

A New Method for the Determination of the Dynamic Isotope Effect and the Deuterium Quadrupole Coupling Constant in Liquids

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Using a self-consistent NMR method, it is now possible to determine both the deuterium quadrupole coupling constant as well as the rotational dynamic isotope effect in liquids. We successfully tested the method on benzene for temperatures between 280 K and 293 K. The average value of 185(3) kHz for the coupling constant is compared with measurements in solid state and gas phase. As might be expected for liquids without hydrogen bonds, no difference can be detected. A rotational dynamic isotope effect of 6(3)% is observed. This value is significantly smaller than 20(5)%, the only other result reported in the literature. The results are corrected for the influence of vibrational motion. © 1998 Academic Press

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INTRODUCTION

We present a new nuclear magnetic resonance (NMR) method for the determination of the dynamic isotope effect as well as the deuterium quadrupole coupling constant in liquids.

The dynamic isotope effect resulting from isotopic substitution, for example, hydrogen/deuterium substitution, is difficult to predict theoretically. It can be calculated from different diffusion models, but yet no satisfactory approach exists. Experimental results for the isotope effect may serve as a test for models in molecular dynamics.

Quadrupole coupling constants probe the electric field gradient at the site of the nucleus. They are therefore a test for electronic wavefunctions, calculated, for example, by *ab initio* methods. For hydrogen bonded systems, the quadrupole coupling constant shows a characteristic temperature dependence. The values in liquids are bracketed by the solid and gas values and increase with temperature. For the study of such systems, accurate experimental results for the coupling constant would be valuable.

The first determinations of the deuterium quadrupole constant in a neat liquid were performed on benzene (1–3) at about 1965. They were based on the isotopic dilution technique, performed for the first time also on benzene (4, 5, 3). This technique requires measurements on several samples with an extrapolation to infinite dilution of a protonated molecule in

deuterated surroundings. It yields the intramolecular proton relaxation rate, arising mainly from magnetic dipole–dipole interaction. However, other contributions are included in the extrapolated rate. When applying this method the isotope effect is neglected and the situation becomes even more complicated for anisotropic motion. Since that time the coupling constant has also been determined from NMR spectra of molecules dissolved in liquid crystal phases. However, the interpretation of the spectra is not straightforward (6–10). We also quote here some measurements of the coupling constant in solid benzene (11–14) as well as in gas phase (15, 16).

To our knowledge, the only study of the isotope effect in the reorientation of benzene has been performed by J. P. Jacobsen (17). For this method, the deuterium quadrupole coupling constant has to be known. Our result is at variance with the effect reported in Ref. (17).

Our method is the first self-consistent method that allows the determination of the dynamic isotope effect as well as the deuterium quadrupole coupling constant. For the latter, only one sample is needed. Provided that extreme narrowing condition is fulfilled, no further assumptions have to be made for the reorientation of the molecule.

In any case, corrections for the influence of vibrational motion have to be considered (18–20).

METHODS

The deuteron relaxation is governed by the interaction of the nuclear quadrupole moment with the electric field gradient at the site of the nucleus. This interaction is accepted to be purely intramolecular. In the case of extreme narrowing, realized for not too viscous liquids, the relaxation rate is frequency-independent and can be expressed as

$$R_Q = \frac{3\pi^2}{2} \left(\frac{e^2 Q q}{h} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \tau_Q. \quad [1]$$

$e^2 Q q / h$ is the quadrupole coupling constant (QCC). The asymmetry parameter η for benzene is small, 0.04 or 0.05 (13), so that the above equation can be simplified to

$$R_Q = \frac{3\pi^2}{2} \left(\frac{e^2 Q q}{h} \right)^2 \tau_Q. \quad [2]$$

R_Q can be measured with an accuracy of about one percent. Concerning the quantities $e^2 Q q / h$ and τ_Q , two different approaches have been adopted up to now.

Additional relaxation measurements are carried out to estimate a value for τ_Q . Under the condition of extreme narrowing, τ_Q is the integral of the autocorrelation function for the reorientation of the C–D bond, i.e., the effective reorientational correlation time. In the case of benzene, it is possible to determine the intramolecular proton relaxation rate by isotopic dilution (4, 5, 3). The dipolar contribution to the proton relaxation rate is given by

$$R_{H-H} = \frac{3}{2} \gamma^4 \hbar^2 \left(\frac{\mu_0}{4\pi} \right)^2 \sum_j r_{eff}^{-6}(H-H_j) \tau_{H-H}. \quad [3]$$

The sum runs over all neighbors. As a good approximation, only the first two neighbors are considered: $\sum_j r_{eff}^{-6}(H-H_j) = 2r_{eff}^{-6}(H-H)$, $r_{eff}(H-H)$ being the effective distance to the first neighbor. The definition of the effective distance will be given at the end of this section. Assuming $\tau_Q = \tau_{H-H}$, the QCC can be calculated by combining Eqs. [2] and [3]:

$$\frac{e^2 Q q}{h} = \frac{\gamma^2 \hbar \mu_0}{\sqrt{8\pi^2}} \sqrt{\frac{R_Q}{R^{H-H}} r_{eff}^{-6}(H-H)}. \quad [4]$$

One problem is that it is difficult to separate the other contributions to the measured proton relaxation rate, such as spin rotation or chemical shift anisotropy. For anisotropic motion, the reorientational correlation times of the C–D bond and the H–H vector are different in general. Benzene is an exception if considered as a symmetric top molecule in the diffusion limit (21). Finally, the effect of the deuteration on the reorientation is not known (dynamic isotope effect).

The other approach that has been adopted is to estimate the QCC from NMR measurements in solid state (11–14), from microwave measurements in the gas phase (15, 16) and from NMR measurements for molecules dissolved in liquid crystal phases (6–10). Then the quantity τ_Q calculated with Eq. [2] can be used to evaluate the dynamic isotope effect (17). This is done by comparing τ_Q to τ_{C-H} . τ_{C-H} is the integral of the autocorrelation function for the reorientation of the C–H bond obtained from the dipolar relaxation rate of the ^{13}C nucleus with the directly bound protons:

$$R_{C-H} = \gamma_C^2 \gamma_H^2 \hbar^2 \left(\frac{\mu_0}{4\pi} \right)^2 \sum_j r_{eff}^{-6}(C-H_j) \tau_{C-H}. \quad [5]$$

The sum runs over all effective intramolecular C–H distances.

Intermolecular contributions can be neglected. As the directly bonded proton accounts for about 95% of the sum, we write for simplicity $r_{eff}^{-6}(C-H)$ instead of $\sum_j r_{eff}^{-6}(C-H_j)$. The dipolar contribution R_{C-H} can be separated from the total carbon relaxation rate $R_{C(H)}$ by measuring the nuclear Overhauser enhancement (NOE) under steady-state proton saturation η_H ,

$$R_{C-H} = \frac{\eta_H}{\eta_H^{max}} R_{C(H)}. \quad [6]$$

η_H^{max} is the maximum NOE,

$$\eta_H^{max} = \frac{\gamma_H}{2\gamma_C} = 1.988. \quad [7]$$

Now the isotope effect τ_Q/τ_{C-H} is calculated by combining Eqs. [2], [5], [6], and [7]:

$$\frac{\tau_Q}{\tau_{C-H}} = \frac{\gamma_C \gamma_H^3 \hbar^2}{3\pi^2} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e^2 Q q}{h} \right)^{-2} \frac{R_Q}{\eta_H R_{C(H)}} r_{eff}^{-6}(C-H). \quad [8]$$

The problems of this method are the uncertainties concerning the correct value for the QCC and the effective C–H distance. An error of 2% for the former and 2% for the latter gives an error of 13% for the isotope effect. This is bigger than the effect itself.

Our new method consists in the determination of the dipolar relaxation rate R_{C-D} for the ^{13}C nucleus in the *deuterated* molecule,

$$R_{C-D} = \frac{8}{3} \gamma_C^2 \gamma_D^2 \hbar^2 \left(\frac{\mu_0}{4\pi} \right)^2 \sum_j r_{eff}^{-6}(C-D_j) \tau_{C-D} = \frac{\eta_D}{\eta_D^{max}} R_{C(D)}. \quad [9]$$

Again we note $r_{eff}^{-6}(C-D)$ instead of the sum. $R_{C(D)}$ is the total carbon relaxation rate in the deuterated molecule; η_D and η_D^{max} are the NOE and maximum NOE under steady-state *deuterium* saturation,

$$\eta_D^{max} = \frac{\gamma_D}{2\gamma_C} = 0.3052. \quad [10]$$

Now both the deuterium quadrupole coupling constant and the dynamic isotope effect can be determined. The former is obtained by combining Eqs. [2], [9], and [10]:

$$\frac{e^2 Q q}{h} = \frac{\hbar \mu_0}{6\pi^2} \sqrt{2\gamma_D^3 \gamma_C \frac{R_Q}{R_{C(D)} \eta_D} r_{eff}^{-6}(C-D)}. \quad [11]$$

R_Q , $R_{C(D)}$, and η_D are measured on the same sample. The

eliminated τ_Q and τ_{C-D} are the integrals over the autocorrelation function of the same C–D bond.

The dynamic isotope effect is given by combining Eqs. [5], [6], [7], [9], and [10]:

$$\frac{\tau_{C-D}}{\tau_{C-H}} = \frac{3\gamma_H^3\eta_D R_{C(D)}}{8\gamma_D^3\eta_H R_{C(H)}} \frac{r_{eff}^{-6}(C-H)}{r_{eff}^{-6}(C-D)}. \quad [12]$$

Due to the influence of mainly zero-point vibrational motion on the dipolar coupling constant, $(r_{eff}^{-3}(C-H))^2/(r_{eff}^{-3}(C-D))^2$ is not equal to one. The problem of vibrational corrections is discussed, for example, by Lucas (18), by Sykora, Vogt, Bösigger, and Diehl (19), or by Henry and Szabo (20). The expression given by the last authors for the approximated effective dipolar coupling constant is

$$\left(\frac{\gamma_C\gamma_H\hbar}{r_{eff}^3}\right)^2 = (\gamma_C\gamma_H\hbar)^2 \left\langle \frac{1}{r^3} \right\rangle^2 \mathcal{S}^2, \quad [13]$$

$\langle 1/r^3 \rangle$ being the vibrational average of the inverse cube distance. \mathcal{S} is the generalized order parameter in the model-free approach of Lipari and Szabo (22). Equation [13] defines an effective distance approximated by Eq. [47] of Ref. (20) to

$$r_{eff} = R + \left[\langle \Delta_z \rangle - \frac{2}{R} \langle \Delta_z^2 \rangle \right] + \left\{ \frac{1}{2R} (\langle \Delta_x^2 \rangle + \langle \Delta_y^2 \rangle) \right\}. \quad [14]$$

The equilibrium distance R for C–H and C–D is taken as 108.0 pm (8). The vibrational mean-square amplitudes for C_6H_6 and C_6D_6 are taken from Refs. (23, 24). The anharmonic contribution $\langle \Delta_z \rangle$ is approximated in Eq. [54] of Ref. (20) by

$$\langle \Delta_z \rangle = -\frac{10^5 f_{rrr}}{\mu^2 \omega^3}, \quad [15]$$

where f_{rrr} is the cubic force constant in $\text{kcal mol}^{-1} \text{\AA}^{-3}$, μ is the reduced mass in g mol^{-1} , and ω is the frequency of the bond stretch in cm^{-1} . The cubic force constant is taken as in Ref. (25); the frequencies for the C–H and C–D bond stretch can be found in Ref. (26).

The QCC calculated by Eq. [11] with the effective distance $r_{eff}(C-D)$ is the appropriate coupling constant for the interpretation of NMR relaxation data. It is the vibrational averaged coupling constant, as the electric field gradient eq at the site of the nucleus depends on the C–D distance. The correction leading to the coupling constant calculated with the field gradient at the equilibrium distance R , $eq(R)$, requires the knowledge of the distance dependence of the field gradient. In Ref. (20), a distance dependence stronger than r^{-3} leads to

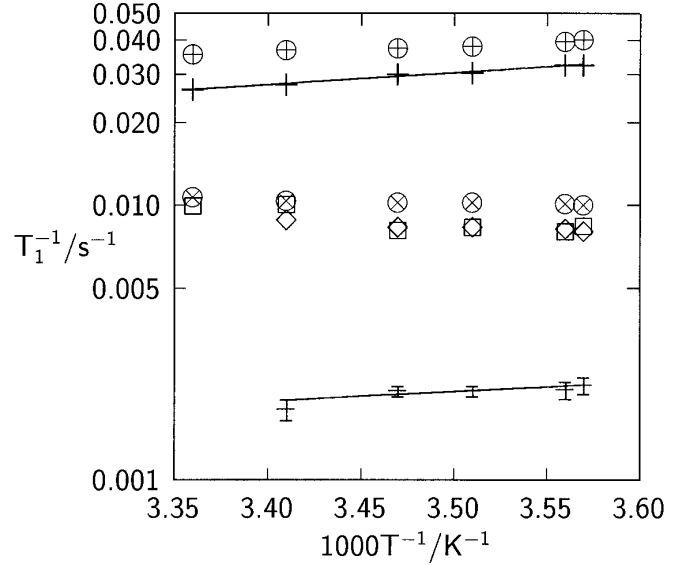


FIG. 1. ^{13}C relaxation rates: \oplus , total relaxation rate for C_6H_6 ; \otimes , total relaxation rate for C_6D_6 ; +, dipolar relaxation rate for C_6H_6 (without errorbars) and C_6D_6 (with errorbars); \square , contributions by other relaxation rates for C_6H_6 ; \diamond , contributions by other relaxation rates for C_6D_6 .

$$\frac{e^2 Q q}{h} = \frac{e Q e q(R)}{h} \left\{ 1 - \frac{6}{R} \langle \Delta_z \rangle + \frac{15}{R^2} \langle \Delta_z^2 \rangle - \frac{3}{2R^2} (\langle \Delta_x^2 \rangle + \langle \Delta_y^2 \rangle) \right\}. \quad [16]$$

A relation of this kind should be used when comparing measured quadrupole coupling constants with the result of *ab initio* calculations. The coupling constants determined by measurements using single crystals, polycrystalline samples, liquid crystal phases, and measurements in the gas phase are also vibrational averaged. Thus our result can directly be compared to these measurements, provided that the vibrational motions are identical in all phases.

RESULTS

Figure 1 summarizes the results for ^{13}C in a semilogarithmic plot of the relaxation rates versus reciprocal temperature. The encircled symbols show the total relaxation rates for the protonated sample (\oplus) and the deuterated sample (\otimes). In the case of C_6H_6 , the dipolar rate calculated with Eq. [6] (+) is the major contribution. The errorbars are too small to be shown. The Arrhenius fit yields an activation energy of 8.3(9) kJ mol^{-1} . In the case of C_6D_6 , the dipolar relaxation obtained from Eq. [9] (+ with errorbars) amounts to only 20% of the total relaxation. The Arrhenius fit gives an activation energy of 7(4) kJ mol^{-1} . Also shown are the contributions by other relaxation rates for C_6H_6 (\square) and C_6D_6 (\diamond). These contributions are calculated as

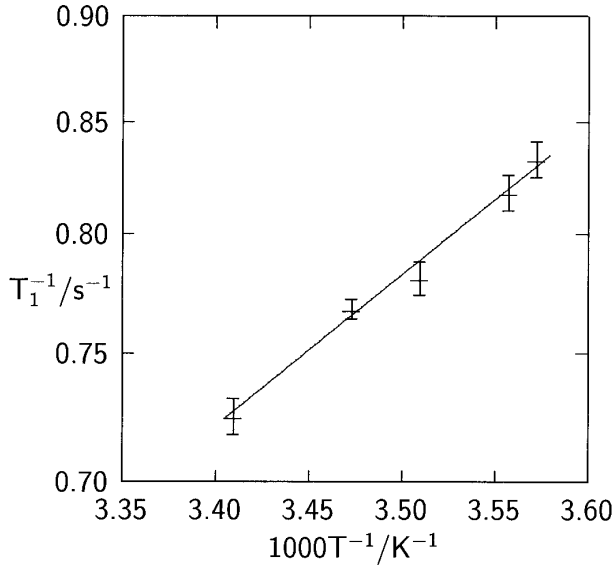


FIG. 2. Deuterium relaxation rates for C₆D₆.

$$R_{C(X)}^{\text{other}} = R_{C(X)} - R_{C-H} \quad [17]$$

and contain the relaxation by spin rotation and chemical shift anisotropy. The contributions of these mechanisms are equal for both samples and larger than the dipolar rate in the case of C₆D₆ (X = D).

Figure 2 shows a semilogarithmic plot of the deuterium relaxation rates as a function of reciprocal temperature for C₆D₆. These data give a more direct way of calculating the activation energy for the deuterated sample. Within the uncertainties, the result of 6.8(6) kJmol⁻¹ agrees with the less accurate result obtained from the dipolar ¹³C–D relaxation rate.

DISCUSSION

The isotope effect τ_{C-D}/τ_{C-H} is calculated with Eq. [12]. The accuracy of the total relaxation rate and the Overhauser enhancement is about one percent for the protonated sample. The accuracy of the total relaxation rate for the deuterated sample is also about one percent. The difficulty here is to get a reliable value for the Overhauser enhancement. The enhancement is calculated from the intensities with (I^*), and without (I) saturation,

$$\eta_D = \frac{I^* - I}{I} \quad [18]$$

It follows for the relative uncertainty,

$$\frac{\Delta\eta_D}{\eta_D} = \frac{I\Delta I^* + I^*\Delta I}{I(I^* - I)} \quad [19]$$

For C₆D₆, $I^* \approx 1.065I$ and $\Delta I^* \approx \Delta I$. Thus for the relative uncertainty of η_D ,

$$\frac{\Delta\eta_D}{\eta_D} \approx 30 \frac{\Delta I}{I} \quad [20]$$

is obtained. As a comparison, the calculation for the protonated molecule yields only a factor of about 3 instead of 30. All parameters have to be set very carefully and a good statistics is important. With our experimental setup, we achieved values between 1.3% at 285 K and 5.7% at 293 K for the relative uncertainty.

The effective C–H and C–D distances are calculated with Eqs. [14] and [15] inserting the values given in the Refs. (23–26). The results are

$$r_{\text{eff}}(C-H) = (108.0 + 2.0 - 1.1 + 1.7) \text{ pm} = 110.6 \text{ pm}$$

for C₆H₆ and

$$r_{\text{eff}}(C-D) = (108.0 + 1.4 - 0.8 + 1.3) \text{ pm} = 109.9 \text{ pm}$$

for C₆D₆. The corresponding vibrational corrections for the dipolar coupling constants are $(108.0/110.6)^3$ or -7% for C₆H₆ and $(108.0/109.9)^3$ or -5% for C₆D₆. This is exactly the same result as obtained in Ref. (10) using the corrections given in Ref. (18) with different vibrational analysis. The correction for the isotope effect given by Eq. [12] is $\sum_j r_{\text{eff}}^{-6}(C-H_j)/\sum_j r_{\text{eff}}^{-6}(C-D_j)$. The vibrational corrections for the protons or deuterons that are not directly bound are much smaller than for the directly bound ones. Moreover, their contribution to the sum is small, about 5%. If they are neglected and only $r_{\text{eff}}^{-6}(C-H)/r_{\text{eff}}^{-6}(C-D)$ is calculated, the result is 0.963 or -3.7% . The other extreme is to consider their contribution without any correction:

$$\frac{\sum_j r_{\text{eff}}^{-6}(C-H_j)}{\sum_j r_{\text{eff}}^{-6}(C-D_j)} = \frac{r_{\text{eff}}^{-6}(C-H) + 0.05 \sum r^{-6}}{r_{\text{eff}}^{-6}(C-D) + 0.05 \sum r^{-6}}.$$

With $0.631 \cdot 10^{60} \text{ m}^{-6}$ for $\sum r^{-6}$ taken from Ref. (27), the result is 0.965 or -3.5% . The mean of the two extremes is 0.964 or -3.6% . This correction leads to the isotope effects listed in Table 1, together with the total relaxation rates and nuclear Overhauser enhancements. The isotope effects scatter between 1% and 8%. A temperature dependence is not detectable in this small temperature range. The weighted mean is 6(3)%. This is at variance with the value given in Ref. (17). There the isotope effect was measured according to Eq. [8] in several 1:1 binary mixtures. The results for C₆X₆, X = H, D in CD₃OD, CD₃COCD₃, CD₃SOCD₃, and CD₃CN are 16%, 23%, 17%, and 19%, respectively. The fact that these results largely

TABLE 1
Dynamic Isotope Effect on the In-Plane Rotational
Correlation Time, Comparing C₆H₆ and C₆D₆

T/K	$R_{C(D)}/s^{-1}$	$R_{C(H)}/s^{-1}$	η_D	η_H	τ_{C-D}/τ_{C-H}
293	0.0104	0.0374	0.0530 (30)	1.46	1.01 (6)
288	0.0102	0.0380	0.0630 (9)	1.57	1.08 (3)
285	0.0102	0.0385	0.0628 (8)	1.56	1.07 (2)
281	0.0101	0.0402	0.0645 (25)	1.60	1.01 (4)
280	0.0100	0.0407	0.0673 (24)	1.58	1.05 (4)

exceed the values determined in our experiments cannot be explained with the choice of the QCC and r in Ref. (17). The use of our corrected value of $((1.106)^{-6} + 0.05 \cdot 0.631) \cdot 10^{60} \text{ m}^{-6}$ for $\sum_j r_{eff}^{-6}(C - H_j)$ and our measured QCC, 185 kHz, lowers the results in Ref. (17) by only 1.4%. Unfortunately, neat benzene has not been studied in Ref. (17) so that a direct comparison is not possible. Although the temperature is not given in Ref. (17), the rates and enhancements suggest a temperature of 298 K. However, we do not believe that the isotope effect is more than three times larger in any of the four 1:1 mixtures at 298 K compared to neat benzene at somewhat lower temperatures. The value of 20% can be related to the isotope effect on the moments of inertia. With $2.96 \cdot 10^{-45} \text{ kg m}^2$ for C₆H₆ and $3.58 \cdot 10^{-45} \text{ kg m}^2$ for C₆D₆, this effect is 21% for the symmetry axis. For a perpendicular axis, the effect is the same. For a liquid without hydrogen bonds, the maximum change of the rotational dynamics with the moment of inertia should be given if inertial effects dominate. In this case, the dynamic isotope effect is the square root of the ratio of the moments of inertia so that the maximum effect should be about 10%. From the activation energy of the deuterium relaxation in C₆D₆, Woessner concludes that the inertia effect is not dominating, and the dynamic isotope effect should thus be smaller than 10% (1). The isotope effect on the self-diffusion, measured with the pulsed gradient NMR spin-echo technique, is 5(2)% at 288 K and 6(2)% at 298 K (28). At the same temperatures, the isotope effects on the viscosity are 6.3(2)% and 6.1(2)%, respectively (28).

The QCC calculated with Eq. [11] and $((1.099)^{-6} + 0.05 \cdot 0.631) \cdot 10^{60} \text{ m}^{-6}$ for $\sum_j r_{eff}^{-6}(C - D_j)$ is given in Table 2 together with the total relaxation rates and the nuclear Overhauser enhancements. It varies between 183(3) and 192(8) kHz; the weighted mean is 185(3) kHz.

Our value of 185(3) kHz can be compared to other values obtained in the neat liquid by the method according to Eq. [4]. Rewriting this equation without assuming $\tau_Q = \tau_{H-H}$ leads to

$$\frac{e^2 Q q}{h} = \frac{\gamma^2 \hbar \mu_0}{\pi 4 \pi} \sqrt{\frac{R_Q}{R_{H-H}}} \sqrt{\frac{\tau_{H-H}}{\tau_Q}} r_{eff}^{-6}(H - H). \quad [21]$$

The very first isotopic dilution experiments by Eisner and

Mitchell (4) were performed on benzene. They obtained $R_{H-H} = 0.017 \text{ s}^{-1}$ at room temperature. Woessner combined this value with his measured R_Q of 0.68 s^{-1} and obtained 143 kHz for the QCC (1). He noted that a maximum isotope effect of 10% would lower the QCC by 5%. Bonera and Rigamonti repeated the measurements with the same result for R_{H-H} (5) and 0.77 s^{-1} for R_Q (2) at 295 K; the QCC obtained is 147 kHz. At the same time Zeidler obtained a much smaller value of 0.009 s^{-1} for R_{H-H} and 0.67 s^{-1} for R_Q at 298 K (3). The QCC was calculated to 206 kHz, but the H-H distance was assumed too small in this calculation. Using 248 pm (15) instead of 244 pm, the result is decreased to 196 kHz. Inserting our isotope effect of 6%, the QCC is further decreased to 190 kHz, in excellent agreement with our present result. For H-H distances, vibrational corrections are much smaller than for C-H bonds (8). A later study of Powles and Figgins attempted to separate the spin-rotational contribution from the intramolecular relaxation rate (29, 30). At 298 K it was found to be small. The extrapolated intramolecular rate was $R_{H-H} = 0.01 \text{ s}^{-1}$ and the intramolecular dipolar rate was $R_{H-H}^{dd} = 0.009 \text{ s}^{-1}$. Bull and Jonas obtained 0.014 s^{-1} for R_{H-H} at 296 K, but this result was measured in a high-pressure probe using only two dilutions (31).

Deuterium QCCs can be determined in nematic solutions by the analysis of proton and deuterium NMR spectra of oriented molecules. Caspary *et al.* obtained 194(4) kHz for benzene-*d*₆ assuming the asymmetry parameter η equal to zero (6). Millett and Dailey reported values for several solvents and solutes (7). They showed that the result depends on the asymmetry parameter as $(1 + \eta)^{-1}$. For C₆D₆, the result is 183(10) kHz with $\eta = 0.06$ and 187(10) kHz for $\eta = 0.04$. Diehl and Reinhold repeated such measurements on benzene-*d*₁, 1,4-benzene-*d*₂, and 1,3,5-benzene-*d*₃ in different solvents at 300 K (8). As the determined QCC is proportional to $r^{-3}(H - H)$, they corrected for molecular vibrations as shown in Ref. (18). Again, the correction for $r^{-3}(H - H)$ is small, about 1.5%. They found that the results for the three molecules are independent of the solvent, 188.4(13), 190.5(12), and 192.4(12) kHz, respectively. They assumed $\eta = 0.041$. Wooten *et al.* determined the QCC for benzene-*d*₁ in nematic oriented phase from ¹³C satellites in proton decoupled deuterium NMR spectra (9). The result of 207(2) kHz was corrected later for the influence of vibrations (−4.87%) and the asymmetry parameter (10). The

TABLE 2
Deuterium Quadrupole Coupling Constant in C₆D₆

T/K	R_Q/s^{-1}	$R_{C(D)}/s^{-1}$	η_D	$e^2 q Q h^{-1}/\text{kHz}$
293	0.725	0.0104	0.0530 (30)	192 (8)
288	0.761	0.0102	0.0630 (9)	183 (3)
285	0.781	0.0102	0.0628 (8)	185 (3)
281	0.818	0.0101	0.0645 (25)	188 (6)
280	0.833	0.0100	0.0673 (24)	186 (5)

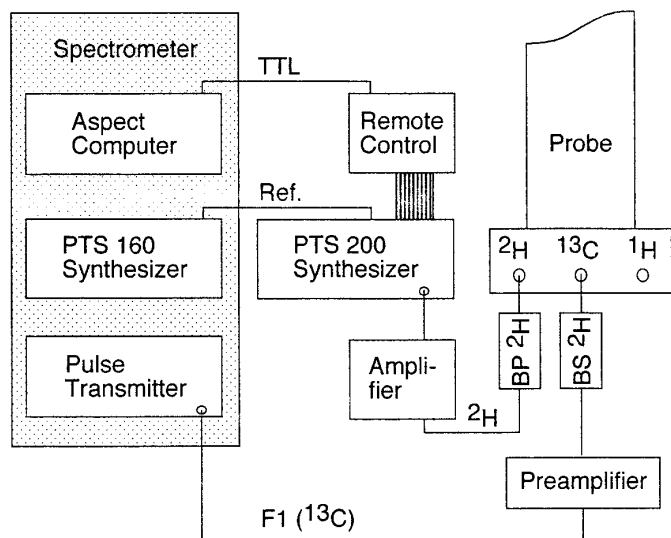


FIG. 3. Experimental setup for deuterium decoupling; BP, bandpass; BS, bandstop.

vibrational correction is important as in this method the result is proportional to $r^{-3}(C - D)$. They obtain 190(2) kHz for $\eta = 0.041$ and 188(2) kHz for $\eta = 0.05$. As a conclusion, the measurements in liquid nematic oriented phases as well as the dilution experiments in the neat liquid agree fully with our result of 185(3) kHz.

The deuterium QCC in solid state can be determined by NMR methods too. From the quadrupole splitting in the deuterium spectrum of polycrystalline C_6D_6 , Rowell *et al.* obtained 193(3) kHz as an average over measurements at 14 temperatures between 109 and 269 K (11). They assumed $\eta = 0$. Pyykkö and Lähteenmäki performed measurements on a single crystal sample at 263 K (12). For $\eta = 0$, their result is 186.6(16) kHz. Using a polycrystalline sample at 77 K, Barnes and Bloom fitted the deuterium lineshape for the QCC and for η . They obtained 180.7(15) kHz for the QCC and 0.041(7) for η (13). The value given by Rinné and Depireux, neglecting the asymmetry parameter, was 193 kHz (14).

In the gas phase, the deuterium QCC can be determined from the hyperfine splittings in rotational transitions. The first investigation by Oldani, Ha, and Bauder gave 223(12) kHz (15). In a later study with higher resolution, 186.1(18) kHz was obtained (16).

All reliable data for the deuterium QCC in benzene containing deuterium lie in the range from 180 to 192 kHz. This holds for the neat solid, liquid, and gas as well as for benzene dissolved in liquid crystal solvents. Within the uncertainties, a difference between the different phases cannot be detected. This is in contrast to the behavior of the deuterium QCC in water. Here the QCC ranges from 212 kHz in ice (32) over 255 kHz in the liquid at room temperature (33, 34) to 315 kHz in gas (32). The QCC probes the electric field gradient (efg) at the site of the nucleus. In the case of water, the efg at the position

of the deuterium is affected by the nature of the hydrogen bonds present. The effect is about 40%, whereas for benzene no effect is detectable within the uncertainty of about 3%.

In Ref. (15), the QCC for benzene calculated by the *ab initio* method scatters between 218 and 230 kHz. It is stated in Ref. (16) that more recent calculations still exceed the experimental value by about 10%. We note that this deviation might well be explained by the influence of vibrational motion, as in Ref. (15) the QCC was simply calculated as $eQeq(108.5 \text{ pm})/h$. The correction given in Eq. [16] reduces the *ab initio* result, calculated at $r(C - D) = 108.5 \text{ pm}$, just by about 10%.

It is interesting to note that the contributions by other relaxation rates shown in Fig. 1 are equal for C_6H_6 and C_6D_6 . This can be explained by the fact that relaxation by chemical shift anisotropy increases when the correlation time increases due to the dynamic isotope effect, whereas the relaxation by spin rotation decreases when the correlation time increases.

CONCLUSIONS

Our self-consistent method gives reliable results for liquid benzene. The dynamic isotope effect of 6(3)% is much smaller than the result of 20% given in Ref. (17). The measured coupling constant of 185(3) kHz agrees with the values in solid and gas. This indicates that no hydrogen bonds are present.

The method requires a sufficiently accurate determination of the nuclear Overhauser effect under deuterium saturation. We showed that the measurements can be performed with a slightly modified single resonance setup. The accuracy would be markedly improved with a spectrometer possessing two hetero-channels and a probe with two hetero-channels and a fluorine lock.

The method can equally be applied to nitrogen ^{15}N and directly bonded protons/deuterons. The effect is even larger because the maximum nuclear Overhauser enhancements are -4.9 and -0.76 , respectively.

EXPERIMENTAL

Chemicals were purchased at Merck Darmstadt and used without further purification. The degree of deuteration for C_6D_6 was better than 99.95%. The sample tubes from Wilmand, Buena, NJ, were constricted in order to confine the sample volume to the region where the radio frequency fields are homogeneous. This minimizes diffusion problems too. The samples were sealed after several freeze-pump-thaw cycles.

All measurements were performed on a Bruker AM spectrometer. The frequencies for 1H , ^{13}C , and 2H were 250.132, 62.896, and 38.398 MHz, respectively. ^{13}C was measured in natural abundance. Temperature was controlled with a modified Bruker VT unit. The accuracy is about 0.5 K and the stability about 0.1 K.

The relaxation times were measured with the inversion recovery method. For the protonated sample, the two level de-

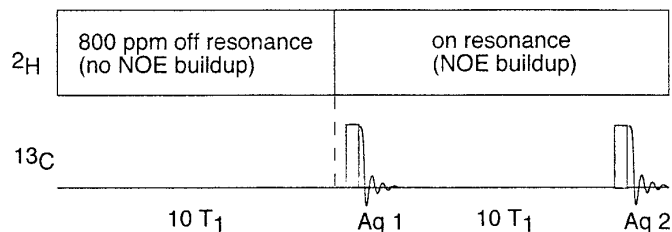


FIG. 4. Pulse sequence for the measurement of the nuclear Overhauser enhancement under continuous wave deuterium decoupling.

coupling technique was applied to determine the nuclear Overhauser effect.

For the deuterated sample, the NOE measurement was not straightforward. The spectrometer did not possess a deuterium decoupling device and the broadband probe was designed for deuterium lock only. Fortunately, the lock circuit can be operated with a power of 200 mW, sufficient for continuous wave decoupling. In order to minimize the resulting noise on the ^{13}C channel, masking all signal, two deuterium filters were used. A bandpass was inserted between the deuterium amplifier and the lock circuit, and an additional bandstop between the ^{13}C channel and the preamplifier, as shown in Fig. 3. The decoupling frequency was generated with an accuracy of 1 Hz by a remote controlled PTS 200 synthesizer. The TTL-pulse which in normal use switches the proton decoupler on and off was used to switch the synthesizer between two frequencies. This allowed the programming of the pulse sequence shown in Fig. 4. Using a low decoupling power has the advantage that the sample temperature remains unchanged. For the measurement without deuterium saturation the frequency was simply set far away from the resonance frequency. This does not affect the sample temperature. As the spectrometer synthesizer and the additional synthesizer were set up in the master and slave mode, the deuterium frequency measured with the spectrometer can be set directly as the decoupling frequency. Of course, field-frequency locking of the spectrometer was no longer possible with the deuterium lock unit. It is therefore advisable not to accumulate FIDs. To have a good statistics, more than 50 experiments were performed at each temperature.

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REFERENCES

1. D. E. Woessner, Molecular reorientation in liquids: Deuteron quadrupole relaxation in liquid deuterium oxide and perdeuterobenzene, *J. Chem. Phys.* **40**, 2341–2348 (1964).
2. G. Bonera and A. Rigamonti, Electric-field gradients in liquids by deuteron quadrupole relaxation, *J. Chem. Phys.* **42**, 175–180 (1965).
3. M. D. Zeidler, Umorientierungszeiten, Sprungzeiten und Quadrupolkopplungskonstanten in einigen organischen Flüssigkeiten aus kernmagnetischen Relaxationszeitmessungen, *Ber. Bunsen. Phys. Chem.* **69**, 659–669 (1965).
4. M. Eisner and R. W. Mitchell, Translational and rotational contributions to nuclear spin-lattice relaxation in benzene, *Bull. Am. Phys. Soc.* **6**, 363 (1961).
5. G. Bonera and A. Rigamonti, Intra- and intermolecular contributions to the proton spin-lattice relaxation in liquids, *J. Chem. Phys.* **42**, 171–174 (1965).
6. W. J. Caspary, F. Millet, M. Reichbach, and B. P. Dailey, NMR determination of deuterium quadrupole coupling constants in nematic solutions, *J. Chem. Phys.* **51**, 623–627 (1969).
7. F. S. Millett and B. P. Dailey, NMR determination of some deuterium quadrupole coupling constants in nematic solutions, *J. Chem. Phys.* **56**, 3249–3256 (1972).
8. P. Diehl and M. Reinhold, Isotope effects on the degree of order and the deuterium quadrupole coupling constants, as measured by N.M.R. of oriented benzene- d_1 , 1,4-benzene- d_2 and 1,3,5-benzene- d_3 , *Mol. Phys.* **36**, 143–149 (1978).
9. J. B. Wooten, A. L. Beyerlein, J. Jacobus, and G. B. Savitsky, Determination of deuteron quadrupole coupling constants from natural abundance ^{13}C satellites in ^2H NMR spectra, *J. Magn. Reson.* **31**, 347–349 (1978).
10. K. Seidman, J. F. McKenna, G. B. Savitsky, and A. L. Beyerlein, The vibrational and asymmetry corrections to quadrupole coupling constants determined from ^{13}C Satellites in ^2H NMR spectra of benzene- d_1 and acetonitrile- d_1 , *J. Magn. Reson.* **38**, 229–232 (1980).
11. J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, NMR studies of some liquid crystal systems, *J. Chem. Phys.* **43**, 3442–3454 (1965).
12. P. Pykkö and U. Lähtenmäki, Measurement of the deuteron quadrupole coupling constant in C_6D_6 single crystals, *Ann. Univ. Turku. Ser. A* **193**, 2–7 (1966).
13. R. G. Barnes and J. W. Bloom, Measurement of the quadrupole coupling constant and asymmetry parameter of the ring deuterons in several deuterated benzene derivatives, *J. Chem. Phys.* **57**, 3082–3086 (1972).
14. M. Rinné and J. Depireux, Nuclear quadrupole coupling constant of deuterium bound to carbon in organic molecules, *Adv. Nucl. Quadrupole Reson.* **1**, 357–374 (1974).
15. M. Oldani, T.-K. Ha, and A. Bauder, Deuterium nuclear quadrupole hyperfine coupling in benzene- d_1 observed by pulsed microwave fourier transform spectroscopy, *Chem. Phys. Lett.* **115**, 317–320 (1985).
16. S. Jans-Bürli, M. Oldani, and A. Bauder, Deuterium quadrupole coupling in rotational spectra of benzene- d_1 and of three isomers of fluorobenzene- d_1 , *Mol. Phys.* **68**, 1111–1123 (1989).
17. J. P. Jacobsen, ^{13}C and ^2H relaxation time studies of selected 1:1 binary mixtures: Isotope effects on correlation times, *J. Magn. Reson.* **41**, 240–246 (1980).
18. N. J. D. Lucas, The influence of vibrations on molecular structure determinations from N.M.R. in liquid crystals. I. Application to methyl fluoride, *Mol. Phys.* **2**, 147–154 (1971).
19. S. Sykora, J. Vogt, H. Bösiger, and P. Diehl, Vibrational corrections in NMR spectra of oriented molecules, *J. Magn. Reson.* **36**, 53–60 (1979).

20. E. R. Henry and A. Szabo, Influence of vibrational motion on solid state line shapes and NMR relaxation, *J. Chem. Phys.* **82**, 4753–4761 (1985).
21. D. E. Woessner, Nuclear spin relaxation in ellipsoids undergoing rotational brownian motion, *J. Chem. Phys.* **37**, 647–654 (1962).
22. G. Lipari and A. Szabo, Model-free approach to the interpretation of nuclear magnetic relaxation in macromolecules. 1. Theory and range of validity, *J. Am. Chem. Soc.* **104**, 4546–4559 (1982).
23. W. V. F. Brooks and S. J. Cyvin, Vibrational mean-square amplitude matrices. XVI. In-plane normal coordinates and mean amplitudes of vibration in benzene molecules, *Acta Chem. Scand.* **16**, 820–826 (1962).
24. W. V. F. Brooks, S. J. Cyvin, and P. C. Kvide, Vibrational mean-square amplitude matrices. XVII. Perpendicular amplitudes and shrinkage effects in benzene molecules, *J. Phys. Chem.* **69**, 1489–1497 (1965).
25. P. Pulay, G. Fogarasi, and J. E. Boggs, Force field, dipole moment derivatives, and vibronic constants of benzene from a combination of experimental and *ab initio* quantum chemical information, *J. Chem. Phys.* **74**, 3999–4003 (1981).
26. B. L. Crawford, Jr., and F. A. Miller, The planar vibrations of benzene, *J. Chem. Phys.* **17**, 249–256 (1949).
27. A. Dölle, M. A. Suhm, and H. Weingärtner, Anisotropic molecular reorientation of liquid benzene revisited: A study using ^{13}C magnetic relaxation through chemical shift anisotropy and spin rotation, *J. Chem. Phys.* **94**, 3361–3365 (1991).
28. M. Holz, X. Mao, D. Seiferling, and A. Sacco, Experimental study of dynamic isotope effects in molecular liquids: Detection of translation-rotation coupling, *J. Chem. Phys.* **104**, 669–679 (1996).
29. J. G. Powels and R. Figgins, Molecular motion in liquid benzene by nuclear magnetic resonance, *Mol. Phys.* **11**, 155–161 (1966).
30. J. G. Powels and R. Figgins, Molecular motion in liquid bromobenzene and 1,3,5 trideutero benzene by nuclear magnetic resonance, *Mol. Phys.* **13**, 253–262 (1967).
31. T. E. Bull and J. Jonas, Effect of pressure on the intramolecular and intermolecular contributions to dipolar spin relaxation in benzene and chlorobenzene in liquid state, *J. Chem. Phys.* **52**, 4553–4558 (1970).
32. E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York (1969).
33. D. Lankhorst, J. Schrieffer, and J. C. Leyte, Determination of the rotational correlation time of water by proton NMR relaxation in H_2^{17}O and some related results, *Ber. Bunsen. Phys. Chem.* **86**, 215–221 (1982).
34. B. C. Gordalla and M. D. Zeidler, Molecular dynamics in the system water-dimethylsulphoxide, a N.M.R. relaxation study, *Mol. Phys.* **59**, 817–828 (1986).