NMR study of hydrogen isotopes to determine the ratio of the proton and deuteron magnetic moments to the eighth decimal place

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The ratio of the proton and deuteron resonance frequencies in HD has been determined with an error of $\pm 2.46\times 10^{-9}$. The $\sigma(\dot{H}D)-\sigma(H_2)$ and $\sigma(D_2)-\sigma(H\dot{D})$ isotope shifts for the proton and deuteron resonances were also determined. The isotope shifts are calculated with allowance for the differences in the rotational-vibrational characteristics of the isotopic analogs of the hydrogen molecule. The calculated shifts are in agreement with experiment provided the asymmetry of the electron cloud of the HD molecule due to coupling between the motions of the nuclei and electrons as well as the mutual screening of the nuclei are taken into account. This agreement is regarded as confirming the estimate of 8.8×10^{-9} for the excess screening of the deuteron over that of the proton in HD. Using this estimate, the ratio of the gyromagnetic ratios is found to be $\gamma_p/\gamma_d = 6.514\,399\,178$ with an error less than 10^{-8}.

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The magnetic moment of the deuteron is a few percent smaller than the sum of the magnetic moments of the proton and neutron. Thus, the noncentral character of the proton-neutron interaction forces is manifest in this simplest of all nuclei. An accurate knowledge of this difference could be useful in testing more accurate ways of describing the strong-interaction potential.

The ratio of the proton and deuteron magnetic moments can be determined with the aid of proton-deuteron NMR spectroscopy by simultaneously recording both the proton and the deuteron resonances from the same region of an isotopically mixed specimen. Then the ratio of the gyromagnetic ratios will be related to the ratio of the resonance frequencies by the formula[1]

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

in which σ_d and σ_p are the deuteron and proton screening constants. One should obviously use a compound for which the difference between the nuclear screening constants is minimal.

Wimett[2] determined the ratio of the proton and deuteron resonance frequencies for HD molecules in the gaseous phase, and the result was subsequently used[3,4] to calculate the magnetic moment of the deuteron. On comparing the value of f_p/f_d for HD with its values for a number of other compounds[5] one finds that the ratio of the resonance frequencies is minimum for HD (Smaller[6] found a lower value for f_p/f_d for a gaseous mixture of H_2 and D_2, but this result proved to be erroneously low).

In the work reported here we investigated HD in the gaseous state using a proton-deuteron spectrometer[5], and we also investigated the isotopic mixtures H_2-HD and D_2-HD, the former at the proton resonance and the latter at the deuteron resonance. At the same time we calculated the isotopic shifts $\sigma(\dot{H}D)-\sigma(H_2)$ and $\sigma(D_2)-\sigma(H\dot{D})$, since only when the calculated and experimental results on the isotopic shifts are in agreement can we expect our calculated estimate of the difference between the proton and deuteron screening[1] for HD to be correct.

EXPERIMENT

The gaseous H_2-HD, D_2-HD, and HD specimens were prepared as follows. A quartz capillary (o.d. 5 mm, wall thickness 1 mm) was first filled about 70% full of water. The empty part of the capillary was separated from the water by a teflon plug. Then we put a few crystals of LiH and LiD on the plug and sealed the capillary off. After shaking the sealed capillary, the crystals fell into the water and reacted with the evolution of an H_2-HD or D_2-HD gaseous mixture, depending on whether the capillary had been filled with H_2O or D_2O. The weight of the crystals (in our case 16 mg) was so chosen as to bring the hydrogen pressure within the tube to about 130 atm. In recording the gas spectra, the part of the capillary containing no liquid was placed within the receiving coil of the radiospectrometer.

The NMR signal from gaseous H_2 has a large intrinsic width (~30 Hz), which is reflected in the accuracy of the results. Thus, Dayan et al.[7] obtained $\sigma(\dot{H}D - \sigma(H_2) = (40 \pm 10)\times 10^{-9}$ for the gaseous mixture of H_2 and HD. Therefore, following Evans[8], we investigated an H_2-HD mixture dissolved in CCl_4. In this case the specimen tubes were filled with gas much as before, but the ampoule was filled to 35 mm with CCl_4 containing ~1% of acetone ($(CH_3)_2CO$) as an internal standard.

The value of $\sigma(\dot{H}D)-\sigma(H_2)$ was determined as follows. The operation of the pulse spectrometer was controlled by an Elektronika-100 computer, which triggered the 90° pulse at the resonant frequency (65 MHz for protons) and recorded the shape of the free-spin precession signal in its memory. An amplitude detector was used to separate the proton signals. The signal consisted of a falling exponential from the $(CH_3)_2CO$ on which could be seen the damped oscillations from the H_2 singlet and HD triplet. There was a 2-sec interval between the 90° pulses, and during this time the computer stored 1792 values of the signal amplitude in its memory.

The Elektronika-100 summed 512 free-precession signals and transferred the data block through a buffer to a Minsk-32 computer, where the results were printed out graphically for preliminary examination. The data blocks were later transferred to a BÉSM-6 computer where the spectra were presented on the frequency scale and the positions of the individual signals were found by the least squares method.

Operation of the spectrometer in this manner does

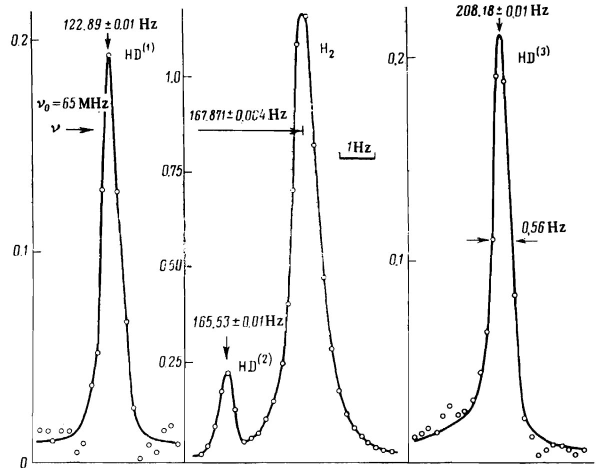

FIG. 1. Positions of the triplet components from HD and the singlet line from H_2 relative to acetone, $(CH_3)_2CO$, in CCl_4. The points were obtained by on-line Fourier transformation of the corresponding data block, extended to 4096 numbers. The instrumental resolution was estimated as 0.56 Hz/65 MHz = 8.6×10^{-9} or better on the basis of the line widths.

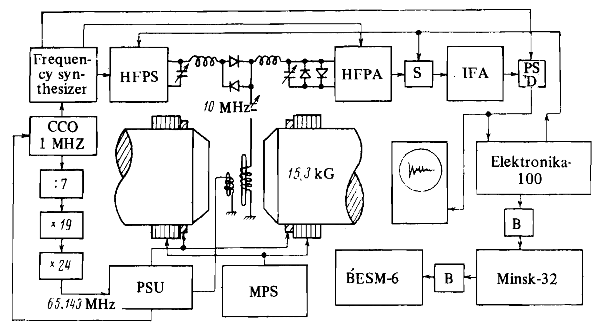

FIG. 2. Block diagram of the equipment for determining the isotope shift at the deuteron resonance: HFPS—high frequency pulse shaper, HFPA—high frequency preamplifier, S—switch, IFA—intermediate frequency amplifier, PSD—phase sensitive detector, B—buffer, CCO—crystal controlled oscillator, PSU—proton stabilizing unit, MPS—magnet power supply.

not require rigid external stabilization of the resonance conditions and permits data to be accumulated for a long time. Fine adjustment of the uniformity of the magnetic field was effected during the data accumulation process on the basis of the duration of the free-precesion signal. The NMR signals from protons in CCl_4 were 0.5 Hz wide (Fig. 1), so the results obtained by processing only a few spectra were accurate enough (in the present study it was not necessary to improve the accuracy of the experimental data beyond the accuracy of the theoretical calculations). The final result obtained from the measurements was $\sigma(\dot{H}D)-\sigma(H_2) = (35.9 \pm 0.2) \times 10^{-9}$, which agrees with the value $(36 \pm 2) \times 10^{-9}$ given in [8].

We determined $\sigma(D_2)-\sigma(HD)$ in a gaseous medium since in this case the NMR signal was only ~4 Hz wide. Figure 2 is a block diagram of the apparatus. The high-frequency 90°-pulse shaper and the high-frequency preamplifier were matched to the inductance of the signal transducer in the same way as in the work of Clark and McNeil[9]. The exciting pulse was ~15 μsec long, the deuteron resonance frequency was 10 MHz, and the resonance conditions were stabilized with the aid of an external proton specimen at 65.143 MHz.

The NMR signals from the deuterons were ~100 times weaker than those from the protons, so a specimen was used that filled the receiving coil as completely as possible without circulation. There was a 1-sec interval between the 90° pulses, and in this time 580 points were stored. To reduce the effect of thermal drift of the magnetic-field gradient on the shape of the NMR signal, the spectrum was accumulated for 1 min, after which the data block was sent to the other computer while the Elektronika-100 machine began to accumulate the next spectrum. After ten spectra had been sent forward the ampoule with the investigated gas was replaced by a standard C_6D_6 specimen and the magnetic field was carefully adjusted for uniformity. Uncontrolled changes in the field uniformity could take place when the specimens were changed. We therefore processed only 30 of the 70 recorded spectra, choosing those for which the width of the D_2 signals due to field nonuniformity did not exceed 5 Hz.

The selected spectra with the best resolution were processed by the least squares method on the BÉSM-6 computer, the experimental data being approximated by the function

$$f(t)=\sum_{k=1}^{3} a_k \cos[2\pi\nu_k(t+\varphi_k)+\varphi_0]\exp(-b_k t)+c, \qquad (2)$$

in which the a_k, b_k, ν_k, φ_k, φ_0, and c are the parameters to be varied. The Fourier transform of the temporal process described by this function is a superposition of three Lorentz curves with the respective frequencies ν_1, ν_2, and ν_3. The highest and lowest of these frequencies correspond to the components of the HD doublet; hence the following constraints were imposed on the parameters: $a_1 = a_3$, $b_1 = b_3$, $\varphi_1 = -\varphi_3$, and $\varphi_2 = 0$.

We used 490 points in optimizing the parameter values and calculated the amplitude of the random noise for estimating the errors from the last 50 points. The value of $\sigma(D_2)-\sigma(H\dot{D})$ and its error $\Delta\sigma$ (which usually amounted to $\sim 10^{-8}$) were determined for each data block, and the weighted mean of these values was calculated using the weights $p_i = 1/\Delta\sigma_i$. The χ^2 criterion was used to check the fit of the experimental to the theoretical function; this led to the rejection of four of the 30 spectra. The final result was

$$\sigma(D_2)-\sigma(H\dot{D})=(42\pm 2.3)\cdot 10^{-9}.$$

The stability of this result against dropping the first 20 experimental points was tested (most of the 30 spectra that were rejected for having broad lines were not stable against dropping those points because of nonuniform broadening and overlapping of the lines).

Using apparatus described earlier, a block diagram of which will be found in [1], we determined the ratio of the proton and deuteron resonance frequencies for gaseous HD. The receiving coil of the two-resonance spectrometer used in this work was the same as that used in [5].

The deuteron channel operated in the pulse mode. The reference frequency for the synchronous detector was 28.54 Hz and was synchronized with the 90° trigger pulses. In this case the left-hand deuteron signal (Fig. 3) represents the component of the doublet that appears in the stronger magnetic field, while the right-hand signal is due to the weak-field doublet component. Thanks to the choice of the reference frequency, the

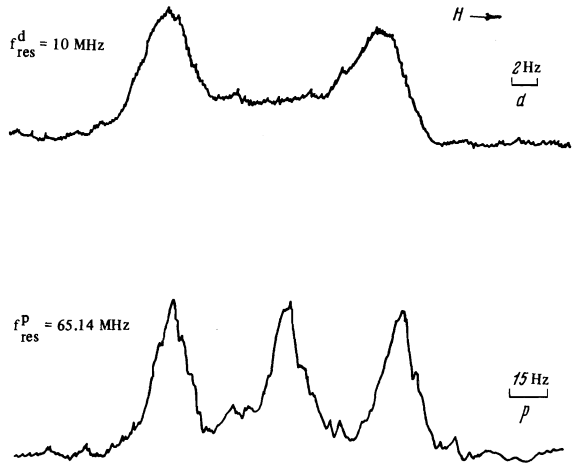

FIG. 3. Proton-deuteron spectrum of gaseous HD, recorded using a 6.514399869 times higher resonance frequency for protons than for deuterons.

proton-deuteron spectrum proved to be compact and convenient to process.

In processing the results we read off coordinates from the upper and lower specta. The resulting numerical data were used to find the separation between the lines with the aid of a computer and by the method of least squares. For the calculations each signal was approximated as the sum of a Lorentz curve and a dispersion curve. The scatter of the data on the 24 spectra (of the type of Fig. 3) that we recorded proved to fit a normal distribution at the ~90% confidence level.

To remove systematic errors, the proton-deuteron spectra were recorded both while increasing the magnetic field strength and while decreasing it. Our recording rate proved to be so slow that the transition processes were too small to cause any difference between the results obtained on increasing and decreasing the magnetic field. The systematic error due to the nonlinearity of the magnetic-field sweep was considerably smaller than the random erros. Our final result is

$$(f_p/f_d)_{\mathrm{HD}}=6.514399235\pm16.$$

This result agrees well with the value 6.514399270 ± 320 obtained by Wimett[2].

In addition to these three basic constants, we also determined the proton-deuteron interaction energy in HD at the same time, obtaining J = 43.115 ± 0.012 Hz for the gas and J = 42.64 ± 0.01 Hz in CCl_4.

CALCULATION OF THE ISOTOPIC EFFECTS OF SCREENING ASSOCIATED WITH THE DIFFERENCE IN THE VIBRATIONAL-ROTATIONAL CHARACTERISTICS

As in [10–13], the calculations were carried through in the Born-Oppenheimer approximation, i.e., the ground-state wave function was represented as the product of an electron wave function in which only the instantaneous positions of the nuclei were taken into account, and a wave function for the motion of the nuclei in the field produced by the electrons.

The external magnetic field H and the nuclear magnetic moment μ determine the value of the vector potential that leads to the appearance in the Hamiltonian of additional operators acting on the electron wave function. Since these additional terms are small, the energy E of the system, which depends on the parameters H and μ, can be calculated by perturbation theory. The screening constant is defined as the second derivative of the energy by these two parameters. Both ordinary perturbation theory and the Hartree-Fock perturbation theory were used, depending on the type of wave function employed to describe the ground state.

The screening constant σ was calculated in three stages: 1) the quantity $\sigma(R_i)$ was determined for several fixed values R_i of the distance between the nuclei; 2) the resulting function $\sigma(R)$ was averaged over the nuclear state characterized by the vibrational and rotational quantum numbers v and J to give the screening constant σ_{vJ} for the corresponding vibrational-rotational state; and 3) σ_{vJ} was averaged over v and J with allowance for the populations of the various levels E_{vJ} at the temperature under consideration.

If we assume that all orientations of the molecule with respect to the external magnetic field are equally probable, we find, on averaging over all orientations, that $\sigma(R)$ for the hydrogen molecule (and its isotopes) will be given by the formula

$$\sigma(R)=\sigma^0(R)+\sigma^g(R)+\sigma^p(R), \tag{3}$$

$$\sigma^0(R)=\frac{2}{3}\alpha^2\left\langle\psi_0\left|\frac{1}{r}\right|\psi_0\right\rangle, \tag{4}$$

$$\sigma^g(R)=-\frac{R}{3}\alpha^2\left\langle\psi_0\left|\frac{z}{r^3}\right|\psi_0\right\rangle, \tag{5}$$

$$\sigma^p(R)=\frac{2}{3}\alpha^2\sum_{n\neq0}\frac{\langle\psi_0|\mathscr{H}_\mu|\psi_n\rangle\langle\psi_n|\mathscr{H}_H|\psi_0\rangle}{E_0-E_n}. \tag{6}$$

Here σ^p is the paramagnetic contribution to the screening constant, while σ^0 and σ^g are the gauge-invariant and gauge-noninvariant parts of the diamagnetic contribution; r and z are the radius vector and its projection onto the molecular axis for the electrons in a coordinate system fixed to the investigated nucleus; ψ_0 and ψ_n are the wave functions for the ground and excited electronic states; E_0 and E_n are the corresponding electronic energies; and α is the fine structure constant.

The operators $\mathscr{H}_H$ and $\mathscr{H}_\mu$ describe the perturbations of the electron cloud due, respectively, to the magnetic field H and to the interaction of the electrons with the magnetic moment μ of the nucleus under consideration. These operators are defined by the formulas

$$\mathscr{H}_\mu=-i\sum_{j=1}^{2}\frac{1}{r_j^3}\left[y_j\frac{\partial}{\partial z_j}-z_j\frac{\partial}{\partial y_j}\right], \tag{7}$$

$$\mathscr{H}_H=-i\sum_{j=1}^{2}\left[y_j\frac{\partial}{\partial z_j}-\left(z_j-\frac{R}{2}\right)\frac{\partial}{\partial y_j}\right], \tag{8}$$

in which r_j, y_j, and z_j are the coordinates of the j-th electron (j = 1, 2).

Because of the symmetry properties of the operators $\mathscr{H}_\mu$ and $\mathscr{H}_H$, only excited states having π symmetry contribute to the sum in (6). To find the wave functions ψ_n and the energies E_n, the unperturbed Schrödinger equation describing the motion of the electrons was solved in matrix form in an auxiliary basis consisting of configurations having π symmetry. The number of these configurations used in the calculations ranged from

TABLE I. Coefficients of the polynomial approximating the screening as a function of internuclear distance

Data on ψ_0	σ_0	σ_1	σ_2	σ_3	σ_4
from [15]	26.3785	−16.039	12.649	−5.06	−3.52
from [16]	26.4030	−15.739	11.710	−6.45	2.05
from [17]	26.3097	−15.371	13.009	−6.67	6.68

TABLE II. Parameters characterizing the mean deviations of the internuclear distance from the equilibrium value for several vibrational-rotational states

	v	J	$\langle\xi\rangle$	$\langle\xi^2\rangle$	$\langle\xi^3\rangle$	$\langle\xi^4\rangle$
H_2	0	0	0.03394	0.01551	0.00182	0.00076
	0	1	0.03549	0.01563	0.00188	0.00076
	1	0	0.10374	0.05425	0.01278	0.00522
HD	0	0	0.02932	0.01323	0.00135	0 00055
	0	1	0.03048	0.01331	0.00139	0.00055
	1	0	0.08930	0.04544	0.00940	0.00368
D_2	0	0	0.02385	0.01060	0.00089	0.00035
	0	1	0.02462	0.01065	0.00091	0.00035
	1	0	0.07236	0.03559	0.00611	0 00226

2 to 16. Both Slater- and Gaussian-type orbitals[14] were used as basis functions.

Three different ground-state wave functions were used in calculating $\sigma(R_i)$, the required data on ψ_0 and E_0 being taken from the work of Fraga and Ransil[15,16] and McLean et al.[17]. The function $\sigma(R_i)$ thus obtained was then approximated by a polynomial of degree M:

$$\sigma(\xi)=\sum_{k=0}^{M}\sigma_k\xi^k,\quad \xi=\frac{R-R_e}{R_e},\tag{9}$$

where R_e is the equilibrium distance between the nuclei. Then the following relation is satisfied:

$$\sigma_{vJ}=\sum_{k=0}^{M}\sigma_k\langle\xi^k\rangle_{vJ}.\tag{10}$$

The case M = 4 proved to be accurate enough for small values of v and J since the $\langle\xi^k\rangle_{vJ}$ decrease rapidly with increasing k. The values we obtained for the coefficients σ_k are listed in Table I.

The $\langle\xi^k\rangle_{vJ}$ were calculated by a method[18] based on the approximate solution of the Schrödinger equation for the motion of the nuclei. The values obtained for some of the $\langle\xi^k\rangle_{vJ}$ are listed in Table II (the constants required for these calculations were taken from [19–21]).

The values of certain quantities analogous to the $\langle\xi^k\rangle_{vJ}$ (namely, $\langle R^k\rangle$, $\langle(R-R_e)^k\rangle$) are given in [22,24] for a few values of v and J. They were obtained using an accurate wave function for the hydrogen molecule[22] and by numerical integration of the corresponding Schrödinger equations[23]. On comparing these results with those obtained in the present work and with the values given in [11,13], we find that the values of the mean nuclear-vibration amplitudes $\langle\xi\rangle_{vJ}$ used by Marshall and by Raynes and collaborators are too small. The isotopic shifts calculated in [11,13] are therefore also too small. Using the data on $\sigma(R)$ given in [10,12], we recalculated the corresponding isotopic shifts, employing corrected values of the $\langle\xi\rangle_{vJ}$. These recalculated values are given in the second and fourth columns of Table III.

To determine the screening of the hydrogen nuclei at room temperature we averaged the constants σ_{vJ} with allowance for the populations of the energy levels, the following formulas being used for the averaging:

TABLE III. Isotopic differences in screening (× 10^9) calculated with allowance for the difference in the rotational-vibrational characteristics

	Source of data on ψ_0					Experiment
	[12, 13]	[15]	[10, 11]	[16]	[17]	
E_0, a.u.	−1.1317	−1.1321	−1.138	−1.1566	−1.1669	−1.1745
$\sigma(HD)-\sigma(H_2)$	55	48	48	49	43	35.9±0.2
$\sigma(D_2)-\sigma(HD)$	65	56	58	57	51	42±2.3

$$\sigma(HD)=\frac{\sum\limits_{vJ}\sigma_{vJ}(2J+1)\exp[(E_{00}-E_{vJ})/kT]}{\sum\limits_{vJ}(2J+1)\exp[(E_{00}-E_{vJ})/kT]},\tag{11}$$

$$\sigma(D_2I)=\frac{\sum\limits_{vJ}\sigma_{v,2J}(2\cdot 2J+1)\exp[(E_{00}-E_{v,2J})/kT]}{\sum\limits_{vJ}(2\cdot 2J+1)\exp[(E_{00}-E_{v,2J})/kT]},\tag{12}$$

$$\sigma(D_2II)=\frac{\sum\limits_{vJ}\sigma_{v,2J+1}2(2J+1)\exp[(E_{01}-E_{v,2J+1})/kT]}{\sum\limits_{vJ}2(2J+1)\exp[(E_{01}-E_{v,2J+1})/kT]}.\tag{13}$$

Here D_2I and D_2II denote the two modifications of the deuteron molecule corresponding to total nuclear spins of 2 and 1, respectively. Only the NMR signal from the ortho-modification of hydrogen (total nuclear spin unity) was observed for the H_2 molecule. The formula for $\sigma(H_2\text{-ortho})$ is the same as formula (13) for $\sigma(D_2II)$. It proved to be sufficient to take into account only levels with v = 0–1 and J = 0–9 for all three molecules at room temperature. The level energies E_{vJ} were calculated from the equations given by Herman, Tipping, and Short[18].

On comparing the results given in Table III, we see that using better ground-state wave functions (i.e., wave functions that give lower values for the total energy E_0) gives values for the isotopic shifts that are lower and agree better with the experimental values.

The five-configuration ground-state wave function that we used[17] is not only better as regards the ground-state energy, but also gives a value for the isotopic effect that is closer to the experimental value. It is apparently important that the wave function include $2\pi p$ orbitals in its basis. Taking these orbitals into account in the configuration-interaction method[17] leads to correct angular correlations in the electron motion.

Increasing the number of auxiliary configurations ψ_n for σ^p from two to 16 does not substantially affect the isotopic difference in the screening. This is due primarily to the fact that term (4) is six times larger than (5) while term (5) is about ten times larger than (6). The error in the calculations associated with inaccurate calculations of the integrals, the quantities $\langle\xi^k\rangle_{vJ}$, etc. can be estimated as ~2%. Hence the observed ~17% excess of the calculated values over the corresponding experimental values (Table III) must be due to something else. We note that the proton and deuteron screening in the HD molecule are the same within the limitations of the approximate calculations presented above.

ESTIMATE OF THE CORRECTIONS TO THE HD ELECTRON CLOUD ASYMMETRY AND TO THE MUTUAL SCREENING OF THE NUCLEI

The electron cloud of the HD molecule is asymmetric because of the coupling between the motions of the nuclei and the electrons, and the molecule consequently has an electric dipole moment $\mu = 1.5 \times 10^{-3}$ D[24] and the screening of the proton differs from that of the deuteron. The correction to the screening constant can be estimated without cumbersome calculations by adopting a simplified model for the electron density distribution. In this connection we shall use the result obtained by Kolos and Wolniewicz, who found that the center of gravity of the electron cloud is displaced a distance $\delta z = 0.304 \times 10^{-3}$ a.u. toward the deuteron[24]. Then the principal term (4) determining the deuteron screening will take the form

$$\sigma_d{}^0 = {}^2/_3\alpha^2\langle\psi_0|[x^2+y^2+(z-\delta z)^2]^{-1/2}|\psi_0\rangle = \sigma^0 + \delta\sigma_d{}^0. \tag{14}$$

Bringing δz outside the brackets, we obtain the following expression for the additional deuteron screening due to the asymmetry:

$$\delta\sigma_d{}^0 = \frac{2}{3}\alpha^2\left\langle\psi_0\left|\frac{z}{r^3}\right|\psi_0\right\rangle\delta z \approx 2.7\cdot10^{-9}. \tag{15}$$

The change in the proton screening will have the same magnitude but the opposite sign.

Consequently, the calculated isotopic differences (Table III) must be decreased by the quantity (15), and the difference between the screening of the proton and that of the deuteron in HD will be twice as large: $\approx 5.4 \times 10^{-9}$.

In addition to the electron screening, we must also examine the screening of one nucleus by the other. The "nuclear" screening is similar in nature to the electron screening. The calculation can be based on the same quasiclassical ideas as are used in deriving the formula for screening in atoms, i.e., it is sufficient to determine the strength of the nuclear current induced by the external magnetic field.

This current is due to the precession of the nuclei about their common center of gravity at the Larmor frequency

$$\omega_k = -e\mathrm{H}/2M_kc, \tag{16}$$

where M_k is the mass of the k-th nucleus. According to the Biot-Savart law, the additional field at nucleus 1 due to the precession of nucleus 2 is

$$\mathbf{H}_1 = -\frac{e}{c}\left\langle\frac{[[\boldsymbol{\omega}_k\times\mathbf{r}_k]\times\mathbf{r}_{12}]}{r_{12}{}^3}\right\rangle, \tag{17}$$

where r_{12} is the distance between the nuclei and r_k is the distance of the k-th nucleus from their common center of gravity. The angular brackets indicate averaging over all orientations. The relation $r_k = r_{12}M_k/(M_1 + M_2)$ obtains. Assuming that all orientations are equally probable, we obtain the following expression for the screening of nucleus 1 by nucleus 2:

$$\sigma_1^{\mathrm{N}} = \frac{\alpha^2}{3}\frac{m_e}{M_1+M_2}\frac{M_1}{M_2}\left\langle\frac{1}{r_{12}}\right\rangle, \tag{18}$$

where m_e is the electron mass.

The same relation can be derived by replacing each nuclear momentum p_N in the initial Schrödinger equation by the sum $p_N + \alpha A$, where A is the vector potential. Equation (18) represents the "diamagnetic" part of the mutual nuclear screening. From Eq. (18) we obtain the following numerical values:

$$\sigma_N(\mathrm{H}_2) = 3.4\cdot10^{-9}, \quad \sigma_N(\mathrm{D}_2) = 1.7\cdot10^{-9},$$
$$\sigma_N(\dot{\mathrm{H}}\mathrm{D}) = 1.1\cdot10^{-9}, \quad \sigma_N(\mathrm{H}\dot{\mathrm{D}}) = 4.5\cdot10^{-9}.$$

The experimental error can be made smaller than these corrections, so the latter must be taken into account both in comparing the isotopic differences in the screening and in determining the ratio of the gyromagnetic ratios. We also considered other effects, but they led to corrections that do not exceed 10^{-9}.

Thus, on taking the asymmetry of the electron cloud and the mutual screening of the nuclei into account we obtain the following calculated values for the isotope effects:

$$\sigma(\dot{\mathrm{H}}\mathrm{D}) - \sigma(\mathrm{H}_2) = 38\cdot10^{-9}, \quad \sigma(\mathrm{D}_2) - \sigma(\mathrm{H}\dot{\mathrm{D}}) = 45\cdot10^{-9}$$

which agree fairly well with the experimental results. Hence the value $\sim 8.8 \times 10^{-9}$ obtained for the difference between the screening of the nuclei in HD can be used to determine the ratio of the gyromagnetic ratios from Eq. (1):

$$\gamma_d/\gamma_p = 6.514399178 \pm 16. \tag{19}$$

As error, we indicate here only the experimental value, which gives the contribution $1 \pm 2.46 \times 10^{-9}$. It may be assumed, however, that our value of γ_p/γ_d is correct with a relative error not exceeding 10^{-8}. The ratio of the magnetic moment of the proton to that of the deuteron is half the ratio (19) of the gyromagnetic ratios because of the different spins.

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