

SO₂Cl₂, SOCl₂: energy dispersive X-ray diffraction, ab initio and molecular dynamics calculation

S. Meloni ^{*}, A. Pieretti, L. Bencivenni, V. Rossi Albertini, C. Sadun, R. Caminiti

Dipartimento di Chimica, Istituto Nazionale per la Fisica della Materia, Universita' La Sapienza, P.le A. Moro 5, 00185 Roma, Italy

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Abstract

This work reports a new protocol for achieving microscopic structural information from theoretical (quantum-chemical (QC) and molecular dynamic (MD) calculations) and experimental methods (X-ray diffraction). The Lennard–Jones (L–J) parameters of the force field (FF) fit satisfactorily the X-ray diffraction results of the liquid samples. The study has been carried out on SOCl₂ and SO₂Cl₂ molecular liquids. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In this work, we propose a new protocol to obtain microscopical structural information by combining the action of different theoretical and experimental techniques.

X-ray diffraction on liquid sample provides important structural information about short-range ordered state of matter. Unfortunately, these measurements do not often admit univocal interpretation. In fact, there is no method for obtaining all the partial radial distribution functions ($D_{ij}(r)$, $i, j = 1, \dots, N$, where N is the number of different atomic species) by a single diffraction pattern, however, it is extended in the reciprocal space.

In case of liquid phase, averaged model in coordinate space must be proposed and tested in terms of capability to fit experimental results

(taking into account that different models having this property may exist). The model includes both intermolecular distances and the intramolecular ones and it is dependent on several independent parameters. Their reduction, simplifying the model, decreases its arbitrariness. This can be done by adding further information from other experimental techniques (electron diffraction, for instance) or theoretical calculations. We will refer to the first case as an *empirical* or *semi-empirical* model and in the other case as an *ab initio* model.

At this point, molecular dynamics (MD) simulations are a great interesting tool in the interpretation of the experimental data. The MDs simulation allows to know about structural information on the single atomic kind needed for the interpretation of experimental data at a microscopic level. In this work, a well-adapted force field (FF) based on Lennard–Jones (L–J) and coulombic interaction was used to reproduce, with good agreement with the experimental data.

^{*} Corresponding author. Fax: +39-6-490631.

E-mail address: r.caminiti@caspur.it (S. Meloni).

2. Experimental section

The measurements were carried out by employing an X-ray energy scanning non-commercial diffractometer [1,2] equipped with an X-ray generator (water-cooled W target having 3.0 kW maximum power), a solid-state detector connected to a multichannel analyzer (MCA) by means of an electronic chain, a collimating system, step motors and sample holder. The X-ray source is a Seifert tube which produces an X-ray beam at 60 kV and 50 mA, whose white Bremsstrahlung component was used. The L fluorescence lines present in the 8–11 KeV range do not disturb the measurements since they are intensively absorbed by the sample and are out of the energetic region of interest. A Seifert and Rich high-voltage power supply, whose stability is better than 0.1%, was used. The detecting system consists of EG and G liquid nitrogen cooled ultra-pure Ge SSD (ORTEC, model 92X) connected to a PC 286 via ADCAM hardware and Maestro II software. The current pulse coming out of the detector is suitably amplified and converted into a digital signal and it is visualized onto a computer screen through a MCA. The collimating system is composed of four slits with adjustable width W , purposely placed to reduce the X-ray beam angular divergence. The X-ray tube and detector holding arms can rotate around a common center in order to reach the desired 2θ scattering angle. The movement is accomplished by step motors by means of a mechanical setting. In this way, a reproducibility within 0.001° for the scattering angles is obtained.

The transmission geometry is employed in order to make absorption correction easier [3].

Since the intense absorption in the low-energy range would largely extend the acquisition time and, on the other hand, uncertainty about polarization of the primary X-ray beam at high energy would cause valuable errors, the usable part of the incident beam energy spectrum must be the central one [3].

For this reason a set of several angles must be chosen for covering entirely the q -space region of interest, by paying attention to maintain a partial superposition (fixed at about 30%) between a zone and the next one, which is indispensable to nor-

malize the experimental data. Since the incident beam energy range used was 50 keV, the following numerical values of the scattering angles (2θ) have been obtained: 26.0° ; 21.0° ; 15.5° ; 10.5° ; 8.5° ; 3.5° ; 3.0° ; 2.0° ; 1.5° ; 1.0° ; 0.5° . The liquid sample holder is a thin amorphous quartz cell.

According to the expression for the intensity of the diffracted radiation that is

$$I_{\text{Obs}}(E, E', \vartheta) = KI_0(E)P(E, \vartheta)A_{\text{Coh}}^{\text{Tot}}(E, \vartheta) \left[I_{\text{Coh}}(E, \vartheta) + \frac{E'I_0(E')P(E', \vartheta)A_{\text{Inc}}^{\text{Sam}}(E, E', \vartheta)}{EI_0(E)P(E, \vartheta)A_{\text{Coh}}^{\text{Sam}}(E, \vartheta)} I_{\text{Inc}}(E', \vartheta) \right] + A_{\text{Coh}}^{\text{Sam}}(E, \vartheta)I_{\text{Emp}}(E, E', \vartheta), \quad (1)$$

the experimental data correction is necessary, and is divided into two categories: the first one being sample independent, and the second one, on the contrary, being connected with the sample's chemical-physical characteristics. These corrections are common to all samples studied, regardless of the chemical composition, and must be crowned by eliminating the possible fluorescence peaks, whenever the sample contains heavy elements. This is done in such a way, that the experimental X-ray data enable us to obtain the structural information in terms of the *reduced intensity*, $qi(q)$.

3. Results and discussion

In this chapter, we discuss in detail our application of the theoretical and experimental techniques used in this work.

3.1. X-ray diffraction data

Referring to what has been stated previously, by the correction and the elaboration of the diffraction data, the static structure functions $i(q)$, in the form of $qi(q) M(q)$ ($M(q)$ being a modification function) were calculated.

The aim of the X-ray scattering is to determine, through Fourier transformation of the reduced intensity, the *radial distribution function* ($D(r)$).

The Fourier transformation of the $i(q)$ function gives the radial distribution

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{q_{\max}} qi(q)M(q) \sin(rq) dq. \quad (2)$$

Here ρ_0 is the average electronic density of the sample.

If the single molecule geometrical parameters were known, the number of free variables decreases simplifying thus the theoretical model and allowing to focalize the attention on the intermolecular organization which is the most interesting data for us.

To determine the structural properties of the single molecule, theoretical quantum-mechanical calculations were carried out. In fact, supposing that the geometry of the isolated molecule is the same as that in the liquid state, it is possible to

attribute a peak of the $D(r)$ to a given atomic couple and to test the reliability of the X-ray method (Figs. 3 and 4). Otherwise, if there were the right number of peaks, but were slightly displaced, one would conclude that a distortion of the molecule in the liquid phase, with respect to its isolated form, is a consequence of the interaction with the other ones.

3.2. *Ab initio* calculation

The Gaussian'94 package programs were used to run the geometry optimizations of SOCl_2 (Table 1) and SO_2Cl_2 (Table 2) molecules. The study was carried out on the second order of the Møller–Plesset theory employing all the active orbitals and with the B3-LYP density functionals

Table 1

Theoretical parameters obtained at different levels of theory and results from gas electron diffraction (G.E.D.) and liquid X-ray diffraction for SOCl_2 molecule (distances in Å and angles in degrees)

	SOCl_2				
	MP2		B3-LYP	G.E.D. ^a	X.D. ^b
	6-311 + G(3d)	6-311 + G(3d,f)	6-311 + G(3d)		
$d_{\text{S-O}}$	1.442	1.437	1.440	1.442	1.440
$d_{\text{S-Cl}}$	2.123	2.073	2.132	2.075	2.087
$d_{\text{O-Cl}}$	2.912	2.860	2.917	2.840	2.840
$d_{\text{Cl-Cl}}$	3.180	3.102	3.223	3.087	3.087
O–S–Cl	108.1	107.8	107.9	106.3	105.8
Cl–S–Cl	97.0	96.9	98.2	96.1	95.4

^a Taken from Ref. [5].

^b This work.

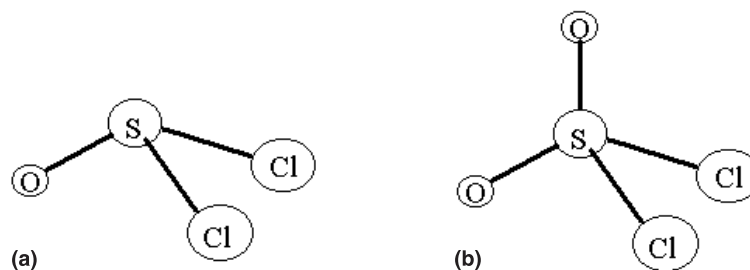
Table 2

Theoretical parameters obtained at different levels of theory and results from gas electron diffraction and liquid X-ray diffraction for SO_2Cl_2 molecule (distances in Å and angles in degrees)

	SO_2Cl_2				
	MP2		B3-LYP	G.E.D. ^a	X.D. ^b
	6-311 + G(3d)	6-311 + G(3d,f)	6-311 + G(3d)		
$d_{\text{S-O}}$	1.422 ₅	1.418	1.422	1.418	1.418
$d_{\text{S-Cl}}$	2.038	2.005	2.059	2.012	2.012
$d_{\text{O-Cl}}$	2.817	2.785	2.836	2.797	2.797
$d_{\text{Cl-Cl}}$	3.125	3.078	3.167	3.089	3.090
O–S–Cl	107.7	107.7	107.7	108.0	108.0
Cl–S–Cl	100.2	100.3	100.5	100.3	100.3
O–S–O	123.5 ₅	123.5	123.2	123.5	123.5

^a Taken from Ref. [5].

^b This work.

Fig. 1. SOCl₂ (a) and SO₂Cl₂; (b) molecules.

(Tables 1 and 2). Several polarized basis sets were used for the geometry optimizations.

The effects of different levels and basis sets on the equilibrium geometry of the molecules can be seen from the values reported. As it may be observed, for the SOCl₂ (Fig. 1(a)) and SO₂Cl₂ (Fig. 1(b)) molecules, there is a good agreement with the experimental geometry [4] at the MP2 and B3-LYP levels when the largest basis sets are used, but the best results were obtained at the MP2 level with the most extended basis set adopted.

The inclusion of multiple polarization functions in all atoms makes the theoretical data closer to the experimental ones. In particular, the most satisfactory agreement with the gas-phase electron diffraction and the X-ray diffraction data of the molecular liquids was accomplished for the SOCl₂ and SO₂Cl₂ molecules when one **f** function was added to the largest basis set used for the MP2 computations. As a general observation, the use of multiple **d** and **f** polarization functions shortens the molecular bonds with respect to the values determined from MP2 calculations employing a less extended basis set. This effect indeed makes the calculated equilibrium geometries of SOCl₂ and SO₂Cl₂ molecules comparable with the experimental ones, determined for liquid and gaseous species.

3.3. Molecular dynamics

In these studies a four/five-site all-atom potential has been developed, respectively, for SO₂Cl₂ and SOCl₂. The molecules are considered as rigid bodies whose geometry has been derived from ab initio calculations (Tables 1 and 2). Fixed atomic

charges and L–J potentials are assigned to each atom in order to reproduce van der Waals and coulombic interactions.

$$U_{\text{tot}} = U_{L-J} + U_{\text{Coul}}, \quad (3)$$

where

$$U_{L-J} = \sum_{i \neq j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (4a)$$

$$U_{\text{Coul}} = \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad (4b)$$

are, respectively, 6–12 (ϵ – σ) L–J potentials, usual coulombic charge pair interactions (Table 3). The MD simulations were carried out using a slightly modified version of the program MOLDFY (for technical programming details we refer to the user's guide on web site www.earth.ox.ac.uk/~keith).

MD simulations were performed on systems consisting of 256 molecules in a cubic simulation cell of 32.444 Å for SO₂Cl₂ and 31.416 Å for

Table 3
L–J parameter and atomic charge used in MD simulations

SOCl ₂			
	σ (Å)	4ϵ (k cal/mol)	$q(e)$
S	3.535	1.051	0.568
O	3.137	0.946	–0.349
Cl	3.456	1.261	–0.109
SO ₂ Cl ₂			
	σ (Å)	4ϵ (k cal/mol)	$q(e)$
S	3.610	0.857	1.043 ₅
O	3.203	0.773	–0.398
Cl	3.529	1.030	–0.124

SOCl_2 . Simulations were carried out in an NVE microcanonical ensemble. Since from the equipartition theorem [5] each degree of freedom in the system has the same average kinetic energy given by $\langle K \rangle = K_B T / 2$, where K is the system's kinetic energy and $\langle O \rangle$ is the average of a generic observable O of the system over the microcanonical ensemble. The effective temperature is therefore given by ensemble average of its kinetic energy

$$T = \frac{2}{gK_B} \sum_{i=1}^g \langle K_i \rangle = \frac{1}{3NK_B} \sum_{i=1}^N \langle mv_i^2 + \omega_i I \omega_i \rangle. \quad (5)$$

Here K_i is the instantaneous kinetic energy of the i th degree of freedom, g the number of degrees of freedom and N is the number of molecules. It is always desirable that a simulation can be conducted so that the temperature is the supplied

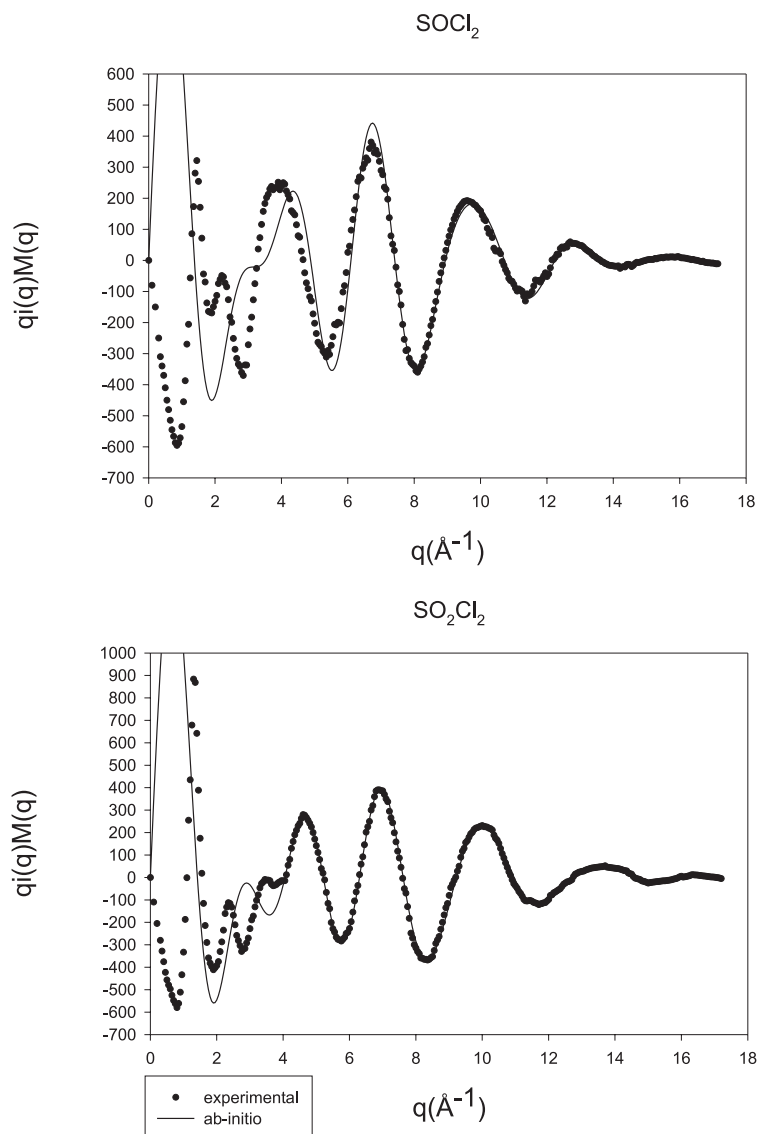


Fig. 2. Experimental and theoretical structure functions calculated using the parameters given in Tables 1 and 2.

parameter rather than the kinetic energy. This requires some kind of technique in order to fix the average kinetic energy at the required value. Initial kinetic energies may be constructed randomly following the Maxwell–Boltzmann distribution at the desired temperature. Unfortunately, initial conditions fall usually far away from the equilibrium status in the direction of a too high potential energy that during the dynamic will be eventually converted into kinetic energy, raising the temperature above the desired value. In order to remove

this problem we rescaled at periodic intervals linear and angular velocities by a factor

$$s = \sqrt{\frac{gK_B T}{2T}}, \quad (6)$$

where T is the desired value and T is the “instantaneous” system temperature. Such a periodic scaling can be viewed as a series of kicks which we give to the system in the direction of the thermodynamical equilibration, and consequently MD

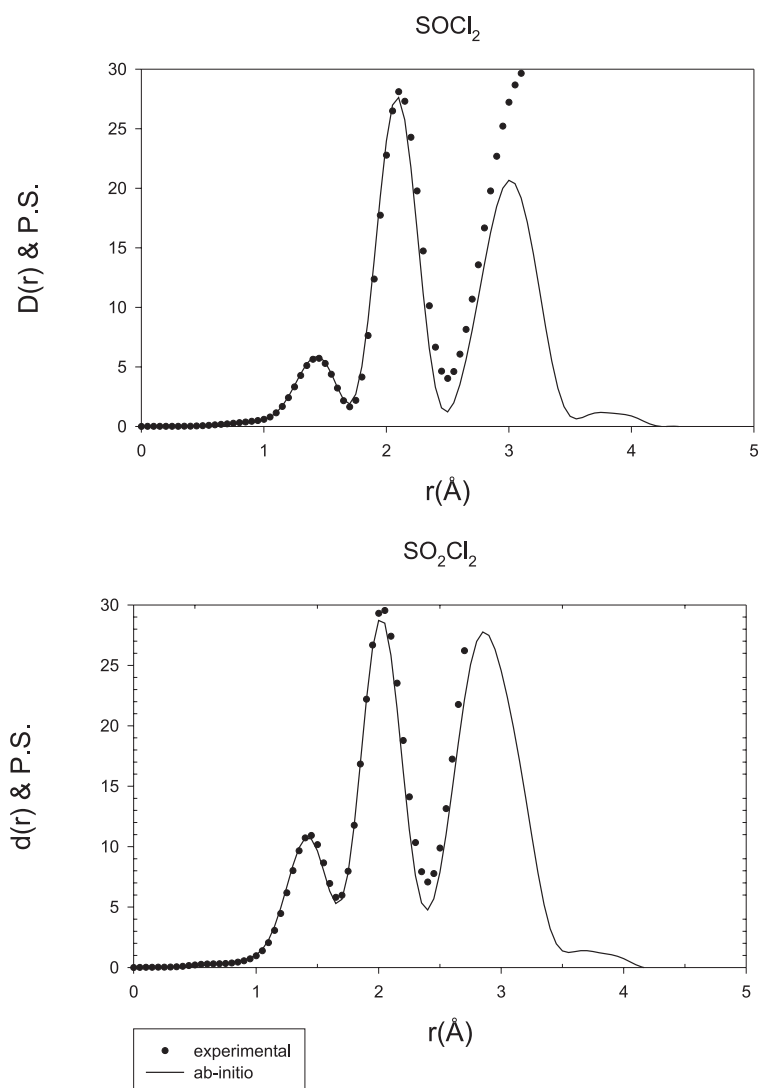


Fig. 3. Experimental radial distribution function and peak shape calculated using the theoretical function reported in Fig. 2.

during rescaling of velocities does not generate the correct statistical ensemble. Only after reasonable time of equilibration (namely 50 ps for both molecules), with a time step of integration of 0.001 ps, we started accumulating microscopical configurations for the thermodynamical averages. Once the system is suitably equilibrated, the total energy fluctuates less than 0.5%. In order to get statistically significant microscopical configurations we save snapshot of the system every 0.1 ps for SO_2Cl_2 and every 0.05 ps for SOCl_2 . We fixed such a conservative time interval in order to be sure to have statistically decorrelated configurations.

The structure of a liquid can be analyzed in terms of the atomic $g_{\alpha\beta}(r)$ defined by

$$g_{\alpha\beta} = \frac{1}{\rho^2} \left\langle \sum_{i \neq j}^N \delta(\mathbf{r} - \mathbf{r}_i^\alpha - \mathbf{r}_j^\beta) \right\rangle, \quad (7)$$

where the angular brackets denote the averages over the distribution probability, N the total number of atoms, α and β are the labels for different atomic species. RDF can be calculated with the following procedure [5]: we fixed a length interval (20 Å in our simulations) which is divided into a certain number of histogram bins (200),

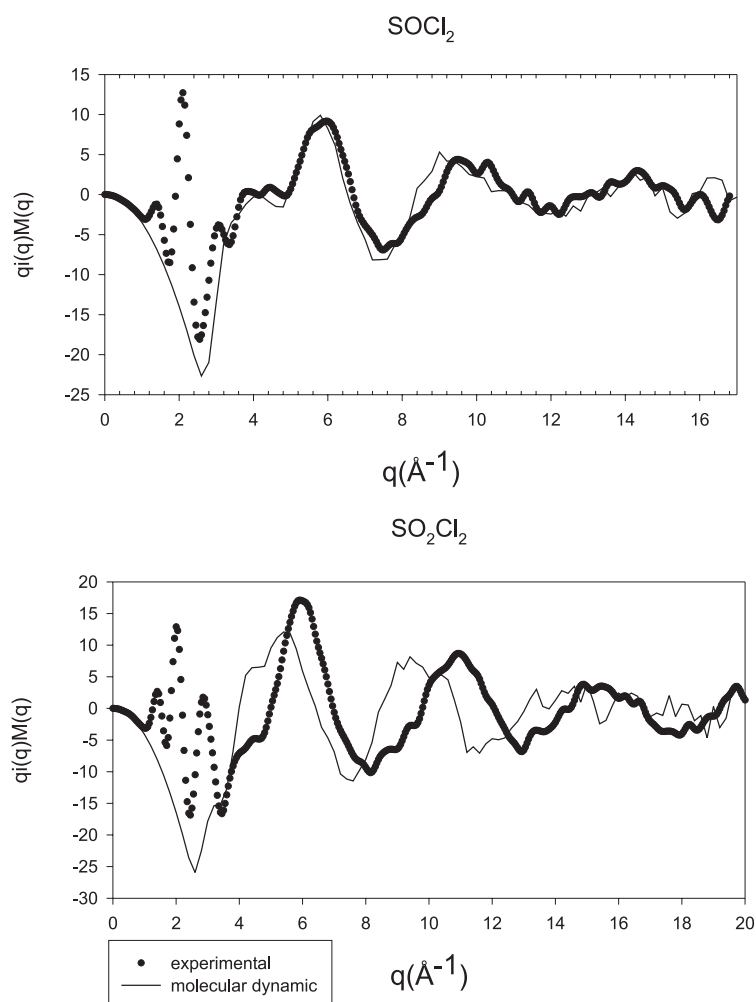


Fig. 4. Experimental radial distribution function in $\text{Diff}(r)$ form and theoretical function obtained from MD calculation.

every accumulated snapshot we update by a histogram of pair distances so that

$$g_{\alpha\beta}(r + \delta r) = \frac{3Nn_{\text{his}}(b)}{4\pi\rho N_{\alpha}N_{\beta}\tau \left[(r + \delta r)^3 - r^3 \right]}, \quad (8)$$

where N_i is the total number of the i th atomic type. It is important to stress that integrating $g_{SS}(r)$ between 0 and the first minimum provides information about the coordination number which is the average number of first neighbor molecules. In X-

ray diffraction experiments the measurable quantity is the total intensity of scattered radiation as a function of the scattering angle 2θ that uses electron units per stoichiometric unit which can be expressed by Carbone et al. and Allen and Tildesly [3,6]

$$I(q) = \sum_{i=1}^m x_i f_i^2 + i(q), \quad (9)$$

where $q = 4\pi\sin(\theta)/\lambda_s$ is the magnitude of momentum transfer related to the scattering angle θ

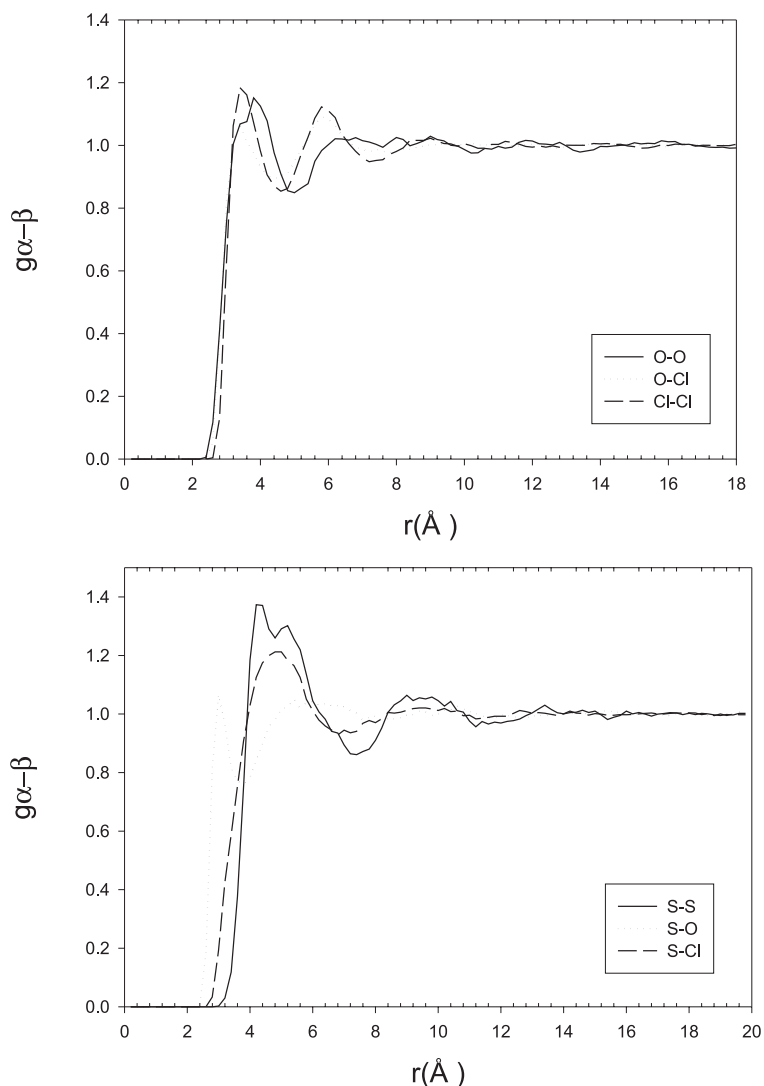


Fig. 5. The S-S, S-O, S-Cl (a) and O-O, O-Cl, Cl-Cl (b) partial correlation function obtained from MD calculations.

and wave length λ , and the summation is extended over the m atomic types. The quantity $x_i f_i^2$ is the atomic independent scattering factor in stoichiometric unit: namely x_i is the stoichiometric concentration of the i -type atom and f_i is the related scattering factor which is assumed to be real. The second term on the left-hand side of (9) is the structural function contribution due to interference. The $I(q)$ is related to RDF according to

$$i(q) = \sum_{i,j=1}^m x_i x_j f_i f_j \tilde{h}_{ij}(q), \quad (10)$$

where

$$\tilde{h}_{ij}(q) = 4\pi\rho_0 \int_0^\infty r [g_{ij}(r) - 1] \frac{\sin(qr)}{q} dr. \quad (11)$$

Comparison of the MD and X-ray diffraction data has been performed using a slightly modified structure function obtained by multiplying the function $qi(q)$ by a modification function $M(q)$

$$M(q) = \frac{f_S^2(0)}{f_S^2(q)} e^{-Kq^2},$$

where $K = 0.01 \text{ \AA}^2$, for the purpose of cutting spurious high-frequency modes. All the data presented hereafter are obtained back by Fourier transformation of the function $qi(q)M(q)$ which gives the Diff(r) RDF that allows a more sharp confrontation of data.

4. Analysis of results

By comparing the X-ray diffraction results of liquid samples with those of gas-phase electron diffraction and ab initio calculations we may conclude that the molecular structure does not undergo significant changes due to the physical state (Figs. 2 and 3).

In the case of SOCl_2 , agreement between the MD and X-ray diffraction results allows us to employ microscopic data to obtain structural information concerning the liquid (Fig. 4). The partial distributions (Figs. 5(a) and (b)) are consistent with a model with direct interaction between sulfur and oxygen (S–O) at 3.0 \AA . This model takes into account the double peak at 4.3 and 5.2 \AA .

From a numerical integration of distribution function of S–S distance between 0.0 \AA and its first “real” minimum value, one might conclude that the first coordination shell consists of 12 molecules. Similar conclusions cannot be drawn for SO_2Cl_2 since a good agreement between MD and X-ray diffraction has not been achieved yet.

Some questions still remain unsolved about the adopted procedure. For example, we are still considering whether FF optimization to reproduce structural data of liquid samples might be used without any comparison with other experimental results such as the thermodynamical data or ab initio calculation.

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