \[ \frac{5}{2} \rightarrow \frac{3}{2} \] and \[ \frac{7}{2} \rightarrow \frac{5}{2} \] at 310K for site B yield: 40µs, 46µs, 28µs, respectively, while the corresponding spin-lattice relaxation times are: 241µs, 108µs, 54µs. Analogously for site A it has been obtained: 7 52µs, 50µs and 44µs for the spin-spin relaxation times and 98µs, 63µs and 46µs for the corresponding spin-lattice relaxation times. The values are by order of magnitude smaller than for other $^{209}$Bi
compounds, for instance triphenylbismuth: $^{7} 277\mu s$ and $436\mu s$ for the spin-spin relaxation times for the $^{|5/2\rightarrow3/2|}$ and $^{|7/2\rightarrow5/2|}$ transitions at $310K$ and $1123\mu s$ and $548\mu s$ for the corresponding spin-lattice relaxation times. Fast relaxation diminishes the QRE effects (the peaks become broader), in the limiting case they disappear. As relaxation of double-quantum coherences (transitions) is slower, the corresponding quadrupole peaks manifest themselves in the $^1H$ spin-lattice relaxation data. The reason why fast quadrupole relaxation leads to a progressive disappearance of the quadrupole peaks is that the relaxation process acts as a source of modulations of the $I-S$ dipole-dipole coupling. When the modulations become fast, the relaxation processes becomes non-sensitive to the energy level structure of the spin system.\textsuperscript{28, 30-32}

Looking at the structure of phenylbismuth dichloride and triphenylbismuth dichloride one can suppose that the $^1H$ spin transitions leading to the QRE peaks involve the protons in the ortho positions. Nevertheless, one has to be aware that the experiment has been performed for a crystal (powder) not for a single molecule. This implies that $^1H$ nuclei belonging to neighboring molecules can also contribute to this process.

It is also worth to stress that the shape of QRE peaks depend on both: the spin-lattice and the spin-spin relaxation of the quadrupole nucleus. This means that one can observe a QRE peak even if the associated NQR line cannot be detected due to too fast spin-spin relaxation.

Before finishing this section let us mention that for phenylbismuth dichloride we have also considered different interpretations of the $^1H$ relaxation results, not based on the correspondence between the I, II, III peaks for triphenylbismuth dichloride and I’, II’, III’ peaks for phenylbismuth dichloride. An example is the set of parameters: $Q_0=1750MHz$, $\eta = 0.05$.

For this set of parameters one obtains for the NQR frequency the value of $74.54MHz$, $145.36MHz$, $218.65MHz$, $291.61MHz$, which is in a better agreement with the experimental value ($75.5MHz$). Fig.9 and Fig.10 of Appendix show how the transition frequencies resulted from these parameters match the positions of the quadrupole peaks; peaks I’ and III’ remain unexplained. In principle, one could attribute them to $^{35}Cl$ (instead of $^{209}Bi$), as many $^{35}Cl$ compounds have NQR transitions in the range between 15 and 45MHz,\textsuperscript{33} but this is unlikely: in such a case one would observe more effects associated with $^{35}Cl$ for both compounds.

V. CONCLUSIONS
The experimental $^1$H spin-lattice NMR relaxation data for triphenylbismuth dichloride and phenylbismuth dichloride and their thorough analysis lead to three main conclusions. The first one is that indeed for high spin quantum numbers ($S=9/2$ in this case) one is able to experimentally detect a rich set of quadrupole peaks. The data available in literature are, in fact, limited to $^{14}$N QRE effects leading to three peaks as expected for $S=1$. The second conclusion is that the experimental data cannot be explained in terms of a model system including a single $^1$H nucleus and a single $^{209}$Bi nucleus. The explanation requires involving double – quantum coherences. Moreover, and this is the third conclusion, the presence of a quadrupole peak is mediated by the $^{209}$Bi relaxation. One can observe well pronounced peaks associated with double-quantum transitions even if corresponding single-quantum peaks (which are theoretically more probable) are not present due to fast quadrupole relaxation.

The analysis presented in this paper has been performed in the context of exploiting QRE as a novel contrast mechanism for MRI. For this purpose it is crucial to understand the origin of the individual quadrupole peaks for $^{209}$Bi. The studies should, however, be considered even in a broader context. QRE effects are exploited as a source of information about molecular dynamics and structure (in particular $^{14}$N QRE for biological systems). One has to be aware of the complexity of this phenomenon to avoid serious misinterpretations. Eventually, this complex, quantum-mechanical phenomenon is by itself worth a deeper understanding.

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Figures

FIG. 1. Structure of triphenylbismuth dichloride (C_{18}H_{15}BiCl_{2}) and phenylbismuth dichloride (C_{6}H_{5}BiCl_{2}).
FIG. 2. $^1$H spin-lattice relaxation rates versus frequency for triphenylbismuth dichloride ($\text{C}_{18}\text{H}_{15}\text{BiCl}_2$) and phenylbismuth dichloride ($\text{C}_6\text{H}_5\text{BiCl}_2$). The numbering of the QRE peaks has been explained in the text.
FIG. 3. Comparison between the calculated single-quantum $^{209}$Bi transition frequencies of triphenylbismuth dichloride (for each transition, the upper and lower continuous lines define the boundaries of the domain of transition frequencies corresponding to all possible orientations of the external magnetic field with respect to the principal axis system of the electric field gradient) and the experimental $^1$H spin-lattice relaxation rates. Black solid and dashed lines correspond to the single- and double-quantum $^1$H spin transitions, $\omega_q$ and $2\omega_q$, respectively. Vertical shaded areas mark the frequency ranges in which $\omega_q$ matches one of the $^{209}$Bi single – quantum transition frequencies: ($|\frac{3}{2}\rangle \rightarrow |\frac{1}{2}\rangle$) – green, ($|\frac{5}{2}\rangle \rightarrow |\frac{3}{2}\rangle$) – pink, ($|\frac{7}{2}\rangle \rightarrow |\frac{5}{2}\rangle$) – blue. “Small” horizontal bars are used to mark the frequency ranges in which $2\omega_q$ matches one of the $^{209}$Bi transition frequencies; the colours correspond to those for $\omega_q$, red bar is associated with the ($|\frac{9}{2}\rangle \rightarrow |\frac{7}{2}\rangle$) $^{209}$Bi spin transition.
FIG. 5. Comparison between calculated double-quantum $^{209}\text{Bi}$ transition frequencies of triphenylbismuth dichloride (for each transition, the upper and lower continuous lines define the boundaries of the domain of transition frequencies corresponding to all possible orientations of the external magnetic field with respect to the principal axis system of the electric field gradient) and the experimental $^1\text{H}$ spin-lattice relaxation rates. The QRE peaks denoted as I, II and III can be attributed to the double-quantum $^{209}\text{Bi}$ transitions $(\frac{3}{2}\rightarrow\frac{1}{2})$, $(\frac{5}{2}\rightarrow\frac{1}{2})$, $(\frac{7}{2}\rightarrow\frac{3}{2})$, respectively, combined with $^1\text{H}$ double-quantum transition.
FIG. 6. Comparison between calculated double-quantum $^{209}$Bi transition frequencies of phenylbismuth dichloride and the experimental $^1$H spin-lattice relaxation rates. The QRE peaks denoted as I', II' and III' can be attributed to the double-quantum $^{209}$Bi transitions ($\frac{3}{2} \rightarrow \frac{-1}{2}$), ($\frac{5}{2} \rightarrow \frac{1}{2}$), ($\frac{7}{2} \rightarrow \frac{3}{2}$), respectively, combined with $^1$H double-quantum transition.
FIG. 7. Comparison between calculated single-quantum $^{209}\text{Bi}$ transition frequencies of phenylbismuth dichloride (for each transition, the upper and lower continuous lines define the boundaries of the domain of transition frequencies corresponding to all possible orientations of the external magnetic field with respect to the principal axis system of the electric field gradient) and the experimental $^1\text{H}$ spin-lattice relaxation rate. The QRE peaks denoted as 2, II’, 3 and 4 can be attributed to the single-quantum $^{209}\text{Bi}$ transitions ($|\frac{5}{2}\rangle \rightarrow |\frac{1}{2}\rangle$, $|\frac{5}{2}\rangle \rightarrow |\frac{3}{2}\rangle$, $|\frac{5}{2}\rangle \rightarrow |\frac{3}{2}\rangle$), respectively, combined with $^1\text{H}$ single-quantum transition, while peaks 1 and I’ can be associated with the $|\frac{5}{2}\rangle \rightarrow |\frac{3}{2}\rangle$ and $|\frac{3}{2}\rangle \rightarrow |\frac{1}{2}\rangle$ $^{209}\text{Bi}$ transition, combined with $^1\text{H}$ double-quantum transition, respectively. “Small” horizontal bars are used to mark the frequency ranges in which $2\omega_I$ matches one of the $^{209}\text{Bi}$ transition frequencies.
APPENDIX

a) Energy level structures

FIG. 8. $^{209}$Bi energy levels versus magnetic field converted to $^1$H resonance frequency for $\Omega = 0$ calculated for a) triphenylbismuth dichloride: $a_0 = 1071\text{MHz}$, $\eta = 0.02$ (site B) and $a_0 = 1039.7\text{MHz}$, $\eta = 0.046$ (site A) - dotted grey lines; b) phenylbismuth dichloride: $a_0 = 915.4\text{MHz}$, $\eta = 0.09$. 
b) Alternative analysis for phenylbismuth dichloride

FIG. 9. Comparison between calculated single-quantum $^{209}$Bi transition frequencies of phenylbismuth dichloride for $a_0=1750$MHz, $\eta = 0.05$ and the experimental $^1$H spin-lattice relaxation rate. The QRE peaks denoted as 1 and II’ can be attributed to the single-quantum $^{209}$Bi transitions ($\left|\frac{3}{2}\right> \rightarrow \left|\frac{1}{2}\right>$), ($\left|\frac{5}{2}\right> \rightarrow \left|\frac{3}{2}\right>$), respectively, combined with $^1$H double-quantum transition, while peaks 3 and 4 can be associated with the $\left|\frac{3}{2}\right> \rightarrow \left|\frac{1}{2}\right>$ and $\left|\frac{5}{2}\right> \rightarrow \left|\frac{3}{2}\right>$ $^{209}$Bi transition, combined with $^1$H single-quantum transition.
FIG. 10. Comparison between calculated double-quantum $^{209}$Bi transition frequencies of phenylbismuth dichloride for $a_\nu=1750\text{MHz}$, $\eta = 0.05$ and the experimental $^1\text{H}$ spin-lattice relaxation rate. The QRE peaks denoted as 2 and 4 can be attributed to the double-quantum $^{209}$Bi transitions $|3/2\rangle \leftrightarrow |1/2\rangle$) and $|5/2\rangle \leftrightarrow |1/2\rangle$, respectively, combined with $^1\text{H}$ double-quantum transition, while peak 4 can also be associated with the $|3/2\rangle \leftrightarrow |1/2\rangle$ $^{209}$Bi transition, combined with $^1\text{H}$ single-quantum transition.
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