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Structure determination of liquid carbon tetrabromide via a combination of x-ray and neutron diffraction data and Reverse Monte Carlo modelling

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ABSTRACT

In order to reveal the atomic level structure of liquid carbon tetrabromide, a new synchrotron x-ray diffraction measurement, over a wide momentum transfer (Q-)range, has been performed. These x-ray data have been interpreted together with a neutron diffraction dataset, measured earlier, using the Reverse Monte Carlo method. The structure is analysed on the basis of partial radial distribution functions and distance dependent orientational correlation functions. Orientational correlations behave similarly to other carbon tetrahalides. Moreover, the information content of the new x-ray diffraction dataset, and in particular, of the varying Q-range, is also discussed. Only very small differences have been found between the results of calculations that apply one single experimental structure factor and the ones that use both x-ray and neutron diffraction data: the latter showed slightly more ordered carbon–carbon radial distribution function, which resulted in seemingly more ordered orientational correlations between pairs of molecules. Neither the extended Q-range, nor the application of local invariance constraints yielded significant new information. For providing a simple reference system, a hard sphere model has also been created that can describe most of the partial radial distribution functions and orientational correlations of the real system at a semi-quantitative level.

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1. Introduction

The covalently bonded tetrahedral shape molecule, carbon tetrabromide (tetrabromomethane, CBr_4) has become a model system for studies on plastic (or orientationally disordered) crystalline phase among carbon tetrahalides. Its diffraction pattern shows only a few, not too intense Bragg-peaks; on the other hand, a significant amount of diffuse scattering contributions appear [1]. To describe this behaviour various models have been refined in the past [2–5]. Apart from its plastic phase, CBr_4 has several high pressure modifications, including phase III that appears to be also plastic crystalline [6]. Studying these exotic variations by total scattering powder diffraction may only be possible in the future, by instrumentation developed very recently for synchrotron x-ray diffraction and high-pressure techniques.

The liquid phase of CBr_4 is stable between 365 and 463 K [7]. In contrast to the solid phases of carbon tetrabromide, only few experiments were performed by neutron [1,8,5] and x-ray [4] diffraction on the liquid. Two of them [1,4] (including the only published x-ray result until now) compared qualitatively the pattern of different phases; however, detailed analyses of the liquid phase were not their subject. The first theoretical investigation [9] using diffraction data was performed by the help of the Reference Interaction Site Model [10], which estimated the atomic radius of bromine atoms. A more detailed analysis performed on measured diffraction datasets by Reverse Monte-Carlo (RMC) simulation was provided by Bakó et al. [8], who reported all of the three partial radial distribution functions and made a simple analysis of orientational correlations. Their most important result was that they ruled out the formerly proposed Apollo-model [11] from the most probable orientations; similarities between plastic crystalline and liquid phase were also surmised. A more recent contribution [12] discussed similarities to XCl_4 liquids by orientational correlations based on molecular dynamics simulation and Rey's classification of mutual orientation of tetrahedral molecules [13]. This classification has been proven to be useful by numerous recent studies for liquids containing tetrahedral molecules [14–19]. Another recent examination [5] provided a systematic study of orientational correlations (again, by means of Rey's classification) in liquid and two crystalline phases by neutron diffraction, proving the similarities of orientational correlations between the plastic crystalline and liquid phases.

For the full determination of the two-particle level structure of a disordered material (containing n different kinds of atoms) purely from diffraction experiments, we must be able to perform $n(n+1)/2$ independent diffraction measurements, varying the scattering parameters of each element in the material in question (wherever such a variation is feasible). However, by applying theoretical considerations, or by performing some sort of structural modelling, the required number of measurements might be reduced (see, e.g. [14,15]).

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Throughout the present work, effects of the new measured x-ray data, its use together with earlier neutron diffraction results [5], and the applied momentum transfer range will be discussed, in terms of atomic radial distribution functions and orientational correlations between molecules. The feasibility of analysing the structure of liquids of tetrahedral molecules based on only one single diffraction experiment, using molecular constraints and RMC, has been discussed by many authors [8,20,5]. This approach has been proven valid [17] for several XCl_4 liquids experimentally. However, such a validation is lacking for the case of CBr_4. Also, the latest publication on the subject [5] used an assumption based on earlier work [21], that the applied Q-range (up to only 8 $Å^{-1}$) is sufficient for describing intermolecular correlations; this assumption also needs to be verified.

2. Experiment

The sample, provided by Sigma-Aldrich, contained 99% pure CBr_4 polycrystals at room temperature.

The x-ray diffraction experiment has been carried out at the BL04B2 high-energy x-ray diffraction beamline [22] of the Japan Synchrotron Radiation Research Institute (JASRI/SPring-8, Hyogo, Japan). The incoming photon energy was chosen to be 37.65 keV (corresponding to a wavelength of 0.329 Å). The capillary transmission geometry with single HPGe detector (in the horizontal plane) setup has been used.

The powdered sample was filled into a 1 mm diameter, thin walled borosilicate glass capillary (GLAS Müller, Germany) mounted in a Canberra vacuum furnace, available at the beamline. The liquid phase measurement was performed at 397.6 ± 0.8 K, recording the intensities of scattered photons by a germanium detector and the incoming beam by a monitor counter. To optimize the performance of the experimental apparatus, the patterns have been recorded in four, slightly overlapping, segments, differing by the incoming beam width and height. After the measurement on the sample, scattered intensities of the empty capillary were also recorded by the same conditions.

Raw intensities were normalised by the monitor counter, corrected for attenuation, polarization, and empty capillary intensities. Then, the whole pattern was reconstructed from the segments, scaled in electron units and corrected for Compton-scattering contributions following the standard procedure [23].

3. Reverse Monte Carlo modelling

Series of Reverse Monte Carlo simulations (RMC_POT [24,25]) have been performed, in order to reveal the information content of the diffraction datasets beyond the already known evidences, such as molecular parameters and density (see Table 1). Taking into account solely the molecular geometry and the density, two hard sphere Monte Carlo simulations have been started: the atomic parameters of *HS0* were identical to RMC calculations with experimental data (see below). In contrast, atomic radii closer to reality have been applied in the *HS1* model. Of the experimentally constrained simulations, three runs were performed using both experimental (x-ray and neutron diffraction) data: *NXl* and *NXlli* made use of the entire measured Q-range of both datasets, whereas in *NXsh* the maximum momentum transfer values were identical for the two experimental datasets. For the 'neutron-only' case the earlier simulated configurations [5] (*N*), as well as a new simulation (*Nli*) were considered.

Table 1
Parameters of the Reverse Monte Carlo simulations performed. For combined runs that apply both neutron and x-ray diffraction data, the Q-ranges and R-factors are also shown.

Run	Experimental data	Q-range [$Å^{-1}$]	R_{wp} [%]	Saved cfg
HS0	None	–	–	195
HS1	None	–	–	184
N [5]	Neutron	0.39–8.0	4.84	50
Nli	Neutron	0.39–8.0	5.12	1
NXsh	Neutron, x-ray	0.39–8.0; 0.65–8.0	4.82; 4.89	68
NXl	Neutron, x-ray	0.39–8.0; 0.65–14.0	4.84; 5.12	84
NXlli	Neutron, x-ray	0.39–8.0; 0.65–14.0	5.29; 5.44	1

A more detailed description of the Reverse Monte Carlo method can be found elsewhere [26,24], and only the way of calculation of the (total scattering) structure factor ($F(Q)$) is shown here. During the RMC calculation, the partial radial distribution functions (prdfs, $g_{xy}(r)$) are calculated from atomic coordinates. The prdfs are then Fourier-transformed to obtain the corresponding partial structure factors ($S_{xy}(Q)$):

$$S_{xy}(Q)-1 = 4\pi\varrho\int_0^\infty r^2\left(g_{xy}(r)-1\right)\frac{\sin(Qr)}{Qr}dr, \qquad (1)$$

where ϱ denotes the number density. To calculate the total scattering structure factor belonging to a given experiment, the partial structure factors are summed by proper coefficients (w_{ij}). Coefficients depend on concentration (c_i) and atomic form factors [27] for x-rays ($f_i(Q)$), and Q-independent scattering lengths [28] for thermal neutrons as follows:

$$w_{ij} = \frac{c_i c_j f_i(Q) f_j(Q)}{\left(\sum c_i f_i(Q)\right)^2}\left(2-\delta_{ij}\right), \qquad (2)$$

where δ_{ij} is the Kronecker symbol. The applied coefficients are shown in Table 2 for both experiments.

Concerning the density of liquid CBr_4, earlier works performed calculations using atomic number densities of 0.031 $Å^{-3}$ [9,8] and 0.02688 $Å^{-3}$ ([12], referring to [29]); these values correspond to bulk densities of 3.41 and 2.961 g/cm^3, respectively. Interestingly, the former value is identical to that of liquid CCl_4 (0.031 $Å^{-3}$ [9] or 0.0319 $Å^{-3}$ [17]). Since the volume of the CBr_4 molecule is larger than that of the CCl_4 molecule, the number density of liquid CBr_4 should be lower than that of liquid CCl_4, unless there are some special orientations that would enable denser packing. Since no long-range orientational correlations have been found earlier [8] in liquid CBr_4 (which might result in a more densely packed structure), it can be concluded that some of the earlier works [8,9] actually used a number density that is far too high. Also, a RMC trial run gave worse agreement (with an R_{wp} about 12% for the neutron dataset) with unphysical features in r space, in comparison with the lower density case (see Table 1). For these reasons, in each calculation reported here, the lower density value was taken.

For each model, the simulation box contained 6912 molecules with an atomic number density of 0.026888 $Å^{-3}$, which provided 54.36 Å half box length. To maintain the geometry of the molecules during the series of single atomic moves, fixed neighbour constraints [30] have been applied between carbon and bromine (1.93 ± 0.05 Å) and between bromine and bromine (3.15 ± 0.1 Å) atoms within the molecule. For pairs of atoms belonging to different molecules, closest distance constraints (cut-offs) have been used between carbon and carbon (3.5 Å), carbon and bromine (2.5 Å) and bromine and bromine (2.8 Å) pairs. At *HS1* run, these limits were 5.0 Å, 3.8 Å and 3.5 Å, respectively.

The RMC procedure provides sets of configurations that agree with diffraction results within the experimental error. In order to improve the statistical accuracy of the results, series of independent particle configurations have been saved; the configurations have been taken so that they were separated by at least one successful move for each atom.

Table 2
Contribution of each partial structure factor to the experimental total scattering structure factors.

Experiment	CC	CBr	BrBr
Neutron	3.9%	31.6%	64.5%
x-Ray (at $Q = 0$)	0.2%	7.09%	91.9%

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