# Molecular Reorientation in Liquid Methanol

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*Dedicated to Karl Heinzinger on the occasion of his 60th birthday*

Oxygen-17 enriched methanol $CD_3^{17}OH$ was synthesized and $^1H$ as well as $^{17}O$ nmr relaxation rates were measured in the temperature range 180–310 K. By varying the $^{17}O$-content different contributions to the proton relaxation rate could be separated and from the $^{17}O-H$ dipolar interaction contribution the correlation time of the OH bond was determined. These results are compared to recent computer simulation data. Additional deuteron relaxation measurements on $CH_3OD$ yielded the quadrupole coupling constant which increases with falling temperature. The $^{17}O$ quadrupole coupling constant shows a similar trend with temperature but not as pronounced.

## Introduction

The mutual interaction of direct experiments and computer experiments is of extremely high value for the solution of specific problems in liquid state research. Karl Heinzinger has devoted most of his scientific career to investigate liquid systems by computer simulation, thus it is appropriate at the present occasion to demonstrate for the case of liquid methanol the importance of such an interplay.
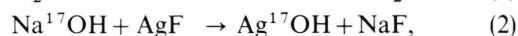
Recently several computer experiments on liquid methanol were carried out [1–8]. They could be compared to a large number of available experimental data like X-ray diffraction [9], neutron diffraction [10], quasielastic neutron scattering [11], self-diffusion [12–15], dielectric relaxation [16] and nuclear magnetic relaxation [15, 17, 18]. It is clear that the best molecular model, probably the OPLS potential of Jorgensen [1], must agree with all experimental data if the latter are conclusive. Unfortunately the experimental data often are not directly comparable to the simulation results, but usually some quantities are extracted from the experiments and these are then compared. Specialists in experimental disciplines and in computer simulation mostly do not collaborate closely enough in order to avoid pitfalls in such comparisons. The aim of the present work is to provide a reliable comparison of the simulation and nmr relaxation results in liquid methanol. The following objections are raised to pre-vious comparisons [3, 8]: in the case of proton relaxation in $CD_3OH$ [17] the reorientational vector is not strictly defined whereas in the case of deuteron relaxation in $CH_3OD$ [15, 18] the quadrupole coupling constant for the deuteron is not known. Instead we derive in this paper the reorientational correlation time $\tau_2$ of the OH bond, which is the one calculated in the simulations [3, 8], from $^{17}O$-induced proton relaxation in $CD_3^{17}OH$. This type of proton relaxation was previously applied to pure water [19–21], aqueous electrolyte solutions [21–23] and binary aqueous mixtures [24] using $H_2^{17}O$. This same approach can be used for any OH bond and we extended it to alcohols, reporting in this paper our results for methanol.

In addition we measured the deuteron relaxation in $CH_3OD$ and extracted the deuteron quadrupole coupling constant over a larger temperature range. The observed temperature dependence of the coupling constant, an increase with falling temperature, might be understood with the help of the simulation results which show a corresponding increase of doubly hydrogen-bonded methanol molecules. Finally the oxygen-17 quadrupole coupling constant was estimated from oxygen relaxation in $CD_3^{17}OH$.

## Experimental

Methanol $CD_3^{17}OH$ with 6%, 11.7%, 26.8% and 37.5% $^{17}O$ enrichment was prepared from the corresponding $H_2^{17}O$ using the following reactions:

$$H_2^{17}O + NaH \rightarrow Na^{17}OH + H_2, \quad (1)$$

$$Na^{17}OH + AgF \rightarrow Ag^{17}OH + NaF, \quad (2)$$

$$Ag^{17}OH + CD_3I \rightarrow CD_3^{17}OH + AgI. \quad (3)$$

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Reaction (1) was carried out in anhydrous dioxane as solvent, which was distilled over sodium metal and stored over NaH before use. The sodium hydride was suspended in the dioxane, and water was added dropwise under flow of a dry nitrogen stream and under cooling in an ice-bath. After the reaction was complete, the dioxane was evaporated. The $Na^{17}OH$ formed was dissolved in $H_2^{17}O$ of the same $^{17}O$-content, and AgF dissolved in the same $H_2^{17}O$ was added to complete reaction (2) under stirring. This was done in a glass autoclave which was actually needed in reaction (3). After adding methyl iodide the glass autoclave was cooled to liquid nitrogen temperature and then sealed under vacuum. It was placed in an oven at 70 °C for 5 hours. Then it was opened under a dry nitrogen stream and the liquid part, $CD_3^{17}OH$ together with excess $CD_3I$ and $H_2^{17}O$, was transferred under vacuum to a distillation flask. On fractional distillation the three fractions $CD_3I$ (42–43 °C), $CD_3^{17}OH$ (63–64 °C) and $H_2^{17}O$ (100 °C) were collected. The yield of $CD_3^{17}OH$ was 65% and the recovery of $H_2^{17}O$ 85%. The product $CD_3^{17}OH$ was carefully dried over 3 Å-molecular sieve until the water content was below 0.2%, as determined by nmr spectra. Concerning the absolute $^{17}O$-content we had to rely on the analysis of the producers of $H_2^{17}O$ (Yeda in Rehovot, Israel, for the two lower concentrations and IRE Diagnostic in Düsseldorf, Germany, for the two higher concentrations), but by taking the nmr spectra of the starting material $H_2^{17}O$ and of the product $CD_3^{17}OH$ we could check the relative $^{17}O$-content in both cases. The intensities were in the correct order and the preparation procedure did not change the $^{17}O$-content.

The relaxation time $T_1$ was measured by the $180-\tau-90$ pulse sequence for protons at 300.13 MHz, for deuterons at 46.05 MHz and for oxygen-17 at 40.67 MHz on a Bruker CXP spectrometer. The temperature control was improved by us and is $\pm 0.3$ K. All samples were degassed by several freeze-pump-thaw cycles.

## Results

The measured proton relaxation rates $(1/T_1)_H$ for $CD_3^{17}OH$ are collected in Table 1 as function of $^{17}O$-content and temperature. From these raw data we obtain by a least-squares fit according to the relation

$$\left(\frac{1}{T_1}\right)_H = \left(\frac{1}{T_1}\right)_H^{H,D} + x \left(\frac{1}{T_1}\right)_H^O, \quad (1)$$

Table 1. Proton relaxation rates $(1/T_1)_H/s^{-1}$ of $CD_3OH$ as function of $^{17}O$-content and temperature.

| $T/K$ | $x_{CD_3^{17}OH}$ | | | | |
|---|---|---|---|---|---|
| | 0.000 | 0.060 | 0.117 | 0.268 | 0.375 |
| 308 | 0.066 | 0.107 | 0.139 | 0.210 | 0.291 |
| 298 | 0.079 | 0.128 | 0.152 | 0.251 | 0.325 |
| 288 | 0.092 | 0.163 | 0.191 | 0.307 | 0.399 |
| 283 | 0.101 | 0.175 | 0.209 | 0.328 | 0.440 |
| 278 | 0.114 | 0.187 | 0.241 | 0.352 | 0.447 |
| 273 | 0.130 | 0.210 | 0.273 | 0.395 | 0.513 |
| 268 | 0.145 | 0.234 | 0.299 | 0.421 | 0.561 |
| 263 | 0.150 | 0.257 | 0.316 | 0.454 | 0.607 |
| 258 | 0.180 | 0.280 | 0.341 | 0.522 | 0.673 |
| 253 | 0.190 | 0.292 | 0.378 | 0.574 | 0.773 |
| 248 | 0.212 | 0.341 | 0.428 | 0.607 | 0.847 |
| 243 | 0.238 | 0.393 | 0.462 | 0.672 | 0.890 |
| 238 | 0.259 | 0.434 | 0.511 | 0.804 | 1.045 |
| 233 | 0.310 | 0.507 | 0.609 | 0.861 | 1.176 |
| 228 | 0.345 | 0.512 | 0.658 | 0.955 | 1.353 |
| 223 | 0.400 | 0.592 | 0.768 | 1.091 | 1.584 |
| 218 | 0.452 | 0.659 | 0.877 | 1.263 | 1.733 |
| 213 | 0.523 | 0.752 | 0.992 | 1.477 | 2.016 |
| 208 | 0.620 | 0.881 | 1.142 | 1.757 | 2.456 |
| 203 | 0.674 | 1.020 | 1.316 | 1.996 | 2.854 |
| 198 | 0.826 | 1.227 | 1.633 | 2.458 | 3.150 |
| 193 | 0.988 | 1.372 | 1.862 | 2.862 | 3.824 |
| 188 | 1.074 | 1.551 | 2.199 | 3.534 | 4.478 |
| 183 | 1.230 | 1.777 | 2.473 | 4.023 | 4.985 |
| 178 | 1.386 | 1.937 | 2.851 | 4.562 | 6.086 |

where $x$ is the mole fraction of $^{17}O$, the two terms to the proton relaxation rate due to magnetic dipolar interactions from other protons and deuterons or from the $^{17}O$ nucleus, denoted as $(1/T_1)_H^{H,D}$ and $(1/T_1)_H^O$ respectively. In the previous work on water [19] a correction was applied to the measured proton rates in order to account for variations in the dynamics of the system due to different isotopic compositions. For example, the variation in $^{17}O$ and $^{18}O$ content in the different samples was compensated by a correction factor calculated from the mole fractions and viscosities of the different species. Such data were available in the case of water, but the different viscosities for the methanol species are not known. Therefore the $(1/T_1)_H$ in (1) are uncorrected data, but this is not too serious a defect since the correction would be definitely smaller than in water where it did not exceed 4%. The results of the least-squares fit are summarized in Table 2.

The contribution $(1/T_1)_H^O$ is completely dominated by intramolecular interactions. This was shown by theoretical estimates for water [19] to be of the order of 98%, and for methanol it should be even larger since the spin density is lower and the molecular di-

Table 2. Contributions to the proton relaxation rate of $CD_3OH$ due to proton/deuteron $(1/T_1)_H^{H,D}$ and oxygen $(1/T_1)_H^O$.

| $T/K$ | $(1/T_1)_H^{H,D}/s^{-1}$ | $(1/T_1)_H^O/s^{-1}$ | Corr. coeff. |
|---|---|---|---|
| 308 | 0.068 | 0.581 | 0.9947 |
| 298 | 0.077 | 0.656 | 0.9968 |
| 288 | 0.091 | 0.790 | 0.9971 |
| 283 | 0.104 | 0.830 | 0.9967 |
| 278 | 0.115 | 0.901 | 0.9966 |
| 273 | 0.133 | 0.982 | 0.9968 |
| 268 | 0.149 | 1.050 | 0.9949 |
| 263 | 0.159 | 1.150 | 0.9940 |
| 258 | 0.179 | 1.278 | 0.9987 |
| 253 | 0.194 | 1.506 | 0.9979 |
| 248 | 0.216 | 1.590 | 0.9929 |
| 243 | 0.232 | 1.637 | 0.9946 |
| 238 | 0.257 | 2.020 | 0.9975 |
| 233 | 0.308 | 2.160 | 0.9927 |
| 228 | 0.344 | 2.563 | 0.9933 |
| 223 | 0.399 | 3.106 | 0.9992 |
| 218 | 0.458 | 3.287 | 0.9958 |
| 213 | 0.517 | 3.866 | 0.9969 |
| 208 | 0.590 | 4.764 | 0.9955 |
| 203 | 0.667 | 5.578 | 0.9939 |
| 198 | 0.829 | 6.093 | 0.9992 |
| 193 | 0.956 | 7.510 | 0.9989 |
| 188 | 1.070 | 9.145 | 0.9995 |
| 183 | 1.232 | 10.157 | 0.9993 |
| 178 | 1.406 | 12.555 | 0.9985 |

ameter is larger than in water. Consequently we have [25]

$$\left(\frac{1}{T_1}\right)_H^O = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_H^2 \gamma_O^2 \hbar^2 S(S+1) r_{OH}^{-6} \tau_2^{OH}, \quad (2)$$

where $\gamma$ are the magnetogyric ratios for protons and oxygen-17 and $S = 5/2$ is the nuclear spin of $^{17}O$. $r_{OH}$ is the intramolecular OH distance in $CD_3OH$, the correct choice of which is very important because of the large effect it has through the 6th power dependence, but which is very difficult to select properly. There is no doubt about its value in the gas phase from very exact microwave data [26] or from less exact electron diffraction data [27], 94–95 pm being the accepted value. But for the liquid state the neutron diffraction data [10, 28] scatter too much between 99–103 pm. The value of 103 pm seems rather high for a gas-liquid shift, in comparison to water where it amounts to 2–3 pm. We favor a value of 99 pm since, as will be apparent from the following evaluation of our deuterium relaxation data, we have to meet some constraints in connection with our experiments. One such constraint is the obvious requirement that the deuterium quadrupole coupling constant for liquid methanol should not fall below the corresponding

value of the solid. The second argument is that a relation between the deuterium quadrupole coupling constant and the intramolecular OH bond length exists [29]. If we use the empirical relation given by Struis et al. [21], an upper limit of 101 pm is calculated from our proton and deuteron relaxation data. Equation (2) is then solved for the rotational correlation time $\tau_2^{OH}$, and the results are listed in Table 3.

From the procedure used we can be sure that this correlation time really concerns the OH vector which is identical with the quantity calculated in the computer simulation. Depending on the potential model used in the simulations [3, 8], $\tau_2^{OH}$ was found in the range 2–5 ps at 300 K, 4–11 ps at 265 K and 48 ps at 200 K. Comparison with our $\tau_2^{OH}$ values in Table 3 gives 5 ps at 300 K, 9 ps at 265 K and 45 ps at 200 K. The activation energies given in the simulations for the more reliable models are 13–16 kJ mol$^{-1}$ as compared to our expermental value of 11.5 kJ mol$^{-1}$.

The contribution $(1/T_1)_H^{H,D}$ from (1) is a mixed term containing both intramolecular and intermolecular parts:

$$\left(\frac{1}{T_1}\right)_H^{H,D} = \left(\frac{1}{T_1}\right)_{H\,intra}^D + \left(\frac{1}{T_1}\right)_{H\,inter}^D + \left(\frac{1}{T_1}\right)_{H\,inter}^H. \quad (3)$$

The terms $(1/T_1)_H^D$ take account of the interactions between the hydroxyl proton and the three methyl deuterons, intramolecular as well as intermolecular, and $(1/T_1)_H^H$ stands for the interactions between hydroxyl protons in different molecules. We did not disentangle these parts experimentally, therefore an evaluation of this contribution is rather crude. The term $(1/T_1)_{H\,intra}^O$ is estimated using the intramolecular distances $\tau_{HD}$ of 210 pm for one pair and 280 pm for two

Table 3. Rotational correlation times of the OH bond in $CD_3OH$ ($\tau_2^{OH}$).

| $T/K$ | $\tau_2^{OH}/ps$ | $T/K$ | $\tau_2^{OH}/ps$ |
|---|---|---|---|
| 308 | 4.5 | 233 | 16.6 |
| 298 | 5.1 | 228 | 19.7 |
| 288 | 6.1 | 223 | 23.0 |
| 283 | 6.4 | 218 | 25.3 |
| 278 | 6.9 | 213 | 29.8 |
| 273 | 7.6 | 208 | 36.7 |
| 268 | 8.1 | 203 | 43.0 |
| 263 | 8.9 | 198 | 46.9 |
| 258 | 10.3 | 193 | 57.9 |
| 253 | 11.6 | 188 | 70.5 |
| 248 | 12.3 | 183 | 78.3 |
| 243 | 13.6 | 178 | 96.7 |
| 238 | 15.6 | | |

Table 4. Deuteron relaxation rates $(1/T_1)_D$ and quadrupole coupling constants $(eQq/h)_D$ of methanol $CH_3OD$ as function of temperature.

| $T/K$ | $(1/T_1)_D/s^{-1}$ | $(eQq/h)_D/kHz$ |
|-------|--------------------|-----------------|
| 308   | 2.80               | 205.6           |
| 298   | 3.29               | 210.0           |
| 288   | 4.00               | 212.0           |
| 283   | 4.54               | 219.5           |
| 278   | 5.00               | 220.5           |
| 273   | 5.62               | 223.4           |
| 268   | 6.17               | 226.2           |
| 263   | 7.06               | 232.0           |
| 258   | 8.28               | 233.0           |
| 253   | 9.81               | 239.0           |
| 248   | 10.70              | 242.8           |
| 243   | 12.26              | 246.0           |
| 238   | 14.11              | 256.9           |
| 233   | 16.43              | 258.2           |
| 228   | 19.45              | 258.4           |
| 223   | 22.83              | 259.0           |
| 218   | 27.70              | 271.8           |
| 213   | 32.90              | 273.0           |
| 208   | 41.03              | 274.8           |
| 203   | 49.88              | 280.0           |
| 198   | 62.10              | 299.0           |
| 193   | 80.39              | 306.3           |
| 188   | 96.15              | 303.6           |
| 183   | 128.54             | 333.1           |
| 178   | 173.31             | 347.4           |

pairs, and $\tau_2^{HD}$ is equated with $\tau_2^{OH}$. Unfortunately, in the simulation work $\tau_2$ values for nmr relevant vectors like HD were not computed. We find that $(1/T_1)_{H\,intra}^D$ is about 3% of the total term $(1/T_1)_H^{H,D}$ over the whole temperature range. The intermolecular term $(1/T_1)_{H\,inter}^D$ could therefore be ignored completely. The remaining $(1/T_1)_{H\,inter}^H$ term was treated in the following way: If the simulation results are consulted which yield mole fractions of methanol molecules with one or two hydrogen bonds of more than 90% and rather long hydrogen bond lifetimes, at least at lower temperatures, then we can treat the associate as a supermolecule with fixed distances. The closest distance between two hydroxyl protons, which yields the largest relaxation contribution, is about 245 pm with a rather broad distribution 216 pm to 331 pm [2]. Again we lack from the simulation work the nmr relevant $r_{HH}^{-6}$ average, thus we only can estimate a crude value of $r_{HH} = 235$ pm by approximating the first peak in the HH radial distribution function by a Gaussian curve. With this $r_{HH}$ value we obtain correlation times $\tau_2^{HH}$ a factor 4–5 longer than $\tau_2^{OH}$ over the whole temperature range. In the simulation work [8] we find separate $\tau_2^{OH}$ data for differently bonded species, but no $\tau_2^{HH}$ values were calculated. The $\tau_2^{OH}$ values increase for the

higher bonding states, therefore a similar increase in $\tau_2^{HH}$ is also expected. Quantitative numbers are not given in [8], but a 4-fold increase above the average seems a little bit high. Differences between $\tau_2^{OH}$ and $\tau_2^{HH}$ are likely to exist, because the higher bonding molecules must reorient in a more anisotropic way than the lower bonding ones. Whether this leads to a stronger slowing-down of $\tau_2^{HH}$ as compared to $\tau_2^{OH}$ depends on details of the dynamics of the associates. Since this information was not extracted from the simulation, we will not speculate any further but conclude by stating that the above evaluation of our $(1/T_1)_{H\,inter}^H$ term is not unreasonable. Alternatively we may turn around, use $\tau_2^{OH}$ from Table 3 and calculate $r_{HH}$ to obtain about 185 pm over the whole temperature range. This latter value which, however, is not present in the simulation data, is in excellent agreement with the HH distance in a cyclic dimer using 195 pm for the intermolecular OH bond [2], the previous value of 99 pm for the intramolecular OH bond [28] and an angle of 71.5° between these two bonds, which corresponds to a linear $C-O\cdots H$ arrangement if an intramolecular COH angle of 108.5° is accepted [26].

The measured deuteron relaxation rates $(1/T_1)_D$ for $CH_3OD$ are collected in Table 4. We apply the relation [25]

$$\left(\frac{1}{T_1}\right)_D = \frac{3}{2}\,\pi^2(eQq/h)^2(1+\eta^2/3)\,\tau_2 \qquad (4)$$

in order to derive the deuterium quadrupole coupling constant $(eQq/h)$ from our relaxation data. For this purpose two points have to be clarified: which asymmetry parameter $\eta$ must be inserted and which value for the correlation time $\tau_2$ is needed. From a theoretical calculation of the coupling constant and the asymmetry parameter [30] we know the values 292 kHz and 0.152, respectively. Since the coupling constant is in good agreement with the experimental gas value of 303 kHz [31], we anticipate a similar accuracy for $\eta$. An experimental determination of $\eta$ does not exist. Such a small asymmetry parameter $\eta = 0.152$ yields $\eta^2/3 \ll 1$ and therefore we safely can neglect this term. From nmr spectra of solid $CH_3OD$ a deuterium coupling constant of 192 kHz was determined [15], again no asymmetry parameter is given. We assume that $\eta^2/3 \ll 1$ remains valid also for the solid and over the whole liquid range. Concerning the correlation time $\tau_2$ we can expect [31] that the electric field gradient tensor is nearly cylindrically symmetric about the

O–D bond, therefore the correlation time $\tau_2$ for the field gradient tensor in (4) is related to the correlation time $\tau_2^{OH}$ obtained from the proton relaxation data through (2). It is possible that $\tau_2$ for the OH and OD bonds may differ due to isotope effects. This was checked by preparing mixtures of $CH_3OD/CH_3OH$ at mole fractions 0.2, 0.4, 0.6 and 0.8 and measuring the deuteron relaxation rate at a selected temperature of 298 K. Since no composition dependence was detected we may conclude that the $\tau_2$ for the OH and OD bonds are equal. With $\tau_2^{OH}$ from Table 3 and the $(1/T_1)_D$ from Table 4 we calculated the deuterium quadrupole coupling constants which are included as $(eQq/h)_D$ in Table 4. It is seen that the coupling constant increases from 206 kHz at 308 K to 347 kHz at 178 K. On the first sight this is an unexpected behaviour, one might rather expect at the lower temperature a value close to the solid state value of 192 kHz and at the higher temperature an approach to the gas value of 303 kHz. However the opposite temperature dependence is found and the gas value does not constitute the upper limit. From the simulation results [3, 8] we know that the mole fraction of methanol molecules engaged in two hydrogen bonds increases from 0.75 at 300 K to 0.90 at 200 K; this corresponds to a factor of 1.2. In comparison the increase of the coupling constant is by a factor of 1.4. At the present state it is not possible to draw any more quantitative conclusions.

The measured oxygen-17 relaxation rates $(1/T_1)_O$ for $CD_3^{17}OH$, yielding the same value in samples of different $^{17}O$-content, are collected in Table 5. Now the relation [25]

$$\left(\frac{1}{T_1}\right)_O = \frac{12}{125}\,\pi^2(eQq/h)^2(1+\eta/3)^2\,\tau_2 \quad (5)$$

holds, where the quadrupole coupling constant $eQq/h$ and the asymmetry parameter $\eta$ refer to oxygen-17. In this case $\tau_2$ is the correlation time for the oxygen-17 field gradient tensor, for which neither the direction nor the asymmetry are known. Therefore the following evaluation is quite arbitrary: we inserted the $\tau_2^{OH}$ values from Table 3 and chose $\eta=0$. This might be quite incorrect if similar $\eta$ values as in water exist, they

Table 5. Oxygen-17 relaxation rates $(1/T_1)_O$ and quadrupole coupling constants $(eQq/h)_O$ of methanol $CD_3^{17}OH$ as a function of temperature.

| $T/K$ | $(1/T_1)_O/s^{-1}$ | $(eQq/h)_O/kHz$ |
|---|---|---|
| 308 | 178.3 | 6.47 |
| 298 | 204.5 | 6.50 |
| 288 | 240.5 | 6.46 |
| 283 | 257.7 | 6.52 |
| 278 | 285.2 | 6.58 |
| 273 | 303.1 | 6.78 |
| 268 | 358.4 | 6.84 |
| 263 | 398.4 | 6.88 |
| 258 | 456.6 | 6.84 |
| 253 | 500.0 | 6.75 |
| 248 | 561.8 | 6.96 |
| 243 | 630.1 | 7.00 |
| 238 | 709.2 | 6.94 |
| 233 | 800.0 | 7.12 |
| 228 | 925.9 | 7.04 |
| 223 | 1087.5 | 7.06 |
| 218 | 1250.0 | 7.22 |
| 213 | 1492.5 | 7.27 |
| 208 | 1850.0 | 7.29 |

range between 0.94 for ice [32] and 0.75 for gaseous water [33]. Thus our coupling constants included in Table 5 could be lower by 20 or 30%. Also in this case we find an increase from 6.47 MHz at 308 K to 7.29 MHz at 208 K, but this amounts to a factor of 1.1 as compared to 1.4 for the deuterium coupling constant. This means that hydrogen bonding affects the deuterium coupling constant stronger than the oxygen-17 coupling constant, quite a reasonable result.

Between the deuterium quadrupole coupling constant and the oxygen-17 coupling constant a linear relation exists, which is expressed by the equation

$$\left(\frac{eQq}{h}\right)_O = 11.64\left(\frac{eQq}{h}\right)_D + 4.07 \cdot 10^6\,s^{-1}, \quad (6)$$

similar to previous observations by Poplett [34].

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