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Structure of liquid methylene chloride: Molecular dynamics simulation compared to diffraction experiments

Szabolcs Bálint, Imre Bakó, Tamás Grósz, Tünde Megyes *

Institute of Structural Chemistry, Chemical Research Center of the Hungarian Academy of Sciences, Pusztaszeri út 59-67, H-1025 Budapest, Hungary

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Abstract

Molecular dynamics simulation and diffraction (X-ray and neutron) studies are compared on methylene chloride with aiming at the determination of the liquid structure. Beyond that, the capabilities of the methods to describe liquid structure are discussed. For the studied liquid, the diffraction methods are performing very well in determination of intramolecular structure, but they do not give detailed structural information on the intermolecular structure. The good agreement between the diffraction experiments and the results of molecular dynamics simulations justify the use of simulations for the more detailed description of the liquid structure using partial radial distribution functions and orientational correlation functions. Liquid dichloromethane is described as a molecular liquid without strong intermolecular interactions like hydrogen bonding or halogen-halogen contacts, but with detectable orientational correlations resulting in antiparallel, tail-to-tail orientation of the first nearest neighbours, which is lost very quickly and slight preference of parallel head-to-tail and L-shaped orientation can be detected. On the other hand some orientational correlations between rather distant molecules can also be observed.

Keywords: Dichloromethane; Methylene chloride; X-ray diffraction; Neutron diffraction; Simulation; Liquid structure

1. Introduction

Methylene chloride (dichloromethane), belongs to a group of low-permittivity, dipolar, aprotic solvents, which are ideal media for a variety of important chemical reactions. It is a widely used solvent in supramolecular [1] and polymer chemistry [2]. Methylene chloride is a particularly suitable organic diluent for liquid–liquid extraction by carriers such as crown ethers, since it can solubilize reasonable amounts of extractants and extracted species [3]. Further on, being a chlorinated hydrocarbon, it has also been widely used as solvent in processing of radioactive materials and contributes significantly to nuclear waste remediation problems [4]. Methylene chloride is a volatile organic compound, which pollutes the environment and adversely affects human health. The European Community has issued directives to restrict chlorinated compounds and currently investigating risks posed by chemicals including chlorohydrocarbons [5]. To obtain detailed understanding of the role of solvent in different chemical systems and environment, it is clearly essential to model the pure solvent and to study its structure.

There exist various theoretical and experimental studies on the structure and properties of methylene chloride. Different spectroscopic methods (IR [6], Raman [7] and microwave [8,9] spectroscopic experiments, Rayleigh scattering [7a] and NMR relaxation [10]) were applied to study methylene chloride. Recently time resolved X-ray diffraction studies of liquid methylene chloride were conducted [11]. The parameters obtainable from spectroscopic experiments were compared to those calculated from molecular dynamics simulation.

Liquid methylene chloride has been investigated by molecular dynamics simulation [12–14] using different potential models, molecular Ornstein–Zernike theory [15] and Monte-Carlo simulation [16]. Methylene chloride was also studied by theoretical methods on liquid–liquid and liquid–vapor interfaces [17] and mixtures [18]. These studies were focused mainly on testing the developed model potentials and comparing their predictions with the experimentally accessible vibrational quantities and the overall dynamic [12a–14a,19] and thermodynamic [15a] behaviour of the liquid. However, the structural analysis did not go beyond the determination of the

* Corresponding author.
E-mail address: megyes@chemres.hu (T. Megyes).

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partial correlation functions and the determination of several structure functions in order to be compared to the experimental results. *Ab initio* molecular orbital calculations were performed by Torii [16] and density functional calculation of methylene chloride clusters by Canepa [20]. Only one attempt has been made on the detailed structural study of liquid methylene chloride by Reverse Monte Carlo (RMC) simulation [21], using early X-ray and neutron diffraction data.

Diffraction techniques serve, in principle, as direct method to determine the structure of the matter in condensed state. The crystalline structure of methylene chloride has been determined using single crystal X-ray diffraction [22]. Recently *in situ* high pressure single crystal X-ray study [23] of methylene chloride has been carried out focusing on the evaluation of crystal cohesion forces and behaviour of halogen contacts under compression. To the best of our knowledge, only one single X-ray diffraction study of liquid methylene chloride was conducted, by Orton et al. [24], but this experiment had been carried out in a limited k (0−10 $Å^{-1}$) range and the resulting structure function supposed to be rather inaccurate above 3 $Å^{-1}$. Jung et al. [25] performed neutron diffraction experiments on samples containing different isotopic mixtures.

In the present study we performed X-ray experiments on methylene chloride, in combination with molecular dynamics simulation. In order to obtain a more reliable picture of the liquid in study, molecular dynamics simulation results are compared to our X-ray diffraction measurements and neutron diffraction performed by Jung et al. [25]. To learn more about the mutual orientation of methylene chloride molecules we have also performed an *ab initio* study of methylene chloride dimer on MP2 level. The paper is organized as follows: In the 'methods' section we describe the quantum chemical calculations, and the simulation details and after the X-ray measurements and data treatments. In 'results and discussion' we present the experimental and theoretical results and compare them before 'conclusions' summarizes the main results.

2. Computational details

2.1. Quantum chemical calculations

All calculations were performed by using the Gaussian 03 program suite [26] at MP2 level of theory using the 6–311+G** basis set. The behaviour of the calculated stationary points was characterized by their harmonic vibrational frequencies. The interaction energies for each minimum were corrected for basis set superposition error (BSSE) with the full counterpoise (CP) procedure, resulting in a more reliable estimate of the interaction energy [27]. The magnitude of the BSSE correction at the energy minimum configuration is about 50–60% of the total interaction energy at MP2 level of theory. In principle, since the BSSE causes the intermolecular interactions to be too attractive, the CP correction is expected to make the complexes less stable [28].

2.2. Molecular dynamics simulation

We have performed a classical MD simulation in the NVT ensemble. The simulation box contained 512 rigid methylene chloride molecules. Three set of intermolecular potentials were used, namely, Torii, model 2 [16], Rothschild [19] and Evans [12] as given in Table 1. The side length of the cube was 37.913 Å corresponding to the experimental density of 1.312 g cm^{-3}. During the 50,000 time steps of equilibration the Nosé–Hoover thermostat was used to control the temperature in the DLPOLY 2.15 software [29]. The simulations were performed for 200,000 time steps leading to the total time of 400 ps.

Table 1
Interaction potential parameters for liquid methylene chloride

	σ (Å)	ε (kcal/mol)	q [a]	q [b]	q [c]
C	3.2	0.1013	−0.640	0.4474	−0.109
H	2.75	0.0266	0.317	−0.0551	0.098
Cl	3.35	0.347	0.003	−0.1686	0.002

[a] Ref. [16].
[b] Ref. [19].
[c] Ref. [12].

3. Experimental details

X-ray diffraction measurement was carried out on liquid methylene chloride, anhydrous, special grade, produced by Aldrich. The physical properties of the methylene chloride were: density $\rho = 1.31\ g \cdot cm^{-3}$, linear X-ray absorption coefficient $\mu_0 = 12.84\ cm^{-1}$, atomic number density $\rho_0 = 0.0464 \cdot 10^{-24}\ cm^{-3}$.

The X-ray scattering measurements were performed at room temperature (24±1 °C), with a Rigaku R-AXIS RAPID image plate diffractometer using MoKα radiation ($\lambda = 0.7107$ Å). Quartz capillaries (1.5 mm diameter, 0.01 mm wall thickness) were used as the liquid sample holder. The scattering angle range of measurement spannedover $4.80 \le 2\Theta \le 138.88°$ corresponding to a range of 0.74 $Å^{-1} \le k \le 16.55\ Å^{-1}$ of the scattering variable $k = (4\pi/\lambda) \cdot \sin(\Theta)$. In order to expand the scattering range to lower angle values another set of measurements was performed at room temperature (24±1 °C), with a Philips X'Pert goniometer in a vertical Bragg-Brentano geometry with a pyrographite monochromator in the scattered beam and proportional detector using MoKα radiation. In this case the scattering angle range of measurement spanned over $1.28 \le 2\Theta \le 130.2°$ corresponding to a range of 0.2 $Å^{-1} \le k \le 16.06\ Å^{-1}$ of the scattering variable $k = (4\pi/\lambda) \cdot \sin\Theta$.

Background and absorption corrections were applied based on an algorithm reported by Paalman and Pings [30] for cylindrical sample holders. This algorithm assumes that significant coupling does not occur between the sample and cell [31], therefore the experimentally observed intensities are considered as linear combination of an independent component from the confined sample and a component from the sample cell. The correction procedure was applied using in house software written in a Fortran language. The polarization and Compton scattering corrections were applied using standard methods given in earlier works [32].

The experimental structure function is defined as:

$$h(k) = I(k) - \sum_{\alpha} x_\alpha f_\alpha^2(k) M(k) \quad (1)$$