

Search for an NMR Signal from Spin Isomers of Water in H₂O/D₂O Mixture

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Abstract—With the aim to detect the existence of spin-isomeric molecules in water by NMR tomography, comparative measurement of NMR signal integral amplitude was performed with pure water and 50/50 water/heavy water mixture. Magnetic field was 0.5 T in tomographic and spectroscopic regimes. No spin-isomeric effect was registered, taking into account that the error of measurements did not exceed 5%.

Keywords: spin isomers of water, NMR

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INTRODUCTION

Despite the many-year practice of using ¹H protons in the capacity of active NMR probes, it remains an open question in what way the protons exhibit their NMR activity in liquid water while distributed pairwise over H₂O molecules. In an H₂O molecule the proton spins ($I = 1/2$) may be oriented in the same or in opposite directions. In the former case the H₂O molecule is an *ortho* molecule, and interacts with an external magnetic field by its total magnetic moment ($I = 1$). In the latter case, the H₂O molecule is a *para* molecule, and its total magnetic moment is zero, i.e., the two protons of *para*-H₂O do not interact with an external magnetic field [1].

Under quantum mechanics, in the gas phase at room temperature the quantities of *ortho*- and *para*-H₂O molecules are in statistical equilibrium with a 3 : 1 ratio. In early works on NMR of water it was believed that liquid water also represents a mixture of *ortho* and *para* spin isomers [2]. In the condensed phase, however, H₂O molecules are united by covalent chemical bonds, with the specifics that along them the H₂O molecules can exchange protons. At what rates and under what laws the proton exchange takes place is still not finally clear [3]. For this reason, obscure is also the role of spin isomerism in the NMR response formation.

We have recently [4] proposed a method that makes it possible to determine which of the two possible carriers of nonzero spin—individual ¹H proton with spin 1/2 or *ortho*-H₂O molecule with spin 1—is the source

of the NMR signal. As the object, we propose a well-studied reaction



By this scheme, upon dilution of usual water H₂O with heavy water D₂O, there arise molecules of mixed water HDO, containing an unpaired and hence NMR-active proton. The concentration of HDO as dependent on the initial concentrations of H₂O and

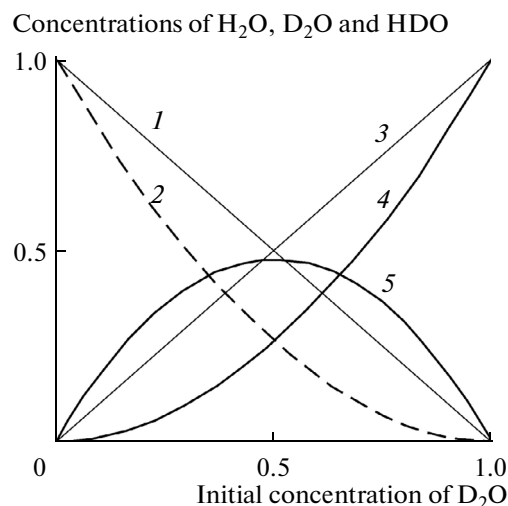


Fig. 1. Concentration diagram of an equilibrium H₂O–D₂O mixture at room temperature: 1, 3 – initial H₂O and D₂O concentrations; 2, 4 and 5 – respective H₂O, D₂O and HDO concentrations.

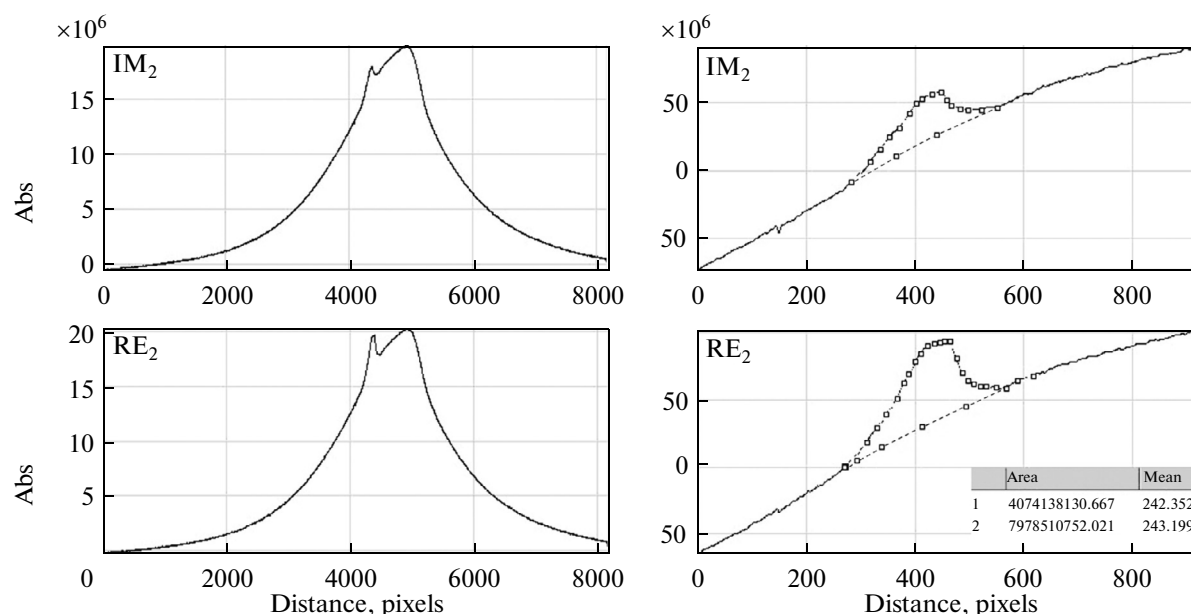


Fig. 2. Comparative NMR spectra of HDO solution (50%) (IM₂ – top) and distilled H₂O (RE₂ – bottom).

D₂O at room temperature (equilibrium constant $K = 3.9$) is shown as a diagram in Fig. 1. It is evident that with increasing D₂O concentration, the content of NMR-active HDO changes nonmonotonically. This allows distinguishing two cases. In the first case, if the NMR signal S is generated by protons regardless of which molecules contain them, in the process of increasing H₂O concentration in the presence of D₂O the signal S grows linearly. In the second case, if *ortho* molecules are NMR-active and *para* molecules inactive, the NMR signal S grows more slowly. As calculated for the two cases, the change in S as dependent on the relationship between H₂O and D₂O has been determined [4] as $S \sim 2[\text{H}_2\text{O}] + [\text{HDO}]$ and $S \sim 1.5[\text{H}_2\text{O}] + [\text{HDO}]$. For a mixture in a 1 : 1 ratio as compared with pure water, the difference in S in the second case makes 12%. The hypothesis of existence of this deviation has come to experimental checking in the present work.

EXPERIMENT

We have performed precision comparison of the concentration of NMR-active protons of an HDO solution (50%) with their concentration in the reference sample—distilled water. The program was implemented in two versions: NMR spectroscopy and NMR tomography. As the test specimens, we used samples of HDO differing in the concentrations of usual and heavy water not more than 0.1%, and samples of distilled water.

Experiments were run in a medium-field tomograph Bruker Tomikon S-50 with magnetic field

intensity 0.5 T at resonance frequency 21.2 MHz. Digitization was performed in XwinNMR 1.0 and Paravision 1.036.

In the spectroscopic regime, we performed alternating recording for two specimens in identical conditions to level off the influence of magnetic gradients. Specimens were placed in the center of the coil in the zone of maximal field uniformity. To work on a unified scale with two samples, the transmission band was adjusted to the signal from the specimen and from the coil itself, making 10 kHz. Pulse duration, 100 μs , was chosen to encompass the entire scanning area 50×50 mm without loss of sensitivity. The discretization rate with the XwinNMR 1.0 package was 4K. The integral amplitude of spectra was calculated with a tomographic data processing program ImageJ, cutting off the spectral component of the coil.

In the tomographic regime, proton-weighted images were obtained with a spin echo pulse sequence MSSE at the following parameters: section thickness 5 mm, spatial resolution 0.9 mm/pixel, scanning area 5×5 cm, time $T_R = 10$ s and $T_E = 15$ s. Large T_R was used to reduce the degree of saturation and accordingly the influence of T_1 relaxation on the signal level. Scanning was performed for several samples simultaneously, scanning time was 40 min. The NMR signal intensity was calculated applying the *smooth image* filter and displayed as a histogram.

Here we used a receiver/transmitter head coil with maximal (for the given tomograph) field uniformity in the chosen working volume of 3500 cm³.

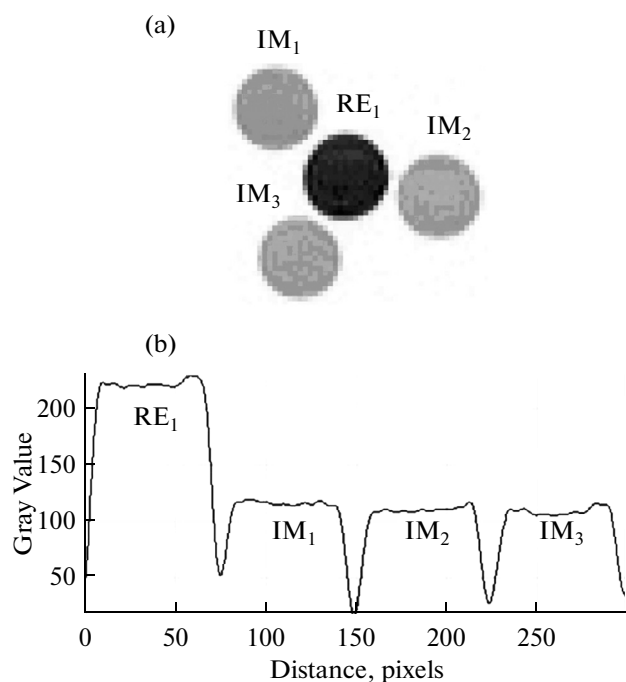


Fig. 3. Typical example of NMR study: (a) inverted proton-weighted images of specimens, (b) their digitization. RE₁ — distilled water; IM₁, IM₂, IM₃ — HDO solution (50%).

Typical results of measurements are shown in Figs. 2 and 3.

All the described experiments have yielded one and the same result: to an accuracy not worse than 5%, for three specimens of HDO (50%) no deviation of the NMR signal from the relative value of 0.5 is registered. The result should be interpreted as indicative of that the NMR signal in liquid water is produced by unpaired protons rather than by *ortho*-H₂O molecules. The high signal intensity is evidence of a high concentration of these protons, the origin of which remains not quite clear. Possibly, their manifestation in NMR reflects processes of intense proton exchange taking place in liquid water at times beyond the NMR limits.

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