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On the local intermolecular ordering and dynamics of liquid chloroform

John J. Karnes, Ilan Benjamin *

Department of Chemistry and Biochemistry, University of California-Santa Cruz, Santa Cruz, CA 95064, United States

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ABSTRACT

Recently published neutron scattering experiments suggest local molecular 'polar stacking' in bulk liquid chloroform. We present molecular dynamics simulations of liquid chloroform that confirm the existence of these structures in relative populations that agree with experiment. Removing the electrostatic contributions to the chloroform force field leaves these structures mostly unchanged. Dynamic studies show that the lifetimes of these short-lived structures are also unchanged when disabling electrostatics. This set of results confirms that these polar-stacked structures are the result of geometrical packing, as opposed to dipole-dipole interactions or other electrostatic driving forces. We also extend this investigation of local intermolecular ordering in chloroform to relate these polar stacking populations to the well-known 'Apollo configuration,' where nearby molecules have collinear, head-to tail-dipole moment vectors. We find that the 'Apollo configuration' represents only a very small fraction of the total population in bulk liquid $CHCl_3$.

1. Introduction

The intermolecular structure and ordering of neat liquids have been investigated with diffraction experiments and computer simulations for several decades [1–11]. Molecules with simple symmetry, like the nearly tetrahedral chloroform ($CHCl_3$), receive particular attention, as knowledge of their structure serves as a stepping-stone toward systems of greater complexity. Understanding intermolecular structure may also lead to insights toward chloroform's outstanding solvation properties that result in its widespread use in both research and manufacturing capacities despite chloroform's well-documented detrimental health effects and safety concerns [12–15]. Understanding the precise nature of $CHCl_3$'s solvation ability could lead toward alternate solvents with similar properties.

We shall not summarize decades of $CHCl_3$ structural research here, but instead direct readers toward the review recently published by Pusztai and co-workers [16]. The present work focuses on a long-standing orientational question related to the existence of the 'Apollo configuration.' In this Apollo configuration nearest-neighbor chloroform molecules have parallel, collinear dipoles with the hydrogen atom being located in the "hollow formed by three chlorine atoms" [17] of the neighboring $CHCl_3$, as illustrated by the cartoon in Fig. 1a. The Apollo configuration has been dismissed by most researchers in the field [16, 18], but its possible existence as an important structural feature in $CHCl_3$ was suggested recently in the neutron diffraction (ND) experiments by Shephard et al. [19] In this work, the authors introduce 'polar stacking:' a quantitative definition of local dipole-dipole ordering in bulk liquid chloroform. The criteria for 'polar stacking' were defined as follows: A vector that begins at the C atom of the reference $CHCl_3$ molecule and points toward its H atom is defined. The neighboring $CHCl_3$ is in a polar stack with the reference $CHCl_3$ molecule if (1) its H atom is between 2.0 and 4.2 Å from the reference C atom and (2) and the H-C⋯H angle is between 150° and 210°. Fig. 1b is a cartoon schematic of this definition, where the green $CHCl_3$ molecule is in a polar stack with the reference molecule and the red $CHCl_3$ molecules are not. Analysis of ND data suggests that 29.3% of $CHCl_3$ molecules participate in these structures and that these head-to-tail dipole orientations may extend well beyond two neighboring $CHCl_3$ molecules to include 'polar stacks' that consist of up to 5 $CHCl_3$ molecules [19]. These stacks are further postulated to form 'super dipole' aggregates, which may enhance solvation and extraction properties. We note the distinction between 'polar stacking' and the Apollo configuration: The 'polar stacking' definition is based on three atomic centers (H, C, and the neighboring H) and is a measure of head-to-tail dipole vector configurations. Quantification of the 'Apollo configuration' requires an additional constraint regarding dipole-dipole collinearity or parallelism and is necessary for the existence of the "super dipole" aggregates.

The present work uses computer simulations to search for and study the dynamics of these stacked structures as described by Shephard et al. In addition, by removing the electrostatic contribution from intermolecular potential energy functions we can gain insight into the role of electrostatic vs. packing effects in determining the existence of these structures. Disabling the electrostatics in MD simulations has been shown to have little effect on the local intermolecular ordering of liquid $CBrCl_3$, a molecule that shares $CHCl_3$'s C_{3v} symmetry and is also of

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* Corresponding author.
E-mail address: benjamin@chemistry.ucsc.edu (I. Benjamin).

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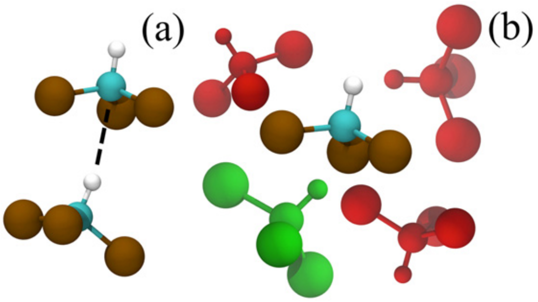

Fig. 1. Cartoon schematics of (a) $CHCl_3$ molecules in the 'Apollo configuration and (b) $CHCl_3$ molecules in a 'polar stack.' The molecule arranged in a 'stack' with the reference molecule is green, those not participating in the stack are red.

similar size [20], although the magnitude of the $CBrCl_3$ dipole moment vector is much smaller than in liquid $CHCl_3$. However, disabling some of the electrostatics in a system with much stronger coulombic interactions, a hydroxylated silica surface, results in a relatively dramatic change in the local ordering of an adjacent liquid alcohol phase [21]. This change in interfacial ordering is due to disruption of the local hydrogen-bonding network between the silica surface and the adjacent liquid phase. We also extend the analysis of $CHCl_3$ local structure to quantify a relationship between polar stacking and the Apollo configuration. Since $CHCl_3$ molecules participating in a 'polar stack' have their dipole moment vectors in a head-to-tail orientation, adding a dipole moment colinearity constraint will reveal the subset of 'polar stacked' $CHCl_3$ molecules that are also in the 'Apollo configuration.'

2. Simulation details

We use a chloroform force field that gives rise to site-site radial distribution functions that are in good agreement with those calculated by other force fields and are in agreement with results of previous experiments. Classical molecular dynamics simulations of neat liquid chloroform are performed using our in-house code. We use an all-atom, 5-site, fully flexible, fixed-charge $CHCl_3$ model where the intermolecular interaction potential is the pairwise sum of Lennard-Jones and Coulombic terms

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{q_i q_j}{4\pi r \varepsilon_0} \tag{1}$$

where r is the distance between atom centers i and j. Standard Lorentz-Berthelot combining rules, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$, are used to generate mixed interaction parameters. Details of this model have been described elsewhere [22,23] but for convenience we include a full listing of the inter- and intramolecular potential energy parameters in Tables 1 and 2. The simulation box consists of 794 $CHCl_3$ molecules in a truncated octahedron whose enclosing cube has an edge length of 59.69 Å. The simulations in this work consist of only fixed-charge (non-polarizable) force fields and sample two extreme cases: the aforementioned fixed partial charges used in our previous studies ($\langle\mu\rangle = 1.4$ D) and the nonphysical case of a zero-charge $CHCl_3$. All molecular dynamics simulation data presented in this work represents the ensemble average of 10^6 configurations obtained during 10 ns of simulation time. Simulations were performed at 298 K with an integration time step of 0.5 fs.

Table 1
Intermolecular potential parameters used in the $CHCl_3$ model.

Atom	σ (Å)	ε (kcal/mol)	q (e)
C	3.20	0.101	0.32
Cl	3.50	0.348	−0.14
H	2.75	0.0266	0.10

Table 2
Stretch and bend equilibrium values and force constants.

Equilib. value	Force const. (×kcal/mol)
$r^{eq}_{CCl} = 1.77$ Å	$k_{CCl} = 630$ Å^{-2}
$r^{eq}_{CH} = 1.07$ Å	$k_{CH} = 725$ Å^{-2}
$\theta^{eq}_{ClCCl} = 112.0°$	$k_{ClCCl} = 149$ rad^{-2}
$\theta^{eq}_{ClCH} = 106.8°$	$k_{ClCH} = 95.6$ rad^{-2}

3. Results and discussion

3.1. Survey of local structure: spatial distribution functions

When considering the molecular structure of a liquid composed of a nearly-spherical or pseudo-spherical species like chloroform, it is reasonable to expect the overall *molecular* arrangement to resemble a model of close-packed spheres, like the common textbook examples of liquid argon [24] or "Lennard-Jonesium" [25]. Following a standard approach, we may first quantitatively describe the structure of a bulk liquid using the radial distribution function, $g_{A\text{-}B}(r)$

$$g_{A\text{-}B}(r) = \frac{1}{\eta_c}\left\langle \sum_{i=1}^{N} \delta(r - r_i) \right\rangle \tag{2}$$

where A is the reference atom center ($CHCl_3$'s central C atom in this work), B is the atom center of interest in the neighboring molecules, η_c is a normalization constant selected so that $g_{A\text{-}B}(r \to \infty) = 1$, and the ensemble average is collected over all N molecules and N possible reference atoms.

Fig. 2 shows the $g(r)$ curves for bulk liquid $CHCl_3$ at 298 K. The first peak of $g_{C\text{-}C}(r)$ (blue curve) is located at 5.4 Å and the first minima at 7.5 Å, in good agreement with previous reports [3,4,6,26]. The overall 'pseudo-spherical' shape of $CHCl_3$ does result in a $g_{C\text{-}C}(r)$ curve that resembles the radial distribution of close-packed spheres. The first two $g_{C\text{-}C}(r)$ peaks integrate to 8.9, indicating that the pseudo-spherical $CHCl_3$ is less tightly packed than actual close-packed spheres (like liquid argon or "Lennard-Jonesium"), whose first two peaks integrate to about 12 [24]. We also draw attention to the visible asymmetry of this first $g_{C\text{-}C}(r)$ peak, a feature that will be discussed at length later in this work. The green and red curves in Fig. 2 are $g_{C\text{-}Cl}(r)$ and $g_{C\text{-}H}(r)$. These curves represent the distribution of the atoms bonded to the central carbon atom in a (nearly) tetrahedral arrangement. The symmetry of the radial distribution function is far less spherical when considering the arrangement of tetrahedral pendant atoms (like Cl in CCl_4) and even less so for the 'nearly tetrahedral' surrounding atoms in $CHCl_3$. In both cases, $g_{C\text{-}Cl}(r)$ and $g_{C\text{-}H}(r)$, the region of r spanned by the first peak of $g_{C\text{-}C}(r)$

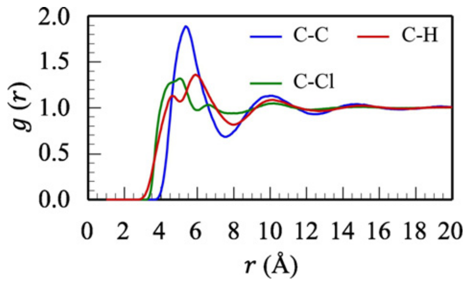

Fig. 2. Radial distribution functions referencing the central carbon atom in bulk liquid $CHCl_3$. Curves are displayed for $g_{C\text{-}x}(r)$ where x = C (blue), x = Cl (green), and x = H (red).