

Hydrogen bonding in liquid methanol and ethanol determined by x-ray diffraction^{a)}

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The x-ray diffraction patterns of liquid methanol and ethanol have been measured at 20 °C. The data are analyzed to yield the molecular structures, and the distinct structure functions $H_d(k)$ are analyzed to obtain the hydrogen bonding in these alcohols. The data show clearly that hydrogen-bonded hydroxyl groups occur in methanol and ethanol with an OH...OH distance of 2.8 Å, and that each hydroxyl group has 1.8 ± 0.1 nearest neighbors at this distance.

I. INTRODUCTION

Alcohols were among the first liquids to which the method of x-ray diffraction was applied.^{1,2} Zachariasen³ applied the method of Fourier analysis to these data and concluded that the hydroxyl groups are linked by hydrogen bonding, each hydroxyl group having about two hydroxyl groups from neighboring molecules at a distance of roughly 2.5 Å. Later investigations⁴⁻⁷ have confirmed this conclusion. Neutron diffraction studies^{8,9} have added some information on hydrogen distances.

As part of a systematic study of liquid hydrocarbons¹⁰⁻¹³ and alcohols,¹⁴ we here present x-ray diffraction data for liquid methanol and ethanol at 20 °C. We will discuss the hydrogen bonding scheme characteristic of these liquids, insofar as it can be deduced directly from the x-ray data. The data will provide a sensitive test for statistical mechanical models of these liquids.

II. EXPERIMENT AND DATA REDUCTION

The alcohols used in the experiments were obtained from Aldrich Chemical Co. The purity claimed by the manufacturer was > 99wt %. The experiments were carried out at 20 °C and atmospheric pressure. Under these conditions the number densities¹⁵ and isothermal compressibilities,¹⁵ used in the data reduction, are as listed in Table I.

The x-ray measurements were made using reflection geometry¹⁶ and monochromatic MoK_α radiation ($\lambda = 0.7107$ Å). The range of scattering angles measured cov-

er the interval $0.3 < k < 16 \text{ Å}^{-1}$, where $k = (4\pi/\lambda) \sin \theta$ and 2θ is the scattering angle. Sufficient counts were accumulated at each scattering angle to keep the statistical errors in the structure functions (defined below) approximately uniform and less than ± 0.003 over the range of k .

Corrections for background, absorption,¹⁷ polarization, incoherent scattering,¹⁸ monochromator discrimination,¹⁶ and multiple scattering¹⁹ were applied. The corrected cross sections were normalized to the scattering from a single, average site in an alcohol molecule, $S_s(k) = n^{-1} \sum_{\alpha} f_{\alpha}^2(k)$ (where this and the following sums are over the n scattering sites in a molecule), with $f_{\alpha}(k)$ the x-ray scattering factor of site α . For the work reported here, the -OH, -CH₂, and -CH₃ groups were treated as single scattering sites.²⁰ Thus, ethanol was considered to be composed of one -CH₃, one -CH₂, and one -OH group. The coherent scattering factors were taken from Table I of Ref. 10. The scattering functions $S(k)$ for the two alcohols thus obtained are shown in Fig. 1. A noteworthy feature of these curves is a shoulder near 1 Å on the first main diffraction peak for methanol, which develops into a peak near 0.8 Å for ethanol. The "inner peak" is characteristic of all alcohols that have been studied by x-ray diffraction and has been much discussed over the years.^{2,14,21,22}

TABLE I. Site number densities ρ and isothermal compressibilities β_T used in the data reduction for methanol and ethanol studied by x-ray diffraction at 20 °C.

| | $\rho (\text{Å}^{-3})$ | $\beta_T (\text{Pa}^{-1})$ |
|----------|------------------------|----------------------------|
| Methanol | 0.029 76 | 1.21×10^{-9} |
| Ethanol | 0.030 96 | 1.11×10^{-9} |

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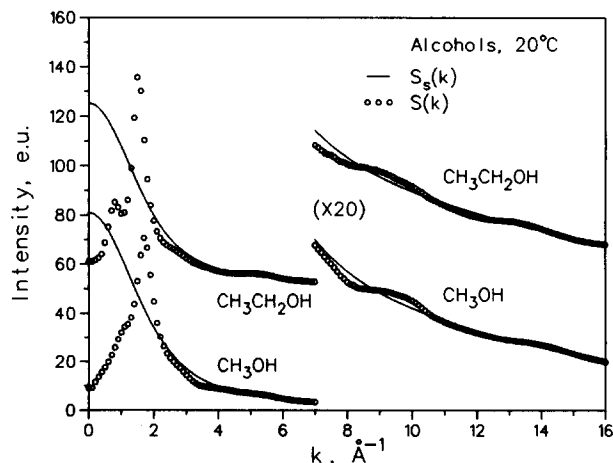


FIG. 1. The normalized static coherent scattering function $S(k)$ and the self-scattering from independent scattering sites $S_s(k)$ for liquid methanol and ethanol at 20 °C. The ethanol curves are displaced by + 50 units.

TABLE II. Intramolecular distances $r_{\alpha\gamma}$ and associated rms-deviations $l_{\alpha\gamma}$ obtained from the x-ray diffraction data on methanol and ethanol.

| | $r_{\alpha\gamma}$ (Å) | $l_{\alpha\gamma}$ (Å) |
|-----|------------------------|------------------------|
| C-O | 1.437(2) | 0.064(2) |
| C-C | 1.540(3) | 0.042(5) |
| C-O | 2.472(4) | 0.056(5) |

The next step in the data reduction was to construct the total structure function $H(k)$, defined as

$$H(k) = H_m(k) + H_d(k) = M(k)[S(k) - S_s(k)]. \quad (1)$$

The factor $M(k)$ is given by

$$M(k) = \left[n^{-1} \sum_{\alpha} f_{\alpha}(k) \right]^{-2}, \quad (2)$$

and the molecular structure function is given by

$$H_m(k) = M(k)n^{-1} \sum_{\alpha} \sum_{\gamma \neq \alpha} f_{\alpha}(k) f_{\gamma}(k) j_0(kr_{\alpha\gamma}) \times \exp(-l_{\alpha\gamma}^2 k^2/2), \quad (3)$$

where $l_{\alpha\gamma}$ is the root-mean-square (rms) deviation of the local instantaneous site-site separation distance $r_{\alpha\gamma}$, and $j_0(x) = x^{-1} \sin x$.

Since, in general, the function $H_d(k)$ decays to zero much faster than $H_m(k)$, $H(k) \simeq H_m(k)$ at large values of k . By a least squares fitting of Eq. (3) to the large k portion of the experimental structure function $H(k)$, we have obtained the molecular parameters $r_{\alpha\gamma}$ and $l_{\alpha\gamma}$ listed in Table II. The procedure was to obtain the parameters for the C-O bond from the methanol data. These values were then used in the analysis of the ethanol data, from which the parameters for the C-C bond and the nonbonded C-O interaction was obtained.

The molecular structure functions $H_m(k)$, calculated from the parameters listed in Table II, are shown in Fig. 2

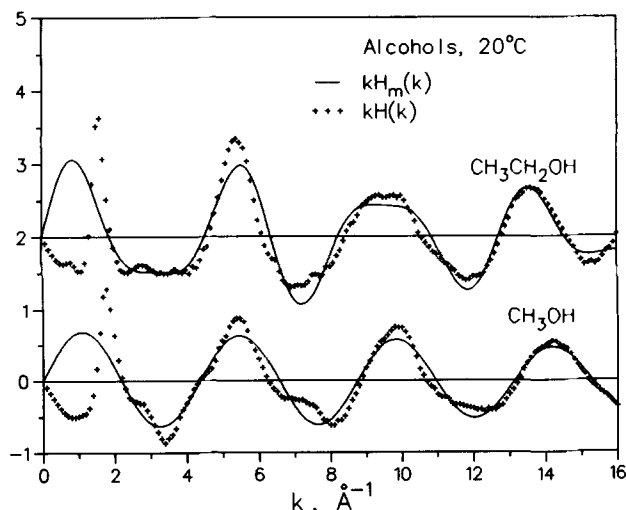


FIG. 2. The k -weighted structure functions for ethanol and methanol at 20°C derived from experiment. Subtraction of the fitted molecular structure functions $H_m(k)$ from the total structure functions $H(k)$ yields the distinct structure functions $H_d(k)$ shown in the next figure. The ethanol curves are displaced by +2 units.

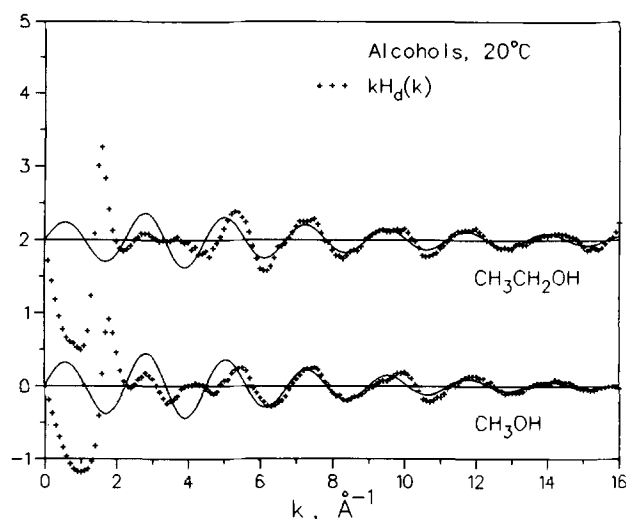


FIG. 3. The k -weighted distinct structure functions $H_d(k) = H(k) - H_m(k)$ describe the intermolecular site-site correlations in liquid methanol and ethanol. The solid curve is the least squares fit to the large- k portion of $H_d(k)$ resulting in 1.8 OH...OH interactions shown in the next figure. The ethanol curve is displaced by +2 units.

together with the total structure functions derived from experiment. The distinct structure functions $H_d(k) = H(k) - H_m(k)$, shown in Fig. 3, contain all information about intermolecular correlations in the liquid alcohols, which is accessible from x-ray diffraction. The function $H_d(k)$ was extrapolated to $H_d(0)$, as calculated²³ from the compressibility. The functions $H(k)$ and $H_d(k)$ are listed in Table III.

III. DATA ANALYSIS

The main focus of our work is the determination of the intermolecular, rather than molecular, structures of molecular liquids, thus the remainder of this paper will deal with the analysis of the distinct structure functions $H_d(k)$. These functions can be written as

$$H_d(k) = M(k) \sum_{\alpha} \sum_{\gamma \neq \alpha} f_{\alpha}(k) f_{\gamma}(k) a_{\alpha\gamma}(k), \quad (4)$$

where the partial structure functions $a_{\alpha\gamma}(k) = \rho \hat{h}_{\alpha\gamma}(k)$ are defined to be

$$\hat{h}_{\alpha\gamma}(k) = 4\pi \int_0^{\infty} r^2 h_{\alpha\gamma}(r) j_0(kr) dr, \quad (5)$$

with $h_{\alpha\gamma}(r) = g_{\alpha\gamma}(r) - 1$. The intermolecular site-site distribution function is defined so that $\rho g_{\alpha\gamma}(r) dr$ is the number of γ sites in a volume element dr a distance r from an α site on another molecule in a fluid of bulk site number density ρ .

Fourier inversion of the function $H_d(k)$ derived from experiment yields a radial distribution function

$$G_d(r) = 1 + (2\pi^2 \rho r)^{-1} \int_0^{\infty} k H_d(k) \sin(kr) dk \quad (6)$$

which, from Eqs. (4) and (5), is seen to be a weighted sum of site-site distribution functions modified by products of the site-site scattering factors. This function is mainly of use in identifying the peak locations of the dominant site-site correlations. Figure 4 shows the radial distribution functions

TABLE III. The total structure function $H(k)$ and the distinct structure function $H_d(k)$ for methanol and ethanol from x-ray diffraction.

| k | H(k) | H _d (k) | k | H(k) | H _d (k) | k | H(k) | H _d (k) | k | H(k) | H _d (k) |
|----------|---------|--------------------|-----|---------|--------------------|------|---------|--------------------|------|---------|--------------------|
| Methanol | | | | | | | | | | | |
| 0.0 | -0.8873 | -1.8820 | | | | | | | | | |
| 0.1 | -0.8873 | -1.8820 | 4.1 | -0.0563 | 0.0029 | 8.1 | -0.0765 | -0.0159 | 12.1 | -0.0338 | 0.0088 |
| 0.2 | -0.8566 | -1.8410 | 4.2 | -0.0288 | 0.0088 | 8.2 | -0.0675 | -0.0147 | 12.2 | -0.0326 | 0.0085 |
| 0.3 | -0.8276 | -1.7950 | 4.3 | -0.0117 | 0.0046 | 8.3 | -0.0664 | -0.0222 | 12.3 | -0.0355 | 0.0033 |
| 0.4 | -0.7991 | -1.7430 | 4.4 | 0.0080 | 0.0035 | 8.4 | -0.0585 | -0.0234 | 12.4 | -0.0313 | 0.0045 |
| 0.5 | -0.7679 | -1.6820 | 4.5 | 0.0169 | -0.0074 | 8.5 | -0.0456 | -0.0203 | 12.5 | -0.0323 | -0.0002 |
| 0.6 | -0.7306 | -1.6090 | 4.6 | 0.0258 | -0.0169 | 8.6 | -0.0318 | -0.0163 | 12.6 | -0.0323 | -0.0045 |
| 0.7 | -0.6837 | -1.5210 | 4.7 | 0.0359 | -0.0237 | 8.7 | -0.0212 | -0.0157 | 12.7 | -0.0287 | -0.0056 |
| 0.8 | -0.6258 | -1.4170 | 4.8 | 0.0574 | -0.0171 | 8.8 | -0.0082 | -0.0125 | 12.8 | -0.0265 | -0.0085 |
| 0.9 | -0.5583 | -1.2990 | 4.9 | 0.0930 | 0.0056 | 8.9 | 0.0066 | -0.0071 | 12.9 | -0.0204 | -0.0077 |
| 1.0 | -0.4916 | -1.1780 | 5.0 | 0.1134 | 0.0153 | 9.0 | 0.0200 | -0.0025 | 13.0 | -0.0145 | -0.0072 |
| 1.1 | -0.4270 | -1.0560 | 5.1 | 0.1233 | 0.0169 | 9.1 | 0.0295 | -0.0012 | 13.1 | -0.0095 | -0.0077 |
| 1.2 | -0.3767 | -0.9458 | 5.2 | 0.1463 | 0.0341 | 9.2 | 0.0405 | 0.0026 | 13.2 | -0.0033 | -0.0068 |
| 1.3 | -0.2895 | -0.7970 | 5.3 | 0.1584 | 0.0429 | 9.3 | 0.0507 | 0.0065 | 13.3 | 0.0028 | -0.0058 |
| 1.4 | -0.1393 | -0.5843 | 5.4 | 0.1635 | 0.0472 | 9.4 | 0.0576 | 0.0082 | 13.4 | 0.0116 | -0.0019 |
| 1.5 | 0.1117 | -0.2706 | 5.5 | 0.1610 | 0.0462 | 9.5 | 0.0613 | 0.0079 | 13.5 | 0.0173 | -0.0006 |
| 1.6 | 0.4242 | 0.1042 | 5.6 | 0.1492 | 0.0383 | 9.6 | 0.0665 | 0.0102 | 13.6 | 0.0230 | 0.0012 |
| 1.7 | 0.6926 | 0.4335 | 5.7 | 0.1243 | 0.0193 | 9.7 | 0.0723 | 0.0143 | 13.7 | 0.0276 | 0.0024 |
| 1.8 | 0.7102 | 0.5102 | 5.8 | 0.0939 | -0.0032 | 9.8 | 0.0768 | 0.0185 | 13.8 | 0.0304 | 0.0024 |
| 1.9 | 0.5281 | 0.3845 | 5.9 | 0.0731 | -0.0144 | 9.9 | 0.0754 | 0.0179 | 13.9 | 0.0325 | 0.0024 |
| 2.0 | 0.3193 | 0.2290 | 6.0 | 0.0506 | -0.0259 | 10.0 | 0.0745 | 0.0189 | 14.0 | 0.0340 | 0.0023 |
| 2.1 | 0.1374 | 0.0967 | 6.1 | 0.0299 | -0.0343 | 10.1 | 0.0679 | 0.0154 | 14.1 | 0.0364 | 0.0040 |
| 2.2 | 0.0221 | 0.0269 | 6.2 | 0.0087 | -0.0424 | 10.2 | 0.0588 | 0.0103 | 14.2 | 0.0383 | 0.0058 |
| 2.3 | -0.0467 | -0.0009 | 6.3 | -0.0065 | -0.0439 | 10.3 | 0.0459 | 0.0023 | 14.3 | 0.0373 | 0.0053 |
| 2.4 | -0.0960 | -0.0138 | 6.4 | -0.0173 | -0.0406 | 10.4 | 0.0317 | -0.0062 | 14.4 | 0.0339 | 0.0031 |
| 2.5 | -0.1078 | 0.0057 | 6.5 | -0.0242 | -0.0334 | 10.5 | 0.0152 | -0.0164 | 14.5 | 0.0323 | 0.0034 |
| 2.6 | -0.1092 | 0.0306 | 6.6 | -0.0337 | -0.0292 | 10.6 | 0.0065 | -0.0184 | 14.6 | 0.0299 | 0.0033 |
| 2.7 | -0.1159 | 0.0452 | 6.7 | -0.0377 | -0.0199 | 10.7 | -0.0020 | -0.0198 | 14.7 | 0.0251 | 0.0014 |
| 2.8 | -0.1135 | 0.0640 | 6.8 | -0.0350 | -0.0048 | 10.8 | -0.0073 | -0.0178 | 14.8 | 0.0197 | -0.0008 |
| 2.9 | -0.1404 | 0.0485 | 6.9 | -0.0352 | 0.0064 | 10.9 | -0.0104 | -0.0136 | 14.9 | 0.0146 | -0.0023 |
| 3.0 | -0.1647 | 0.0312 | 7.0 | -0.0373 | 0.0145 | 11.0 | -0.0178 | -0.0138 | 15.0 | 0.0102 | -0.0029 |
| 3.1 | -0.1974 | 0.0010 | 7.1 | -0.0390 | 0.0217 | 11.1 | -0.0207 | -0.0099 | 15.1 | 0.0063 | -0.0028 |
| 3.2 | -0.2226 | -0.0259 | 7.2 | -0.0371 | 0.0309 | 11.2 | -0.0205 | -0.0032 | 15.2 | 0.0012 | -0.0038 |
| 3.3 | -0.2433 | -0.0518 | 7.3 | -0.0409 | 0.0328 | 11.3 | -0.0225 | 0.0007 | 15.3 | -0.0028 | -0.0038 |
| 3.4 | -0.2548 | -0.0721 | 7.4 | -0.0445 | 0.0332 | 11.4 | -0.0279 | 0.0006 | 15.4 | -0.0051 | -0.0020 |
| 3.5 | -0.2284 | -0.0574 | 7.5 | -0.0455 | 0.0345 | 11.5 | -0.0290 | 0.0041 | 15.5 | -0.0084 | -0.0014 |
| 3.6 | -0.2076 | -0.0511 | 7.6 | -0.0502 | 0.0304 | 11.6 | -0.0290 | 0.0080 | 15.6 | -0.0114 | -0.0009 |
| 3.7 | -0.1784 | -0.0385 | 7.7 | -0.0592 | 0.0204 | 11.7 | -0.0300 | 0.0098 | 15.7 | -0.0134 | 0.0004 |
| 3.8 | -0.1320 | -0.0106 | 7.8 | -0.0694 | 0.0075 | 11.8 | -0.0309 | 0.0110 | 15.8 | -0.0164 | 0.0003 |
| 3.9 | -0.1029 | -0.0014 | 7.9 | -0.0712 | 0.0016 | 11.9 | -0.0316 | 0.0114 | 15.9 | -0.0198 | -0.0006 |
| 4.0 | -0.0794 | 0.0012 | 8.0 | -0.0773 | -0.0100 | 12.0 | -0.0319 | 0.0113 | 16.0 | -0.0227 | -0.0014 |
| Ethanol | | | | | | | | | | | |
| 0.0 | -0.8560 | -2.8390 | | | | | | | | | |
| 0.1 | -0.8560 | -2.8390 | 4.1 | -0.1251 | -0.0324 | 8.1 | -0.0443 | -0.0258 | 12.1 | -0.0461 | 0.0094 |
| 0.2 | -0.8470 | -2.7950 | 4.2 | -0.0972 | -0.0221 | 8.2 | -0.0315 | -0.0269 | 12.2 | -0.0438 | 0.0056 |
| 0.3 | -0.8320 | -2.7210 | 4.3 | -0.0999 | -0.0452 | 8.3 | -0.0232 | -0.0310 | 12.3 | -0.0418 | -0.0002 |
| 0.4 | -0.8070 | -2.6160 | 4.4 | -0.0738 | -0.0422 | 8.4 | -0.0070 | -0.0256 | 12.4 | -0.0339 | -0.0013 |
| 0.5 | -0.7360 | -2.4460 | 4.5 | -0.0396 | -0.0333 | 8.5 | 0.0086 | -0.0187 | 12.5 | -0.0273 | -0.0047 |
| 0.6 | -0.6340 | -2.2290 | 4.6 | -0.0297 | -0.0502 | 8.6 | 0.0187 | -0.0156 | 12.6 | -0.0196 | -0.0075 |
| 0.7 | -0.5200 | -1.9850 | 4.7 | 0.0242 | -0.0236 | 8.7 | 0.0224 | -0.0172 | 12.7 | -0.0100 | -0.0086 |
| 0.8 | -0.4450 | -1.7710 | 4.8 | 0.0667 | -0.0081 | 8.8 | 0.0328 | -0.0105 | 12.8 | 0.0015 | -0.0076 |
| 0.9 | -0.4540 | -1.6330 | 4.9 | 0.1099 | 0.0094 | 8.9 | 0.0458 | 0.0002 | 12.9 | 0.0101 | -0.0087 |
| 1.0 | -0.4740 | -1.5030 | 5.0 | 0.1555 | 0.0316 | 9.0 | 0.0507 | 0.0040 | 13.0 | 0.0187 | -0.0091 |
| 1.1 | -0.4368 | -1.3160 | 5.1 | 0.1982 | 0.0541 | 9.1 | 0.0551 | 0.0080 | 13.1 | 0.0306 | -0.0047 |
| 1.2 | -0.3038 | -1.0360 | 5.2 | 0.2296 | 0.0693 | 9.2 | 0.0580 | 0.0111 | 13.2 | 0.0384 | -0.0030 |
| 1.3 | 0.0072 | -0.5842 | 5.3 | 0.2475 | 0.0758 | 9.3 | 0.0604 | 0.0140 | 13.3 | 0.0410 | -0.0047 |
| 1.4 | 0.5203 | 0.0610 | 5.4 | 0.2489 | 0.0711 | 9.4 | 0.0605 | 0.0149 | 13.4 | 0.0440 | -0.0044 |
| 1.5 | 1.0117 | 0.6737 | 5.5 | 0.2347 | 0.0563 | 9.5 | 0.0564 | 0.0116 | 13.5 | 0.0480 | -0.0012 |
| 1.6 | 1.0185 | 0.7894 | 5.6 | 0.2169 | 0.0436 | 9.6 | 0.0558 | 0.0117 | 13.6 | 0.0487 | 0.0003 |
| 1.7 | 0.6291 | 0.4954 | 5.7 | 0.1816 | 0.0188 | 9.7 | 0.0573 | 0.0139 | 13.7 | 0.0478 | 0.0018 |
| 1.8 | 0.2860 | 0.2338 | 5.8 | 0.1339 | -0.0134 | 9.8 | 0.0580 | 0.0154 | 13.8 | 0.0462 | 0.0039 |
| 1.9 | 0.0536 | 0.0689 | 5.9 | 0.0854 | -0.0419 | 9.9 | 0.0538 | 0.0121 | 13.9 | 0.0425 | 0.0050 |
| 2.0 | -0.0786 | -0.0093 | 6.0 | 0.0384 | -0.0652 | 10.0 | 0.0559 | 0.0154 | 14.0 | 0.0362 | 0.0044 |
| 2.1 | -0.1652 | -0.0546 | 6.1 | 0.0089 | -0.0682 | 10.1 | 0.0490 | 0.0101 | 14.1 | 0.0310 | 0.0054 |
| 2.2 | -0.2083 | -0.0675 | 6.2 | -0.0191 | -0.0680 | 10.2 | 0.0387 | 0.0021 | 14.2 | 0.0252 | 0.0060 |
| 2.3 | -0.2154 | -0.0544 | 6.3 | -0.0375 | -0.0575 | 10.3 | 0.0323 | -0.0013 | 14.3 | 0.0190 | 0.0063 |
| 2.4 | -0.2061 | -0.0330 | 6.4 | -0.0471 | -0.0386 | 10.4 | 0.0201 | -0.0096 | 14.4 | 0.0125 | 0.0059 |
| 2.5 | -0.1830 | -0.0043 | 6.5 | -0.0500 | -0.0143 | 10.5 | 0.0049 | -0.0200 | 14.5 | 0.0067 | 0.0057 |
| 2.6 | -0.1654 | 0.0141 | 6.6 | -0.0726 | -0.0120 | 10.6 | -0.0023 | -0.0214 | 14.6 | -0.0003 | 0.0036 |
| 2.7 | -0.1444 | 0.0326 | 6.7 | -0.0892 | -0.0068 | 10.7 | -0.0082 | -0.0205 | 14.7 | -0.0051 | 0.0030 |
| 2.8 | -0.1400 | 0.0326 | 6.8 | -0.0962 | 0.0042 | 10.8 | -0.0139 | -0.0186 | 14.8 | -0.0098 | 0.0016 |
| 2.9 | -0.1373 | 0.0300 | 6.9 | -0.0995 | 0.0149 | 10.9 | -0.0196 | -0.0159 | 14.9 | -0.0159 | -0.0021 |
| 3.0 | -0.1475 | 0.0144 | 7.0 | -0.0974 | 0.0264 | 11.0 | -0.0229 | -0.0104 | 15.0 | -0.0213 | -0.0059 |

TABLE III. (continued).

| k | H(k) | H _d (k) | k | H(k) | H _d (k) | k | H(k) | H _d (k) | k | H(k) | H _d (k) |
|---------|---------|--------------------|-----|---------|--------------------|------|---------|--------------------|------|---------|--------------------|
| Ethanol | | | | | | | | | | | |
| 3.1 | -0.1505 | 0.0064 | 7.1 | -0.0930 | 0.0358 | 11.1 | -0.0284 | -0.0069 | 15.1 | -0.0254 | -0.0092 |
| 3.2 | -0.1586 | -0.0059 | 7.2 | -0.0939 | 0.0355 | 11.2 | -0.0327 | -0.0023 | 15.2 | -0.0243 | -0.0078 |
| 3.3 | -0.1489 | 0.0002 | 7.3 | -0.0913 | 0.0346 | 11.3 | -0.0346 | 0.0042 | 15.3 | -0.0230 | -0.0067 |
| 3.4 | -0.1504 | -0.0045 | 7.4 | -0.0830 | 0.0357 | 11.4 | -0.0388 | 0.0076 | 15.4 | -0.0244 | -0.0087 |
| 3.5 | -0.1454 | -0.0027 | 7.5 | -0.0698 | 0.0387 | 11.5 | -0.0419 | 0.0110 | 15.5 | -0.0218 | -0.0068 |
| 3.6 | -0.1347 | 0.0043 | 7.6 | -0.0675 | 0.0283 | 11.6 | -0.0471 | 0.0109 | 15.6 | -0.0173 | -0.0032 |
| 3.7 | -0.1214 | 0.0127 | 7.7 | -0.0686 | 0.0126 | 11.7 | -0.0495 | 0.0118 | 15.7 | -0.0127 | 0.0007 |
| 3.8 | -0.1294 | -0.0019 | 7.8 | -0.0666 | -0.0011 | 11.8 | -0.0515 | 0.0113 | 15.8 | -0.0102 | 0.0026 |
| 3.9 | -0.1287 | -0.0100 | 7.9 | -0.0530 | -0.0035 | 11.9 | -0.0505 | 0.0119 | 15.9 | -0.0055 | 0.0068 |
| 4.0 | -0.1146 | -0.0074 | 8.0 | -0.0512 | -0.0175 | 12.0 | -0.0462 | 0.0137 | 16.0 | 0.0024 | 0.0146 |

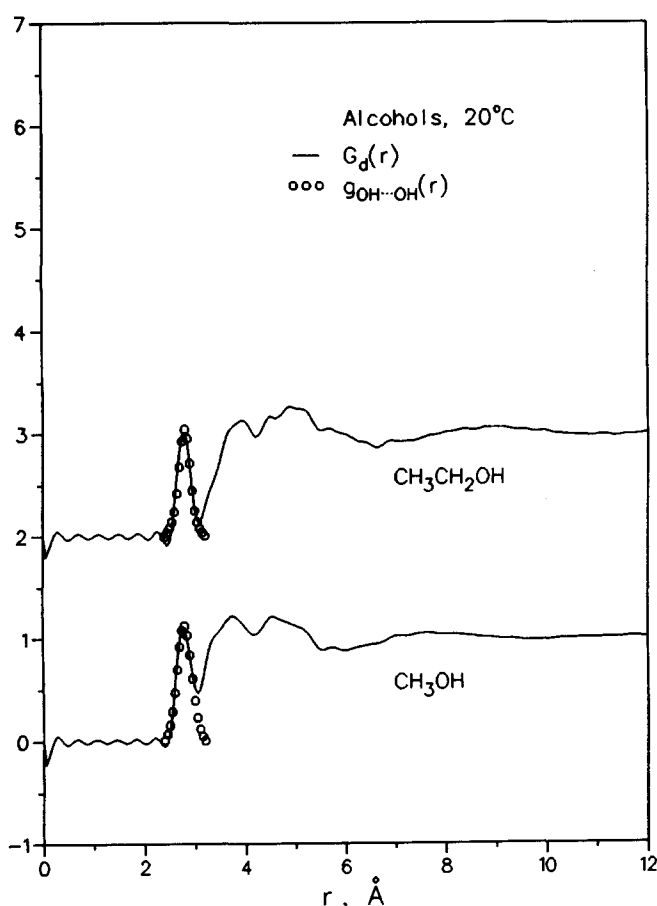


FIG. 4. The intermolecular radial distribution functions obtained by Fourier inversion of the curves shown in Fig. 3. The upper curve is displaced by + 2 units.

TABLE IV. Number of hydrogen-bonded OH...OH interactions n , per molecule, at distance r , with rms-deviation l , for methanol and ethanol studied by x-ray diffraction at 20 °C.

| | n | r (Å) | l (Å) |
|----------|---------|----------|----------|
| Methanol | 1.77(7) | 2.798(6) | 0.142(6) |
| Ethanol | 1.81(9) | 2.808(8) | 0.113(7) |

$G_d(r)$ for the alcohols studied here. The most striking feature of these plots is the presence of a strong peak near 2.8 Å which is absent in the curves for the alkanes.¹⁰⁻¹³ This peak must be ascribed to hydrogen-bonded hydroxyl groups.

The peak near 2.8 Å in the radial distribution functions of the alcohols is almost completely resolved, and well described by a peak computed for 1.8 OH...OH interactions (Fig. 4, circles). This result was obtained by fitting the large k part of the distinct structure functions $H_d(k)$ as described in Sec. II for the intramolecular interactions, with the coordination number as an additional parameter. The results are shown in Fig. 3 and listed in Table IV.

IV. SUMMARY AND CONCLUSIONS

Our x-ray data show clearly that, on the average, each hydroxyl group in the two alcohols studied has 1.8 hydroxyl neighbors from other molecules at a well defined intermolecular OH...OH distance of 2.8 Å. While further experimental information and/or statistical mechanical modelling^{24,25} are needed to completely define the intermolecular structure of the alcohols, our results could be understood in terms of chain formation. The molecules within such a chain are connected by OH...OH hydrogen bonds. The description of the arrangement of alcohol molecules in chains is, of course, an average one. There are large local and instantaneous deviations from the average configuration and, hence, we expect the correlations to extend only a few molecular diameters from any given molecule. At larger distances, the radial distribution functions of liquid alcohols differ from uniformity only by the small variations caused by the random fluctuations in density expected for a liquid consisting of single molecules. This view is in agreement with small-angle x-ray diffraction studies,²⁶ which show that the scattering function $S(k)$ for several alcohols is constant, with a value $S(0)$ equal to that computed from the isothermal compressibility.

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