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Nuclear electric quadrupole interactions in liquids entrapped in cavities

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Abstract Liquids entrapped in cavities and containing quadrupole nuclei are considered. The interaction of the quadrupole moment of a nucleus with the electric field gradient is studied. In such a system, molecules are in both rotational and translational Brownian motions which are described by the diffusion equation. Solving this equation, we show that the intra- and intermolecular nuclear quadrupole interactions are averaged to zero in cavities with the size larger than several angstroms.

Keywords Nuclear quadrupole resonance · Cavity · Rotational and translational Brownian motions · Averaged quadrupole Hamiltonian

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1 Introduction

In a crystalline solid, the electric quadrupole moment, eQ, of a nucleus possessing a spin greater than $I > 1/2$, interacts with the gradient of the electric field, $\frac{\partial^2 V}{\partial x_i \partial x_j}\left(x_i,\, x_j = x,\, y,\, z\right)$ generated by the surrounding electrons or external charges of other nuclei. The interaction results in splitting of the energy levels which are separated by distances proportional to the quadrupole coupling constant $\frac{e^2 Qq}{h}$, where $eq = \frac{\partial^2 V}{\partial z^2}$, and V is the potential of the electric field and e is the proton charge [1, 2].

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Without application of an external magnetic field, in solids for which the direction of the electric field gradient (EFG) does not vary in time, the nuclear quadrupole interaction (NQI) creates a discrete spectrum, which can be detected by the pure nuclear quadrupole resonance (NQR) [1–4].

Analysis of the properties of the NQI of a spin system of solids and liquids reveals some significant similarities to the nuclear magnetic dipole-dipole interaction (DDI) [1–4]. In particular, in an isotropic bulk liquid, continual tumbling of molecules averages the secular parts of both interactions to zero, while the non-secular ones cause relaxation of the spin system [1–4].

In a liquid entrapped in nanocavities the motion of molecules is restricted but they still move randomly. The DDIs are not averaged to zero [5] and they are observed in NMR spectrum if the characteristic time t_{tran} of the translational diffusion is much less than the characteristic time of flip-flop process t_{mag} [6–12]. Estimations show that DDI in the NMR signal can be detected if the characteristic size of a nanocavity does not exceed 10^3 of the typical size of a molecule [13].

Below we show that the situation is radically different in the case of NQI. In this case the EFG is not averaged to zero in a nanocavity if $t_{tran} < t_{rot}$, where t_{rot} is the characteristic time of the molecular rotational diffusion. The condition $t_{tran} < t_{rot}$ corresponds to a cavity with a size of the order of a molecule. Only in such small cavity NQIs are not averaged to zero and NQR signals can be detected.

2 Averaged nuclear quadrupole Hamiltonian

Let us consider a quadrupole nucleus with spin $I > 1/2$. Quadrupole coupling exists between a non-spherical nuclear charge distribution and the EFG generated by the charges in its surroundings. These field gradients are averaged to zero in liquids due to molecular motion

To demonstrate this effect, let us assume for simplicity that the EFG is axially symmetric and the rotation of a molecule occurs around an axis $\vec{l}$, which direction is determined by polar θ angle in the laboratory frame (LF) [14]. The quadrupole Hamiltonian can be presented in the following form [14]

$$H_Q^{(1)}(\theta) = \frac{e^2qQ}{16I(2I-1)\hbar}\left(3I_z^2 - \vec{I}^2\right)\left(3\cos^2\theta - 1\right), \tag{1}$$

where I_z is the projection of the angular spin momentum operator $\vec{I}$ on the z-axis of the LF.

In a bulk liquid, the z-axis of the laboratory frame does not point into a preferred direction, and therefore all values of the angle θ in (1) become equiprobable. Then, taking into account the ergodic theorem [6, 7], the spin evolution in a nanocavity can be described by the averaged Hamiltonian, which can be find by integrating (1) over the surface area

$$\left\langle H_Q^{(1)}\right\rangle_{(\theta)} = \frac{1}{2\pi}\frac{e^2qQ}{16I(2I-1)\hbar}\left(3I_z^2 - \vec{I}^2\right)\int_0^{\pi}\sin(\theta)\left(3\cos^2\theta - 1\right)d\theta\int_0^{2\pi}d\varphi. \tag{2}$$

The integral over θ in (2) from 0 to π equals to zero. So, the NQI necessarily vanishes at $t \to \infty$ if there is no obstacle to the random rotation of molecules.

It is possible that the NQI is not averaged through a limited period of time or when the distribution of the z-axis direction is nonuniform. Among various NQIs it is useful to distinguish between intramolecular interactions inside a molecule and intermolecular interactions of different molecules. It is necessary to emphasize that due to the $\frac{1}{r^3}$ dependence and the zero electric charge of the molecules, the charges of electrons close to the nucleus have the most important effect. Therefore, the intramolecular NQIs make a decisive contribution to the quadrupole energy splitting.

To estimate the time dependence of the averaged Hamiltonian,

$$\left\langle H_Q^{(1)} \right\rangle (t) = \frac{e^2 q Q}{16 I (2I-1)\hbar} \left(3 I_z^2 - \vec{I}^2 \right) \left(3 \left\langle \cos^2 \theta \, (t) \right\rangle - 1 \right) \tag{3}$$

let us consider a molecule, such as heavy water D_2O.

We assume, following Abragam [3], that rotational and translational Brownian motions of the molecules are described by the diffusion equations.

3 Rotational Brownian motion

We suppose that $\Psi(\theta,\ t)\ d\theta$ is the probability of finding the z-axis in the direction between θ and $\theta + d\theta$ at the time t and the molecule can be represented as a sphere with the effective hydrodynamic radius of the water molecule λ and the viscosity σ in a liquid. We measure the angle θ from the direction of the z-axis at the time t_0. Moreover, we assume that the random process is homogeneous in time and the probability of changing the direction of the axis depends on the duration of the time t, so that, without loss of generality, we can set $t_0 = 0$. Under these suppositions, the probability density $\Psi(\theta,\ t)$ can be described by the rotational diffusion equation [15]

$$\frac{\partial \Psi(\theta,\ t)}{\partial t} = \frac{1}{\sin\theta} D_{rot} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Psi(\theta,\ t)}{\partial \theta} \right), \tag{4}$$

with the normalization condition $\int_0^\pi \Psi(\theta,t) \sin\theta d\theta = 1$ and the rotational diffusion constant D_{rot} is given by Stokes's formula

$$D_{rot} = \frac{kT}{8\pi\lambda^3\sigma}. \tag{5}$$

Since the expression in the last brackets in (3) may be expressed in terms of sine, following Leontovich [15] let us calculate the average square of the sine

$$\left\langle \sin^2\theta \right\rangle = \int_0^\pi \Psi(\theta,t) \sin^3\theta d\theta. \tag{6}$$

Using (4) we will find the time dependence of $\left\langle \sin^2\theta \right\rangle$ assuming that $\left\langle \sin^2\theta \right\rangle = 0$ at $t = 0$. Multiplying (4) by $\sin^2\theta$ and integrating over the angle θ, we get

$$\frac{d\left\langle \sin^2\theta \right\rangle}{dt} = \int_0^\pi \sin^3\theta \frac{\partial \Psi(\theta,\ t)}{\partial t} d\theta = D_{rot} \int_0^\pi \sin^2\theta \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial \Psi(\theta,\ t)}{\partial \theta} \right) d\theta. \tag{7}$$

Converting the right part of (7) by double integration by parts and using (4), we obtain

$$\frac{d\left\langle \sin^2\theta \right\rangle}{dt} = 2D_{rot} \left(2 - 3 \left\langle \sin^2\theta \right\rangle \right). \tag{8}$$

Solving (8), we get

$$\left\langle \sin^2\theta \right\rangle (t) = \frac{2}{3}\left(1 - e^{-6D_r t}\right). \tag{9}$$

Substituting (9) into (3), we obtain

$$\left\langle H_Q^{(1)} \right\rangle (t) = \frac{e^2 q Q}{8I(2I-1)\hbar}\left(3I_z^2 - \vec{I}^2\right) e^{-6D_{rot} t}. \tag{10}$$

To estimate the diffusion coefficient D_{rot} for heavy water D_2O, we use (5) with the following parameters at room temperature: $\sigma = 8.94 \times 10^{-4}\,\frac{Ns}{m}$; $\lambda = 2 \times 10^{-10}$ m, which gives $D_{rot} = 4.3 \times 10^{10}\,\frac{1}{s}$. Thus, for heavy water, the NQI is averaged to zero during the time of the order $t \approx \frac{1}{6D_{rot}} = 3.9 \times 10^{-12}\,s$.

4 Translational Brownian motion

In the case of restricted geometry, random Brownian motion of the molecules is also limited, that in turn restricts rotational motion. The restriction can prevent averaging NQI to zero, as it occurs in the cavities with dimensions on the order of nanometers for the DDI [6–12]. In order to estimate sizes of the cavity where the NQI does not vanish, let us estimate the time, during which a molecule arrives at the cavity wall, using the one-dimensional diffusion equation [15]

$$\frac{\partial W(x,\,t)}{\partial t} = D_{tran}\frac{\partial^2 W(x,\,t)}{\partial x^2}, \tag{11}$$

for the probability $W(x,\,t)$ which means that the water molecule, located at a point with coordinate x at $t = 0$, at least once achieves a boundary ($x = a$ or $x = b$). $\frac{\partial W(x,t)}{\partial t}dt$ determines the probability that a molecule will reach one of the boundaries in the time interval between t and $t + dt$. Translational diffusion constant D_{tran} is given by

$$D_{tran} = \frac{kT}{6\pi\lambda\sigma} \tag{12}$$

At the boundaries $x = a$ and $x = b$ the probability for each t is $W(a,\,t) = W(b,\,t) = 1$. For all values of x inside of the interval $(a,\,b)$ at $t = 0$ the probability equals zero: $W(x,\,0) = 0$.

Using (11), we can find the average time required by a water molecule, initially located at point x inside of the interval $(a,\,b)$, to reach the boundaries. This time is determined as [15]

$$\langle t\rangle\,(x) = \int_0^\infty t\frac{\partial W(x,t)}{\partial t}dt, \tag{13}$$

The average time should satisfy the differential equation, which can be obtained in the following way. First, (11) is differentiated respect to t, then multiplied by t and integrated over t from 0 to ∞ [15]:

$$\int_0^\infty t\frac{\partial^2 W(x,t)}{\partial t^2}dt = D_{tran}\frac{\partial^2}{\partial x^2}\int_0^\infty t\frac{\partial W(x,t)}{\partial t}dt. \tag{14}$$

Integrating by parts the left side of (14), we have

$$\int_0^\infty t\frac{\partial^2 W(x,t)}{\partial t^2}dt = -1. \tag{15}$$

Substituting this value into (14), we obtain the differential equation for the average time of achievement of the boundaries

$$D_{tran}\frac{d^2\left\langle t\right\rangle\,(x)}{dx^2}=-1 \tag{16}$$

with the boundary condition $\langle t\rangle(a)=\langle t\rangle(b)=0$.

Solution of (16) is

$$\left\langle t\right\rangle\,(x)=\frac{(b-x)\,\,(x-a)}{2D_{tran}} \tag{17}$$

and it has a maximum

$$\left\langle t\right\rangle_{\max}(x)=\frac{(a-b)^2}{8D_{tran}} \tag{18}$$

at $x=\frac{1}{2}\,(a+b)$.

Substituting (5), (12) and (18) into (10) we have

$$\left\langle H_Q^{(1)}\right\rangle\,(t)=\frac{e^2qQ}{8I(2I-1)\hbar}\left(3I_z^2-\vec{I}^2\right)\,e^{-\left(\frac{3(a-b)}{4\lambda}\right)^2}. \tag{19}$$

Therefore, even in relatively small cavities with a characteristic size of a few molecular diameters, the NQI is averaged to zero. Only if the index of the exponential function is on the order of unity $\left(\frac{3(a-b)}{4\lambda}\right)^2\sim 1$, then the quadrupole splitting of the energy levels in liquid can be observed.

5 Conclusion

It was shown that the both kinds of NQI, intramolecular and intermolecular, are averaged to zero even for extremely small cavities with size of a few times larger than size of molecules. NQR signals can be detected only in materials with very small cavities with the size of few angstroem. This is a significant distinction from DDIs. The intramolecular DDIs are also averaged while the NMR signals due to intermolecular DDI are observed till the size of cavities of 750 nm.

In gases at low pressures, the probability of intermolecular collisions is small, and the direction of the z-axis, around which the molecules rotate, is not changed. Therefore, in gases at low pressures one can observe the effects of the NQI [1]. The fact of observing NQR can be taken as an evidence of a preferred orientation of the z-axis.

We note that the considered model can be easily extended to the case of with non- axially symmetric of the EFG.

In conclusion, we note that the results obtained in this paper are also valid for the case when the spin system is located in an external magnetic field. The quadrupole part of the Hamiltonian is described by the same (1) [14].

The observation NQR signals is possible if the water molecules stick to the walls of the cavity. In this case, the rotation of the molecules occurs around axes fixed in space, that does not lead to averaging the NQI.

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