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Experimental Verification of the Theory of Nuclear Quadrupole Relaxation in Liquids over the Entire Range of Molecular Tumbling Motion

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S Supporting Information

ABSTRACT: Nuclear magnetic resonance (NMR) spectra of quadrupolar nuclei ($I > 1/2$) in liquids often consist of broad resonances, making it difficult to obtain useful chemical information. The poor NMR spectral resolution commonly observed for quadrupolar nuclei is a direct consequence of nuclear quadrupole relaxation processes. Although all key aspects of nuclear quadrupole relaxation processes have been known for decades within the framework of the Redfield relaxation theory, direct experimental NMR relaxation data that cover a wide range of molecular motion in liquids for quadrupolar nuclei are generally lacking. Here we report a complete set of experimental nuclear quadrupole relaxation data that are obtained for ^{17}O , a half-integer quadrupolar nucleus, over the entire range of molecular motion within the limit of the Redfield theory. A general approach utilizing the quadrupole relaxation properties in the slow motion limit will be particularly beneficial for studies of quadrupolar nuclei in biomolecules of medium and large sizes.

SECTION: Kinetics, Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopic studies of quadrupolar nuclei ($I > 1/2$) in liquids are far less common in the literature than those of spin-1/2 nuclei such as ^1H , ^{13}C , and ^{15}N , despite the fact that over 70% of the elements in the periodic table have NMR-active isotopes with quadrupolar nuclei. The paucity of such studies is primarily because the nuclear quadrupole relaxation in fast tumbling molecules is so rapid that the observed NMR resonances are generally very broad, hence, making it rather difficult to extract useful chemical information. For the same reason, it is also widely believed that NMR spectroscopy is not so useful for studying quadrupolar nuclei in large biomolecular systems in solution. However, the true reality of nuclear quadrupole relaxation processes is more complex. First, both transverse and longitudinal nuclear quadrupole relaxation processes are multiexponential.^{1–8} Second, the spectral behavior depends critically on how the molecular motion, characterized by a molecular rotational correlation time (τ_c), is related to the Larmor frequency (ω_0) of the nucleus under detection. For example, when $\omega_0\tau_c \ll 1$, the so-called extreme narrowing condition or fast motion limit, the transverse quadrupole relaxation rate, and thus the observed NMR line width would increase with the size of the molecule under study. In contrast, when $\omega_0\tau_c \gg 1$, known as the slow motion limit, the transverse quadrupole relaxation rate is inversely proportional to τ_c , a trend exactly opposite that seen under the extreme narrowing condition. In the literature, nuclear quadrupole relaxation

properties in the slow motion limit have been utilized in studies of metal ion binding in metalloproteins,^{9–15} multiple-quantum NMR,^{16–20} and protein–ligand complexes.^{21–24} In addition, the same nuclear quadrupole relaxation properties are important for understanding dynamical processes in solid materials^{25–27} and, for example, for detecting Na^+ ions in tissues by magnetic resonance imaging (MRI).^{28,29} We should note that the nuclear quadrupole relaxation process can also manifest itself in the NMR spectra of spin-1/2 nuclei when they are J -coupled to quadrupolar nuclei.^{30–34} However, previous studies either dealt with nuclear quadrupole relaxation within narrowly defined ranges of molecular motion or probed it indirectly via detection of spin-1/2 nuclei. To the best of our knowledge, there has not been a single case in which NMR relaxation properties of a half-integer quadrupolar nucleus were fully examined over the entire range of molecular motion within the limit of the Redfield relaxation theory, that is, from the extreme narrowing to the slow motion limit. In this work, we report natural abundance ^{17}O ($I = 5/2$) NMR spectroscopic and relaxation results obtained for neat liquid glycerol, $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH})$, over a temperature range in which the value of τ_c changes nearly four orders of magnitude. These results represent the first direct

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Figure 1. Experimental (upper traces) and simulated (lower traces) ^{17}O 21.14 T NMR spectra of glycerol at different temperatures. NMR spectra were recorded at 122.0 MHz on a Bruker Avance-II spectrometer with a home-built solenoid probe (7 mm i.d.) using the following parameters: recycle delay, 10 ms; 60 000 transients; excitation pulse, $4\ \mu\text{s}$ (a selective 90° pulse for the CT; the B_1 field was $\sim 21\ \text{kHz}$); spectral window, 100 kHz. All experimental spectra were scaled to the same vertical height. In the spectral analysis, we assumed the same dynamic frequency shift and line width for the two components. All ^{17}O chemical shifts were referenced to external $\text{H}_2\text{O}(\text{liq})$. Sample temperatures were carefully calibrated using ^1H NMR spectra of pure methanol. The vertical dashed line is used to highlight the dynamic frequency shifts.

experimental verification of the theoretical predictions for nuclear quadrupole relaxation properties in liquids.

Figure 1 shows representative natural abundance ^{17}O NMR spectra of neat glycerol (99.5%) recorded at 21.14 T between 340 and 240 K. Even though the crystallization/melting temperature of neat glycerol is 291.8 K (18.6°C), it stays as a supercooled liquid well below this temperature down to the glass-transition temperature T_g of $\sim 190\ \text{K}$. Within the studied temperature range, the viscosity of glycerol changes over four orders of magnitude, from $5.3 \times 10^{-2}\ \text{Pa}\cdot\text{s}$ at 340 K to $1.7 \times 10^3\ \text{Pa}\cdot\text{s}$ at 240 K.³⁵ At the elevated temperature, 339 K, the ^{17}O NMR spectrum exhibits two resonances at 12 and $-10\ \text{ppm}$ with an integrated intensity ratio of 1:2, each having a full width at half-height (FWHH) of $\sim 2.4\ \text{kHz}$. The two ^{17}O NMR resonances

Figure 2. Experimental (data points) and theoretical (solid lines) results on the dependence of ^{17}O relaxation rates (R_1 and R_2) and dynamic frequency shift ($\Delta\delta_d$) on $\omega_0\tau_c$ for glycerol at two magnetic fields. To best-fit the experimental data, we added a small constant term in the theoretical curves ($2.0 \times 10^3\ \text{s}^{-1}$ for R_1 and $2.5 \times 10^3\ \text{s}^{-1}$ for R_2). See the text for discussion of other NMR parameters used for data analyses.

correspond to the two chemically different OH groups in glycerol. As the temperature is decreased, so τ_c increases, the spectral resolution worsens drastically. For example, at 282 K, the FWHH value exceeds 15 kHz. As a result, the two ^{17}O NMR signals cannot be resolved. These spectral features, well-known to most researchers, are often used, for example, in various textbooks, to highlight the nuisance of nuclear quadrupole relaxation processes and, as such, to argue against NMR applications of quadrupolar nuclei in large molecular systems. Once again, the common argument is that as τ_c increases NMR signals would become very broad. However, as clearly seen from Figure 1, when the sample temperature is further decreased, the ^{17}O NMR signal of glycerol actually becomes narrow again and, most remarkably, at 242 K, the two sharp ^{17}O NMR resonances (FWHH = 2.1 kHz) reappear again. It is striking that for glycerol the spectral resolution observed at 242 K is even somewhat better than that observed at 339 K. The origin of this spectral behavior is the multiexponential nature of the quadrupole transverse relaxation process. For $I = 5/2$, whereas the two satellite transitions ($m_I = +3/2 \leftrightarrow +1/2$ and $-3/2 \leftrightarrow -1/2$) are indeed too broad to be detectable in the slow motion limit, the

central transition (CT: $m_I = +1/2 \leftrightarrow -1/2$) exhibits a relatively slow transverse relaxation rate. As a result, only CT is observable in the slow motion region, having a line width inversely proportional to τ_c .

Another important feature of the CT signal is that its position is shifted from the true chemical shift position (very often toward the low-frequency direction) because of the presence of the dynamic frequency shift, as first shown by Werbelow.⁶ In general, the dynamic frequency shift depends on both the quadrupole coupling product, $P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$ and the applied magnetic field, B_0 (vide infra).

It is also important to mention two additional aspects of acquiring NMR spectra of quadrupolar nuclei in the slow motion limit. One is that the selective 90° pulse for the CT is known to be shorter than the conventional nonselective 90° pulse by a factor of $(I + 1/2)$. The other is that the maximum CT signal intensity observed in the slow motion limit is considerably reduced from the total signal intensity expected under the extreme narrowing condition where all transitions are detected. For $I = 3/2, 5/2, 7/2$, and $9/2$ nuclei, the maximum CT signal after a selective 90° pulse is only 20.0, 8.6, 4.8, and 3.0% of the total signal intensity, respectively.³⁶ Although this loss of signal intensity in the slow motion limit is undesirable, the benefit in resolution gain clearly outweighs the drawback.

Figure 2 shows the experimental results of ^{17}O NMR relaxation rates (transverse and longitudinal) and the dynamic frequency shift observed at 14.09 and 21.14 T for glycerol. Because no analytical expressions exist that can be used to describe the observed nuclear quadrupole relaxation rates over the entire range of $\omega_0\tau_c$, we performed numerical diagonalization of the Redfield relaxation matrices following a procedure previously described in the literature.^{37,38} The dynamic frequency shift can be calculated using the equations given by Werbelow.⁶ Assuming a single τ_c with an Arrhenius behavior, $\tau_c = \tau_0 \times \exp(E_a/RT)$, we were able to simultaneously fit all experimental ^{17}O NMR data obtained at two magnetic fields with a single set of parameters: $P_Q = 9.2 \pm 0.2$ MHz, $\tau_0 = 5.1 \pm 0.2 \times 10^{-20}$ s, $E_a = 57.3 \pm 0.5$ kJ mol⁻¹. The calculated τ_c values at various temperatures for glycerol are in qualitative agreement with the literature values from ^2H NMR for deuterated glycerol;^{32,39} details are given in the Supporting Information. For hydroxyl groups, because $\eta_Q \approx 1$, a $C_Q(^{17}\text{O})$ value of 8.0 MHz can then be estimated for liquid glycerol. This value is somewhat less than the 11 MHz computed for glycerol in the gas phase. The reduction in C_Q from gas to liquid is expected, in line with the previous observations for ^{17}O in water, H_2O ($C_Q = 10.2, 7.6$, and 6.9 MHz for vapor, liquid, and ice, respectively), which reflects the different degrees of hydrogen bonding between water molecules in different phases.^{40,41} We should add that although the agreement between experimental and theoretical results shown in Figure 2 is reasonable, visible deviations do exist, especially for data recorded at the lower magnetic field. Several factors may contribute to these observed discrepancies. First, the quality of the low-field experimental data is generally lower than that of the corresponding high-field data. Second, our assumption of a single τ_c with an Arrhenius behavior over a wide temperature range for supercooled glycerol is certainly an oversimplification. Third, dynamic heterogeneities may become significant at very low temperatures.

Here it is also important to comment on the entire range of molecular tumbling motion within which the Redfield relaxation theory is valid. Because the Redfield theory is based on a

perturbation approach, the upper limit for $\omega_0\tau_c$ is given by $(\nu_0/C_Q)^2$. For example, if $\nu_0 = 122$ MHz (the Larmor frequency of ^{17}O at 21 T) and $C_Q = 10$ MHz, then the entire range of motion is approximately $150 > \omega_0\tau_c > 0$. This range is consistent with those shown in Figure 2. For very slow motions that are beyond this range, the high order effects will become important.⁴²

In summary, we report the complete set of direct experimental NMR measurements on nuclear quadrupole relaxation properties over the entire range of motion within the limit of the Redfield relaxation theory. Our experimental results have fully verified the theoretical predictions on nuclear quadrupole relaxation properties including both transverse and longitudinal relaxation rates as well as dynamic frequency shifts. These new results further reinforce the argument that NMR studies of quadrupolar nuclei in liquids can be advantageous if carried out under the slow motion limit, as opposed to the common misconception that such studies should be done only in the fast motion limit. We hope that this work will help shift the existing paradigm regarding the feasibility of NMR in studying quadrupolar nuclei in liquids. This is of particular importance in the context of biological applications of NMR spectroscopy because many biological macromolecules would automatically be in the slow motion limit when placed in high magnetic fields.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details of quadrupole relaxation measurements. A complete set of ^{17}O NMR spectra of glycerol recorded at 14.09 and 21.14 T over different temperatures. A table containing τ_c values for glycerol and relevant literature values. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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