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# Temperature dependence of self-diffusion in compressed monohydric alcohols

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The  $p, T$ -dependence of the self-diffusion coefficient  $D$  for methanol, methan(<sup>2</sup>H)ol and ethanol has been studied between 150 and 450 K at pressures up to 250 MPa. The experiments were performed in strengthened high-pressure glass cells by the application of the nuclear magnetic resonance (NMR) spin-echo technique with pulsed magnetic-field gradients. Upon cooling, molecular mobility is strongly reduced, leading to a pronounced non-Arrhenius temperature dependence of  $D$ . Applying the rough hard-sphere model (Chandler) to our data, a dramatic decrease of the  $A$ -parameter with falling temperature is observed. This behavior indicates that attractive intermolecular interactions dominate translational mobility. The best description of the data is given by the empirical Vogel–Tammann–Fulcher (VTF) equation, with ideal glass transition temperatures  $T_0$ , that are in excellent agreement with those obtained from calorimetric studies. The isotope effect for self-diffusion in methanol and methan(<sup>2</sup>H)ol increases from  $\sim 5\%$  at high temperatures to about 40% in the supercooled region. This drastic increase is assumed to originate from a difference in hydrogen bond strength of the isotopes, as has already been found for light and heavy water.

## I. INTRODUCTION

The self-diffusion coefficient  $D$  characterizes the single-molecule translational mobility in homogeneous liquid phases.

For the determination of  $D$  the nuclear magnetic resonance (NMR) spin-echo method in a pulsed magnetic-field gradient has become the method of choice.<sup>1</sup>

An independent variation of temperature and pressure allows one to separate the influences of kinetic energy and density upon molecular motion. Over the last years the pressure and temperature dependence of translational motion for a series of halomethanes<sup>2–7</sup> and supercooled water<sup>8,9</sup> has been studied in our group.

The results for the halomethanes led Speedy<sup>10</sup> to an extension of existing hard-sphere models<sup>11,12</sup> which explicitly includes the retarding effects of attractive interactions on translational diffusion.

Liquid water shows an unusual pressure and temperature dependence for all dynamic properties. This is due to the ability of the water molecule to form a three-dimensional approximately tetrahedral network of hydrogen bonds. The monoalcohols studied here can form hydrogen-bonded chains, branched chains, and ring structures only.<sup>13</sup> They should thus exhibit a less complex behavior than liquid water.

The data given in the following cover a much wider temperature range than studied hitherto and extend for the first time into the deeply supercooled metastable region of the phase diagram. To examine the retarding effect of hydrogen bonding upon translational diffusion it is necessary to measure  $D$  over a wide temperature range. Especially in the su-

percooled region, attractive interactions should significantly lower translational mobility. Due to the formation of hydrogen bonds, at low temperatures the molecules exhibit correlated motion, which can often be described by the empirical Vogel–Tammann–Fulcher (VTF) equation. A possible change in intermolecular potential by isotopic substitution should result in a temperature-dependent isotope effect of  $D$ .

## II. EXPERIMENTAL

### A. Substances

Methanol (99.8% purity), methan(<sup>2</sup>H)ol (99% <sup>2</sup>H), and ethanol (99.8%) were purchased from E. Merck (Darmstadt, FRG). Residual water was removed by the addition of a piece of metallic sodium to the storage flask. After the dissolution of the sodium, the flask was connected to a vacuum line and degassed by several freeze–pump–thaw cycles to a final pressure at liquid nitrogen temperature of  $5 \times 10^{-3}$  Pa.

### B. Capillaries and filling procedure

High-pressure capillaries were drawn from Duran 50 glass and glued with an alumina-filled epoxy resin into the bore of a copper–beryllium nipple. A Teflon shrink hose serves as pressure-transmitter and -separator. Below 300 K capillaries with an i.d. of about 150  $\mu\text{m}$  and an o.d. of 800  $\mu\text{m}$  were used [Fig. 1(c)]. The small amount of substance reduces the probability for nucleation and thus allows measurements to be extended into the deeply supercooled region. In order to increase the filling factor in the high-temperature region, we employed capillaries with i.d. 0.8 mm and o.d. 5.0 mm [Fig. 1(b)]. From the flask, a small portion of the substance was sublimated into the filling apparatus and pressed into the capillaries by flushing the high-vacuum line with

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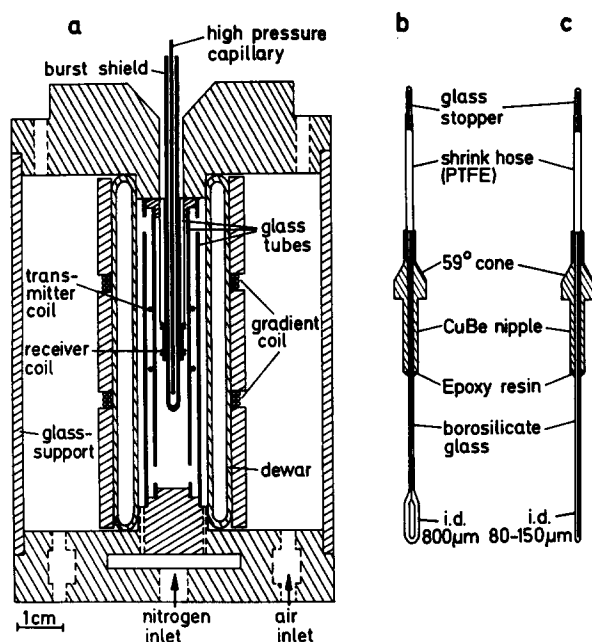


FIG. 1. Probehead and capillaries: (a) NMR probehead with Helmholtz coil, (b) high-pressure cell for measurements above 300 K, (c) narrow capillary for supercooling.

argon. Upon removal from the apparatus the capillaries became flame sealed at their upper end. The design of the complete high-pressure apparatus and the connection to the pressure-generating system have been given previously.<sup>9,14,15</sup>

### C. Measurements

The self-diffusion coefficients  $D$  were obtained in a Bruker MSL 300 NMR spectrometer. The home-built probehead for the determination of  $D$  by the pulsed field gradient spin-echo technique<sup>16</sup> is shown in Fig. 1(a). The gradient is produced by a pair of opposite Helmholtz coils wound onto the outside wall of a glass Dewar and connected to a Bruker gradient unit. This design holds the coil at room temperature and eliminates any temperature effect on the gradient strength. The temperature was regulated by a Bruker temperature accessory by blowing a stream of thermostatted nitrogen around the capillary. A thermocouple was inserted before and after each measurement to determine the temperature at the position of the sample.

During one measurement, the temperature varied  $< \pm 0.3$  K while the temperature gradient over the probe did not exceed 0.5 K at extreme temperatures. Pressure was measured with a Bourdon gauge (Heise, Connecticut, USA) to  $\pm 0.5$  MPa.

The determination of  $D$  was most conveniently accomplished by increasing the current intensity  $I$  and thus raising the gradient strength  $g = kI$  while keeping all other variables constant. The coil constant  $k$  has been obtained from a calibration with the known self-diffusion coefficient of water

at ambient pressure and 298 K provided by Mills<sup>17</sup> which is generally acknowledged to be the most reliable value.<sup>18</sup> It was controlled by a redetermination of  $D$  for benzene known from tracer measurements.<sup>19</sup>

Problems with echo modulation originating from homonuclear  $J$ -coupling in ethanol and methanol could be minimized by using the constant  $\tau$  technique.<sup>20</sup> Evaluation of the echo was accomplished by Fourier transforming the second half of the spin-echo and measuring the methyl-peak intensity.

The low-temperature limit for the determination of  $D$  was set by a rapid decrease of  $T_2$  with falling temperature combined with the low filling factor in the thin capillaries.

The self-diffusion coefficients are considered accurate to  $\pm 5\%$ . Their reproducibility was  $\pm 1$ – $2\%$ . Due to the weak signal at the lowest temperatures, the reproducibility deteriorates to about  $\pm 4\%$ .

## III. RESULTS

Tables I–III present our experimental data for the self-diffusion coefficients of the three substances. The isotherms collected in Fig. 2 compare the pressure dependence of the translational mobility of the alcohols.

For each liquid, the measured self-diffusion coefficient covers a range of approximately four orders of magnitude. Where the data overlap, our measurements agree within experimental error with the values presented by Jonas and Akai<sup>21</sup> (MeOD: 223–323 K), Hurle *et al.*<sup>22</sup> (MeOD: 214–343 K, MeOH: 278–313 K, EtOH: 298 K) and Meckl and Zeidler<sup>23</sup> (EtOH: 285–320 K). However, for methan(<sup>2</sup>H)ol at temperatures above 283 K, where the two data sets diverge by up to 20%, our results lie in between these data.

## IV. DISCUSSION

### A. Rough hard-sphere model

The retarding influence of hydrogen bonding upon molecular mobility becomes evident when the 178 K isotherm for methylfluoride<sup>3</sup> given in Fig. 2(a) is compared to the low-temperature isotherms of methanol. The molecules have very similar masses, moments of inertia, and dipole moments ( $\text{CH}_3\text{F}$ : 1.85 D,  $\text{CH}_3\text{OH}$ : 1.70 D). However, the formation of hydrogen bonds reduces the translational mobility in the alcohol by approximately two orders of magnitude.

For the rigid halomethanes which are unable to form hydrogen bonds, the  $\rho$ ,  $T$ -dependence of  $D$  can be described quantitatively by the interacting sphere model. In this approach Speedy<sup>10</sup> considers the effects of attractive interactions in a hard-sphere liquid in the form of a Lennard-Jones potential. A hard-sphere diameter, decreasing with temperature, is modelled to fit the  $T$ -dependence of the effective molecular diameter.

This description must fail for the alcohols studied here, since the H-bonds cause a much steeper decrease of  $D$  with falling temperature.

The individual isotherms of the three monoalcohols, however, can be very well described by Chandler's rough hard-sphere model.<sup>11,12</sup> According to Chandler, the experi-

TABLE I. Experimental results for the self-diffusion coefficient in methanol.

$P(\text{MPa})/$ $T(\text{K})$	0.1	5	50	MeOH 100	150	200	250
453		$1.86 \times 10^{-8}$	$1.37 \times 10^{-8}$	$1.12 \times 10^{-8}$	$9.52 \times 10^{-9}$	$8.42 \times 10^{-9}$	
418		$1.31 \times 10^{-8}$	$9.99 \times 10^{-9}$	$8.37 \times 10^{-9}$	$7.37 \times 10^{-9}$	$6.46 \times 10^{-9}$	
387		$8.54 \times 10^{-9}$	$7.05 \times 10^{-9}$	$6.00 \times 10^{-9}$	$5.25 \times 10^{-9}$	$4.69 \times 10^{-9}$	
355		$5.80 \times 10^{-9}$	$4.92 \times 10^{-9}$	$4.06 \times 10^{-9}$	$3.71 \times 10^{-9}$	$3.45 \times 10^{-9}$	
323		$3.83 \times 10^{-9}$	$3.31 \times 10^{-9}$	$2.91 \times 10^{-9}$	$2.55 \times 10^{-9}$	$2.20 \times 10^{-9}$	
292	$2.30 \times 10^{-9}$		$2.05 \times 10^{-9}$	$1.73 \times 10^{-9}$	$1.56 \times 10^{-9}$	$1.40 \times 10^{-9}$	$1.25 \times 10^{-9}$
240	$7.82 \times 10^{-10}$		$6.68 \times 10^{-10}$	$5.77 \times 10^{-10}$	$4.96 \times 10^{-10}$	$4.30 \times 10^{-10}$	$3.71 \times 10^{-10}$
213	$3.63 \times 10^{-10}$		$2.98 \times 10^{-10}$	$2.41 \times 10^{-10}$	$2.01 \times 10^{-10}$	$1.68 \times 10^{-10}$	$1.44 \times 10^{-10}$
201	$2.43 \times 10^{-10}$		$1.96 \times 10^{-10}$	$1.56 \times 10^{-10}$	$1.26 \times 10^{-10}$	$1.02 \times 10^{-10}$	$8.13 \times 10^{-11}$
187	$1.44 \times 10^{-10}$		$1.07 \times 10^{-10}$	$8.00 \times 10^{-11}$	$5.88 \times 10^{-11}$	$4.46 \times 10^{-11}$	$3.33 \times 10^{-11}$
174	$7.25 \times 10^{-11}$		$5.27 \times 10^{-11}$	$3.64 \times 10^{-11}$	$2.47 \times 10^{-11}$	$1.72 \times 10^{-11}$	$1.17 \times 10^{-11}$
164	$3.68 \times 10^{-11}$		$2.47 \times 10^{-11}$	$1.52 \times 10^{-11}$	$1.01 \times 10^{-11}$	$5.98 \times 10^{-12}$	
157	$2.13 \times 10^{-11}$		$1.27 \times 10^{-11}$	$7.24 \times 10^{-12}$	$4.15 \times 10^{-12}$		
154	$1.61 \times 10^{-11}$		$8.92 \times 10^{-12}$	$5.37 \times 10^{-12}$			

TABLE II. Experimental results for the self-diffusion coefficient in methan( $^2\text{H}$ )ol.

$P(\text{MPa})/$ $T(\text{K})$	0.1	5	50	MeOD 100	150	200	250
455		$1.88 \times 10^{-8}$	$1.34 \times 10^{-8}$	$1.09 \times 10^{-8}$	$9.63 \times 10^{-9}$	$8.58 \times 10^{-9}$	
428		$1.39 \times 10^{-8}$	$1.05 \times 10^{-8}$	$8.81 \times 10^{-9}$	$7.64 \times 10^{-9}$	$6.89 \times 10^{-9}$	
397		$9.51 \times 10^{-9}$	$7.63 \times 10^{-9}$	$6.45 \times 10^{-9}$	$5.69 \times 10^{-9}$	$5.13 \times 10^{-9}$	
367		$6.51 \times 10^{-9}$	$5.38 \times 10^{-9}$	$4.64 \times 10^{-9}$	$4.13 \times 10^{-9}$	$3.73 \times 10^{-9}$	
339		$4.42 \times 10^{-9}$	$3.70 \times 10^{-9}$	$3.25 \times 10^{-9}$	$2.88 \times 10^{-9}$	$2.60 \times 10^{-9}$	
314		$3.00 \times 10^{-9}$	$2.57 \times 10^{-9}$	$2.23 \times 10^{-9}$	$2.20 \times 10^{-9}$	$1.81 \times 10^{-9}$	
294	$2.08 \times 10^{-9}$		$1.75 \times 10^{-9}$	$1.54 \times 10^{-9}$	$1.39 \times 10^{-9}$	$1.26 \times 10^{-9}$	
257	$1.10 \times 10^{-9}$		$8.76 \times 10^{-10}$	$7.84 \times 10^{-10}$	$6.58 \times 10^{-10}$	$6.09 \times 10^{-10}$	$5.36 \times 10^{-10}$
230	$5.29 \times 10^{-10}$		$4.33 \times 10^{-10}$	$3.97 \times 10^{-10}$	$3.33 \times 10^{-10}$	$2.63 \times 10^{-10}$	$2.33 \times 10^{-10}$
199	$1.84 \times 10^{-10}$		$1.50 \times 10^{-10}$	$1.19 \times 10^{-10}$	$9.22 \times 10^{-11}$	$7.13 \times 10^{-11}$	$6.02 \times 10^{-11}$
180	$8.50 \times 10^{-11}$		$6.41 \times 10^{-11}$	$4.00 \times 10^{-11}$	$2.89 \times 10^{-11}$	$2.29 \times 10^{-11}$	$1.59 \times 10^{-11}$
166	$3.46 \times 10^{-11}$		$2.26 \times 10^{-11}$	$1.57 \times 10^{-11}$	$9.28 \times 10^{-12}$	$5.62 \times 10^{-12}$	$3.41 \times 10^{-12}$
156	$1.47 \times 10^{-11}$		$7.99 \times 10^{-12}$	$4.84 \times 10^{-12}$			
151	$7.85 \times 10^{-12}$						

TABLE III. Experimental results for the self-diffusion coefficient in ethanol.

$P(\text{MPa})/$ $T(\text{K})$	0.1	5	50	EtOH 100	150	200	250
437		$1.20 \times 10^{-8}$	$8.01 \times 10^{-9}$	$6.26 \times 10^{-9}$	$5.27 \times 10^{-9}$	$4.55 \times 10^{-9}$	
403.5		$7.07 \times 10^{-9}$	$5.25 \times 10^{-9}$	$4.23 \times 10^{-9}$	$3.51 \times 10^{-9}$	$3.01 \times 10^{-9}$	
380		$5.30 \times 10^{-9}$	$3.97 \times 10^{-9}$	$3.18 \times 10^{-9}$	$2.69 \times 10^{-9}$	$2.34 \times 10^{-9}$	
352		$3.26 \times 10^{-9}$	$2.56 \times 10^{-9}$	$2.07 \times 10^{-9}$	$1.76 \times 10^{-9}$	$1.52 \times 10^{-9}$	
333	$2.37 \times 10^{-9}$		$1.82 \times 10^{-9}$	$1.49 \times 10^{-9}$	$1.26 \times 10^{-9}$	$1.10 \times 10^{-9}$	
315	$1.60 \times 10^{-9}$		$1.27 \times 10^{-9}$	$1.05 \times 10^{-9}$	$8.89 \times 10^{-10}$	$7.73 \times 10^{-10}$	
290	$9.46 \times 10^{-10}$		$7.59 \times 10^{-10}$	$6.37 \times 10^{-10}$	$5.46 \times 10^{-10}$	$4.68 \times 10^{-10}$	$4.12 \times 10^{-10}$
263	$4.80 \times 10^{-10}$		$3.84 \times 10^{-10}$	$3.21 \times 10^{-10}$	$2.72 \times 10^{-10}$	$2.26 \times 10^{-10}$	$1.95 \times 10^{-10}$
239	$2.37 \times 10^{-10}$		$1.85 \times 10^{-10}$	$1.52 \times 10^{-10}$	$1.29 \times 10^{-10}$	$1.03 \times 10^{-10}$	$8.65 \times 10^{-11}$
218	$1.22 \times 10^{-10}$		$9.40 \times 10^{-11}$	$7.53 \times 10^{-11}$	$5.99 \times 10^{-11}$	$4.87 \times 10^{-11}$	$3.95 \times 10^{-11}$
196	$5.00 \times 10^{-11}$		$3.58 \times 10^{-11}$	$2.67 \times 10^{-11}$	$2.06 \times 10^{-11}$	$1.55 \times 10^{-11}$	$1.22 \times 10^{-11}$
183	$2.53 \times 10^{-11}$		$1.77 \times 10^{-11}$	$1.25 \times 10^{-11}$	$9.25 \times 10^{-12}$	$6.90 \times 10^{-12}$	$5.38 \times 10^{-12}$
173	$1.46 \times 10^{-11}$		$9.36 \times 10^{-12}$	$6.61 \times 10^{-12}$	$4.40 \times 10^{-12}$	$3.09 \times 10^{-12}$	

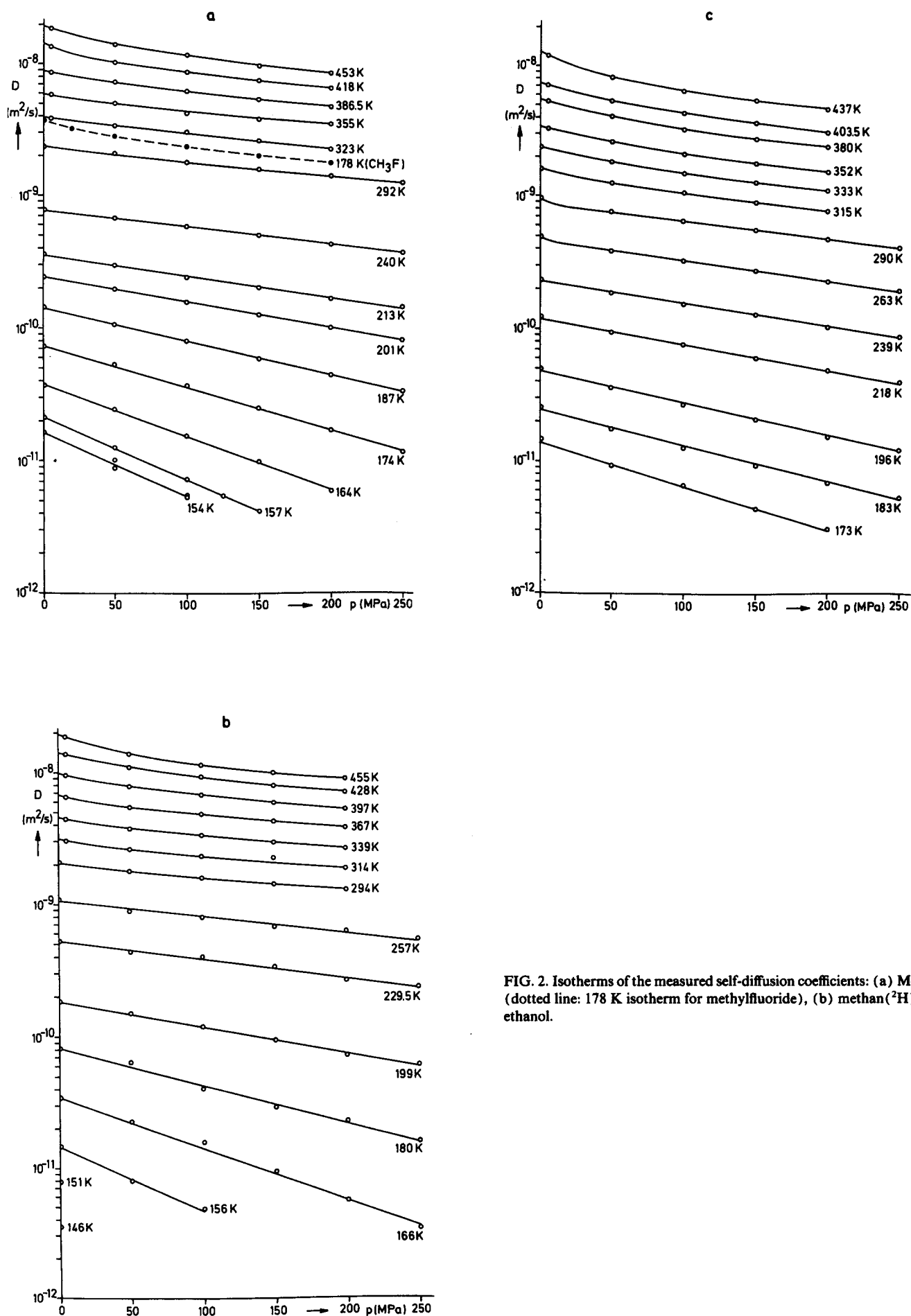


FIG. 2. Isotherms of the measured self-diffusion coefficients: (a) Methanol (dotted line: 178 K isotherm for methylfluoride), (b) methan( $^2\text{H}$ )ol, (c) ethanol.

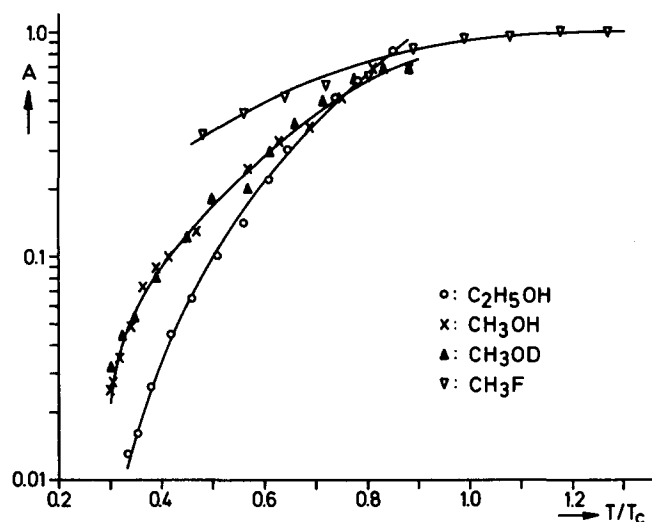


FIG. 3. Temperature dependence of the  $A$ -parameter for methanol ( $T_c = 513$  K), methan( $^2\text{H}$ )ol, ethanol ( $T_c = 516$  K), and methylfluoride ( $T_c = 318$  K).

mental diffusion coefficient  $D_{\text{exp}}$  can be expressed in terms of the hard-sphere diffusion coefficient  $D_{\text{HS}}$ :

$$D_{\text{exp}} = A D_{\text{HS}} = A \frac{D_0}{n} P(n) \quad (1)$$

where  $D_0$  is derived from the Chapman-Enskog solution of the Boltzmann equation.  $P(n = \rho\sigma^3)$  is an empirical polynomial in the packing fraction, that has been deduced from a recent reassessment<sup>24</sup> of available computer simulations of the hard-sphere fluid and accommodates correlated motions and backscattering effects. Chandler ascribed the difference between  $D_{\text{exp}}$  and  $D_{\text{HS}}$  to rotation-translation coupling, which is taken into account by introducing the coupling parameter  $A$  ( $0 < A \leq 1$ ).

In halomethanes, this factor decreases with falling temperature and this decrease becomes really dramatic in the cold alcohols. Figure 3 shows the fitted  $A$ -values on a reduced temperature scale for methanol, methan( $^2\text{H}$ )ol, and ethanol in comparison to data obtained previously for methylfluoride.<sup>3</sup> As can be seen, the temperature dependence of  $A$  for  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  is identical within the limits of error. For ethanol, the decrease of  $A$  with falling temperature is even more pronounced.

TABLE IV. Fit results (rough hard-sphere model) for the three alcohols compared with those for methylfluoride.

Substance	Temperature range (K)	$A$	$\sigma (10^{-10} \text{ m})$
$\text{CH}_3\text{OH}$	154–453	0.025–0.68	3.88–3.59
$\text{CH}_3\text{OD}$	156–455	0.032–0.67	3.91–3.59
$\text{CH}_3\text{F}$	150–375	0.4–1.0	3.47–3.61
$\text{C}_2\text{H}_5\text{OH}$	173–437	0.013–0.82	4.39–4.25

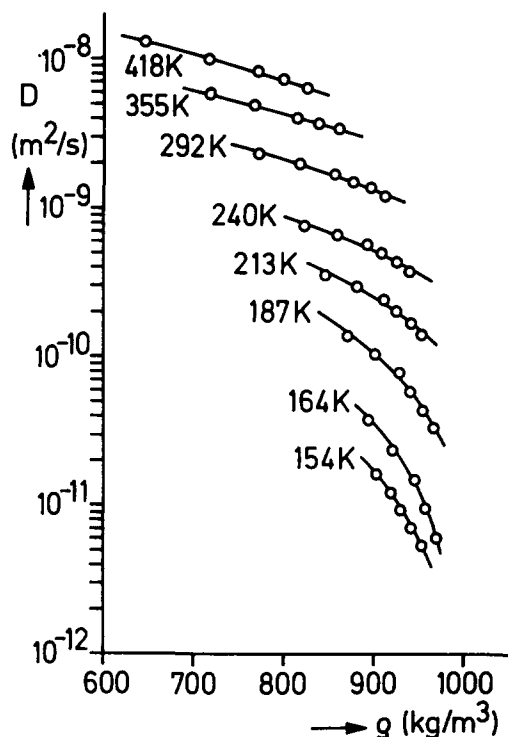


FIG. 4. Self-diffusion coefficient for  $\text{CH}_3\text{OH}$  plotted against density. For clarity several isothermal data sets are omitted. The solid lines represent calculated values with Eq. (1).

In Table IV, best fit results for  $A$  and  $\sigma$  are collected and compared to  $\text{CH}_3\text{F}$ . Our data are in excellent agreement with those given by Hurle *et al.*<sup>22</sup> for methanol and methan( $^2\text{H}$ )ol and with the values presented by Meckl and Zeidler<sup>23</sup> for ethanol. In all liquids, the effective hard-sphere diameter rises only slightly when temperature is reduced. The smallest variation of  $\sigma$  is seen in methylfluoride.

The quality of the least-squares fits (LSF) for the density dependence of  $D$  in methanol is illustrated in Fig. 4. The standard deviations of the fits for the alcohols vary between 2–3%. Larger deviations at the lowest temperatures are believed to originate from uncertainties in density which were not available over the whole  $p, T$ -range covered by our experiments. Densities were taken from the sources compiled in Table V. At the extreme temperatures the values had to be extrapolated graphically.

The drastic decrease of  $A$  with falling temperature cannot be ascribed to a coupling of rotational and translational motions only. Besides this coupling, the  $A$ -parameter comprises all other effects neglected in the RHS-model such as the influence of attractive parts of the intermolecular potential as well as strongly anisotropic interactions, e.g., hydrogen bonding.

For the alcohols,  $(1-A)$  is considered to describe approximately the degree of hydrogen bonding.<sup>22</sup> The variation of  $A$  agrees with the expected temperature dependence of the extent of hydrogen bonding in associated liquids. It

TABLE V. Sources of density.

	<i>T</i> (range) (K)	<i>p</i> range (MPa)	References
CH <sub>3</sub> OH	278–323	0.1–275	25
	298–623	50–800	26
	298–473	0.1–100	27
	175–800	0.1–70	28
	203–263	0.1–280	37
CH <sub>3</sub> OD	223–323	1–500	21
C <sub>2</sub> H <sub>5</sub> OH	293–318	0.1	29
	273–333	0.1–280	30

becomes thus obvious that a strongly temperature-dependent interaction has to be incorporated into any physically meaningful description of the self-diffusion coefficient for hydrogen-bonded liquids by a modified hard-sphere treatment.

## B. VTF description

At the present state of knowledge, the best description of the isobaric temperature dependence of *D* in hydrogen-bonded liquids is offered by the empirical VTF equation:<sup>31</sup>

$$D_{\text{exp}} = D_0 \exp\left(\frac{-B}{T - T_0}\right), \quad (2)$$

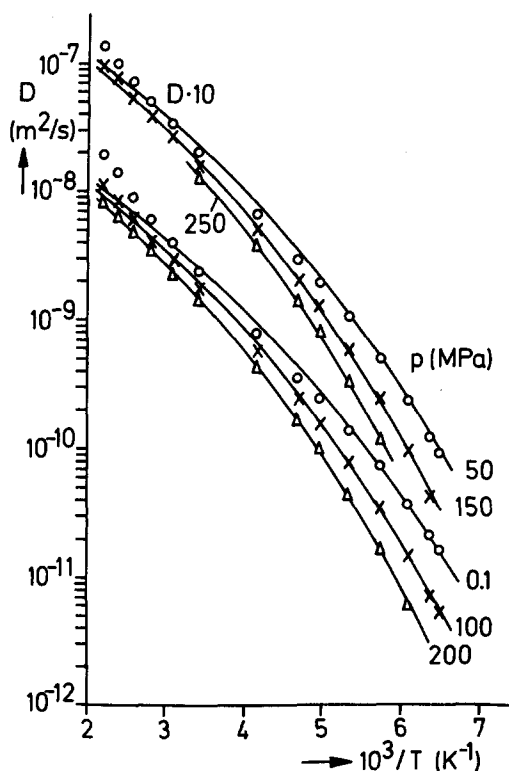


FIG. 5. Isobars of the self-diffusion coefficient for methanol. The solid lines represent calculated values with Eq. (2). For clarity the isobars at 50, 150, and 250 MPa are multiplied by a factor of 10.

TABLE VI. Fit results (VTF equation) for methanol, methanol(<sup>2</sup>H)ol, and ethanol.

	<i>p</i> (MPa)	<i>T</i> <sub>0</sub> (K)	<i>B</i> (K)	<i>B</i> × <i>T</i> <sub>0</sub> <sup>−1</sup>
MeOH	0.1	62	775	12.5
	50	64	800	12.5
	100	67.5	820	12.1
	150	69	850	12.3
	200	70	875	12.5
	250	71	900	12.7
MeOD	0.1	66	775	11.7
	50	68	800	11.8
	100	71.5	820	11.5
	150	73	850	11.6
	200	74	875	11.8
	250	75	900	12.0
EtOH	0.1	57	1000	17.5
	50	59.5	1040	17.5
	100	61.5	1050	17.1
	150	63.5	1080	17.0
	200	65	1110	17.1
	250	66	1135	17.2

*T*<sub>0</sub> represents the ideal glass-transition temperature while *B* is proportional to the change in heat capacity at the glass transition and thus accessible by experiments. In the case of liquids with an Arrhenius dependence of *D*, the parameter *B* is proportional to the activation energy *E*<sub>A</sub>.

Within the precision of the data, all alcohols can be described by the VTF equation with a pressure-independent factor *D*<sub>0</sub> that is identical for all compounds. Figure 5 gives the fits of the individual isobars according to Eq. (2) together with the experimental values for methanol. The fit parameters for the three compounds are collected in Table VI.

*D*<sub>0</sub> was kept at a value of  $7.5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$  for the three alcohols. In order to relate the pre-exponential factor *D*<sub>0</sub> in the VTF equation to a physically meaningful quantity, we compared it to the Enskog diffusion coefficient for a dilute gas<sup>32</sup>

$$D_0 = 3\sigma/8(k_B T/\pi m)^{1/2}.$$

This seems justified, because *D*<sub>0</sub> represents the high-temperature limit of Eq. (2). At the respective critical temperatures for the measured alcohols and at  $\sigma$ -values obtained from the rough hard-sphere calculation, a *D*<sub>0</sub> value of  $2.8 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$  is revealed. Although VTF and hard-sphere treatment are based on quite different concepts, the qualitative agreement of *D*<sub>0</sub> (they differ by a factor of 2.8) gives an indication that the VTF equation does not just provide an empirical formula but can be related to physically accessible quantities.

The ideal glass-transition temperature *T*<sub>0</sub> for methanol at 0.1 MPa was taken from Ref. 33. *B* values and the pressure dependence of *T*<sub>0</sub> were obtained by fitting the single isobars. For methan(<sup>2</sup>H)ol, no reliable glass-transition temperature was available and so both, *T*<sub>0</sub> and *B* were regarded as fit parameters.

Since no dependable *T*<sub>0</sub> value for ethanol could be found

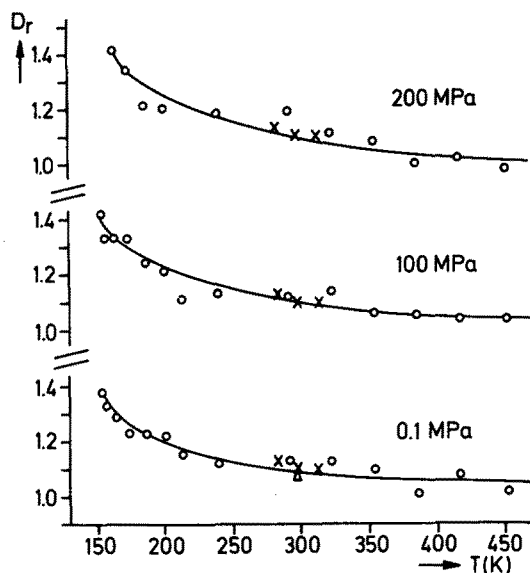


FIG. 6.  $D_r = D_{\text{CH}_3\text{OH}}/D_{\text{CH}_3\text{OD}}$  plotted against temperature at 0.1, 100, and 200 MPa.  $\circ$ : our results,  $\times$ : results from Hurle *et al.* (Ref. 22),  $\triangle$ : Weingärtner *et al.* (Ref. 36).

in the literature, we compared values of the experimental glass-transition temperature  $T_g$  of  $\text{CH}_3\text{OH}$  (Refs. 33 and 34) and  $\text{C}_2\text{H}_5\text{OH}$  (Ref. 35) and assumed a  $T_0$  of 57 K at 0.1 MPa.

Increasing the pressure to 250 MPa forces the glass temperatures to rise by approximately 10 K. As is shown in Table IV, the ratio  $B T_0^{-1}$  is pressure independent with values of 12.4, 11.7, and 17.2 for methanol, methan( $^2\text{H}$ )ol, and ethanol, respectively. The ratios for  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  are close to the value of 12.7 given by Angell<sup>33</sup> resulting from dielectric relaxation measurements for a series of alcohols.

While the hard-sphere treatment is based on single-particle motion, the VTF equation describes the dynamics of associated liquids. However, the apparent incompatibility of these two approaches can be resolved, when the retarding influence of collective motion on the diffusion coefficient is incorporated into the temperature dependence of the  $A$ -parameter in the rough hard-sphere treatment.

For the technical reasons given before, the data sets end well above the ideal glass transition and the fitting thus extrapolates over a fairly wide temperature range. This is especially the case for ethanol, where  $T_0$  lies about 115 K below the lowest measured isotherm. For this alcohol, a description of the diffusion data with an Arrhenius dependence is also possible. Hitherto unavailable results in the closer vicinity of  $T_0$  should provide a more stringent test for the validity of the VTF description.

### C. Dynamic isotope effects

In order to study the influence of isotopic substitution on translational mobility, the self-diffusion coefficients of

TABLE VII. Moments of inertia and masses for methanol and methan( $^2\text{H}$ )ol;  $I_r = I(\text{CH}_3\text{OD})/I(\text{CH}_3\text{OH})$  and  $m_r = m(\text{CH}_3\text{OD})/m(\text{CH}_3\text{OH})$ .

	Moments of inertia ( $10^{-46}$ kg m <sup>2</sup> ).		
	<i>a</i>	Axis <i>b</i>	<i>c</i>
$I(\text{CH}_3\text{OH})$	0.658	3.401	3.532
$I(\text{CH}_3\text{OD})$	0.767	3.576	3.818
$(I_r)^{1/2}$	1.08	1.02	1.04
Molecular masses ( $10^{-3}$ kg)			
$m(\text{CH}_3\text{OH})$	32.04		
$m(\text{CH}_3\text{OD})$	33.07		
$(m_r)^{1/2}$	1.016		

methanol and partially deuterated methanol ( $\text{CH}_3\text{OD}$ ) were measured over the same wide temperature range. Figure 6 gives the ratios of  $D$  for three isobars from 150–450 K. Especially in the supercooled region, the ratios reveal a pronounced temperature dependence.

At the lowest temperature,  $D_r = D_{\text{CH}_3\text{OH}}/D_{\text{CH}_3\text{OD}}$  reaches a maximum value of 1.4. This cannot be attributed to differences in molar volume, since for  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  it differs by < 1%.

According to kinetic theories for simple liquid dynamics, one would expect  $D_r$  to depend on the square root of the inverse mass ratio. For methanol and methan( $^2\text{H}$ )ol this leads to a value of 1.016, which cannot account for the differences in  $D$ .

The data for  $D_r$  presented by Hurle *et al.*<sup>22</sup> between 283–313 K and the value given by Weingärtner *et al.*<sup>36</sup> for 298 K are in very good agreement with our results. Keeping in mind that there seems to exist a strong rotation–translation coupling in methanol, Hurle *et al.* as well as Weingärtner *et al.* compared their results for  $D_r$  with the inverse ratios of the square roots of the moments of inertia (Table VII). However, the temperature dependence of  $D_r$  as presented in Fig. 6 cannot be explained by this approach. It follows that the  $p, T$ -dependence of the mobility of the methanol molecules is not determined by the mechanics of the single free methanol molecule but is a collective property reflecting the dynamics of the hydrogen-bond network.

A similar temperature dependence of the isotope effect can be observed in other hydrogen-bonded liquids such as water.<sup>9</sup> Most probably the observed temperature dependence of the isotope effect in methanol originates from the same effect. In liquid water this difference was assigned to the formation of more and stronger hydrogen bonds in  $\text{D}_2\text{O}$ . Their influence should become more pronounced at low temperatures.

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