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Quadrupole Enhanced Proton Spin Relaxation for a Slow Reorienting Spin Pair:(I)--(S). The stochastic Liouville Approach

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Quadrupole Enhanced Proton Spin Relaxation
for a Slow Reorienting Spin Pair: (I)—(S)
A Stochastic Liouville approach

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July 14, 2009

Abstract

The field dependence of the proton (I) spin-lattice relaxation rate is calculated for a dipole-dipole coupled spin pair, $(I=\frac{1}{2})-(S=1)$ where the quadrupole nucleus (S) is ^2H or ^{14}N with asymmetry parameter $\eta = 0$. The observed relaxation profile shows a marked enhancement

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8 for equal proton Larmor and quadrupole spin frequencies (i.e. $\omega_I =$
9 ω_Q), This phenomenon is referred to as the quadrupole dip, and has
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11 been observed for instance in $^{14}\text{N} - ^1\text{H}$ amide groups of immobilized
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13 proteins.
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17 In this work an analysis of the observed relaxation enhancement is
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19 presented when the dipole-dipole coupling and the quadrupole inter-
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21 action are modulated by the overall reorientational motion.
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24 A characteristic low field dispersion is observed when $\frac{3}{2}\tau_R\omega_I \geq 1$
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26 where τ_R is the rotational correlation time and ω_I is the proton Larmor
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28 frequency. At higher fields the relaxation peak exhibits a Lorentzian
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30 like lineshape; $L(\omega_I) = [(\omega_Q - \omega_I)^2\tau_R^2(\frac{3}{5})^2 + 1]^{-1}$ which is centred at
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32 the quadrupole frequency. The quadrupole spin system shows a spin-
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34 lattice T_{1Q} and a spin-spin relaxation time T_{2Q} which become equal
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36 in the zero field limit. In the slow tumbling limit, **the quadrupole**
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38 **spin relaxation times**, T_{1Q}, T_{2Q} are equal to $\frac{3}{2}\tau_R$.
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46 1 Introduction

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49 The fast field-cycling technique is one of the most important NMR exper-
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51 iment for studies of molecular dynamics and structure. It has been used
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8 measuring the field dependent proton spin-lattice relaxation rate, R_1 - NMR
9 dispersion(NMRD) profile, for a large variety of systems [1] - [3]. In NMRD
10 measurements the relaxation rates $R_i(\omega)$ ($i=1,2$) of a spin system I are mea-
11 sured at the proton Larmor frequency that ranges between 10 kHz and about
12 40 MHz. In the strong narrowing regime, the proton(I) relaxation rates can
13 be expressed in terms of a spectral density function of the spin-lattice in-
14 teraction, which thereby determine the measured NMRD profile. When the
15 dipole-dipole interaction is the dominant spin-lattice interaction, this dipole-
16 spectral density function is the crucial quantity, which contains all the inter-
17 action parameters and information about molecular motions.
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33 During the last thirty years the Solomon-Bloembergen-Morgan theory[4]
34 of water proton R_1 -NMRD profiles of paramagnetic systems have been gener-
35 alised to describe different contrast agents[8]-[11] of high electron spin tran-
36 sition metal complexes including the slow-motion electron spin relaxation
37 problem[5]-[7]. Several experimental studies of 1H NMRD profiles obtained
38 for different paramagnetic systems have been reported [12]-[15], and vari-
39 ous computational methods have been developed to describe these systems
40 [16]-[19].
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53 There are also a large number of both theoretical and experimental NMRD
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8 studies reported on aqueous (diamagnetic) protein solutions[20]-[28]. For
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10 instance the NMRD experiment has been used to study the self associa-
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12 tion of proteins[29]-[31]. The theoretical description and characterization
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14 of the NMRD dispersion profile of protein solutions provides a challenging
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16 problem[23, 24, 28]. Among published NMRD studies a few observations of
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18 quadrupole dips(QD's) were reported[32]-[39]. That is, when the measured
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20 relaxation rate $R_1(\omega_I)$ displays a marked increase at the proton Larmor fre-
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22 quencies matching the resonance frequencies of a quadrupole spin system.
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24 (The "quadrupole dip" is observed in $1/R_1(\omega_I)$ profile). This enhanced re-
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26 laxation rate of an I-spin, coupled via a spin dipole-spin dipole interaction
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28 to a quadrupole nucleus(S), is a cross relaxation phenomenon, in which the
29
30 relatively fast relaxing quadrupole nucleus acts as a relaxation sink for a
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32 dipole coupled I-spin [1],[32]-[36]. The theoretical analysis presented in the
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34 literature is generally limited to the static regime. For instance, the QD's
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36 was observed and analysed in the plastic crystals phases of CFC1_3 [32], in
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38 the biaxial smectic mesophase of HpAB[33], and for amide protons or water
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40 in immobilized proteins[1], [34]-[39]. Nuclear quadrupole resonance (NQR)
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42 studies are relevant for the theory of cross relaxation, because at zero field,
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44 the spin quantisation is defined by the molecular fixed principal axes of the
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8 electric field gradient, NQR reports directly on the quadrupole spin system.
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10 The aim is to determine the transition frequencies of the quadrupole spin
11 system[33, 40].
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14 The present work focuses on reorientational effects in the proton spin
15 lattice relaxation enhancement of protons residing in the vicinity of a deu-
16 terium nucleus(^1H - ^2H) or for amide proton in a slightly simplified spin pair
17 ^1H - ^{14}N with an asymmetry parameter, $\eta=0$. The spin pairs may be present
18 in a globular macromolecule, that undergoes a slow tumbling motion. The
19 condition for slow tumbling is expected to be more important in proteins
20 studies which are carried out in "crowded", or more cell-like systems, as well
21 as for membrane proteins in vesicles. The characteristic rotation diffusion
22 correlation time $\tau_R \equiv 1/6D_R$, (D_R is the rotational diffusion coefficient) is
23 then expected to range between 50-100 ns for crowded protein solutions, to
24 about 1-2 μs for membrane proteins in giant vesicles.
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42 The proton R_1 -NMRD profile is measured over a wide range of proton
43 Larmor frequencies(ω_I), ranging from the low field regime $\omega_I \ll \omega_Q$ where
44 the quadrupole spin is quantized in a molecular fixed frame to the high field
45 regime when $\omega_I \gg \omega_Q$ and the spins are quantized in the laboratory frame.
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8 the quadrupolar frequencies of the S-system. In the high field regime the
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10 quadrupole NMR lineshape is often far too broad to be detectable. Con-
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12 sequently, when a NMRD profile detects a marked cross relaxation peak, it
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14 provides indirect information about the quadrupolar spin frequencies through
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16 the resonance conditions $\omega_I = \omega_Q$, but also about the dynamics which is re-
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18 vealed by the profile dispersions.
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23 A theoretical complication arises in the description of NMRD profiles for
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25 slow reorientations and when slow-motion conditions occur, that is, when the
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27 strong narrowing condition ($\omega_Q \tau_R \ll 1$) is violated. When $\omega_Q \tau_R \geq 1$ the QD's
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29 may be observed, while the quadrupole spin relaxation cannot be described
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31 within the Redfield/perturbation theory. Then it is most convenient to use
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33 the stochastic Liouville (SLE) formalism in the analysis of NMR/EPR slow-
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35 motion spectra. The SLE was developed by Kubo[41] and for the analysis
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37 of EPR line shapes it was further applied by Freed[42]. Actually, the SLE
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39 developed for paramagnetic systems describes the cross relaxation between
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41 protons and an electron spin system. This theory is applicable for the cross
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43 relaxation in reorienting spin pairs; $(I = 1/2) - (S = 1, \frac{3}{2}, 2, \frac{5}{2}, \dots)$ -pairs by
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45 replacing the electron spin system (S) by the quadrupole spin system(S)
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8 In a previous paper[43] we outlined how the QD's may be analysed within
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10 this SLE formalism for a $I=\frac{1}{2}$ — $S=1$ coupled spin pair. This work extends
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12 the analysis and it reveals previously not known dynamic features of the
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14 relaxation profile.
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19 • The NMRD profile displays a low field dispersion(cf. Figs.1 and 2)
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21 when $\frac{3}{2}\tau_R\omega_I \geq 1$
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25 • The enhancement peak can be approximated by the Lorentzian line-
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27 shape; $[(\omega_I - \omega_Q)^2(\frac{3}{5}\tau_R)^2 + 1]^{-1}$ which indicates a second characteristic
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29 correlation time $\frac{3}{5}\tau_R$.
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33 • In the zero field regime, the spin-spin and the spin-lattice relaxation
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35 times of the quadrupole spin system become identical and for slow
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37 tumbling systems they are equal to $\frac{3}{2}\tau_R$.
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41 The latter observation has also been reported for paramagnetic systems
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43 ($S=1$)[45, 17, 18] and it was also recently analysed in detail[19].
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2 The Stochastic Liouville (SLE) Relaxation

Theory

Consider a proton spin ($I=1/2$) which is dipole-dipole coupled to a quadrupole spin with spin quantum number $S=1$ (assuming an axial symmetry $\eta = 0$). When $\eta \neq 0$ the quadrupole spin degeneracy is lifted resulting in three quadrupole frequencies, i.e. $\omega_{Q1} = \omega_Q(1 + \eta/3)$, $\omega_{Q2} = \omega_Q(1 - \eta/3)$ and $\omega_{Q3} = 2\omega_Q\eta/3$ [40]. This makes the calculation more demanding, and instead leads to three dips in the static limit. For instance, the peptide bond display two transition frequencies at about 2.4 and 2.8 MHz which yield an asymmetry parameter $\eta = 0.23$. For deuterium in most compounds the asymmetry parameters is very small or 0. The axial symmetry considerably simplifies the numerical calculations as well as the influence of the quadrupole spin relaxation rate at high fields and the resonance conditions of the NMRD at low fields. However, the effects of rotational dynamics on the quadrupole spin relaxation and the NMRD profile are well demonstrated in the symmetric case (i.e. $\eta = 0$).

The relaxation path of the I-system is due to a nuclear spin(I)-quadrupole spin(S) dipole-dipole coupling. Thus, from the proton spin system point of

view the lattice comprises both a quadrupole spin system and the molecular reorientation diffusion degrees of freedom. The relaxation of the composite lattice, a spin $S=1$ system and the reorientational degrees of freedom, is rather complex in the presence of a strong quadrupole interaction, $\omega_Q \approx 1/\tau_R$. The quadrupole spin relaxation can not be described by using second order time dependent perturbation theory. Furthermore, it is not possible to treat the quadrupole spin relaxation separately from the reorientation motion. Instead, the lattice dynamics comprises both the reorientation and the quadrupole spin relaxation.

The field dependent proton spin-lattice relaxation $R_1(\omega_I)$ which defines the NMRD profile is given by[5, 6, 43]:

$$R_1(\omega_I) = 30 \left(\frac{\mu_0}{4\pi} \right)^2 \hbar^2 \gamma_I^2 \gamma_S^2 \frac{1}{(2S+1)r_{IS}^6} \times \sum_{p=\pm 1,0} \sum_{q=\pm 1,0} \begin{pmatrix} 2 & 1 & 1 \\ 1-p & p & -1 \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ 1-q & q & -1 \end{pmatrix} \times \int_0^\infty tr_L \{ S_p^{1\dagger} D_{0,1-p}^{2*} [\Omega_{LM}(\tau)] e^{i\mathcal{L}\tau} S_q^1 D_{0,1-q}^2 [\Omega_{LM}(0)] \frac{1}{8\pi^2} \} e^{-i\omega_I\tau} d\tau. \quad (1)$$

In Eq.(1) $\begin{pmatrix} 2 & 1 & 1 \\ 1-p & p & -1 \end{pmatrix}$ is a 3-j symbol[46] and the physical

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8 constants γ_I, γ_S and μ_0 are the proton nuclear magnetogyric ratio,
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10 the quadrupole nuclear magnetogyric ratio, and the permeability of
11 space, respectively; r_{IS} is the I-S interspin distance. The quantities
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13 $D_{n,m}^L[\Omega_{LM}(t)]$ are Wigner rotation matrix elements of rank L ; and
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15 they are functions of the Euler angles $\Omega(t)$ relating the laboratory
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17 fixed frame(L) to the molecular fixed frame (M). S_σ^1 is a standard
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19 spherical nuclear spin operator of rank 1 whereas \hbar is the Planck
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21 constant divided by 2π , ω_I is the proton Larmor frequency and τ
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23 refers to the time difference of the time correlation function
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30 It is presupposed that the principal frame of the quadrupole interaction
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32 coincides with the dipole-dipole r_{IS} vector. This simplification can be lifted,
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34 changing only the absolute level of the relaxation enhancement at low field
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36 region [47]. The relaxation rate R_1 is described by a 3×3 spectral density
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38 matrix defined as the Fourier-Laplace transform of the complex reorientation
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40 and quadrupole spin correlation function. The theory allows for a correlation
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42 between the reorientational motion and quadrupole spin relaxation. Conse-
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44 quently, it is not generally permissible to decompose the complex dipole-
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46 dipole correlation functions into a product of a quadrupole spin-spin or a
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48 spin-lattice correlation function and a reorientation correlation function. An
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element of the composite dipole-dipole spectral density matrix is exemplified by:

$$\int_0^{\infty} \text{tr}_L \{ S_p^{1\dagger} D_{0,1-p}^{2*} [\Omega_{LM}(\tau)] e^{i\mathcal{L}_L \tau} S_q^1 D_{0,1-q}^2 [\Omega_{LM}(0)] \sigma^T \} e^{-i\omega_I \tau} d\tau. \quad (2)$$

The time-dependence of this dipole-dipole correlation function is governed by the Liouville super operator, \mathcal{L}_L

$$\mathcal{L}_L = \mathcal{L}_Z + \mathcal{L}_Q(\Omega) + iD_R\Gamma_\Omega, \quad (3)$$

which is decomposed into a Zeeman term (\mathcal{L}_Z), the stochastic time dependent quadrupole interaction ($\mathcal{L}_Q(\Omega)$) and the reorientational diffusion Markov operator $D_R\Gamma_\Omega$ with $D_R = 1/6\tau_R$. The Liouville super operators of Zeeman and the cylindrical symmetric quadrupole interaction are generated by the corresponding hamiltonian:

$$H_Z + H_Q(t) = \omega_0 S_0^1 + V_0 \sum_n (-1)^n S_n D_{0-n}^{(2)} [(\Omega(t))]. \quad (4)$$

The field gradient is $V_0 = \chi\pi\sqrt{\frac{3}{2}}$ and the quadrupole coupling constant is $\chi \equiv \frac{eQV_{zz}}{h}$. The quadrupole frequency is given by $\omega_Q = \sqrt{3/2}V_0 = \frac{3}{2}\pi\chi$.

The spherical spin tensor operators are defined according to:

$$\begin{aligned}
 S_0^{(2)} &= \frac{1}{\sqrt{6}}[3S_z^2 - S(S+1)] \\
 S_{\pm 1}^{(2)} &= \mp \frac{1}{2}[S_z S_{\pm} + S_{\pm} S_z] \\
 S_{\pm 2}^{(2)} &= \frac{1}{2}S_{\pm}^2.
 \end{aligned} \tag{5}$$

In Eq(5) $S_m^{(2)}$ is a standard second rank spin operator and $D_{0-n}^{(2)}[(\Omega(t))]$ is a second rank Wigner rotation matrix element[46] with stochastic time dependent Euler angles $(\Omega(t))$ specifying the orientation of the principal frame of the quadrupole tensor.

2.1 The SLE Description of Lattice Dynamics

In order to determine the spectral density of Eqs.(1,2) one needs to solve the SLE of motion, which determines the time dependence of the lattice density matrix $\sigma(t, \Omega)$:

$$\frac{d}{dt}\sigma(t, \Omega) = -i\mathcal{L}_L(\Omega)\sigma(t, \Omega). \tag{6}$$

However, Eq.(1) expresses the NMRD profile in terms of the dipole-dipole spectral density matrix. It is therefore more convenient to solve the Fourier-

Laplace transformed equation of motion reading,

$$\sigma(0, \Omega) = i[\mathcal{L}_L(\Omega) - 1\omega]\tilde{\sigma}(\omega, \Omega), \quad (7)$$

where $\tilde{\sigma}(\omega, \Omega) = \int_0^\infty \sigma(t, \Omega)e^{i\omega t} dt$. The lattice density operator $\tilde{\sigma}(\omega, \Omega)$ satisfies the equation,

$$\begin{aligned} \tilde{\sigma}(\omega, \Omega) &= [i\mathcal{L}_Z - i\omega 1 + i\mathcal{L}_Q(\Omega) - D\nabla_\Omega^2]^{-1} \sigma(\Omega, 0) \\ &= [\mathcal{M}]^{-1} \sigma(\Omega, 0). \end{aligned} \quad (8)$$

In slowly reorienting spin systems the spin density operator is thus a function of both spin operators and Wigner rotation matrix elements[45]. The SLE(cf.Eq.8) can be solved by introducing a complete basis set of operators which span the composite spin and orientational Liouville space. The inverse of the Liouville matrix, $[\mathcal{M}]^{-1}$ thus contains all information about the observables of the spin systems and it is obtained by introducing a set of basis operators spanning the composite Liouville space. This set of basis operators can, for instance, be formed as the direct product of spherical irreducible spin operators($|\Sigma, \sigma\rangle$) and eigenfunctions($|L, M\rangle$) of the Markov diffusion operator Γ_Ω , thus forming the infinite basis set $\{|\Sigma, \sigma\rangle \otimes |L, M\rangle\}$.

The dipole-dipole spectral density of Eq.(1) is a submatrix of $[\mathcal{M}]^{-1}$ whereas the quadrupole lineshape function (cf.Eq.(12)) and the spin-lattice spectral density function(cf. Eq.(13)) are single matrix elements. The problem of solving the SLE in the time domain (Eq.(6) has been transformed to inverting a infinite Liouville matrix in the frequency domain(Eq.(8)). The details of this procedure are given elsewhere(ref.[44]) and in more general terms in ref.[5].

The irreducible spherical spin operators are given by[46, 48],

$$|\Sigma, \sigma\rangle = \sqrt{2\Sigma + 1} \sum (-1)^{S-\sigma-m} \begin{pmatrix} S & S & \Sigma \\ m + \sigma & -m & -\sigma \end{pmatrix} |S, \sigma + m\rangle \langle S, m|, \quad (9)$$

where the rank of the operators are $\Sigma = 0, 1, \dots, 2S$ and the components $\sigma = -\Sigma, -\Sigma + 1, \dots, \Sigma - 1, \Sigma$ and the ket-bra electron spin operator $|S, m\rangle \langle S, n|$ is formed as an outer product of spin eigenfunctions of S_0^1 and S^2 .

The molecular orientation space is spanned by the symmetric top functions $|LM\rangle$ which are eigenfunctions to the Markov operator Γ_Ω :

$$|LM\rangle = \sqrt{\frac{2L+1}{8\pi^2}} D_{0,M}^L(\Omega). \quad (10)$$

3 Results and Discussions

Before proceeding to the relaxation profiles, it is appropriate to define a reduced relaxation rate,

$$R = \frac{3R_1(\omega_I)}{4\gamma_I^2\gamma_S^2R^{-6}\tau_R}, \quad (11)$$

which is dimensionless and only depends on the dimensionless products $\omega_I\tau_R$, $\omega_Q\tau_R$ and $\omega_S\tau_R$. The marked relaxation peak is observable when $\omega_Q\tau_R \geq 1$ and the reduced relaxation rate $R=1$ when the dipole-dipole correlation time is equal τ_R . The quadrupole coupling constant $\chi = 3.596$ MHz is chosen to match the quadrupole frequency of the QD's of a $H-^{14}N$ pair[2, 35, 36]. The quadrupole frequency for ^{14}N with $\eta=0$ is then 2.7 MHz whereas for deuterium it is 0.15 MHz and $\chi=0.2MHz$.

In Fig.(1) the reduced relaxation rate of Eq(11) is displayed for a symmetric $^1H-^{14}N$ pair attached to a slow(isotropic) tumbling macromolecules. The characteristic NMRD profiles are calculated for four reorientation correlation times: $\tau_R = 50, 100, 150$ and 200 ns. The NMRD profiles have a characteristic low field dispersion determined by $\omega_I\tau_R\frac{3}{2} \geq 1$ and a marked increase in proton relaxation determined by the resonance condition $\omega_I = \omega_Q$.

Fig.2a-2c, the reduced relaxation rate is displayed for a dipole-dipole cou-

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pled proton-deuterium pair, $^1H-^2H$ ($\eta = 0.0$), attached to a slow(isotropic) tumbling macromolecules. The R_1 -NMRD profiles are calculated for three reorientation correlation times: $\tau_R = a) 1.4\mu s, b) 2.0\mu s, c) 3.0\mu s$, displaying NMRD profiles similar to Fig.1 but where the relaxation peak has moved to lower frequencies (0.15 MHz) . Fig.2c₂ shows the low field dispersions $\frac{1}{(\omega_I)^2(\frac{3}{2}\tau_R)^2+1}$. It should be remembered that for both Fig.1 and Fig.2 the low field dispersion changes to $\omega_I\tau_R \geq 1$ if the quadrupole coupling constant is made small enough to satisfy the strong narrowing conditions ($\omega_Q\tau_R \ll 1$). In Fig.(2c₃) the characteristic enhanced relaxation peak is described by a Lorentzian lineshape function $L(\omega_I) = \frac{X}{(\omega_Q-\omega_I)^2(\tau_c)^2+1}$. The effective correlation time τ_c is determined by the relaxation times of the spin correlation function and the reorientation correlation time; $\frac{1}{\tau_c} = \frac{1}{\tau_R} + \frac{1}{3/2\tau_R} = \frac{1}{3/5\tau_R}$. However, when $\omega_Q\tau_R \gg 1$ the approximate Lorentzian peak disappears and the lineshape becomes more complicated (not shown) displaying two or three maxima (still with $\eta = 0$).

3.1 The Lineshape Function $I(\omega)$ and the Spin-Lattice Relaxation $\tilde{C}_0(\omega)$ of the Quadrupole Spin $S=1$

The quadrupole line shape function at zero magnetic field as well as the NMR line shape function at high fields is obtained from the frequency dependence of one Liouville matrix element reading:

$$I(\omega) \equiv \int_0^\infty \langle S_1^{1,\dagger}(t) S_1^1(0) \rangle e^{-i\omega t} dt$$

$$\frac{S(S+1)}{2S+1} \text{Re}(1, 1|00|[\mathcal{M}]^{-1}|1, 1|00). \quad (12)$$

Here we use the notation introduced in Eqs(9) and (10) where $(1,1|00|$ refer to the basis set; $(\Sigma, \sigma|(L, M|^*$ with $|1,1|00)$ as its complex conjugate, in analogy with the ket-bra notation. The Fourier-Laplace transform of the quadrupole spin-lattice correlation function $C_0(t)$ is given by the lattice density matrix element $\sigma(\omega, \Omega)$ proportional to $|1,0\rangle 0,0)$ and obtained as the Liouville matrix element $(1, 0|(00|[\mathcal{M}]^{-1}|1, 0)|00)$,

$$\tilde{C}_0(\omega) \equiv \int_0^\infty \langle S_0^{1,\dagger}(t) S_0^1(0) \rangle e^{-i\omega t} dt =$$

$$\frac{S(S+1)}{2S+1} \text{Re}(1, 0|(00|[\mathcal{M}]^{-1}|1, 0)|00). \quad (13)$$

Fig.(3) displays the ^{14}N line shapes calculated for three correlation times: $\tau_R = 50, 100, 200$ ns, at a static field of 5 T with $\chi = 3.596 \text{ MHz}$ and $\eta = 0.0$. The spectra are very broadened and display a typical slow-motion character. The corresponding lineshapes at the low static magnetic field of $B_0 = 0.1$ T are displayed in Fig (4).

The NQR lineshape function $I(\omega)$ at zero field has been obtained in a closed form by using a low-field operator representation derived by Lynden-Bell[45]. The lineshape function was obtained for an electron spin system $S=1$, with an axially symmetric zero field splitting tensor:

$$I(\omega) = \frac{(\omega_Q^2/3 - \omega^2)\tau_R^2 + 1 - i2\tau_R\omega}{\omega(\omega_Q^2 - \omega^2)\tau_R^2 + 1 - i2\tau_R(\omega^2 - \omega_Q/3)}. \quad (14)$$

The ^{14}N line shapes were calculated using Eq.(12), displayed at low field (0.1 T) and for three correlation times $\tau_R = 50, 100$ and 200 ns corresponding to NMRD profiles displaying a quadrupole dip. In this case when $H_Q \gg H_{Zeeman}$ and slow tumbling ($\omega_Q\tau_R \gg 1$) Eq(14) display a single Lorentzian line shape at $\omega_Q = \frac{3}{2}\chi\pi$ with half width at half height equal to $4D_R$ or $T_{2Q} = \frac{3}{2}\tau_R$ [45]. This observation has recently been reported by Sharp[17] and Fries and Belorizky[18].

In the zero field limit and slow tumbling, the quadrupole spin-lattice

correlation function decays also with a single exponential $T_{1Q} = \frac{3}{2}\tau_R$ which reads,

$$\langle S_0^{1,\dagger}(t)S_0^1(0) \rangle = \frac{2}{9}(1 + 2\cos(\omega_Q t))e^{-t/T_{1Q}}. \quad (15)$$

This form of the correlation function is also discussed by Fries and Belorizky for a paramagnetic spin system with electron spin quantum number $S=1$ [18].

The Fourier-Laplace transform of Eq.(15) is,

$$\begin{aligned} \tilde{C}_0(\omega) \equiv \int_0^\infty \langle S_0^{1,\dagger}(t)S_0^1(0) \rangle e^{-i\omega t} dt = \frac{2T_{1Q}}{9} & \left(\frac{1}{1 + \frac{9}{4}(\omega\tau_R)^2} \right. \\ & \left. + \frac{1}{1 + \frac{9}{4}((\omega + \omega_Q)\tau_R)^2} + \frac{1}{1 + \frac{9}{4}((\omega - \omega_Q)\tau_R)^2} \right), \quad (16) \end{aligned}$$

and give the same shape as Eq.(14) when $\omega_Q\tau_R \rightarrow \infty$ and $T_{1Q} \rightarrow \frac{3\tau_R}{2}$. In Fig.(5a) $\tilde{C}_0(\omega)$ of Eq(13) is displayed for the resonance condition $\omega_I = \omega_Q$ and $\tau_R = 100$ ns ,whereas in 5b-d the magnetic field is 0.1 T and the correlation time has increased to 200 ns. **It is evident that with an increasing reorientation correlation time, $\tilde{C}_0(\omega)$ in Fig. 5.c approaches the result predicted by Eq. (16), which is displayed in Fig. 5d. Consequently, Eq.15 is only valid in the zero field limit and $\omega_Q\tau_R \rightarrow \infty$ with $T_{1Q} = \frac{3}{2}\tau_R$**

In the low (zero) field regime and slow motion the spin-spin relaxation

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8 time T_{2Q} thus becomes identical with the "spin-lattice" relaxation time T_{1Q}
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10 given by $\frac{3}{2}\tau_R$.
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13 14 15 16 4 Final Remarks

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19 The Stochastic Liouville approach was applied for calculating the quadrupole
20 enhanced proton spin relaxation profiles, which display the characteristic
21 peak or the quadrupole dip (if the frequency dependent relaxation time is
22 plotted). The quadrupole spin systems studied are $^{14}N(\eta = 0)$ and $^2H(\eta = 0)$
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24 For proton in the vicinity of the quadrupole nuclei, the R_1 -NMRD profiles
25 show two interesting features related to the reorientation dynamics. Firstly,
26 a low field dispersions at $\omega_I 3/2\tau_R = 1$ and and a Lorentzian shaped relax-
27 ation peak with a characteristic relaxation time $\tau_c = 3/5\tau_R$. At very slow
28 reorientation this simple lineshape disappear and a more complicated line-
29 shape appears. In the limit of large quadrupole interaction compared with
30 the Zeeman and slow motion $\omega_Q\tau_R \gg 1$ the quadrupole spin system have a
31 spin-lattice, T_{1Q} , and a spin-spin relaxation time, T_{2Q} , which both approach
32 $\frac{3}{2}\tau_R$ and the line shape function of Eq(14) predict the same relaxation as
33 given by Eq(16).
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11
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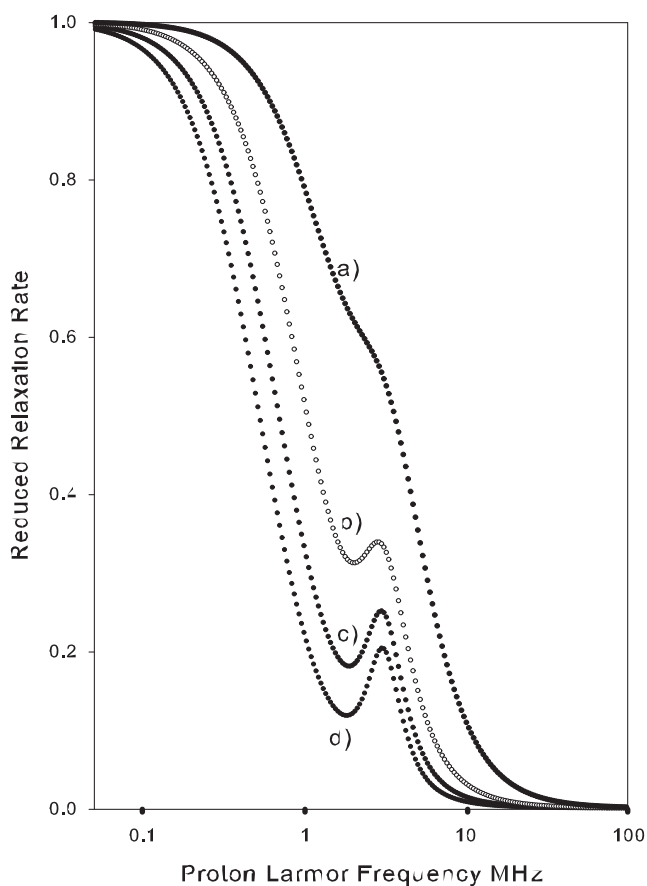


Figure 1: The reduced proton spin lattice relaxation rate as a function of proton Larmor frequency (MHz) displayed for $^1H^{14}N$ coupled pair ($S=1$, $\eta = 0.0$) with a quadrupole coupling constant of $\chi = 3.596 MHz$ and reorientation correlation times $\tau_R =$ a) 50, b) 100, c) 150 d) 200 ns

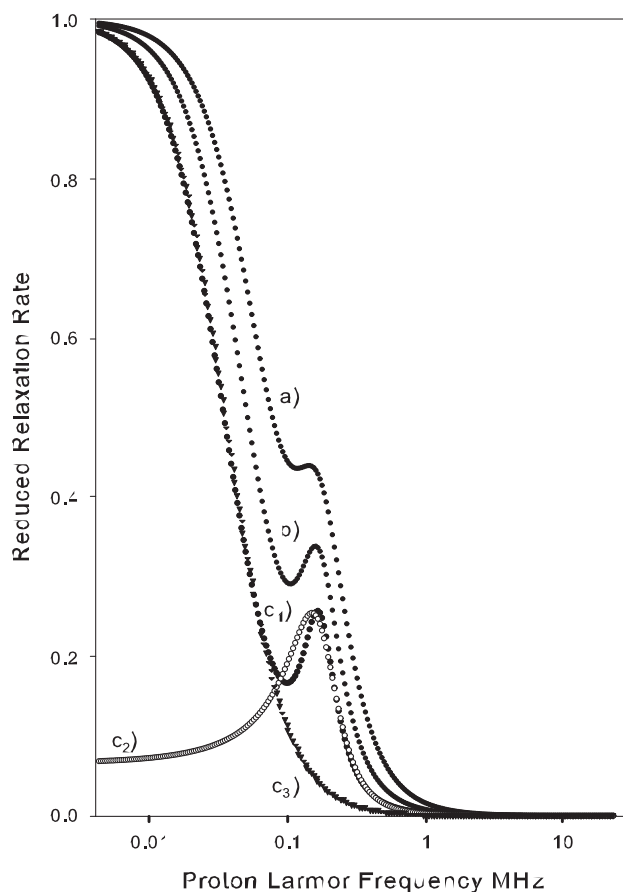


Figure 2: The reduced proton spin lattice relaxation rate is displayed as a function of proton Larmor frequency (MHz) for a $^1H^2H$ coupled pair ($S=1$, $\eta = 0.0$). The deuterium quadrupole coupling constant is $\chi = 0.2 \text{ MHz}$ and reorientation correlation times are $\tau_R =$ a) $1.4 \mu\text{s}$, b) $2.0 \mu\text{s}$, c) $3.0 \mu\text{s}$. In c_2) the "dip" lineshape is approximated with a Lorentzian $\frac{X}{(\omega_I - \omega_Q)^2 (\frac{3}{5}\tau_R)^2 + 1}$ with $X=0.255$. In c_3) the dispersion function $\frac{1}{(\omega_I - \omega_Q)^2 (\frac{3}{2}\tau_R)^2 + 1}$ is shown

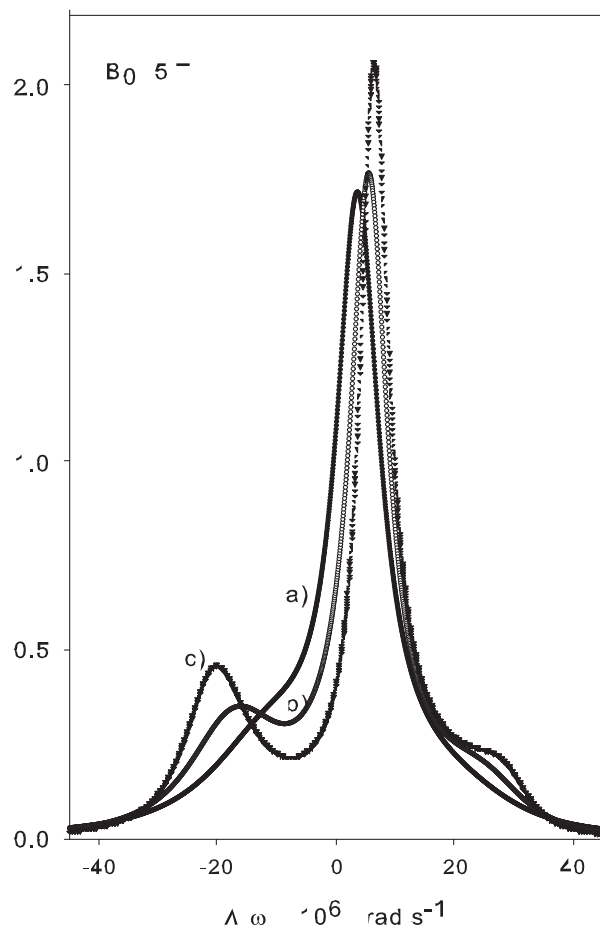


Figure 3: The ^{14}N lineshapes at 5 T and with $\chi = 3.596 \text{ MHz}$ and $\eta = 0.0$ is displayed for the correlation times $\tau_R =$ a) 50, b) 100 c) 200 ns

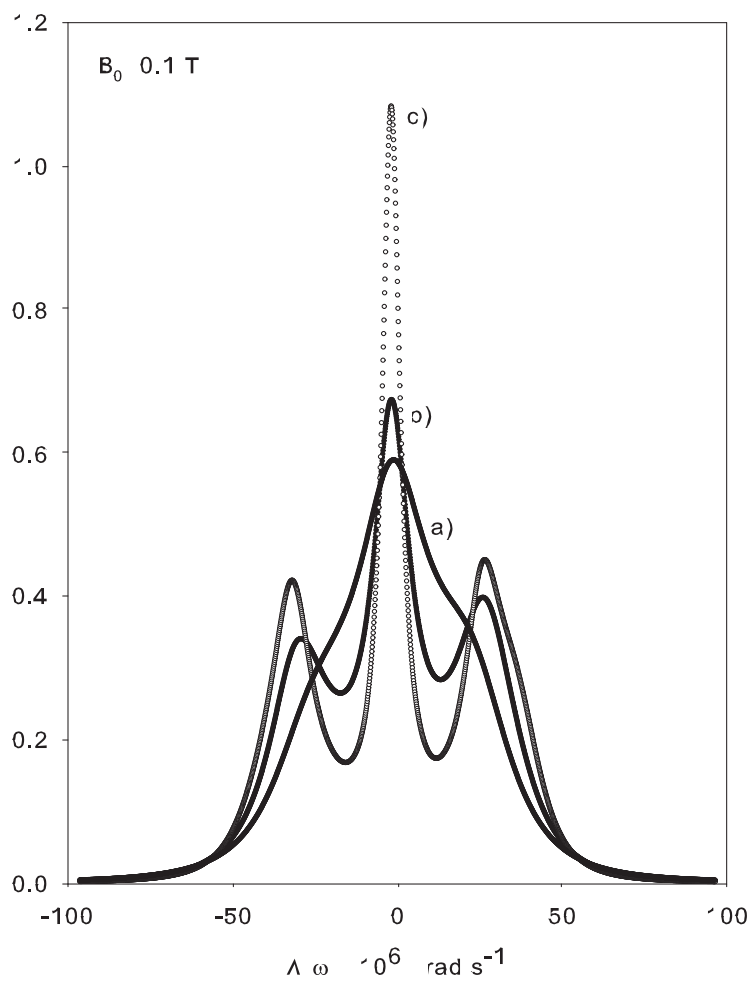


Figure 4: The ^{14}N lineshapes at 0.1 T and with $\chi = 3.596 \text{ MHz}$ and $\eta = 0.0$ is displayed for the correlation times $\tau_R =$ a) 50, b) 100 c) 200 ns

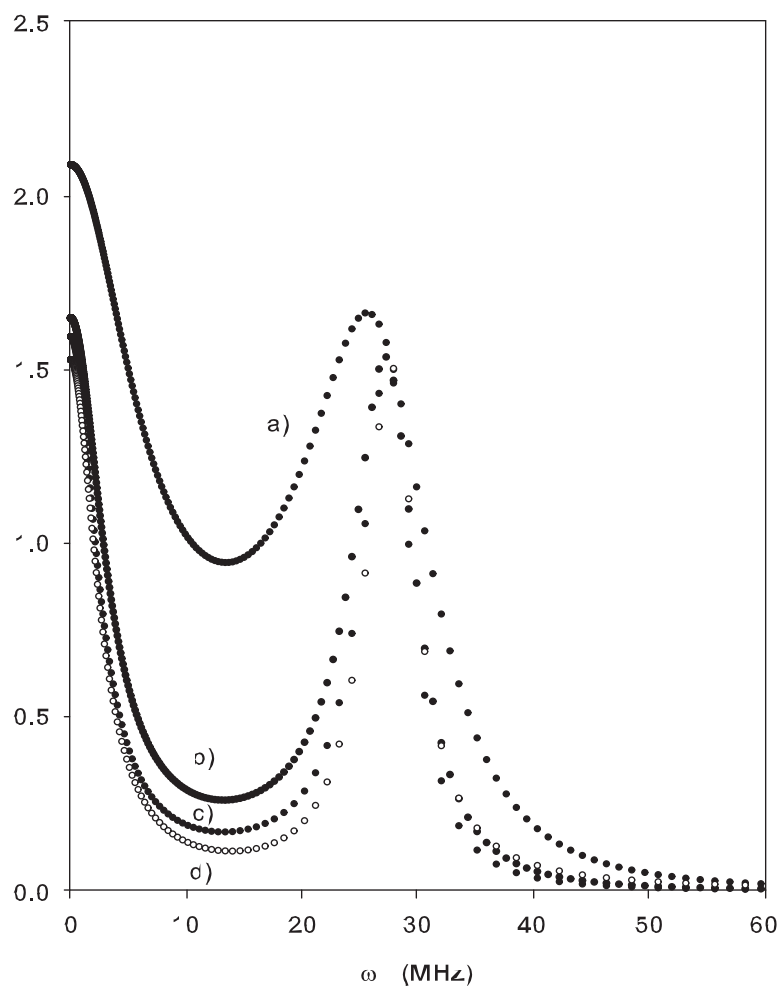


Figure 5: $\tilde{C}_0(\omega)$ are displayed for N-14 and quadrupole interaction $\chi = 3.596$ MHz in a) $B_0 = 0.8769$ T, $\tau_R = 100$ ns and b) 0.01 for $\tau_R = 200$ ns, and in (c) and (d) $\tau_R = 250$ where Eq (16) is displayed in d)