

Magnetic field-induced effects on NMR properties

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Abstract

In principle, all the NMR observables, spin-spin coupling J , nuclear shielding σ and quadrupole coupling q , are magnetic field-dependent. The field dependence may be classified into two categories: direct and indirect (apparent) dependence. The former arises from the magnetic field-induced deformation of the molecular electronic cloud, while the latter stems from a slightly anisotropic orientation distribution of molecules, due to the interaction between the anisotropy of the molecular susceptibility tensor and the external magnetic field. Here we use 1,3,5-D₃-benzene as a model system to investigate the indirect effect on the one-bond ¹H-¹³C and ²H-¹³C spin-spin couplings (J couplings) and the ²H quadrupole coupling. Experiments carried out at four magnetic fields (4.7, 9.4, 14.1, and 18.8 Tesla) show that the indirect effect is significant already at the magnetic fields commonly used in NMR spectrometers. A joint fit of the data extracted at the different field strengths provides experimental results for the susceptibility anisotropy, ²H quadrupole coupling constant and the related asymmetry parameter as well as the one-bond CH and CD coupling constants extrapolated to vanishing field strength. The field-induced contributions are found to exceed the commonly assumed error margins of the latter. The data also indicate a primary isotope effect on the one-bond CH coupling constant. There is a tendency to further increase the magnetic field of NMR spectrometers, which leads to more pronounced indirect contributions and eventually significant direct effects as well.

Keywords: Isotropic liquid, molecular orientation, diamagnetic anisotropy, isotope effect, 1,3,5-D3-benzene

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1. Introduction

Generally the nuclear magnetic resonance (NMR) parameters, nuclear shielding, spin-spin coupling and quadrupole splitting are considered independent of the applied magnetic field. However, as early as 1970, Ramsey¹ published a theoretical study in which he concluded that “in some molecules, especially where the magnetic shielding is abnormally large, it is possible that the field dependence of the shielding could be large enough to be observable”. Inspired by this prediction, Bendall and Doddrell carried out ⁵⁹Co NMR experiments of some cobalt compounds and found a field dependence of shielding in Co(¹⁵NH₃)Cl₃ and Co(acac)₃.² About 25 years later, Manninen and Vaara presented a theory and computed from first principles the field-dependence of -6×10^{-3} ppmT⁻² in Co(acac)₃, which is an order of magnitude smaller than the experimentally derived value.³ Boyd *et al.*, in turn, computed field dependence of the order of 10^{-5} ppmT⁻² for nitrogen shielding in some nitroso and isodiazene compounds.⁴ Similarly to nuclear shielding, the spin-spin coupling can be expected to be field-dependent as well. The semi-empirical study by Raynes and Stevens suggested that the coupling varies as 0.5×10^{-5} HzT⁻² for “strongly magnetic nuclei in large molecules”.⁵ There is, however, no experimental evidence of the field dependence of spin-spin couplings.

The only experimentally observed and computationally confirmed field dependence of an NMR parameter is that of ¹³¹Xe quadrupole coupling.^{6,7,8,9} The ¹³¹Xe NMR spectrum consists of a 3:4:3 triplet when the electric quadrupole moment interacts with a non-zero electric field gradient (EFG) at the nuclear site. The non-zero EFG stems from the slight deformation of the electron cloud induced by the magnetic field. Apart from the *direct* magnetic field effect on the NMR parameters, discussed above, there may appear also an *indirect* (aka *apparent*) contribution due to the field-induced partial orientation of molecules. The partial orientation leads to incomplete averaging of the anisotropic parts of the NMR tensors. In other words, dipole-dipole couplings, quadrupole couplings, and the anisotropies of spin-spin coupling and chemical shift affect the observables. Such effects were

detected already in the mid-1980's for the ^2H quadrupole coupling in substituted benzenes, pyridine and aniline,^{10,11} and for the ^1H - ^{13}C coupling in *o*-dichlorobenzene.¹² In 1995, the field-induced effect on the *ortho* ^1H - ^1H coupling in benzene and halobenzenes was reported by Laatikainen *et al.*¹³ and, for the ^{15}N chemical shift in a protein-DNS complex, by Ottiger, Tjandra and Bax.¹⁴

For this study, we recorded the ^2H , $^2\text{H}\{-^1\text{H}\}$, ^{13}C and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of 1,3,5- D_3 -benzene at four different magnetic fields. From these spectra we reveal information about (a) the orientational order arising from the interaction of the magnetic field with the anisotropy of the diamagnetic susceptibility tensor of benzene, (b) the ^2H quadrupole splitting and its sign, and (c) the apparent magnetic-field dependence of the one-bond ^{13}C - ^1H and ^{13}C - ^2H J couplings. Our findings indicate that, indeed, the J couplings contain a significant contribution from the respective dipolar coupling at the present field strengths. When this part is stripped out, *i.e.*, the coupling values at zero magnetic field are determined, the $^1\text{H}/^2\text{H}$ isotope effect on the one-bond J coupling is revealed.

2. Experimental

The sample of ca. 0.8 ml 1,3,5- D_3 -benzene was prepared into 5 mm (o.d.) NMR tube and degassed by a two freeze-pump-thaw cycles. Small amount of CH_4 gas was added to act as the ^1H - ^{13}C spin-spin coupling reference. Eventually the sample tube was sealed with a flame. The NMR spectra were measured on Bruker DPX200, AVANCE III 400, AVANCE III 600 and AVANCE III 800 (equipped with a TCI cryoprobe) spectrometers, which have ^1H resonance frequencies of 200, 400, 600 and 800 MHz, respectively. In addition to ^1H spectra, ^{13}C and ^2H spectra were measured both with and without broadband proton decoupling. All the experiments were carried out at 300 K. The temperature was calibrated using the standard calibration sample of ethylene glycol. The ^{13}C spectra were analyzed with PERCH,¹⁵ while the ^2H quadrupole splittings were determined from the ^{13}C satellites in the $^2\text{H}\{-^1\text{H}\}$ spectra using line shape analysis on the dmfit¹⁶ program.

3. Results and discussion

The proton-coupled ^{13}C NMR spectrum of 1,3,5- D_3 -benzene consists of a doublet of triplets and a triplet of multiplets due to the ^{13}C - ^1H and ^{13}C - ^2H interactions, as shown in Figure 1. Figure 1 also shows the proton-decoupled ^2H spectrum revealing the doublet splitting due to the ^2H quadrupole coupling. On the contrary, the ^{13}C - $\{^1\text{H}\}$ NMR spectrum consists of a singlet and a triplet of quintets. The doublet splitting is due to the one-bond ^{13}C - ^1H interaction, Δ_{CH} , which is shown, as an example, in Figure 2 as a function of the magnetic flux density at 300 K. Generally, the doublet and triplet splittings are considered to be due to the respective one-bond scalar J couplings. Here we use the Δ symbols for the reason explained below. The dependence of Δ_{CH} on B may result (a) from the direct field dependence of the electronic property of J_{CH} coupling or (b) indirectly via the dependence of the orientational order parameter S (*vide infra*) on the magnetic field. The latter renders visible the anisotropic contributions, dipole-dipole coupling (D_{CH}) and/or the spin-spin coupling, $J_{\text{CH}}^{\text{aniso}}$, which average out in non-oriented liquids. The direct field dependence of J_{CH} is hardly of observable magnitude and it was ruled out in the present study by using $^{13}\text{CH}_4$ as an internal reference. The J_{CH} parameter of $^{13}\text{CH}_4$ was measured at three fields and was found to be constant, $J_{\text{CH}} = 125.668 \pm 0.001$ Hz. As methane is a molecule that, on account of its symmetry, is not oriented by magnetic field (its diamagnetic susceptibility is zero), the constancy of J_{CH} as a function of B implies that any apparent field dependence of the Δ_{CH} parameter arises solely via the indirect mechanism also in 1,3,5- D_3 -benzene.

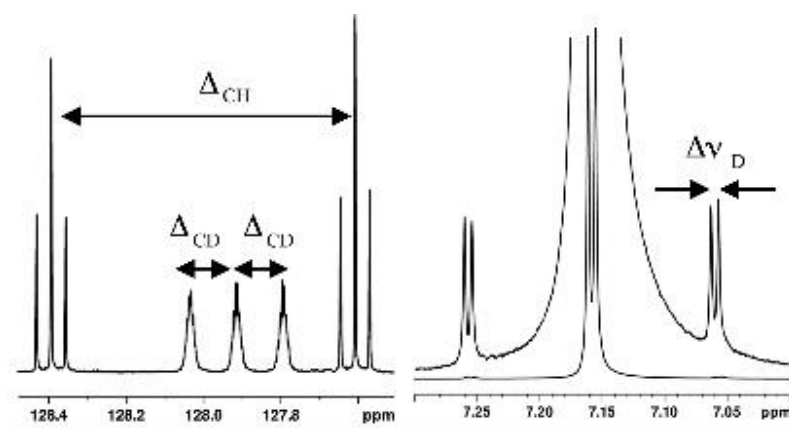


Figure 1. ^{13}C NMR spectrum (left) and $^2\text{H}\{-^1\text{H}\}$ spectrum (right) of 1,3,5- D_3 -benzene recorded in the magnetic field of 18.7829 T (proton Larmor frequency 800 MHz). The extracted quantities are defined in the spectra.

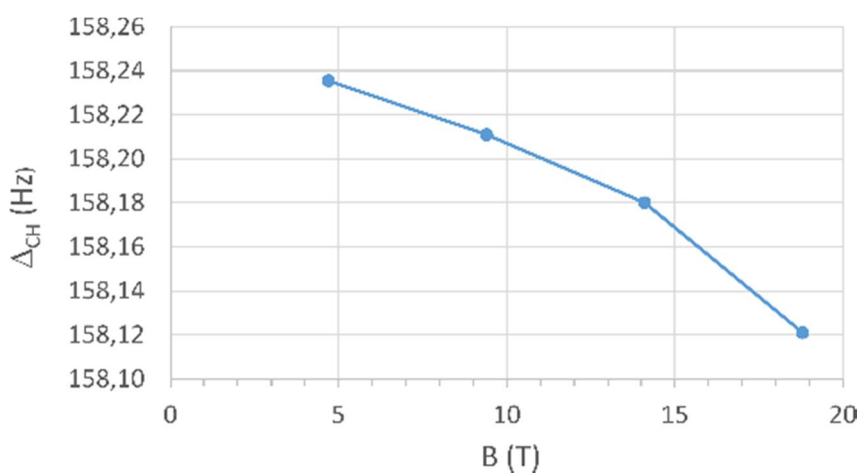


Figure 2. The splitting Δ_{CH} in 1,3,5- D_3 -benzene as a function of the magnetic flux density.

In 1,3,5- D_3 -benzene, similar field dependence is seen for the one-bond $^2\text{H}\text{-}^{13}\text{C}$ splitting and ^2H quadrupole splitting as for Δ_{CH} . Obviously, the reason for the observed field dependence is the slight orientation of the 1,3,5- D_3 -benzene molecule, in the formally isotropic medium. This phenomenon was recently reported for D_6 -benzene and D-chloroform at very high magnetic fields.^{17,18} Consequently, a plausible explanation for the observed behavior shown in Figure 2 is a small contribution from the direct $^{13}\text{C}\text{-}^1\text{H}$ coupling, D_{CH} , and (possibly) from $J_{\text{CH}}^{\text{aniso}}$ due to the anisotropy of the spin-spin coupling tensor.

The dipolar couplings between a pair of nuclei in the benzene ring can be presented in the form

$$D_{KL} = -\frac{\mu_o \hbar \gamma_K \gamma_L}{8\pi^2} \frac{1}{r_{KL}^3} S_{\perp} = K_{KL} \frac{1}{r_{KL}^3} S_{\perp}. \quad (1)$$

Here, S_{\perp} is the orientational order parameter perpendicular to the symmetry axis of benzene, while the other symbols have their usual meanings. One should note that in some earlier papers, the definition of D_{KL} differs by a factor of 2 from that in Eq. (1), *i.e.*, the present values should be multiplied by 2 when compared with the earlier ones.

The contribution from the anisotropy of the spin-spin coupling tensor \mathbf{J}_{KL} is

$$J_{KL}^{\text{aniso}} = \frac{2}{3} \Delta J_{KL} S_{\parallel}, \quad (2)$$

where $\Delta J_{KL} = J_{KL,\parallel} - J_{KL,\perp}$ is the anisotropy relative to the symmetry axis of the axially symmetric molecule and S_{\parallel} is the orientational order parameter of the symmetry axis. These two contributions cannot be measured separately but as a combination

$$D_{KL}^{\text{exp}} = D_{KL} + \frac{1}{2} J_{KL}^{\text{aniso}}. \quad (3)$$

The anisotropy of the one-bond ^1H - ^{13}C spin-spin coupling tensor is small. There are no experimental results available but computations indicate that $\Delta^1 J_{\text{CH}}$ is only a few Hz at maximum.^{19,20,21} Moreover, S_{\parallel} is small, as shown below and, therefore, the term $\frac{1}{2} J_{\text{CH}}^{\text{aniso}}$ is negligible and can be omitted. One should note that J_{KL}^{aniso} may not always be negligible in the case of heavier nuclei.^{21,22}

The orientational order parameters, S_{\parallel} and S_{\perp} , which arise from the interaction between the magnetic field and the anisotropy of the diamagnetic susceptibility of benzene, can be obtained using

Boltzmann statistics. The component of the diamagnetic susceptibility in the direction of the magnetic field, which defines the Z axis of the laboratory frame, is

$$\chi_{ZZ} = \chi^{\text{iso}} + \frac{2}{3}\Delta\chi P_2(\cos\theta) \quad , \quad (4)$$

where χ^{iso} is the isotropic average and $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ is the anisotropy of the cylindrically symmetric susceptibility tensor in the molecule-fixed frame, and $P_2(\cos\theta)$ is the second Legendre polynomial with θ the angle between the molecular symmetry axis and the external magnetic field. The magnetic energy is, consequently,

$$E_B = -\frac{1}{2}\mathbf{B} \cdot \boldsymbol{\chi} \cdot \mathbf{B} = -\frac{1}{2}\chi_{ZZ}B^2 \quad . \quad (5)$$

The orientational order parameter of the symmetry axis, S_{\parallel} , is obtained as follows (one should note that the isotropic part in χ_{ZZ} can be neglected because it does not affect the orientation):

$$S_{\parallel} = \langle \frac{1}{2}(3\cos^2\theta - 1) \rangle_B = \frac{\int_0^{\pi} \frac{1}{2}(3\cos^2\theta - 1) \exp(\frac{1}{3}\frac{\Delta\chi P_2(\cos\theta)B^2}{kT}) \sin\theta d\theta}{\int_0^{\pi} \exp(\frac{1}{3}\frac{\Delta\chi P_2(\cos\theta)B^2}{kT}) \sin\theta d\theta} \approx \frac{\Delta\chi}{15kT} B^2 \quad . \quad (6)$$

In Eq. (6), k is the Boltzmann constant and T the temperature. The exponent $\frac{1}{3}\frac{\Delta\chi P_2(\cos\theta)B^2}{kT}$ is of the order of 10^{-5} - 10^{-4} at the magnetic fields and temperature used in the present study and, consequently, the exponential function can be replaced by a series expansion. The simple final form in Eq. (6) is obtained when higher than the second-order terms in B are omitted. The order parameter in the plane of benzene thus becomes

$$S_{\perp} = P_2(\cos 90^\circ)S_{\parallel} = -\frac{1}{2} \frac{\Delta\chi}{15kT} B^2. \quad (7)$$

The experimentally detected splittings due to the ^1H - ^{13}C and ^2H - ^{13}C interactions are sums of the respective J and D couplings, *i.e.*, $\Delta = J+2D$. Thus, substitution of the right-hand side of Eq. (7) for S_{\perp} in Eq. (1) results in the following equation:

$$\Delta_{\text{CX}} = J_{\text{CX}}(0) + 2D_{\text{CX}} = J_{\text{CX}}(0) + \frac{\mu_0 \hbar \gamma_{\text{C}} \gamma_{\text{X}}}{8\pi^2} \frac{1}{r_{\text{CH}}^3} \frac{\Delta\chi}{15kT} B^2, \quad (8)$$

where X = H or D, indicating linear dependence of the observed splittings on B^2 . The Δ_{CH} and Δ_{CD} parameters are dominated by the respective one-bond J couplings, which are generally known to be positive. Thus the sign of Δ_{CX} is positive, too. In the least-squares fit, the C-H bond length was fixed to $r_{\text{CH}} = 1.0841 \text{ \AA}$, while the C-D bond length was fixed to 1.0830 \AA .²³ The third field-dependent quantity, the ^2H quadrupole splitting, is

$$\Delta\nu_{\text{D}} = \frac{3}{2} q_{zz}(1 + \eta)S_{\perp} = \frac{3}{2} q_{zz}(1 + \eta) \left(-\frac{1}{2} \frac{\Delta\chi}{15kT} B^2 \right) = -\frac{3}{4} \frac{q_{zz}(1+\eta)\Delta\chi}{15kT} B^2, \quad (9)$$

where q_{zz} is the ^2H quadrupole coupling tensor component in the C-D bond direction and η is the asymmetry parameter of the tensor, defined as

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}}. \quad (10)$$

Eqs. (8) and (9) contain a common parameter, the susceptibility anisotropy $\Delta\chi$. Consequently, the joint least-squares fit of functions (8)-(9) to the experimental splittings is based on the adjustable parameters $\Delta\chi$, $J_{\text{CH}}(0)$, $J_{\text{CD}}(0)$, q_{zz} , and η . The results are shown in Table 1 and Figs. 3 and 4.

Table 1. Results from the joint fit of Eqs. (8)-(9) to the experimental splittings Δ_{CH} , Δ_{CD} and $\Delta\nu_{\text{D}}$.

Parameter	Fitted value	Literature value / ref.
$\Delta\chi$	$(-889.5 \pm 0.2) \times 10^{-30} \text{ JT}^{-2}$	$-1026 \times 10^{-30} \text{ JT}^{-2} / 11$
$J_{\text{CH}}(0)$	$158.244 \pm 0.003 \text{ Hz}$	$158.380 \text{ Hz} / 13$
$J_{\text{CD}}(0)$	$24.247 \pm 0.001 \text{ Hz}$	$24.267 \pm 0.006 \text{ Hz} / 24$
q_{zz}	$185.940 \pm 0.003 \text{ kHz}$	$184.7 \pm 0.3 \text{ kHz} / 28$
η	0.054 ± 0.001	$0.056 / 28$

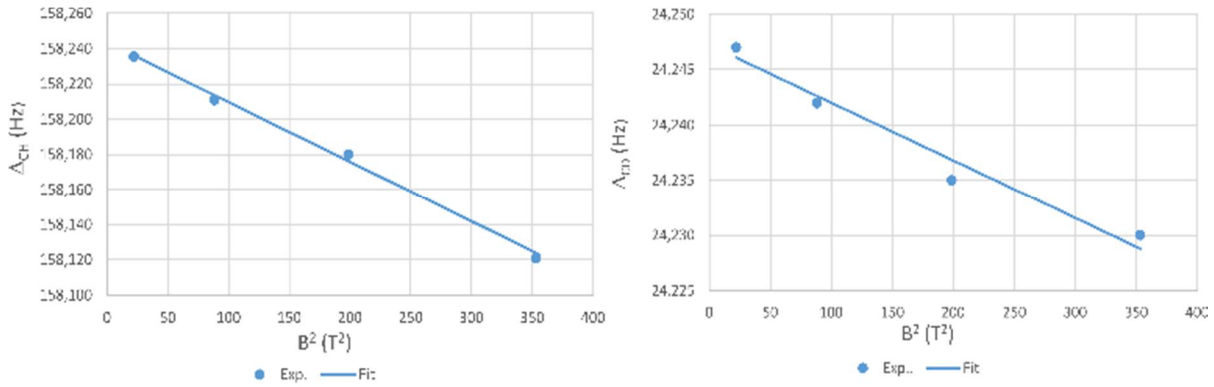


Figure 3. The splittings Δ_{CH} and Δ_{CD} as a function of the square of the magnetic flux density.

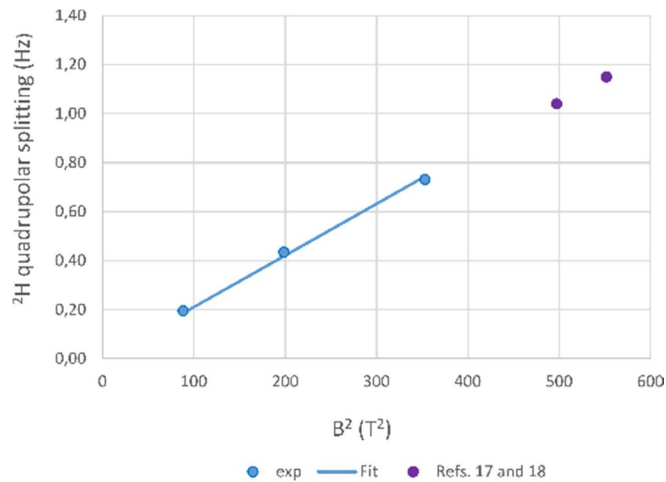


Figure 4. ^2H quadrupole splitting, $\Delta\nu_{\text{D}}$, as a function of the square of the magnetic flux density. The two points at the highest fields are from refs. 17 and 18, for C_6D_6 . The least-squares fit is based on the three lower field points only.

The $\Delta\chi$ value of $-889.5 \times 10^{-30} \text{ JT}^{-2}$ results in the orientational order parameter of the benzene symmetry axis of

$$S_{\parallel} = -1.432 \times 10^{-8} B^2 \left(\frac{1}{\text{T}^2} \right) , \quad (11)$$

where T refers to the SI unit Tesla of the magnetic flux density.

First-principles calculations of the susceptibility tensor were performed using the Dalton 2015 program.²⁵ First, the susceptibility tensor at the benzene equilibrium geometry of Gauss and Stanton²² ($r_{\text{CC}} = 1.3914 \text{ \AA}$; $r_{\text{CH}} = 1.0802 \text{ \AA}$) was computed using the second-order polarization propagator with coupled-cluster singles and doubles amplitudes [SOPPA(CCSD)] method²⁶ with the cc-pCV5Z basis set.²⁷ The results at this level for the isotropic susceptibility χ and susceptibility anisotropy $\Delta\chi$ are -883.3 and -1010.1 , respectively, in units of 10^{-30} J/T^2 . To these equilibrium geometry values we can add rovibrational contributions at 300 K using the same method as employed earlier for the corresponding contributions to the deuterium quadrupole coupling tensor²⁸ and susceptibility¹⁷ in benzene. Carrying out these corrections at the density-functional theory (DFT) level using the 3-parameter hybrid exchange-correlation functional B3LYP²⁹ and the cc-pCVTZ basis²⁶ leads, at 300 K, to the final values of -871.0 and -973.5 (in units of 10^{-30} J/T^2) for χ and $\Delta\chi$, respectively. These results are obtained as the sum of the SOPPA(CCSD) data at the equilibrium geometry and the DFT-based rovibrational corrections. The fact that a roughly 10% larger absolute value of $\Delta\chi$ is obtained from the computations than from the joint fit to the experimental data described above, is due to deficiencies in the present electronic structure treatment (electron correlation and basis set) and, as the main source of imprecision, the lack of solvent/medium corrections in the theoretical calculations,

when comparing to liquid-state experiments. Other recent, entirely DFT-based computations led to the values of $\Delta\chi$ equal to $-1056 \times 10^{-30} \text{ J/T}^2$,¹⁷ at the B3LYP/aug-cc-pVTZ level including rovibrational corrections at 300 K for the perdeuterated isotopomer) and $-1065 \times 10^{-30} \text{ J/T}^2$ (B3LYP/aug-cc-pVTZ without rovibrational corrections).¹⁸

The joint fit results in the one-bond ^1H - ^{13}C spin-spin coupling constant at zero magnetic field of $J_{\text{CH}}(0) = 158.244 \pm 0.003 \text{ Hz}$. Jackowski, Maciaga and Wilczek measured the value of $157.78 \pm 0.02 \text{ Hz}$ at 11.7 T for gaseous benzene.³⁰ (We note in passing that this value may include a contribution from $2D_{\text{CH}}$, of about -0.10 Hz , as estimated on the basis of the present results.) It can be observed from comparison to our present liquid-state data that the coupling increases by about 0.4 Hz at the gas-to-liquid phase transition. The corresponding $J_{\text{CD}}(0)$ is $24.247 \pm 0.001 \text{ Hz}$. The ratio $J_{\text{CH}}(0)/J_{\text{CD}}(0)$ thus equals $6.5262 \pm 0.008\%$ differing from the gamma ratio $\gamma_{\text{H}}/\gamma_{\text{D}} = 6.51439804$ (Ref. 31) significantly, by 0.18%. The deviation of the ratio of the couplings from the gamma ratio suggests the existence of an isotope effect. The primary isotope effect of the one-bond ^1H - ^{13}C coupling is generally defined as³²

$$\Delta_{\text{p}}^1 J(^{13}\text{C}^{2/1}\text{H}) \equiv {}^1 J_{\text{CD}} \frac{\gamma_{\text{H}}}{\gamma_{\text{D}}} - {}^1 J_{\text{CH}}. \quad (12)$$

In the present case the value $-0.288 \pm 0.009 \text{ Hz}$ is obtained for $\Delta_{\text{p}}^1 J(^{13}\text{C}^{2/1}\text{H})$ at zero magnetic field. The negative sign seems to be general for this kind of effects.³²

In fact, the primary isotope effect is, in principle, dependent on the magnetic field. Eq. (12) can be presented in the more complete form

$$\Delta_{\text{p}}^1 J(^{13}\text{C}^{2/1}\text{H}) = ({}^1 J_{\text{CD}} + 2D_{\text{CD}}) \frac{\gamma_{\text{H}}}{\gamma_{\text{D}}} - ({}^1 J_{\text{CH}} + 2D_{\text{CH}}), \quad (13)$$

including the corresponding direct coupling contributions. Using the definition of Eq. (1) for the D coupling, Eq. (13) becomes

$$\Delta_p {}^1J({}^{13}\text{C}^{2/1}\text{H}) \equiv {}^1J_{\text{CD}} \frac{\gamma_{\text{H}}}{\gamma_{\text{D}}} - {}^1J_{\text{CH}} + 2D_{\text{CH}} \left[\left(\frac{r_{\text{CH}}}{r_{\text{CD}}} \right)^3 - 1 \right]. \quad (14)$$

In the present case, $2D_{\text{CH}}$, which is proportional to B^2 , obtains values between -7.5 and -120 mHz depending on the strength of the magnetic field, and the third power of the ratio of the bond lengths is 1.00305. Consequently, the effect of the direct dipolar coupling term in Eq. (14) is negligible in the present case.

As was concluded above, the order parameter S_{\parallel} is negative and, due to the tracelessness of the orientation tensor, its component S_{\perp} is, correspondingly, positive. If the signs are not known, they can be determined from the proton-coupled ${}^2\text{H}$ NMR spectra, as shown below. Namely, the dipolar couplings can be calculated from Eq. (1) when the internuclear distances and orientational order parameter are known. From Eqs. (1) and (9) we can further conclude that the D_{KL} couplings and ${}^2\text{H}$ quadrupole splitting $\Delta\nu_{\text{D}}$ must possess opposite signs. This conclusion follows from the opposite signs of $q_{\text{CD}} (> 0)$ and $K_{KL} (< 0)$, while both D_{KL} and $\Delta\nu_{\text{D}}$ are dependent on the same orientational order parameter, S_{\perp} . The estimate for the magnitude of the latter order parameter is obtained from Eq. (9) using $\Delta\nu_{\text{D}} = 0.73$ Hz from the ${}^2\text{H}$ NMR spectrum at 800 MHz, $q_{zz} = 184.7$ kHz and $\eta = 0.056$.²⁷ The ${}^2\text{H}$ spectra were simulated on the PERCH program¹⁵ using two sign combinations: (1) D_{KL} ($K, L = {}^1\text{H}, {}^2\text{H}$) couplings are negative and $\Delta\nu_{\text{D}}$ positive, and (2) D_{KL} couplings are positive and $\Delta\nu_{\text{D}}$ negative. The resulting spectra are compared with the experimental spectrum (taken at 800 MHz) in Fig. 5. The internuclear distances and the K_{KL} factors are shown in Table 2. The J couplings, in turn, are from C_6H_6 (see ref. 13) scaled by the gyromagnetic ratios. Table 3, in turn, lists the dipolar couplings.

Table 2. D-D and D-H internuclear distances and the K_{KL} factors used in the calculation of the dipolar couplings for the simulation of the proton-coupled ^2H NMR spectrum shown in Fig. 5. The corresponding J couplings are listed as well. ^{a)}

$R_{\text{DH}}^o = 2.47 \text{ \AA}$	$K_{\text{HH}} = -120120 \text{ Hz\AA}^3$	$J_{\text{HD}}^o = 1.158 \text{ Hz}$
$R_{\text{DD}}^m = 4.28 \text{ \AA}$	$K_{\text{DH}} = -18440 \text{ Hz\AA}^3$	$J_{\text{DD}}^m = 0.032 \text{ Hz}$
$R_{\text{DH}}^p = 4.94 \text{ \AA}$	$K_{\text{DD}} = -2830.6 \text{ Hz\AA}^3$	$J_{\text{HD}}^p = 0.100 \text{ Hz}$
$R_{\text{HH}}^m = 4.28 \text{ \AA}$		$J_{\text{HH}}^m = 1.373 \text{ Hz}$

a) The symbols o , p and m refer to *ortho*, *meta* and *para*, respectively.

Table 3. The magnitudes of the dipolar couplings in 1,3,5- D_3 -benzene at variable magnetic fields B . The D couplings are in mHz while B values are in Tesla. ^{a)}

B	o - D_{DH}	m - D_{DD}	p - D_{DH}	m - D_{HH}
18.79	3.09	0.09	0.39	3.88
14.09	1.74	0.05	0.22	2.18
9.40	0.77	0.02	0.10	0.96
4.70	0.19	0.00	0.02	0.24

a) For the meaning of o , p , and m , see footnote in Table 2.

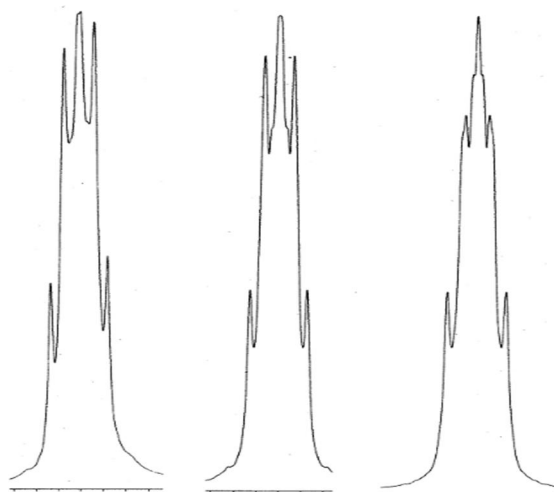


Figure 5. Experimental and simulated ^2H NMR spectra of 1,3,5- D_3 -benzene oriented by magnetic field. Left: Experimental spectrum measured on an 800 MHz spectrometer. Mid: simulated spectrum with positive ^2H quadrupole splitting and negative dipolar couplings. Right: simulated spectrum with negative ^2H quadrupole splitting and positive dipolar couplings.

Figure 5 clearly proves that the ^2H quadrupole splitting must be positive and the dipolar couplings negative. This further means that the orientational order parameter in the benzene plane, *i.e.*, in the perpendicular direction relative to the symmetry axis, must be positive. It is important to note that although the dipolar couplings are small (see Table 3), they affect the fine structure of the spectrum. A nice example is given in ref. 13 in which a very high-resolution spectrum of benzene is analyzed.

4. Conclusions

Isotropic liquids are defined as being uniform in all directions. In such environments the NMR tensors average to their isotropic values, equal to one third of the trace of the tensor. This means that the anisotropic parts of the corresponding tensors vanish. However, this situation breaks down in cases where the anisotropy of the diamagnetic susceptibility of the molecules is large and the NMR experiments are performed at high magnetic fields. The interaction of the magnetic flux density with

the diamagnetic susceptibility leads to a slightly anisotropic orientational distribution of the molecules and, consequently, the NMR tensors include non-zero anisotropic contributions. Presently, efforts are made toward higher and higher magnetic fields, meaning that both the directly field-induced and indirectly field-dependent anisotropic contributions are becoming more pronounced. In this study, we have shown that already at the magnetic field of 4.7 T, the dipolar contribution to the one-bond ^1H - ^{13}C coupling in benzene exceeds the generally reported error limits. The application of high magnetic field in liquid-state NMR experiments is generally considered beneficial. As shown here, the emerging anisotropic contributions affect the accuracy of the extracted NMR parameters.

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