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Quantum effects in the electronic structure of liquid methanol measured by γ -ray diffraction

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Abstract. The electronic structure factors for liquid light methanol (CH_3OH) and heavy methanol (CD_3OD) have been measured at 23°C under their normal vapour pressures using a γ -ray beam from an ^{241}Am radio-isotope source. Observable differences between the electronic structure factors of the two liquids reveal small, but real changes in their r -space correlation functions. This is due to quantum effects in the intermolecular and intramolecular electron density correlation functions and will be discussed in terms of the structures of light and heavy liquid methanol.

1. Introduction

Classical molecular fluids are often assumed to be comprised of rigid, heavy molecules. However, for hydrogenous molecules several quantum corrections to this model are required. For example, there are quantum effects due to zero-point librations and the finite wavelength of light atoms. In the case of a system such as liquid methanol, these effects lead to both intramolecular and intermolecular structural changes. Perhaps the best known change is that in the intramolecular C–O distance [1–3], which has been found by neutron scattering to be $1.418(7)$ Å in the deuterated liquid at room temperature and by x-ray scattering to be $1.437(3)$ Å in the hydrogenated liquid. Some of this difference may be related to the choice of independent atomic form factors in the x-ray work, but we shall discuss this possibility elsewhere and assume the correctness of these data here.

Since the scattering amplitudes of electromagnetic radiation are identical for H and D isotopes, the quantum effects will lead to small changes between the x-ray or γ -ray diffraction patterns for hydrogenated and deuterated samples. These measurements therefore provide a direct test of the theory of quantum effects in nearly classical fluids.

Liquid methanol is a good candidate for the study of quantum effects because it is sensitive to hydrogen-bonding effects and its structure is well known [1–3]. In particular, figure 6 of [3] shows that the intramolecular correlations occur below about 2.5 Å whereas the intermolecular interactions occur beyond 2.5 Å. The quantum effects are also reflected in the thermodynamic properties of the hydrogenated and deuterated liquids, reported in standard tables.

2. Experimental details

The γ -ray experiments were performed on an in-house diffractometer at the University of Guelph using a 2.8 Ci, ^{241}Am radiation source ($\lambda = 0.2083$ Å), see [4, 5] for details. The

scattered intensity was measured as a function of angle by rotating the source in small steps of 0.16° about the sample. A NaI scintillation detector situated in the low-angle region ($\theta = 1^\circ$ to 20°) recorded the scattered γ -rays, whilst the Compton intensity was monitored by another detector at angles slightly greater than 90° and was used for the absolute normalization of the data. The Bragg peaks from a 9 mm diameter aluminium rod were used to calibrate the geometrical angles in the low- θ region. Numerical averaging was performed over the beam and sample cross sectional areas to give the intensity-averaged scattering angles [6].

High-purity methanol, CH_3OH (99.9+% supplied by Sigma-Aldrich Ltd) and CD_3OD (99.8% , Matheson Ltd) were used for the experiments. The corresponding number densities are 0.01487 and 0.01483 \AA^{-3} , respectively. Mass spectrometry was performed on the samples at the end of the experiment to check for any contamination and impurities were found to be much less than 0.1% abundant. The liquid samples were kept at a temperature of 22.6°C throughout the entire experiment. They were contained in Teflon (CF_2) sample vessels of inner diameter 11.1 mm and outer diameter 12.1 mm.

Data collection involved the repeated interchanging of CH_3OH and CD_3OD samples every 2–4 days with the diffractometer stepping through angular positions at 17 min intervals. The change in temperature between these interleaved runs was only 0.4°C . Empty vessel and background measurements were also performed to the same statistical accuracy. The total measurement time was 6 months. In addition a series of γ -ray transmission measurements was performed to measure the total attenuation of the main beam by the sample.

3. Data analysis

A full set of equations required to extract the single-scattering electronic structure factor for the sample, $S_s(Q)$, using this diffractometer has already been given in the literature [4, 5]. For methanol the total x-ray structure factor, $S_s(Q)$, will approach 18 electron units at large Q , namely the asymptotic level due to Compton scattering. It includes the intermolecular structure factor, $D(Q)$, an intramolecular form factor, $\langle F^2 \rangle$, and a Compton-scattering term $C(Q)$. We observed that the principal peak near 1.8 \AA was about 1% higher in the H compound.

The required quantity is the difference between the methanol CH_3OH and CD_3OD structure factors, written $\Delta S_s(Q)$ (see equation (7) of [4]), which is given by

$$\Delta S_s(Q) = \Delta D(Q) + \Delta \langle F^2 \rangle + \Delta C(Q) \approx \Delta D(Q) + \Delta \langle F^2 \rangle. \quad (1)$$

Subsequently we assumed that there is no difference in the Compton scattering from light and heavy methanol so that $\Delta C(Q) = 0$. The experimental data were smoothed by a maximum entropy technique [8], and the original and smoothed results are shown in figure 1. The intramolecular form factors $\langle F^2 \rangle$ for the two compounds were calculated using the independent atom approximation given, for example, by equation (6b) of Narten and Levy [9] using the atomic form factors of [7, 10] and bond lengths of [1–3]. It is useful to compare this result for $\Delta \langle F^2 \rangle$ with the observed liquid data shown in figure 1.

The interpretation of the difference function is simplified and more easily understood by transforming the smoothed $\Delta S_s(Q)$ into real space, to yield the difference in electronic pair correlation functions, $\Delta g(r)$. The transformed data are shown in figure 2 (full line) together with the transform of $\Delta \langle F^2 \rangle$ (broken line). In performing this transform a window function was applied (see [9]) to terminate the data smoothly at their limit of $Q_{\text{max}} = 10.3 \text{ \AA}^{-1}$. This has the effect of slightly broadening the peaks in figure 2. Also the data in figure 2 were

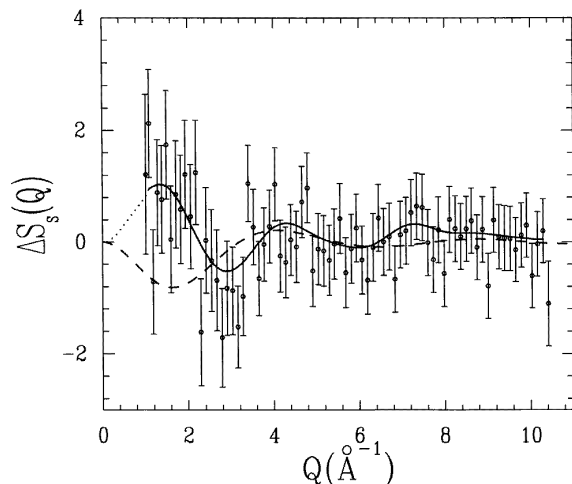


Figure 1. The experimental difference $\Delta S_s(Q)$ for CH_3OH minus CD_3OD at 23°C is given by the points and error bars and the full line is a maximum entropy fit to these data. The broken line corresponds to $\Delta(F^2)$ for the atomic form-factor model of [9].

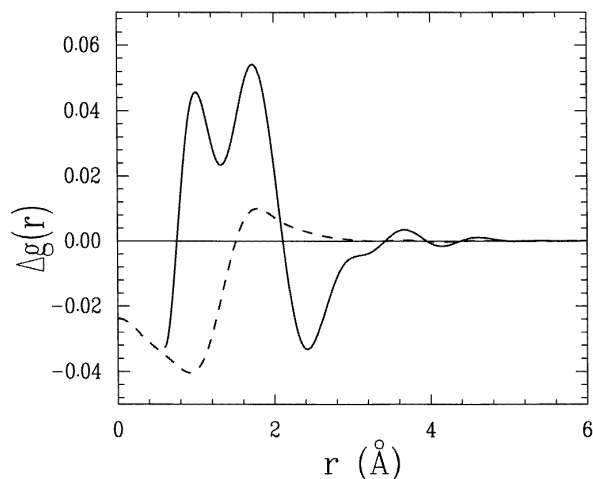


Figure 2. The full line is the Fourier transform of the full line in figure 1, including both intramolecular and intermolecular contributions. The broken line is the transform of our model $\Delta(F^2)$ given in figure 1. The $\Delta g(r)$ scale is per electron.

terminated at $r = 0.6 \text{ \AA}$, to correspond with the requirement $r > 2\pi/Q_{\text{max}}$. The error in the experimental data has been estimated by transforming alternative smooth lines through the data of figure 1. This showed that the experimental errors are about 0.005 on the scale of figure 2.

4. Discussion and conclusions

Several measurements of the structure of methanol have been reported. Neutron diffraction measurements of liquid CD_3OD [3] at 20°C have shown clear peaks in the nuclear $g(r)$, corresponding to the intramolecular C–D, O–D, D–D and C–O correlations. Also conventional x-ray diffraction data for liquid methanol at 20°C have been reported by several authors [1, 2].

It may be seen from figure 2 that, for the model of the single molecule, the electron density near the molecular centre (about 0.71 \AA) is greater in the D than it is in the H

compound. This is to be expected due to the slightly smaller C–O distance in the deuterated compound. For the same reason the anti-bonding electron density, near 2 Å, yields a positive difference. At higher r , corresponding to the intermolecular region, the broken line drops to zero as expected.

For liquid methanol the electron distribution clearly differs from that of the model. The intramolecular difference is shifted to higher r and most noticeably it is positive. This suggests that the independent atom model is a poor representation of the molecule in the liquid. Possibly the greater wavelength of the hydrogen atoms, compared with that of the deuterium atoms, leads to a wider density distribution for the lighter molecule. As a result the negative dip related to the electron density of deuterium atoms would be smaller and the anti-bonding peak wider.

In addition the experimental data show oscillations over the intramolecular to intermolecular region when $r > 2$ Å. The largest intramolecular O–H distance is about 2 Å and this is close to the smallest intermolecular distance. Because the electron distributions are more localized in the D molecule this region of $\Delta g(r)$ is negative. A rise is seen in $\Delta g(r)$ at higher r due to the wider electron distribution in the hydrogenated molecule. The intensity levels out at about 2.8 Å, corresponding to the O...O intermolecular distance between adjacent molecules. Also minor structure is observable beyond this distance.

It would be useful if quantum molecular dynamics simulations could be performed to compare with our experiments. In the case of water they have already been performed [11]. These simulations have shown that structural differences between light and heavy water provide a sensitive test of the intermolecular potential for water. Also, it would be interesting if the electron distribution for the free molecule could be obtained for the calculation of $\Delta\langle F^2 \rangle$, for example from accurate molecular orbital calculations. In addition, with the use of modern-day synchrotron radiation sources it is anticipated that a more extensive range of experimental data will be obtained in this field [12] eventually. A full report will be published elsewhere.

Acknowledgments

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