Communication

An approximate analytical expression for the nuclear quadrupole transverse relaxation rate of half-integer spins in liquids

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Abstract

The nuclear quadrupole transverse relaxation process of half-integer spins in liquid samples is known to exhibit multi-exponential behaviors. Within the framework of Redfield’s relaxation theory, exact analytical expressions for describing such a process exist only for spin-3/2 nuclei. As a result, analyses of nuclear quadrupole transverse relaxation data for half-integer quadrupolar nuclei with spin >3/2 must rely on numerical diagonalization of the Redfield relaxation matrix over the entire motional range. In this work we propose an approximate analytical expression that can be used to analyze nuclear quadrupole transverse relaxation data of any half-integer spin in liquids over the entire motional range. The proposed equation yields results that are in excellent agreement with the exact numerical calculations.

1. Introduction

One of the distinct features in NMR spectra obtained for quadrupolar nuclei (I > 1/2, e.g., 14N, 23Na, 17O) in liquid samples is that the signals are very often much broader than those arising from spin-1/2 nuclei such as 1H, 13C, and 15N. The low spectral resolution for quadrupolar nuclei is intrinsically linked to the fact that the nuclear quadrupole interaction is usually significantly larger than the spin interactions encountered by spin-1/2 nuclei (such as dipole-dipole coupling, magnetic shielding, indirect spin-spin coupling, and spin-rotation interactions). The large nuclear quadrupole interaction, once coupled with the fast molecular tumbling motion in liquids, induces very rapid transverse relaxation processes (short T2’s), which is a severe obstacle for NMR applications of quadrupolar nuclei. As a result, it is widely believed that NMR spectroscopy is not so useful for studying quadrupolar nuclei in large biomolecular systems in solution. However, it is also well established in the literature for several decades that the transverse relaxation process of a half-integer spin exhibits multi-exponential relaxation characteristics [1–13] and that one may be able to detect only the so-called central transition (CT) under the slow motion condition (\(\omega_0 \tau_c \gg 1\), where \(\omega_0\) is the angular Larmor frequency of the nucleus under detection and \(\tau_c\) is the molecular rotational correlation time). This is because, under the slow motion condition, the transverse quadrupole relaxation rate for the CT is inversely proportional to \(\tau_c\). As a result, reasonably high spectral resolution can in fact be achieved for half-integer spins in large molecular systems. In the literature, utilization of this special property of half-integer spins in liquids is termed as quadrupole central-transition (QCT) NMR spectroscopy [14–25]. An analogous situation is seen in 13C1H3 systems where the transverse relaxation process also contains fast and slow components [26–28]. In a recent study, Zhu et al. [29] presented natural-abundance 17O (I = 5/2) NMR data for neat liquid glycerol as experimental verification of the aforementioned relaxation properties of half-integer spins over the entire range of molecular motion. Since exact analytical expressions for quadrupole relaxations exist only for the case of I = 3/2 [3,4], a standard approach for analyzing quadrupole relaxation data is to diagonalize the Redfield relaxation matrix at each point over the entire range of motion [5]. In the present work, we propose a general analytical expression for the quadrupole transverse relaxation rate of any half-integer spin over the entire motional range within the limit of Redfield’s relaxation theory. This closed form expression not only yields useful insight into the quadrupole relaxation process, but also provides a simple tool for practical data analysis.

2. Results and discussion

2.1. The extreme narrowing (fast) and intermediate motion regimes

Under the extreme narrowing or fast motion condition (i.e., \(\omega_0 \tau_c \ll 1\)), the nuclear quadrupole transverse relaxation rate is given by [11]
\[ R_Q^2 = \frac{3\pi^2}{10} \frac{2I + 3}{P_Q^2(1 - 1)} P_Q^2 \tau_c \]

(1)

where \( P_Q \), known as the quadrupole product parameter, is defined as a function of the nuclear quadrupolar coupling constant \( C_Q \) and asymmetry parameter \( \eta_Q \):

\[ P_Q = C_Q \sqrt{1 + \eta_Q^2 / 3} \]

(2)

Eq. (1) suggests that the quadrupole transverse relaxation rate (and thus the line width of the observed NMR signal) increases with \( P_Q \) and \( \tau_c \). Because Eq. (1) appears in all NMR textbooks for describing quadrupole transverse relaxation, a common mistake is to apply this equation to conditions outside the extreme narrowing regime (vide infra).

For convenience, we define a reduced quadrupole transverse relaxation rate as:

\[ \langle R_Q^2 \rangle' = \frac{R_Q^2}{P_Q^2} R_Q^2 \]

(3)

where \( \nu_0 = \omega_0/2\pi \). Therefore, under the extreme narrowing condition, we have

\[ \langle R_Q^2 \rangle' = \omega_0 \tau_c = \omega_0 J(0), \]

(4)

where the normalized spectral density function, \( J(\omega) \), is defined as:

\[ J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2}. \]

(5)

When the molecular tumbling motion is slow enough to reach the intermediate regime where \( \omega_0 \tau_c \approx 1 \), the NMR signal of a half-integer quadrupolar spin generally begins to exhibit a multi-Lorentzian line shape containing \( I + 1/2 \) components. Under this condition, exact analytical expressions for quadrupole relaxation rates exist only for \( I = 3/2 \). For \( I > 3/2 \), one has to carry out numerical diagonalization of the Redfield relaxation matrix [5]. However, because the signal in the intermediate motion regime is “nearly exponential”, Halle and Wennerström [30] used a perturbation approach to obtain the following approximate analytical expression (referred to as the HW model in this study):

\[ \langle R_Q^2 \rangle' = \omega_0 [0.3J(0) + 0.5J(\omega_0) + 0.2J(2\omega_0)] \]

(6)

It can be readily shown that Eq. (6) reduces to Eq. (4) under the extreme narrowing condition. Thus Eq. (6) can be used to describe quadrupole transverse relaxation for any half-integer spin in both fast and intermediate regimes.

2.2. The slow motion limit

Under the slow motion limit, in which \( \omega_0 \tau_c > 1 \), it is very often the case that, among the \( I + 1/2 \) components of the multi-exponential NMR signal, only the CT signal is observable. Werbelow and Pouzard [7] obtained the following analytical expression for the CT signal (referred to as the WP model in this study):

\[ \langle R_Q^2 \rangle' = \frac{\omega_0}{2} J(\omega_0) + \frac{I(I + 1) - 3}{2} J(2\omega_0) \]

(7)

Under the limiting condition of \( \omega_0 \tau_c \gg 1 \), Eq. (7) can be further simplified to

\[ \langle R_Q^2 \rangle' = \frac{I(I + 1) + \eta_Q^2}{16} \frac{1}{\omega_0 \tau_c} \]

(8)

Eq. (8) has been widely used in previous QCT NMR studies [14–25]. The most important implication of Eq. (8) is that, as the transverse quadrupole relaxation rate is inversely proportional to \( \tau_c \), favorable spectral resolution may be achievable for biomolecular systems with relatively large \( \tau_c \) values. This is exactly opposite to what predicted by Eq. (4) under the extreme narrowing condition. Another important feature of the CT signal is that its line width (in Hz) is also inversely proportional to \( \nu_0^2 \); thus, spectral resolution can be further improved by performing experiments at very high magnetic fields.

2.3. An approximate analytical expression

As we have discussed in the previous sections, for half-integer spins with \( I > 3/2 \) one has to use different equations to treat quadrupole transverse relaxation in different motion regimes. It is highly desirable to have a unified approach for all half-integer spins. In addition, it is also important to utilize the commonly used spectral density functions, as seen in Eqs. (4)–(7), to be consistent with well-known equations for describing relaxation processes from all other relaxation mechanisms [1]. Here we propose to use the following analytical expression to describe the quadrupole transverse relaxation rate over the entire range of motion:

\[ \langle R_Q^2 \rangle' = \frac{\omega_0}{2} [J(\omega_0) + J(2\beta \omega_0)] \]

(9)

where

\[ \beta = \sqrt{\frac{2}{I(I + 1) - 4}} \]

(10)

Thus \( \beta \) is equal to \( 1, (2/7)^{1/2}, (2/14)^{1/2}, \) and \( (2/23)^{1/2} \) for \( I = 3/2, 5/2, 7/2 \) and \( 9/2 \), respectively. The expression for \( \beta \) is linked to the coefficient in front of \( J(2\omega_0) \) in Eq. (7). It is clear that Eq. (9) is the exact analytical expression for \( I = 3/2 \) [4]. In addition, it can be readily shown that Eq. (9) becomes identical to Eqs. (4) and (8) under the extreme narrowing \( (\omega_0 \tau_c < 1) \) and slow motion \( (\omega_0 \tau_c > 1) \) conditions, respectively. Fig. 1 shows the comparison between different models and the exact results from numerical diagonalization of the Redfield relaxation matrix. It is clear that, while HW and WP models are useful only under the two limiting conditions, Eq. (9) gives an excellent agreement with the exact results over the entire range of motion. To further examine the discrepancy between Eq. (9) and the exact numerical calculations, Fig. 2 shows the results from Eq. (9) for \( I = 5/2, 7/2 \), and \( 9/2 \). In general, the relative error increases slightly with \( I \) and the largest errors (\(< 15\%) occur in a very narrow range around the intermediate motion regime, \( \omega_0 \tau_c \approx 1 \). In other regions, the relative errors are minimal (\(< 1\%). The reason for the discrepancy occurring around \( \omega_0 \tau_c \approx 1 \) is the absence of \( \beta \) in \( J(\omega_0) \) in Eq. (9). In practice,
A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press.

However, as the NMR signals are the broadest in this regime \((\omega_0 \tau_c \approx 1)\), they are usually either unobservable or cannot be reliably measured. Thus, Eq. (9) can be used in practical data analysis in order to extract NMR parameters from quadrupole transverse relaxation data. As an example, Fig. 3 shows a comparison between the experimental \(^{17}\)O NMR data obtained for neat liquid glycerol at 21 T [29] and the result from Eq. (9). The NMR parameters used for data fitting are: \(v_0 = 122\) MHz, \(P_0 = 9.2 \pm 0.2\) MHz. A simple model for rotational correlation time, \(\tau_c = \tau_0 \exp(E_\text{D}/RT)\), was used as described in [29]. In general, Eq. (9) produces excellent results over a wide range where the value of \(\omega_0 \tau_c\) varies over 4 orders of magnitude. It is important to point out that Eq. (9) is valid within the limitation of Redfield’s relaxation theory. When the molecular motion becomes ultraslow so that \(\tau_c \approx (2\pi C_2)^{-1}\), one will have to consider higher-order contributions such that from the second-order quadrupole interaction, as discussed previously in the literature [8,12,31]. Of course, other relaxation mechanisms such as dipole-dipole and anisotropic magnetic shielding interactions may also be operative for half-integer spins; inclusion of these is straightforward.

### 3. Conclusion

In this work, we propose an approximate analytical expression for the transverse relaxation rate of the observable NMR signal from any half-integer spin over the entire range of motion within the limit of Redfield’s relaxation theory. The proposed explicit expression utilizes the same spectral density terms as in the long-established expressions for other relaxation mechanisms such as dipole-dipole and magnetic shielding anisotropy. Thus a unified approach is now available for describing all NMR relaxation mechanisms. We anticipate that, as QCT NMR continues to attract more interests, the proposed simple analytical expression will be useful in practical data analysis.

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### References