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DETERMINATION OF THE RATIO OF THE PROTON AND DEUTERON NUCLEAR MAGNETIC MOMENTS

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The ratios of the proton and deuteron resonance frequencies have been determined in the mixtures H_2O–D_2O, $(CH_3)_2CO$–$(CD_3)_2CO$, and for partially deuterated acetones. The data obtained are compared with those from the literature. Determination of the magnetic-moment ratio requires corrections both for the difference in vibrational amplitude and for the quadrupole interaction, these two corrections having opposite signs. As the result of discussion, it is proposed to use the ratio of resonance frequencies obtained for the HOD molecule as the most probable value of the ratio of proton and deuteron gyromagnetic ratios. For this molecule the two corrections apparently compensate each other to a substantial degree.

WITH the discovery of the nuclear magnetic resonance method the possibility appeared of accurately determining nuclear magnetic moments and their ratios. Very convenient objects for such investigations are mixtures of isotopes in the liquid phase, which give narrow resonance absorption signals of rather high intensity.

Smaller et al.[1,2] have determined the ratio of the proton and deuteron resonance frequencies for the liquid solution H_2O—D_2O and the gaseous mixture H_2—D_2. Subsequently Wimett[3] determined the ratio of proton and deuteron resonance frequencies for HD molecules in the gaseous phase. Wimett's data are used for calculation of the deuteron magnetic moment[4,5], since corrections for the difference in the vibrational amplitude of the protons and deuterons are not required for the HD molecule. However, comparison of the data of Smaller and Wimett with inclusion of possible corrections shows that correction only for the difference in proton and deuteron vibrational amplitudes is still insufficient for accurate determination of the magnetic-moment ratio, and therefore HD is not the best object for this type of investigation.

In recent years the accuracy with which the proton magnetic moment has been determined has been significantly increased. Thus, Mamyrin et al.[6] have determined the proton magnetic moment in nuclear magnetons $\mu_p = 2.7927745 \pm 0.0000012$—without correction for diamagnetic screening of the proton in the water molecule. In this connection it is of interest to obtain a more accurate value of the ratio of proton and deuteron magnetic moments in order to improve the value of the deuteron magnetic moment. The present paper is devoted to this question.

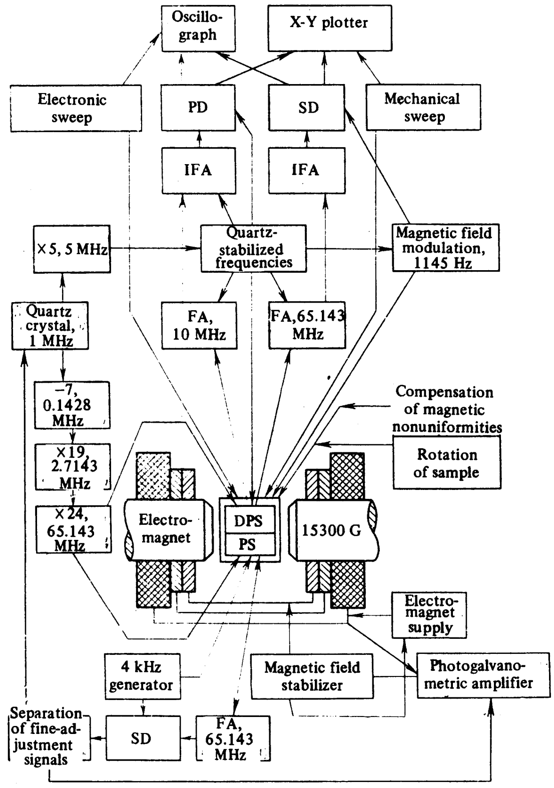

FIG. 1. Block diagram of proton-deuteron NMR spectrometer: PS—proton sample, DPS—deuteron-proton sample, PD—phase detector, SD—synchronous detector, FA—frequency amplifier, IFA—intermediate frequency amplifier.

EXPERIMENTAL APPARATUS

In order to determine the ratio of proton and deuteron resonance frequencies, we assembled a proton-deuteron NMR spectrometer based on a RYa-2303 apparatus. The liquid materials which we investigated were sealed in cylindrical ampoules and were rotated in a system of perpendicular detecting coils of the proton and deuteron channels. A block diagram of the experimental equipment is shown in Fig. 1. The resonance frequencies were obtained from a single quartz-stabilized frequency $f_0 = 1$ MHz, which was supplied from a ChZ-19 standard frequency meter. The proton-channel resonance frequency was obtained by means of a seven-to-one frequency divider and nineteen-to-one and twenty-four-to-one frequency multipliers: $f'_p = f_0 \times 19 \times 24/7$; the deuteron-channel resonance frequency was

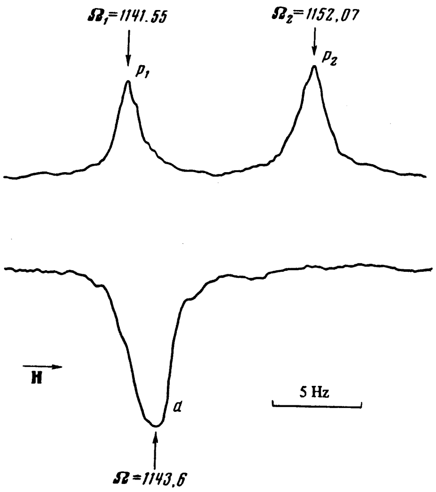

FIG. 2. Proton-deuteron spectrum: d–deuteron signal, for which the frequency Ω corresponding to coincidence of the signals is determined; p_1 and p_2 are proton signal side bands obtained by modulation of the magnetic field on successive application of frequencies Ω_1 and Ω_2. The resolution is $\sim 10^{-8}$.

$f_d = f_0 \times 10$. The frequency f'_p was used also for stabilization of the resonance conditions on the basis of the proton signal itself. The control sample of the proton-stabilization channel was located at a distance of 15 mm from the main proton-deuteron sample.

The proton and deuteron spectra were recorded simultaneously on an X-Y plotter with independent two-channel recording. When our resonance frequencies f'_p and f_d are used, the deuteron-resonance absorption signal is recorded at a higher magnetic field value than the proton signal. In order to observe the proton and deuteron signals simultaneously with a small magnetic-field sweep amplitude, we used the method of detecting a proton-signal side-band which was separated by means of a synchronous detector. The magnetic-field modulation frequency Ω also was obtained from the standard frequency f_0 = 1 MHz by means of a three-decade step divider and was monitored by recording the spectra in the numerical tableau of the ChZ-19 frequency meter.

Figure 2 shows one of the spectra obtained by us for a sample with a $(CH_3)_2CO$-$(CD_3)_2CO$ mixture. The first proton signal was recorded at a modulation frequency $\Omega_1 = f_0/876$. After recording the first signal the modulation was switched to a frequency $\Omega_2 = f_0/868$ and the second proton signal was recorded. In the deuteron channel the absorption signal of the CD_3 group was recorded. The frequency Ω corresponding to coincidence of the proton and deuteron resonance signals was determined from the spectrum by interpolation. The magnetic-field sweep was accomplished by means of a slide wire mechanically connected with the motion of the paper tape of the X-Y plotter. This assured linearity of the sweep.

EXPERIMENTAL DATA

Two of the samples studied by us contained seven isotopes; these consisted of H_2O—D_2O and $(CH_3)_2CO$—$(CD_3)_2CO$ with equal molecular concentrations 1 : 1. The third sample contained H_2O and D_2O separately: a thin-walled capillary tube with D_2O was placed in an ampoule with H_2O. We experimentally determined the ratio of resonance frequencies:

Table I. Experimental results

Sample	Ω, Hz	$\frac{f'_p+\Omega}{f_d}\cdot 10^8$
H_2O—D_2O	1139.7±0.2	651439968±2
$(CD_3)_2CO$ — $(CH_3)_2CO$	1143.6±0.2	651440007±2
H_2O, D_2O	1142.1±0.2	651439992±2

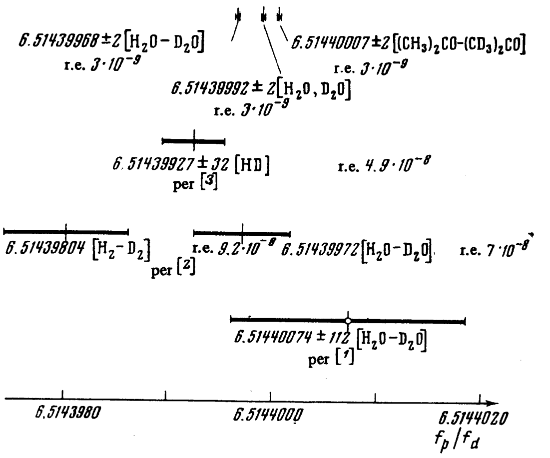

FIG. 3. Comparison of our results (upper values) and those from the literature, with the corresponding errors (r.e.—relative error).

Table II. Shifts of resonance frequencies and frequency ratio for partially deuterated analogs of acetone

Group of acetone atoms	$\delta_p \cdot 10^9$ relative to $-CH_3$	$\delta_D \cdot 10^9$ relative to $-CD_3$	$\frac{f_p}{f_d}\cdot 10^8$
$-CH_2D$	15±2 [7]	29±1 [8]	651439978±4
$-CHD_2$	34±2 [7]	17±2 [8]	651439974±4

$$\frac{f_p' + \Omega}{f_d} = \frac{19 \cdot 24}{7 \cdot 10} + \frac{\Omega}{10^7} \tag{1}$$

where $f'_p + \Omega = f'_p$. The results obtained are shown in Table I. Comparison of the experimental data and their errors from Table I and from refs. 2 and 3 is carried out in Fig. 3.

In order to deal with smaller corrections in determination of the magnetic-moment ratio, it was possible to study not the mixture $(CH_3)_2CO$—$(CD_3)_2CO$, but the partially deuterated analog of this material $(CH_2D)_2CO$ or $(CHD_2)_2CO$. However, the shifts between the proton signals from the $-CH_3$, $-CH_2D$, and $-CHD_2$ groups and between the deuteron signals from $-CD_3$, $-CD_2H$, and $-CDH_2$ are simpler to determine by means of proton and deuteron spectrometers, respectively. Since work of this type has already been carried out and the results published[7,8], it is sufficient to utilize these results. In Table II we have listed the appropriate data from refs. 7 and 8.

The ratio of the resonance frequencies for the $-CH_2D$ and $-CHD_2$ groups was calculated by means of these data and our experimental data from Table I. Here we took into account that the screening constant increases (i.e., the resonance frequency decreases) if a neighboring nucleus is replaced by a heavier isotope. The calculation was made with the formula

$$\left(\frac{f_p}{f_d}\right)=\frac{f_p-\Delta f_p}{f_d+\Delta f_d}=\frac{f_p}{f_d}[1-(\delta_p+\delta_d)]. \qquad (2)$$

The results of the calculations are shown in Table II. The ratios of the resonance frequencies for the $-CH_2D$ and $-CHD_2$ groups agree within experimental error.

NMR spectroscopy has a time resolution no better than 10^{-4} sec. Isotopic exchange in a $H_2O—D_2O$ mixture is a rapid process in relation to this time. From the sample with the $H_2O—D_2O$ isotopic mixture, only common signals are recorded. Here the proton-signal intensity is half due to H_2O molecules (there are 25% of them in the solution) and half due to HOD molecules (there are 50% of them in the solution). As the result of the equal population of the two proton states the common signal is observed halfway between the signal from the H_2O molecule and the assumed signal from the HOD molecule. A similar statement can be made also for the deuteron signal of this sample. Consequently, on the basis of Table I we can calculate the ratio of the resonance frequencies for HOD molecules by means of the following formula:

$$\left(\frac{f_p}{f_d}\right)_{HOD}=\left(\frac{f_p}{f_d}\right)_{H_2O-D_2O}-\left[\left(1+\frac{2\pi}{3}\Delta\chi\right)\left(\frac{f_p}{f_d}\right)_{H_2O, D_2O}-\left(\frac{f_p}{f_d}\right)_{H_2O-D_2O}\right]. \qquad (3)$$

Here we take into account for the third sample the correction for the difference in volume diamagnetic susceptibilities of H_2O and D_2O. From data on the density of H_2O and D_2O the calculation gives $(2/3)\pi\Delta\chi = 5 \times 10^{-9}$. This correction is close to the accuracy of our measurements. According to Eq. (3) the ratio of the proton and deuteron resonance frequencies for HOD molecules is 6.51439940 ± 6 in the last place.

DISCUSSION OF CORRECTIONS FOR THE DIFFERENCE IN DIAMAGNETIC SCREENING OF PROTONS AND DEUTERONS

The resonance magnetic field for deuterons H_d is related to the value of f_d by the expression

$$H_d = 2\pi f_d/\gamma_d(1-\sigma_d), \qquad (4)$$

where γ_d is the deuteron gyromagnetic ratio and σ_d is the electronic screening constant of the deuteron. The corresponding expression for the resonance magnetic field of the side-band proton signal has the form

$$H_p = 2\pi(f_p'+\Omega)/\gamma_p(1-\sigma_p), \qquad (5)$$

where γ_p and σ_p are the analogous constants for protons. For values of Ω corresponding to coincidence of the signals, the resonance magnetic fields are equal: $H_d = H_p$. Consequently we can determine from (4) and (5) the ratio of the gyromagnetic ratios for protons and deuterons:

$$\frac{\gamma_p}{\gamma_d}=\frac{f_p'+\Omega}{f_d}\,\frac{1-\sigma_p}{1-\sigma_d}\approx\frac{f_p}{f_d}[1-(\sigma_d-\sigma_p)]. \qquad (6)$$

In order to determine the magnetic-moment ratio, it is necessary to take into account in accordance with Eq. (6) the difference in the electronic screening of protons and deuterons.

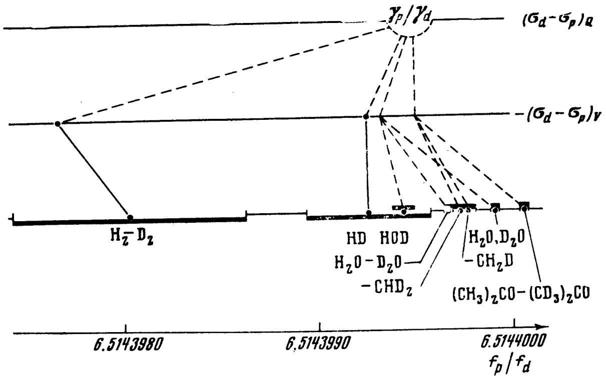

FIG. 4. Graphical determination of the ratio of magnetic moments from comparison of data with inclusion of suggested corrections. Above the frequency-ratio scale are given values of this ratio for several materials as determined from the literature (H_2-D_2, HD), values obtained by us (H_2O-D_2O, $(CH_3)_2CO$-$(CD_3)CO$, H_2O, D_2O), and calculated values (HOD, $-CH_2D$, $-CHD_2$). The heavy lines indicate the uncertainty with which they are known. On the first and second horizontal lines these frequency ratios are given with inclusion of the first and second corrections respectively. The first correction takes into account the difference in vibration of the atoms: $-(\sigma_d-\sigma_p)_V$, and the second—the quadrupole interaction: $+(\sigma_d-\sigma_p)_Q$. The dashed lines indicate the corrections suggested by us. The correction for the difference in vibrational amplitude $-(\sigma_d-\sigma_p)_V$ for the H_2-D_2 mixture was calculated by Marshall and Pople and is shown by the solid line. Correction for $-(\sigma_d-\sigma_p)_V$ is not required for HD.

The isotopic shift, which is associated with the change in oscillation amplitude in the ground state, can be calculated on the basis of the vibrational-spectrum characteristics of the molecules. Such a calculation has been made by Marshall and Pople[9,10] for hydrogen. They obtained

$$\delta(D_2)-\delta(H_2)=55\cdot10^{-9}.$$

However, inclusion only of this correction does not improve, but rather spoils the agreement between the data of Smaller and Wimett[2,3]. This is evident from Fig. 4, where we have compared the existing data with inclusion of possible corrections. To determine the ratio of the nuclear magnetic moments of the proton and deuteron it is necessary further to take into account the correction due to deformation of the electron cloud by the deuteron quadrupole moment Q.

The quadrupole interaction energy of the deuteron is determined by the value of Q and the gradient of the intramolecular electric field. On replacement of a proton by a deuteron, the asymmetry of the electron cloud increases as a result of the quadrupole interaction. It is well known[10] that destruction of spherical symmetry of the electron distribution decreases the screening constant. Thus, the isotopic shift consists of a component due to the difference in vibrational amplitude and a component due to the quadrupole interaction. Here it is important to take into account that these components have opposite signs. In agreement with this, Eq. (6) can be written in the form

$$\frac{\gamma_p}{\gamma_d}=\frac{f_p}{f_d}[1-(\sigma_d-\sigma_p)_V+(\sigma_d-\sigma_p)_Q], \qquad (7)$$

where $(\sigma_d-\sigma_p)_V$ is the correction for the difference in screening as the result of change in the vibrational amplitude, $(\sigma_d-\sigma_p)_Q$ is the correction for deformation of the electron cloud by the deuteron quadrupole moment.

In Fig. 4 we have shown the correction for the difference in vibrational amplitude for a H_2—D_2 mixture, calculated by Marshall and Pople. Of the compounds represented in this figure, the deutero-acetone molecule has the smallest quadrupole coupling constant[11,12]. Since acetone is an inert material with an electron shell only slightly deformed, we can neglect the correction for the quadrupole interaction in that case. If we further assume that for acetone the correction due to change in vibrational amplitude is of the order calculated by Marshall and Pople, the region of occurrence of γ_p/γ_d values indicated in Fig. 4 is defined. As can be seen from this figure, the value of f_p/f_d for partially deuterated isotopes lies closer to the value γ_p/γ_d than for the mixture of $(CH_3)_2CO$ and $(CD_3)_2CO$, which is natural, since the correction $(\sigma_d - \sigma_p)_V$ will be smaller for them. As follows from Fig. 4, the two corrections for the HOD molecule compensate each other to a significant degree, and we can take the frequency ratio obtained by us for HOD, 6.51439940 ± 6 in the last place, as an estimate of the ratio of the gyromagnetic ratios of the proton and deuteron, even though accurate calculations of the corrections have not yet been carried out.

To calculate the deuteron magnetic moment we will use the data of Mamyrin et al.[6] According to these authors the proton magnetic moment is somewhat higher than the adjusted value recommended in 1969[13]. However, Taylor et al.[14] in their latest publications are inclined to the view that the value recommended by them is underestimated. Using the data of Mamyrin et al.[16] and making a correction for diamagnetic screening of the proton in the water molecule, we obtain $\mu_p = 2.7928475$. With inclusion of our experimental data for HOD, the deuteron magnetic moment will be

$$\mu_d = 0.85743821$$

with the uncertainty given by Mamyrin et al.[6], i.e., $4.3 \times 10^{-5}\%$.

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