# Molecular Reorientation of Methanol in Mixtures with Carbon Tetrachloride

R. Ludwig, D. S. Gill *, and M. D. Zeidler
Institut für Physikalische Chemie der RW-Technischen Hochschule Aachen, Aachen

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Proton and oxygen-17 nmr relaxation rates of $CD_3{}^{17}OH$ as well as deuteron nmr relaxation rates of $CH_3OD$ were measured in mixtures with carbon tetrachloride at different compositions and temperatures. 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 $\tau_2^{OH}$ of the OH bond was determined. Using these correlation times the composition dependence of the deuterium and oxygen-17 quadrupole coupling constants of methanol was derived. A strong variation of the coupling constants over the measured composition range is evident.

*Key words:* Relaxation rates, Correlation time, Deuteron quadrupole coupling constant, Oxygen-17 quadrupole coupling constant, Methanol + Carbon tetrachloride mixtures.

## Introduction

The dynamical behaviour as well as the structure of the methanol molecule in binary liquid mixtures with carbon tetrachloride have been the subject of many spectroscopic investigations. Mostly the attention of the spectroscopists was focused on the association of methanol which occurs by hydrogen bonding. Using several methods, like chemical shifts of OH protons in nmr spectra [1], shifts of OH frequencies in IR spectra [2, 3], and proton or deuteron relaxation measurements [4, 5, 6], they followed the extent of molecular association of methanol on dilution with the inert solvent.

In 1956 Liddel and Becker [7] observed that the IR frequency of even the free OH band in a dilute solution of methanol in carbon tetrachloride depends on temperature. Otterstedt and Missen [8] noticed that at high alcohol concentration the enthalpy of mixing is negative for mixtures of alcohols and carbon tetrachloride, but not for mixtures of alcohols and hydrocarbons, such as hexane [9]. Wolff and Hoeppel found the solvation enthalpy of methanol in carbon tetrachloride to be by 0.5 to 1 kcal/mol greater than that for the mixture of methanol with hexane [10]. These and similar results show that there is a specific interaction between the alcohol and the carbon tetrachloride molecule.

In our recent work [11] we determined the reorientational correlation times and the quadrupole coupling constants for deuterium and oxygen-17 in the methanol molecule which gave us information about the dynamics and structure in pure methanol at different temperatures. By the oxygen-17 substitution method we were able to separate intramolecular and intermolecular relaxation rates, and then using the former we calculated the reorientational correlation times $\tau_2^{OH}$ of the OH bond in liquid methanol, which were in good agreement with those obtained from computer simulations [12, 13]. In the past there existed two difficulties in obtaining the correct reorientational correlation time $\tau_2^{OH}$ as in the case of proton relaxation in $CD_3OH$ [14] the reorientational vector is not strictly defined, and in the case of deuteron relaxation in $CH_3OD$ [4, 15, 16] the quadrupole coupling constant is not known. The quadrupole coupling constants of D and $^{17}O$ in the liquid are though expected to be intermediate between the ice and gas values, but their exact values so far were unknown. By measuring the deuteron relaxation rates in $CH_3OD$ and oxygen-17 relaxation rates in $CD_3{}^{17}OH$, we were able to determine the respective quadrupole coupling constants in pure liquid methanol [11]. The value of the deuteron coupling constant at 298 K we found was 210 kHz. As expected, this value is intermediate between the ice value of about 192 kHz [15] and the gas phase value of about 303 kHz [17].

In the present contribution we extend our measurements of pure methanol to the binary mixture methanol + carbon tetrachloride. Similar experiments have

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* Chemistry Department, Panjab University, Chandigarh, India.

Reprint requests to Prof. Dr. M. D. Zeidler, Institut für Physikalische Chemie, Technische Hochschule Aachen, Templergraben 59, D-5100 Aachen.

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been done for water in mixtures with organic solvents [18–20]. The $\tau_2^{OH}$ values in some previous studies [4, 15, 16] were obtained from the deuteron relaxation rates with the assumption that the quadrupole coupling constant was independent of solvent composition. We, however, have found here that the deuteron quadrupole coupling constant is by no means composition independent but increases by about 20% from its value in pure methanol on dilution with carbon tetrachloride at a mole fraction $x_{methanol} = 0.1$. This is in the same direction as the change observed for the transition from liquid methanol to vapour. The molecular background is probably the breakdown of hydrogen bonding between methanol molecules. At $x_{methanol} = 0.1$ the deuteron quadrupole coupling constant begins to decrease from 248 kHz and reaches a value of 230 kHz at $x_{methanol} = 0.03$. We explain this behaviour by the formation of cyclic dimers in agreement with many other investigations [1, 2, 21–24]. The oxygen-17 quadrupole coupling constant which we obtained from oxygen relaxation rates in $CD_3{}^{17}OH$ also provides information on the same line.

## Experimental

The preparation of $CD_3{}^{17}OH$ from $H_2{}^{17}O$ with 6%, 11.7%, 26.8% and 37.5% $^{17}O$-enrichment was described previously [11]. $H_2{}^{17}O$ with the two lower concentrations was obtained from Yeda, Rehovot, Israel, whereas the two higher concentrations were purchased from IRE Diagnostic, Düsseldorf, Germany. $CD_3OH$ (99.9 atom% D) and $CH_3OD$ (99.5 atom% D) were obtained from Aldrich-Chemie, Steinheim, Germany. The different methanol samples were dried over 3 Å molecular sieve. Carbon tetrachloride was used as received from Aldrich-Chemie. From $^1H$ nmr spectra of $CH_3OD$ it was ensured that there was no indication of water in the methanol samples. For the detection of water in $CD_3OH$ samples, however, $^1H$ spectra were recorded in the presence of anhydrous dimethylsulfoxide-d$_6$ which shifts the OH peak of water to a different position than that observed for methanol.

The mixtures of methanol and carbon tetrachloride were prepared by weight, the methanol content in carbon tetrachloride was varied between 3 and 100 mol%. All samples were degassed by several freeze-pump-thaw cycles. The relaxation time $T_1$ was measured by the 180–τ–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.

## Results and Discussion

The measured proton relaxation rates $(1/T_1)_H$ for $CD_3{}^{17}OH$ in the binary mixtures with carbon tetrachloride are collected in Table 1 as function of composition, $^{17}O$-enrichment and temperature. The data at 298 K are also shown in Figure 1.

When at a fixed composition of the methanol + carbon tetrachloride mixture the relaxation rates are plotted against $^{17}O$-enrichment, we obtain straight lines, the slopes of which yield the $^{17}O$-induced proton relaxation contribution $(1/T_1)_H^O$. The $(1/T_1)_H^O$ values are completely dominated by intramolecular dipolar interaction, and thus the relation

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

holds, from which the rotational correlation time of the OH bond, $\tau_2^{OH}$, is directly calculated. Here the γ's are the magnetogyric ratios and $S = 5/2$ is the nuclear

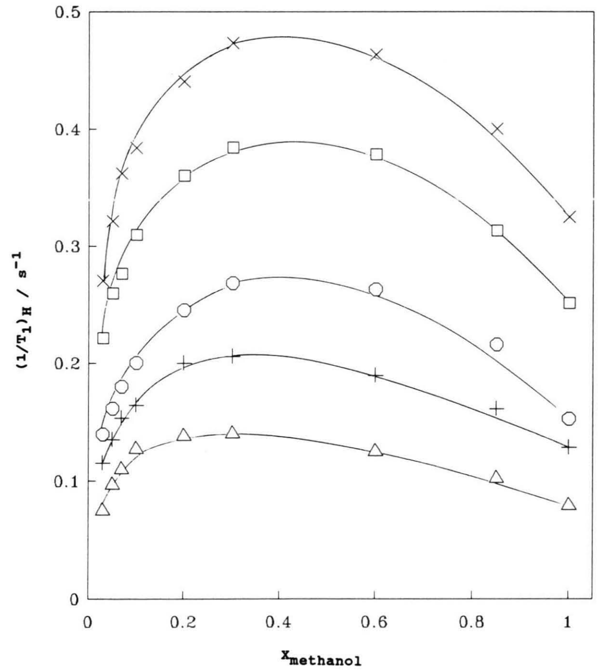


Fig. 1. Proton relaxation rates $(1/T_1)_H$ of methanol $CD_3{}^{17}OH$ in carbon tetrachloride as functions of composition and oxygen-17 enrichment (△ 0%, + 6%, ○ 11.7%, □ 26.8%, × 37.5%) at 298 K.

Table 1. Proton relaxation rates $(1/T_1)_H$ in $s^{-1}$ of methanol $CD_3{}^{17}OH$ in carbon tetrachloride as functions of composition ($x_{methanol}$), $^{17}O$ enrichment ($x_{^{17}O}$) and temperature.

| $x_{^{17}O}$ | $x_{methanol}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.03 | 0.05 | 0.07 | 0.10 | 0.20 | 0.30 | 0.60 | 0.85 | 1.00 |
| | | | | | $T = 288$ K | | | | |
| 0.000 | 0.111 | 0.127 | 0.146 | 0.160 | 0.174 | 0.178 | 0.156 | 0.122 | 0.092 |
| 0.060 | 0.159 | 0.185 | 0.198 | 0.211 | 0.259 | 0.270 | 0.220 | 0.189 | 0.163 |
| 0.117 | 0.189 | 0.219 | 0.241 | 0.273 | 0.317 | 0.353 | 0.310 | 0.250 | 0.191 |
| 0.268 | 0.301 | 0.327 | 0.363 | 0.379 | 0.453 | 0.491 | 0.472 | 0.382 | 0.307 |
| 0.375 | 0.380 | 0.420 | 0.463 | 0.510 | 0.580 | 0.600 | 0.574 | 0.510 | 0.399 |
| | | | | | $T = 298$ K | | | | |
| 0.000 | 0.075 | 0.097 | 0.110 | 0.127 | 0.138 | 0.140 | 0.125 | 0.102 | 0.079 |
| 0.060 | 0.115 | 0.135 | 0.153 | 0.164 | 0.200 | 0.206 | 0.190 | 0.161 | 0.128 |
| 0.117 | 0.139 | 0.161 | 0.180 | 0.200 | 0.245 | 0.268 | 0.263 | 0.216 | 0.152 |
| 0.268 | 0.221 | 0.259 | 0.276 | 0.309 | 0.360 | 0.384 | 0.378 | 0.313 | 0.251 |
| 0.375 | 0.270 | 0.321 | 0.362 | 0.384 | 0.440 | 0.473 | 0.463 | 0.400 | 0.325 |
| | | | | | $T = 308$ K | | | | |
| 0.000 | 0.061 | 0.081 | 0.092 | 0.109 | 0.126 | 0.135 | 0.113 | 0.084 | 0.066 |
| 0.060 | 0.097 | 0.114 | 0.126 | 0.142 | 0.168 | 0.181 | 0.147 | 0.130 | 0.107 |
| 0.117 | 0.109 | 0.133 | 0.150 | 0.185 | 0.210 | 0.230 | 0.206 | 0.174 | 0.139 |
| 0.268 | 0.170 | 0.180 | 0.218 | 0.254 | 0.314 | 0.329 | 0.294 | 0.249 | 0.210 |
| 0.375 | 0.218 | 0.260 | 0.280 | 0.339 | 0.370 | 0.398 | 0.383 | 0.330 | 0.291 |

Table 2. Rotational correlation times $\tau_2^{OH}$ in ps for the OH bond of methanol $CD_3OH$ in carbon tetrachloride as functions of composition and temperature. $E_A$ is the activation energy at the different compositions.

| $x_{methanol}$ | $T$/K | | | $E_A$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| | 288 | 298 | 308 | |
| 0.03 | 5.41 | 4.00 | 3.10 | 20.5 |
| 0.05 | 5.85 | 4.67 | 3.40 | 19.9 |
| 0.07 | 6.44 | 5.07 | 3.80 | 19.4 |
| 0.10 | 6.86 | 5.54 | 4.20 | 18.0 |
| 0.20 | 8.00 | 6.13 | 5.07 | 16.8 |
| 0.30 | 8.40 | 6.67 | 5.37 | 16.4 |
| 0.60 | 8.66 | 6.83 | 5.50 | 16.4 |
| 0.85 | 7.78 | 5.93 | 4.90 | 17.1 |
| 1.00 | 6.10 | 5.06 | 4.50 | 11.5 |

spin of $^{17}O$. For the intramolecular OH distance, $r_{OH}$, we favoured a value of 99 pm [25]. The rotational correlation times $\tau_2^{OH}$ are listed in Table 2. Table 2 also includes the corresponding activation energies derived from their temperature dependence. Plots of the data for all temperatures are shown in Figure 2. Hertz and Holz [4] estimated the rotational correlation time of the hydroxyl group OD in the limit of infinite dilution in methanol using a deuteron quadrupole coupling constant of 222 kHz. Although our measurements were made at relatively higher concentration than those of Hertz and Holz, yet our value of the deuteron

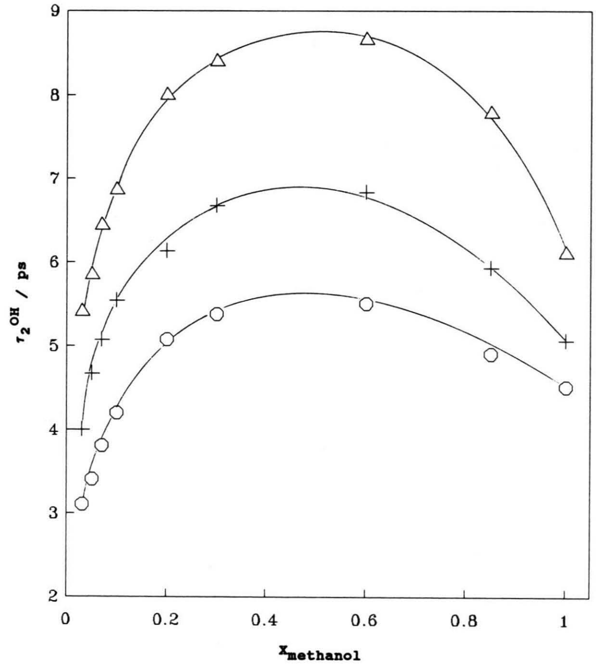


Fig. 2. Rotational correlation times $\tau_2^{OH}$ of the OH bond in methanol $CD_3OH$ in carbon tetrachloride as functions of composition and temperature (△ 288 K, + 298 K, ○ 308 K).

quadrupole coupling constant from Fig. 4 is in very good agreement with the above value. This should be considered, however, as a fortunate coincidence since, as we are aware now, the deuteron quadrupole coupling constants of the OD group in different compounds can vary considerably. For example the values of water and methanol differ by 20% [11, 26], and furthermore the coupling constant depends on the concentration of methanol in the binary mixture. The $\tau_2^{OD}$ value reported by Hertz and Holz and the $\tau_2^{OH}$ values calculated from our data (Table 2) do not contradict each other.

With addition of carbon tetrachloride the rotational correlation time of methanol increases up to a maximum at $x_{methanol} = 0.6$ and then decreases to a value which is smaller than $\tau_2^{OH}$ for pure methanol. At zero $^{17}O$ content the hydroxyl proton of $CD_3OH$ essentially relaxes by intermolecular dipolar interaction. Figure 1 contains this relaxation rate, and we observe a maximum at $x_{methanol} = 0.3$. As the $^{17}O$ content is increased, this maximum shifts to $x_{methanol} = 0.6$; this is now, however, an intramolecular relaxation rate. This fact leads to the conclusion that the translational motion of the $CD_3OH$ molecules is relatively less hindered by the carbon tetrachloride molecules as compared to their rotational motion.

Our relaxation rates at zero $^{17}O$ content are in good agreement with measurements by Koch, Leiter and Mal [6]. Their results were shown to conform to the self and mutual diffusion coefficients. They were also used to determine the velocity correlation function which characterizes the correlated motions between the methanol molecules [27].

The measured deuteron relaxation rates $(1/T_1)_D$ for $CH_3OD$ and the corresponding activation energies are collected in Table 3 and shown in Fig. 3 as functions of composition and temperature. In this case we have the relation

$$(1/T_1)_D = 3/2\,\pi^2\,(e\,Q\,q/h)_D^2\,(1 + \eta_D^2/3)\,\tau_2 \qquad (2)$$

connecting the deuteron relaxation rates $(1/T_1)_D$ with the correlation time $\tau_2$. The deuteron quadrupole coupling constant is denoted as $(e\,Q\,q/h)_D$. The additional factor $(1 + \eta_D^2/3)$ can be neglected since theoretical calculations showed that the asymmetry parameter $\eta_D$ is smaller than 0.152 [28]. The reliability of the $\eta_D$ value equal to 0.152 is supported by the agreement of the theoretically calculated value for the deuteron quadrupole coupling constant 292 kHz with the experimental gas value of 303 kHz [17].

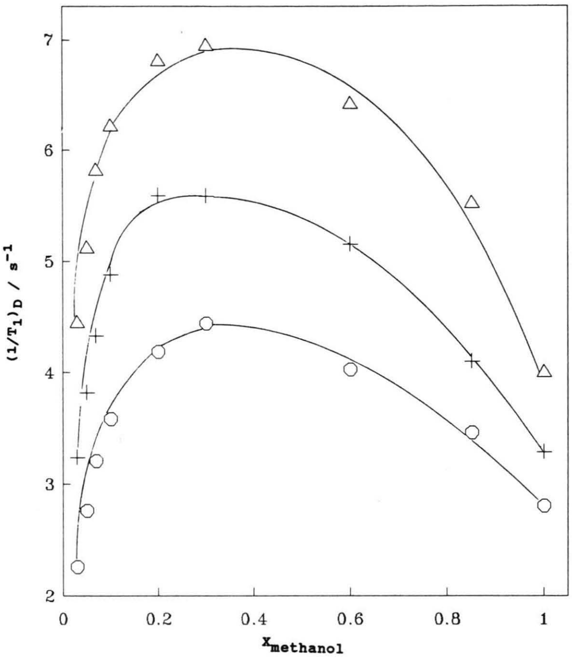


Fig. 3. Deuteron relaxation rates $(1/T_1)_D$ of methanol $CH_3OD$ in carbon tetrachloride as functions of composition and temperature (△ 288 K, + 298 K, ○ 308 K).

Table 3. Deuteron relaxation rates $(1/T_1)_D$ in $s^{-1}$ of methanol $CH_3OD$ in carbon tetrachloride as functions of composition and temperature. $E_A$ is the activation energy at the different compositions.

| $x_{methanol}$ | $T$/K | | | $E_A$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| | 288 | 298 | 308 | |
| 0.03 | 4.44 | 3.24 | 2.25 | 25.1 |
| 0.05 | 5.12 | 3.82 | 2.76 | 22.9 |
| 0.07 | 5.81 | 4.33 | 3.21 | 22.0 |
| 0.10 | 6.21 | 4.88 | 3.58 | 20.3 |
| 0.20 | 6.80 | 5.59 | 4.18 | 17.9 |
| 0.30 | 6.94 | 5.59 | 4.44 | 16.5 |
| 0.60 | 6.42 | 5.16 | 4.02 | 17.2 |
| 0.85 | 5.53 | 4.10 | 3.46 | 17.3 |
| 1.00 | 4.00 | 3.29 | 2.80 | 13.2 |

The correlation time $\tau_2$ in (2) is related to the correlation time $\tau_2^{OH}$ in (1). Since the electric field gradient tensor is nearly cylindrically symmetric about the OD bond we can put both correlation times equal. In the case of pure methanol we have experimentally checked that the correlation times of OH and OD bonds to not differ significantly due to the isotope effect. For this purpose we measured deuteron relaxation rates for the mixture $CH_3OD + CH_3OH$ at mole fractions 0.2, 0.4, 0.6, and 0.8 at a selected tem-

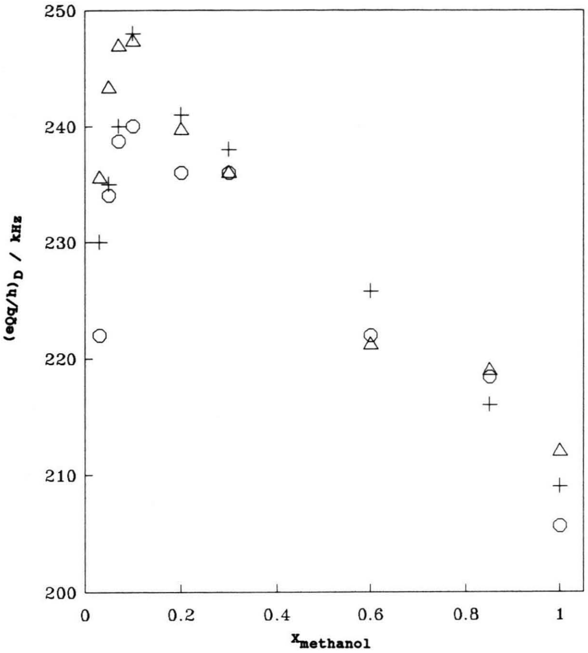


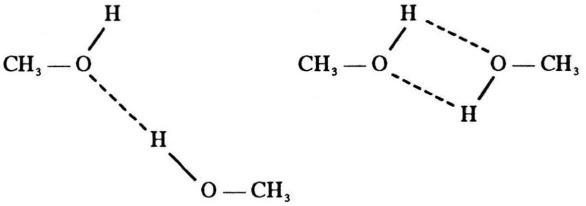
Fig. 4. Deuteron quadrupole coupling constants $(eQq/h)_D$ of methanol $CH_3OD$ in carbon tetrachloride as functions of composition and temperature (△ 288 K, + 298 K, ○ 308 K).

Table 4. Deuteron quadrupole coupling constants $(eQq/h)_D$ in kHz of methanol $CH_3OD$ in carbon tetrachloride as functions of composition and temperature.

| $x_{methanol}$ | $T$/K | | |
|---|---|---|---|
| | 288 | 298 | 308 |
| 0.03 | 236 | 230 | 222 |
| 0.05 | 243 | 235 | 234 |
| 0.07 | 247 | 240 | 239 |
| 0.10 | 247 | 248 | 240 |
| 0.20 | 240 | 241 | 236 |
| 0.30 | 236 | 238 | 236 |
| 0.60 | 221 | 226 | 222 |
| 0.85 | 219 | 216 | 218 |
| 1.00 | 212 | 209 | 206 |

perature of 298 K. The measured relaxation rates were independent of composition, and thus we conclude that the isotope effect is negligible.

Using the $\tau_2^{OH}$ values from Table 2 we evaluated the deuteron quadrupole coupling constant from (2). The deuteron quadrupole coupling constants so obtained are listed in Table 4 and are also shown in Figure 4. A systematic variation of the coupling constant with temperature is apparent, it is the same as for pure methanol [11] i.e. the coupling constant increases with decreasing temperature. Not a single value of the coupling constant in the mixture falls below the solid phase value of 192 kHz [15] or exceeds the gas phase value of 303 kHz [17]. Moreover for all temperatures the composition dependence is the same. We therefore discuss the values just at 298 K. Starting from 209 kHz for pure methanol the coupling constant first increases nearly linearly to about 248 kHz at the mole fraction $x_{methanol} = 0.1$ and then decreases to 230 kHz at $x_{methanol} = 0.03$. Such a concentration dependence of the deuteron quadrupole coupling constant for methanol in a binary mixture with an organic solvent is demonstrated here for the first time. The initial increase of the coupling constant on adding the nonpolar solvent carbon tetrachloride is due to a breakage of hydrogen bonds of methanol with the result that the fraction of free OH bonds increases. A surprise, however, is the decrease of the coupling constant when the composition of methanol falls below a mole fraction of 0.1. A possible explanation could be that we find different kinds of methanol aggregates at the different compositions of the mixture. From IR measurements on pure methanol we know that at 298 K less than 2% monomers but higher aggregates like dimers, trimers and perhaps even longer chains exist [29]. From computer simulation results at 300 K [13] we know that 75% of the methanol molecules are engaged in two hydrogen bonds, 16% form dimers, 7% tetramers and only 1–2% exist as monomers. Linear and cyclic dimers possess different hydrogen bonds, and therefore we expect to have variable coupling constants, for example



If $\beta$ is the angle between the OH axis and the lone electron pair orbital, then for linear dimers $\beta = 0°$ and the strongest hydrogen bond is formed. Cyclic dimers on the other side form an angle $\beta = 110°$ and have weaker hydrogen bond energies. From IR measurements using the matrix isolation technique Luck [29] could identify hydrogen bonds of different methanol aggregates with respect to the corresponding angles $\beta$. We might suppose that in the sequence oligomers ($\beta = 0°$), tetramers ($\beta = 20°$), trimers ($\beta = 50°$), cyclic dimers ($\beta = 110°$) and monomers the quadrupole coupling constant increases because of decreasing hydrogen bond strength. On the basis of this we can explain the behaviour of the deuteron quadrupole coupling constant. At first the hydrogen bonds will be destroyed, thus the mole fraction of free OH bonds and the coupling constant increase. At the lower concentrations of methanol more cyclic dimers exist and the quadrupole coupling constant decreases. The limiting value at 230 kHz lies above the coupling constant of pure methanol, where we find mainly oligomers. Such cyclic dimers were indeed found from IR measurements in the mixtures methanol + carbon tetrachloride [1, 2, 21–24]. In the region of low concentration of methanol a specific hydrogen bond peak appears and again disappears at higher concentration. This intermediate band between the monomer and polymer vibration bands has been observed in different alcohols by several authors. Its appearance is observed in the concentration range where the dipole moment shows a minimum [30–34]. In view of this minimum the assignment of the band to a small aggregate with a cyclic structure is conclusive.

Pimentel [35] has shown that the hydrogen bond energy between two water molecules can be estimated quantitatively under the assumption of dipole-dipole interaction. Assuming that every OH group consists of a dipole with charge 0.32 electron charges and a charge separation of 100 pm, they obtained a hydrogen bond energy of 3.8 kcal/mol for the interaction of two such dipoles at a distance of 276 pm. They stressed that their dipole model gives an angle dependence of the hydrogen bond energy. Luck [29] compared the angle dependence of such dipole interactions with his IR results.

Dixon [36] compared the nmr chemical shifts of the OH proton of methanol in carbon tetrachloride with the one for hydrocarbons like cyclopentane and cyclohexane. From the smaller upfield shift at infinite dilution in the carbon tetrachloride solutions he concluded that hydrogen bonds between methanol and carbon tetrachloride are formed. Hints to the fact that chlorine atoms may act as hydrogen bond acceptors were published earlier by Brandt and Chojnowski [37] and by Fletcher [38]. Such hydrogen bonds we have to expect for all mixtures of methanol with carbon tetrachloride, as was shown by Wolff and Hoeppel [10]. However a maximum of the chemical shift or a minimum of the dipole moment at lower methanol concentrations cannot be explained by OH ··· Cl associates but only with cyclic dimers.

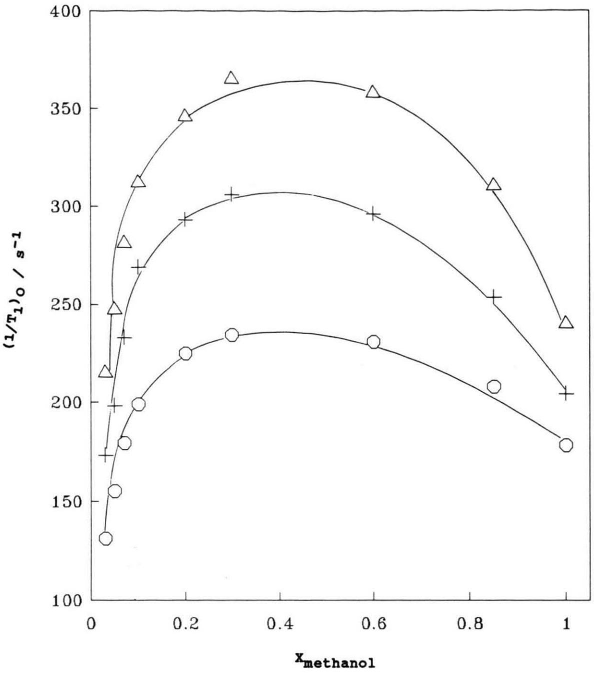


Fig. 5. Oxygen-17 relaxation rates $(1/T_1)_O$ of methanol $CD_3{}^{17}OH$ in carbon tetrachloride as functions of composition and temperature (△ 288 K, + 298 K, ○ 308 K).

Table 5. Oxygen-17 relaxation rates $(1/T_1)_O$ in $s^{-1}$ of methanol $CD_3{}^{17}OH$ in carbon tetrachloride as functions of composition and temperature. $E_A$ is the activation energy at the different compositions.

| $x_{methanol}$ | $T$/K |  |  | $E_A$/kJ mol$^{-1}$ |
|---|---|---|---|---|
|  | 288 | 298 | 308 |  |
| 0.03 | 215 | 173 | 131 | 18.3 |
| 0.05 | 247 | 198 | 155 | 17.3 |
| 0.07 | 281 | 233 | 179 | 16.7 |
| 0.10 | 312 | 269 | 199 | 16.6 |
| 0.20 | 346 | 293 | 225 | 15.8 |
| 0.30 | 365 | 306 | 234 | 16.4 |
| 0.60 | 358 | 296 | 231 | 16.2 |
| 0.85 | 311 | 254 | 208 | 14.8 |
| 1.00 | 241 | 205 | 178 | 11.1 |

The measured oxygen-17 relaxation rates $(1/T_1)_O$ for $CD_3{}^{17}OH$ are listed in Table 5 and plotted in Figure 5. In the relation

$$(1/T_1)_O = 12/125\,\pi^2\,(e\,Q\,q/h)_O^2\,(1 + \eta_O^2/3)\,\tau_2 \qquad (3)$$

the quadrupole coupling constant $(e\,Q\,q/h)_O$ and the asymmetry parameter $\eta_O$ now refer to oxygen-17. For

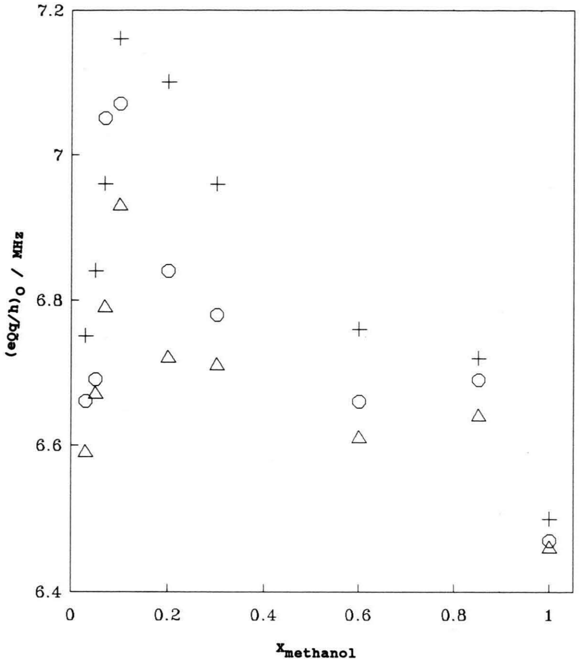


Fig. 6. Oxygen-17 quadrupole coupling constants $(e\,Q\,q/h)_O$ of methanol $CD_3{}^{17}OH$ in carbon tetrachloride as functions of composition and temperature (△ 288 K, + 298 K, ○ 308 K).

Table 6. Oxygen-17 quadrupole coupling constants $(e\,Q\,q/h)_O$ in MHz of methanol $CD_3{}^{17}OH$ in carbon tetrachloride as functions of composition and temperature.

| $x_{\text{methanol}}$ | $T$/K | | |
|---|---|---|---|
| | 288 | 298 | 308 |
| 0.03 | 6.59 | 6.75 | 6.66 |
| 0.05 | 6.67 | 6.84 | 6.69 |
| 0.07 | 6.79 | 6.96 | 7.05 |
| 0.10 | 6.93 | 7.16 | 7.07 |
| 0.20 | 6.72 | 7.10 | 6.84 |
| 0.30 | 6.71 | 6.96 | 6.78 |
| 0.60 | 6.61 | 6.76 | 6.66 |
| 0.85 | 6.64 | 6.72 | 6.69 |
| 1.00 | 6.46 | 6.50 | 6.47 |

the oxygen-17 field gradient tensor we know neither the direction nor the asymmetry, consequently the correlation time $\tau_2$ might differ from $\tau_2^{OH}$. In order to proceed with the evaluation of our data we chose $\eta_O = 0$ and used the $\tau_2^{OH}$ values from Table 2. The quadrupole coupling constants $(e\,Q\,q/h)_O$ were calculated with these assumptions and are listed in Table 6 and plotted in Figure 6. If an $\eta_O$ value as in the case of water in the range between 0.94 for ice [39] or 0.75 for vapour [40] should apply, then our coupling constants as listed in Table 6 would be lower by as much as 20 or 30%. The behaviour of the oxygen-17 coupling constant is similar to that of the deuteron coupling constant but not as pronounced. Hydrogen bonding affects the deuteron coupling constant much more strongly than the oxygen-17 coupling constant.

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[1] E. D. Becker, U. Liddel, and J. N. Shoolery, J. Mol. Spectr. **2,** 1 (1958).
[2] W. C. Coburn and E. Grunwald, J. Amer. Chem. Soc. **80,** 1318 (1958).
[3] W. A. P. Luck and W. Ditter, Ber. Bunsenges. Phys. Chem. **71,** 365 (1967).
[4] H. G. Hertz and M. Holz, Z. Phys. Chem. N.F. **136,** 81 (1983).
[5] M. Gruener and H. G. Hertz, Adv. Mol. Relax. Proc. **3,** 75 (1972).
[6] W. Koch, H. Leiter, and S. Mal, Z. Phys. Chem. N.F. **136,** 89 (1983).
[7] U. Liddel and E. D. Becker, J. Chem. Phys. **25,** 113 (1956).
[8] J. E. Otterstedt and R. W. Missen, Trans. Faraday Soc. **58,** 879 (1962).
[9] G. von Elbe, J. Chem. Phys. **2,** 73 (1934).
[10] H. Wolff and H. E. Hoeppel, Ber. Bunsenges. Phys. Chem. **72,** 1173 (1968).
[11] R. Ludwig, D. S. Gill, and M. D. Zeidler, Z. Naturforsch. **46a,** 89 (1991).
[12] M. Haughney, M. Ferrario, and I. R. McDonald, J. Phys. Chem. **91,** 4934 (1987).
[13] M. Matsumoto and K. E. Gubbins, J. Chem. Phys. **93,** 1981 (1990).
[14] R. Goeller, H. G. Hertz, and R. Tutsch, Pure Appl. Chem. **32,** 149 (1972).
[15] D. E. O'Reilly and E. M. Peterson, J. Chem. Phys. **55,** 2155 (1971).
[16] H. Versmold, Ber. Bunsenges. Phys. Chem. **84,** 168 (1980).
[17] K. H. Casleton and S. G. Kukolich, Chem. Phys. Letters **22,** 331 (1973).
[18] B. C. Gordalla and M. D. Zeidler, Mol. Phys. **59,** 817 (1986).
[19] B. C. Gordalla and M. D. Zeidler, Mol. Phys. **74,** 975 (1991).

[20] R. Ludwig and M. D. Zeidler, J. Mol. Liquids, in press (1992).
[21] F. A. Smith and E. C. Creitz, J. Res. Nat. Bur. Std. U.S. **46,** 145 (1951).
[22] M. M. Maguire and R. West, Spectrochem. Acta **17,** 369 (1961).
[23] L. J. Bellamy and R. C. Pace, Spectrochem. Acta **25,** 319 (1969).
[24] R. Mecke, Z. Elektrochem. **52,** 280 (1948).
[25] Y. Tanaka, N. Ohtomo, and K. Arakawa, Bull. Chem. Soc. Japan **57,** 644 (1984).
[26] J. R. van der Maarel, D. Lankhorst, J. de Bleijser, and J. C. Leyte, Chem. Phys. Letters **122,** 541 (1985).
[27] S. Prabhakar and H. Weingaertner, Z. Phys. Chem. N.F. **137,** 1 (1983).
[28] H. Huber, J. Chem. Phys. **83,** 4591 (1985).
[29] W. A. P. Luck, in: The hydrogen bond – recent developments in theory and experiments (P. Schuster, G. Zundel, and C. Sandorfy, eds.), North-Holland Publ. Co. 1976.
[30] R. Mecke and A. Reuter, Z. Naturforsch. **4a,** 371 (1949).
[31] R. Mecke, A. Reuter, and R. L. Schupp, Z. Naturforsch. **4a,** 182 (1949).
[32] R. L. Schupp, Z. Elektrochem. **53,** 12 (1949).
[33] D. A. Ibbitson and L. F. Moore, J. Chem. Soc. (B) **76,** 80 (1967).
[34] R. van Loon, J. P. Dauchot, and A. Mellemans, Bull. Soc. Chim. Belges **77,** 397 (1968).
[35] G. C. Pimentel, in: Formation and trapping of free radicals (A. M. Bass and H. P. Broida, eds.), Academic Press, New York 1960.
[36] W. B. Dixon, J. Phys. Chem. **74,** 1396 (1970).
[37] W. W. Brandt and J. Chojnowski, Spectrochem. Acta **25a,** 1639 (1969).
[38] A. N. Fletcher, J. Phys. Chem. **73,** 2217 (1969).
[39] H. W. Spiess, B. B. Garett, R. K. Sheline, and S. W. Rabideau, J. Chem. Phys. **51,** 1201 (1969).
[40] J. Verhoeven, A. Dynamus, and H. Bluyssen, J. Chem. Phys. **50,** 3330 (1969).