



New assignment of ^{14}N NQR spectral lines for tetrazoles derivatives

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ABSTRACT

In recent years, considerable interest has been shown in the study of tetrazole derivatives, which attract attention as highly nitrogenous compounds for use as an isosteric substitutes for various functional groups that leads to creation of novel biologically active substances. NQR techniques, being sensitive to the local environment of ^{14}N nuclei, provide great opportunities to study these new substances. To make investigation of complex compounds containing tetrazoles derivatives easier and more reliable a correctly assigned ^{14}N NQR spectra of tetrazoles are required. Here we report on the results of our DFT B3LYP calculations of ^{14}N NQR spectral parameters (quadrupole coupling constant Q_{cc} and the asymmetry parameter of the electric field gradient η) for tetrazole, 5-aminotetrazole and 5-aminotetrazole monohydrate. It has been found that the commonly accepted assignment of the ^{14}N NQR spectral lines for these molecules is incorrect. A new assignment for these molecules is proposed.

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1. Introduction

Nuclear quadrupole resonance (NQR) is one of the effective methods to study molecular structures and dynamic in solid state. The main physical parameter that can be determined from the NQR spectra is the tensor of quadrupole interactions, which are interactions between the nuclear quadrupole moment and intercrystalline electric field gradients (EFG). As soon as the latter is very sensitive to the local environment of the studied nuclei [1,2] NQR allows us to obtain detailed information on crystal symmetry and bonding, phase transitions [2–6] and so on. Even though the NQR method has several practical limitations due to its high sensitivity it may compete with such commonly used structural methods as X-ray diffraction, infrared Fourier spectroscopy and nuclear magnetic resonance. This method is especially powerful to study polymorphic structures [7]. A number of NQR techniques have been developed for detection of explosives [8,9], drugs identification [4,5] and medicines authentication [10,11].

In recent years, considerable interest has been shown in the study of tetrazole derivatives, which attract attention as highly nitrogenous compounds for use as a component of rocket fuels and blended explosives [7,12–14]. Tetrazole derivatives are used

as inhibitors of corrosion in copper and aluminum [15,16] and as a convenient starting material for the synthesis of other tetrazole derivatives. Moreover, tetrazole rings are increasingly being used as isosteric substitutes for various functional groups, which are used for creation of novel biologically active substances [12]. From this perspective, a correct assignment of the NQR lines of tetrazole derivatives is highly required as it will facilitate the analysis of NQR spectra of more complex structures containing tetrazole rings and will provide additional or refining information on the structure of compounds [17]. Some recent investigations have been devoted to the study of tetrazoles by the ^{14}N NQR methods [7,18].

For the first time, the assignment of the NQR lines of ^{14}N nuclei in tetrazole (TZ) was carried out using the double NQR resonance and *ab initio* molecular orbital method for a tetrazole trimer [18]. The authors noted the difficulty in identifying the NQR frequencies for ^{14}N at the positions N2 and N3 in tetrazole [18]. Further, based on these results the ^{14}N NQR frequencies and spin–lattice relaxation times measured in 5-aminotetrazole (ATZ) and 5-aminotetrazole monohydrate (ATZH) within temperature range from 77 to 300 K were assigned [7]. A comparative analysis of theoretical and experimental data for TZ, ATZ and ATZH obtained in Refs. [7,18] has revealed some inconsistencies. In particular, the EFG asymmetry parameters calculated for ^{14}N nuclei in tetrazoles significantly differs from the values determined from experimental spectra. It should be noted that the abnormal change in the EFG temperature dependence at N1 and N5 nitrogen nuclei observed in Ref. [7] was not explained.

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We have assumed that a possible issue of such a discrepancy between the experimental and calculated ^{14}N NQR data is either an imperfection of the computational model or an incorrect assignment of the ^{14}N NQR spectral lines. Due to the growing interest in the synthesis of new drugs, which include tetrazole rings with substituents [19], theoretical data consistent with experimental ones are highly required for unambiguous interpretation of ^{14}N NQR spectra of new compounds.

Moreover, correct quantum-chemical description of tetrazole derivatives will provide information about chemical bonding that is extremely important for further development of these materials.

In this paper to verify the assignment of the signals in ATZ ^{14}N NQR spectra the *ab initio* calculations of the EFG tensor and NQR frequencies have been carried out.

2. NQR theory

Hamiltonian of quadrupole interaction in EFG principal axis frame (PAF) can be written as follows:

$$\hat{H}_Q = \frac{eQq_{zz}}{4} \left(3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2} (\hat{I}_+^2 + \hat{I}_-^2) \right) \quad (1)$$

where e is the electron charge; eq_{zz} is the principal component of the EFG tensor; Q is the nuclear quadrupole moment; \hat{I} is the nuclear spin operator; \hat{I}_z is the operator of the nuclear spin projection on the direction of the principal axis of the EFG tensor; $\eta = |(q_{xx} - q_{yy})/q_{zz}|$, is the asymmetry parameter of the EFG tensor; \hat{I}_+ , \hat{I}_- are the ladder operators. We remind that in PAF the axes are determined in such a way that $|q_{xx}| \leq |q_{yy}| \leq |q_{zz}|$.

For nuclei with spin $I = 1$, such as ^{14}N , the matrix representation of Eq. (1) is

$$H_Q = eQq_{zz} \begin{pmatrix} \frac{1}{4} & \frac{\eta}{4} & 0 \\ \frac{\eta}{4} & \frac{1}{4} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix} \quad (2)$$

The eigenvalues of the Hamiltonian can be found by reducing the matrix (2) to the diagonal form and are

$$\lambda_{1,2} = \frac{eQq_{zz}}{4} (1 \pm \eta); \quad \lambda_3 = -\frac{eQq_{zz}}{2} \quad (3)$$

Thus, for a nucleus with $I = 1$ in an inhomogeneous electric field there are three energy levels and three transitions can be excited by radio-frequency field at the corresponding resonant frequencies, which for ^{14}N NQR are:

$$\nu_{\pm} = \frac{\lambda_{1,2} - \lambda_3}{h} = \frac{eQq_{zz}}{4h} (3 \pm \eta); \quad \nu_0 = \frac{\lambda_1 - \lambda_2}{h} = -\frac{eQq_{zz}}{2h} \eta \quad (4)$$

As soon as ^{14}N NQR frequencies obey the following equation: $\nu_+ = \nu_- + \nu_0$, it is easy to see that the quadrupole coupling constant Q_{cc} and the anisotropy parameter η can be calculated from the NQR frequencies as follows:

$$Q_{cc} = \frac{eQq_{zz}}{h} = \frac{2(\nu_+ + \nu_-)}{3} \quad \text{and} \quad \eta = \frac{(\nu_+ - \nu_-)eQq_{zz}}{2h} \quad (5)$$

3. Experimental and computational methods

5-aminotetrazole monohydrate samples of technical purity 95% have been purchased from Sigma Aldrich (Product of Germany, P-code 101419441). ^{14}N NQR experiments have been carried out on Tecmag Apollo NQR/NMR consoles (0.1–100 MHz) with two-channel transmitter and one-channel receiver modules. Tomco power amplifiers with output power of up to 500 W (or 250 W) has been used. To record ^{14}N NQR signal from ATZH we have used a single

coil 3 mL probe consisting of a solenoid coil connected with a variable capacitor. The coil diameter is 0.8 cm and its length is 3 cm. A low-noise single-channel preamplifier Miteq and auxiliary electronic circuits have been inserted between the probe and the Tecmag NMR/NQR Console.

A two-frequency NQR experiment with the pulse parameters: $t_1 = 100 \mu\text{s}$, $t_2 = 2 \mu\text{s}$, interval between series equal 200 ms has been applied to determine the bound transitions. Two NQR methods with two orthogonal coils and single coil were used which were described early in [8,10,11]. The detector unit for such an experiment consists of a system of two orthogonal coils, each of which is connected to variable capacitor to form a serial/parallel resonance circuit tuned to its own resonance frequency [11]. For single coil measurements the probe consisting of solenoid coil connected to a variable capacitor has been used. A low-noise single-channel preamplifier Miteq and auxiliary electronic circuits (Q-spoiler, cross-diode boxes) have been connected between the probe and Tecmag NMR/NQR Console.

To calculate the ^{14}N NQR parameters in tetrazole derivatives a density functional theory (DFT) method with B3LYP hybrid exchange-correlational functional has been used. This functional has confirmed itself as appropriate to provide trustworthy results for various properties of tetrazole derivatives, such as geometry, optical and electronic properties, thermal decomposition. It should be noted that the calculated properties can be rather sensitive to the choice of the basis set. That is why first we studied the influence of the basis set quality (as well as the role of polarization and diffuse functions, which provide a certain flexibility to the basis, that is especially important for correct description of hydrogen bonds) on the geometry and NQR frequencies of ATZH. All the DFT calculations have been carried out using the GAUSSIAN09 package [20].

In our calculations, if not specified, we used experimental structural parameters. 1H-Tetrazole crystallizes into a triclinic $P1$ space group [21,22] and lattice parameters $a = 3.7370(2) \text{ \AA}$, $b = 4.7818(3) \text{ \AA}$, $c = 4.9443(4) \text{ \AA}$, $\alpha = 106.977(9)^\circ$, $\beta = 107.17(1)^\circ$, $\gamma = 101.715(7)^\circ$. 5-aminotetrazole monohydrate has a monoclinic space group $P21/c$ with four molecules per unit cell and lattice parameters $a = 6.392(1) \text{ \AA}$, $b = 7.277(2) \text{ \AA}$, $c = 9.803(2) \text{ \AA}$, $\beta = 90.24(2)^\circ$ [23,24]. The anhydrous 5-amino-1H-tetrazole has a $P2_12_12_1$ space group and lattice constants $a = 5.090(1) \text{ \AA}$, $b = 3.666(1) \text{ \AA}$, $c = 18.073(2) \text{ \AA}$ [25].

The molecular structures of TZ, ATZ and ATZH are shown in Fig. 1. The ATZ molecule contains 5 non-equivalent nitrogen atoms. The numbering of nuclei in the ring begins with protonated nitrogen and ends with the nucleus of the ^{14}N amino group. The ATZH molecules are bonded by hydrogen bonds $\text{N1} \cdots \text{N4}$ [23].

4. Results

4.1. Experimental study

Experimental ^{14}N NQR frequencies for ATZH (95%) at room temperature are listed in Table 1. The frequencies obtained in Ref. [7] for ATZH (97%) produced by Aldrich Chemical Co. are also given in Table 1 for a comparison. The frequency assignment is used so as proposed in Ref. [7]. It should be noted that there are some differences in NQR frequencies for ATZH provided by different manufacturers. The largest difference between the frequencies is observed for the N1 nucleus, which reaches tens of kilohertz. This difference can be explained by two main reasons: (i) the impurity of compound and (ii) a possible existence of different polymorphic structures in the sample [7,26]. In order to detect interconnected transitions ν_+ and ν_- , two-frequency experiments were carried out. The following related transitions were found $\nu_+ = 2.74 \text{ MHz}$ with $\nu_- = 1.5 \text{ MHz}$, and $\nu_+ = 3.143 \text{ MHz}$ with $\nu_- = 1.908 \text{ MHz}$ and

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