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Local order in fully deuterated liquid acetic acid as studied by neutron scattering. Complementarity to X-ray results

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ABSTRACT

A structural investigation of fully deuterated liquid acetic acid (AA_{d4}) was performed at 298 K and atmospheric pressure by using neutron scattering. The recorded data are analyzed to yield the total structure factor $S_M(q)$, the molecular form factor $F_1(q)$, the distinct pair correlation function $g_L(r)$ and the second signature of H-bonding, i.e. the deuterium oxygen interaction. Neutron scattering data, as well as recent X-ray studies, clearly show that the local order of the liquid is largely described by the short-range crystal structure.

1. Introduction

Understanding the nature of the hydrogen-bonding interaction is very important, considering its role as a special type of chemical bond and also its pervasive presence in biochemical systems [1–3]. In fact, the structure of biomolecules, the most prominent being double-stranded DNA, is determined by these bonds between nucleic acid base pairs [4]. In a more general sense, protein structures are stabilized by hydrogen bonding interactions. Moreover, they largely determine the physical properties of many common condensed-phase systems. Indeed, short-range ordering is much better developed in hydrogen-bonded liquids than in liquids where molecules interact solely by normal Van der Waals forces. Over the last decades, there has been an impressive progress in elucidating a hydrogen-bonded molecular structure. The first step in these processes involves the investigation of small model molecules. Acetic acid (AA), one of the simplest carboxylic acids, is among the liquid media in which the intermolecular hydrogen bond plays a significant part in the determination of the properties of a substance and thus, can be studied as a prototype of the $O-H\cdots O$ hydrogen bond. It is also used in many different industrial products and considered as a main chemical reagent [5].

The structure of acetic acid molecules, containing the fragment $O{=}C-O-H$, is favorable to the formation of various hydrogen-bonded complexes in different arrangement forms. Short-range order of acid acetic has been a subject of extensive investigations for many years [6–25]. AA has one hydrogen-bond donor and one hydrogen-bond acceptor. The carbonyl $C{=}O$ and the hydroxyl $O-H$ are active hydrogen acceptor and donor groups respectively. They tend to form double $O_{C=O}\cdots H_{O-H}$ H-bonds, resulting in the centrosymmetric cyclic dimer in the gas phase [6,7] and some nonpolar solvents. Using the X-ray diffraction, Nahringbauer [9] investigated the crystal structure of AA; he showed that acetic acid molecules form hydrogen-bonded zigzag chains made up of cis molecules joined by $O-H\cdots O$ bonds with the length 2.63 Å. The conformer cis designs that the hydrogen atom of hydroxyl group is at the same side of the carbonyl oxygen atom. – Neutron diffraction investigations [26,27] illustrated that the molecules formed an H – bonded chain structure. Neutron results also confirmed that the hydrogen bond length is equal to 2.63 Å. In 2000, a density functional theory was applied by Rovira and Novoa [28] to study the structure of solid acetic acid. The computed structure of the acetic acid crystal, optimized without symmetry constraints, replicates the changes in the intramolecular structure when going from the gas to the solid phases. A quantum calculation of the solid structure was performed by Allouche and Bahr [29] in 2006. They exhibited that intramolecular distances are very comparable to the experimental ones and the experimental hydrogen-bond length is about 0.05 Å shorter than the calculated value.

Information on the liquid structure is, however, more limited than that on the gaseous and crystalline phases. In fact, the liquid-state structure of acetic acid continues to be a significant and challenging problem. It is also the subject of many experimental and theoretical studies including spectroscopic measurements, ab-initio calculations and diffraction techniques [30–37]. In the recent experimental study [38,39], the measurements of neutron diffraction on the pure liquid structure showed that the associated cyclic dimer structure yields a good and predominant model. The same molecular association was supported by many authors such as Waldstein and Blatz [30], Nielsen and Lund [31], Flakus and Tyl [32] and Benmalti et al. [33] by using different

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experimental and theoretical techniques. In contrast, recent investigations dealing with short-range order in the liquid suggested that acetic acid molecules prefer to be arranged in linear chains [34,35,39]. Theoretically, Monte Carlo simulations and ab-initio MO calculation on Raman spectroscopy have indicated that liquid acetic acid is mainly composed of hydrogen-bonded chains as the fragments of the crystalline networks and not of cyclic dimers [13,16,17,34–36].

In considering this diversity of the formed clusters in the liquid acetic acid, we have performed a structural investigation of the liquid (AA) by X-ray scattering at 298 K [35]. By considering the intramolecular geometry as it has been found in the crystalline state, the intermolecular parameters have been experimentally deduced and the short-range order is described by a trimer organization similar to that existing in the crystalline state whereas cyclic dimer formation is excluded.

In this paper, in order to obtain further insight into the local order of the liquid, we report on the structural investigation of fully deuterated liquid acetic acid (AA_{d4}) by using neutron scattering. This study is considered as complementary to the one performed by X-ray scattering. Experimental data are first analyzed to yield the total structure factor and the intermolecular pair correlation function. Second, the substitution effect H/D on the intra- and intermolecular interactions is examined. Third, the more probable model as deduced from a previous X-ray study [35] is reexamined to describe the short-range in fully deuterated liquid AA_{d4}.

2. Experiment details

The fully deuterated acetic acid (AA_{d4}) was supplied by C/D/N isotopes (chemical purity of 99%+). In the experiments, AA was used without further purification. The sample holders were filled and sealed in a glove box in order to avoid contamination by atmospheric water.

The neutron scattering experiments were performed at the reactor Orphée of the Laboratoire Léon Brillouin, at Saclay (France) using a 7C2 spectrometer. All details about this spectrometer are reported by Ambroise, Bellissent-Funel, and Bellissent [37,38]. This spectrometer is equipped with a BF_3 position sensitive detector with 640 cells; the angular step between two adjacent cells is equal to 0.2°, which leads to a maximum diffraction angle of 125.15°. We select an incident wavelength of $\lambda = 0.718$ Å by means of a Cu (111) monochromator. The sample is contained inside a vanadium cell, having an inner diameter of 3 mm and an outer diameter of 3.1 mm. All experiments are carried out at 298 K. The usual measurements of the vanadium rod, the cadmium rod and the empty cryostat were also performed.

3. Theoretical considerations: Neutron scattering

The coherent contributions of differential scattering cross-section of an assembly of N molecules each with m atoms is given, in the static approximation, by [39]

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \frac{1}{N}\left\langle \sum_{j,k=1}^{N} \sum_{\alpha,\beta=1}^{m} b_{j\alpha} b_{k\beta} expiq\left(r_{j\alpha} - r_{k\beta}\right) \right\rangle \tag{1}$$

where $b_{j\alpha}$ is the coherent scattering length of the nucleus after averaging over all isotopes and nuclear spins; $q = k_0 - k$ is the scattering wave vector, where k_0 and k are the wave vectors of incident and scattered radiations, respectively ($|q| = q = {}^{4\pi \sin\Theta}\!/_{\lambda}$ in the case of elastic scattering), 2Θ is the scattering angle, λ is the wavelength of the radiation and $r_{j\alpha}$ is the position vector of the atom α in the molecule j. The ⟨ ⟩ brackets denote an average over the grand canonical ensemble.

It is convenient to divide the coherent contributions of the differential cross-section into separate compounds corresponding to self and distinct parts [40]

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{self} + \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{distinct}, \tag{2}$$

where

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{self} = \sum_{\alpha=1}^{m} b_{coh,\alpha}^{2}; \tag{3}$$

the distinct part can be separated into intra- and inter-molecular terms corresponding to correlations between atoms within the same molecule or atoms belonging two different molecules, respectively,

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{distinct} = \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{intra} + \left(\frac{d\sigma}{d\Omega}\right)_{coh}^{inter}. \tag{4}$$

The intramolecular part of the differential cross-section is [41]

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{intra} = \sum_{\substack{\alpha,\beta=1\\ \alpha\neq\beta}}^{m} b_{coh,\alpha} b_{coh,\beta} J_0\left(q r_{\alpha\beta}\right) \exp\left[-\left\langle \Delta r_{\alpha\beta}^{2}\right\rangle \frac{q^2}{2}\right], \tag{5}$$

where $J_0(x) = \sin x/x$ is the spherical Bessel function of the zero order and $\langle \Delta r_{\alpha\beta}^2 \rangle^{1/2} = \mu_{\alpha\beta}$ is the root mean-square (r.m.s.) vibrational amplitude for the α–β atom pair.

The intermolecular part is

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{inter} = \sum_{\alpha=1}^{m} b_{\alpha}^{2} \times D_M(q), \tag{6}$$

where $D_M(q)$ contains the information on the intermolecular pair correlation function.

The interference function or total structure factor $S_M(q)$ of liquid is given by (AA):

$$S_M(q) = \left[\left(\frac{d\sigma}{d\Omega}\right)_{coh}^{distinct} + \sum_{\alpha=1}^{m} b_{coh,\alpha}^{2}\right] \Big/ \left(\sum_{\alpha=1}^{m} b_{coh,\alpha}\right)^{2}. \tag{7}$$

At large q, $S_M(q)$ goes to the asymptotic value $S_M(\infty) = \left(\sum_{\alpha=1}^{m} b_{coh,\alpha}^{2}\right) / \left(\sum_{\alpha=1}^{m} b_{coh,\alpha}\right)^{2}$.

For $q \to 0$, $\lim_{Q\to 0}\left(\frac{d\sigma}{d\Omega}\right)_{coh} = \rho K_B T \chi_T \left(\sum_{\alpha=1}^{m} b_{coh,\alpha}\right)^{2}$, where ρ is the molecular number density; K_B, the Boltzmann's constant; T, the absolute temperature; and, χ_T, the isothermal compressibility.

For molecular liquids, it is convenient to separate the structure factor into two parts [42]:

$$S_M(q) = F_1(q) + D_M(q), \tag{8}$$

where $F_1(q)$ contains the intramolecular and self parts of the interference function [42]

$$F_1(q) = \sum_{\alpha,\beta=1}^{m} b_{coh,\alpha} b_{coh,\beta} J_0\left(q r^{\alpha\beta}\right) \exp\left[-\left\langle \Delta r_{\alpha\beta}^{2}\right\rangle \frac{q^2}{2}\right] \Big/ \left(\sum_{\alpha=1}^{m} b_{coh,\alpha}\right)^{2}. \tag{9}$$

At high q-values, the $F_1(q)$ curve oscillates around the asymptotic value $S_M(\infty) = 0.12$.

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