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Structural Studies of Liquid 1,1,1-Trichloroethane by Means of X-Ray Diffraction[1]

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The X-ray scattering intensities from liquid 1,1,1-trichloroethane (TCE) were measured at room temperature by the energy-dispersive method. By the use of the real space expansion and the reciprocal space expansion based on the local lattice structure model, structure simulation studies for TCE were carried out. A bcc model with a random orientation of the methyl group reproduces the experimental intensities well. The number of molecules in the structure region, n, was determined by a trial-and-error method, and a least-squares refinement was carried out to determine the following four parameters; the lattice constant of the bcc cell, a; the Prins parameter, D; the radius up to the continuous region, R_c; and its damping factor, l_c. The refined parameters with the standard deviations in parentheses are: a=6.78 (0.11) Å, D=0.049 (0.009) Å, R_c=12.70 (0.48) Å, and l_c=1.76 (1.22) Å with n=51.

In order to understand the orientational correlation of molecular liquids, it has been proved to be useful to construct a local lattice structure model[2–4] and to test it against the experimental intensity. The present authors previously reported that the scattering intensities of tetrahedral molecular liquids, such as carbon tetrachloride[3–5] and neopentane,[6] were reproduced well by the bcc (body-centered cubic) local-lattice-structure model.

In the bcc model, a chlorine atom (or a methyl group) of one molecule lies in a hollow formed by three off-axis chlorine atoms (or methyl groups) of the neighboring molecule, and the three-fold axes of these molecules are aligned. This packing has been named "head-tail head-tail packing." By the repetition of the packing over a three-dimensional space, a bcc lattice is obtained.[3]

In the present work a structural study of 1,1,1-trichloroethane (TCE) has been carried out. A molecule of TCE is a quasi- tetrahedral molecule; it is obtained by replacing one of the chlorine atoms of carbon tetrachloride by a methyl group. Because the radius of the van der Waals spheres of a methyl group is almost equal to that of a chlorine atom, an appropriate structure model for liquid TCE can be expected to be similar to that of liquid carbon tetrachloride[3–5] or liquid neopentane.[6]

Both the real space expansion and the reciprocal space expansion are applied in the simulation study. The former expansion is a traditional calculation. However, it has the limitation that it is difficult to simulate scattering intensities in the small-s region because of the inevitable appearance of ghosts. The reciprocal space expansion was previously pesented by the present authors to overcome this difficulty in the real space expansion.[5,7]

It is reported that the scattering intensities of liquid TCE can be simulated well by the same bcc model as is used for liquid carbon tetrachloride, where one of the chlorine atoms of carbon tetrachloride is replaced at random by a methyl group. This random replacement of a methyl group is called "random orientation of a methyl group" in the present paper.

Experimental

The sample, TCE (Kanto Kagaku), was purified by careful distillation. The scattering intensities from liquid TCE were measured at 20 °C. An energy-dispersive diffractometer with a horizontal scattering plane and a θ—2θ scanning system was used. A fine-focus X-ray tube with a tungsten target was used under the operating condition of 47.5 kV and 25 mA (or 20 mA). The scattered photons were detected by means of a pure Ge SSD (ORTEC) equipped with a multichannel pulse height analyzer (NAIG). The transmission method was applied to the collection of the data at the scattering angles (2θ) of 2.5, 5, 10, 20, and 40°. The details of the experimentation by the energy-dispersive method and the analysis of the intensity data have been reported elsewhere.[8]

Intensity Simulation of Liquid TCE

In constructing a local lattice structure model,[2,4] we assume a certain nearest-neighbor configuration around a central molecule and repeat this structural unit by some specific rule. According to this model the average molecular positions, as viewed from the location of a given central molecule, conform to a certain lattice structure and any molecule in the liquid can be a central molecule. Unlike the crystalline case, however, the repetition of the structural unit is imperfect and is, therefore, accompanied by a rapid loss of positional correlation as the distance between the central molecule and the surrounding ones increases. This loss of correlation may be embodied in the model in the form of a mean-square deviation of the distribution of the separation between atoms, which increases rapidly with the distance. At least beyond a few molecular radii away from any starting point, the structure can be regarded as a continuum. This distance is denoted by R_c in the present paper.

By using the group scattering factor for a methyl group introduced by Narten,[9] a methyl group is treated as an "atom" in the following calculations.

The coherent scattering intensity per molecule from liquid TCE in the form of the real-space expansion[4)] is given by:

$$I(s)=\sum_{i}\sum_{m}f_if_mj_0(sr_{im})\exp(-l_{im}{}^2s^2/2)+I_c \qquad (1)$$

where $j_0(x)$ is given by $\sin(x)/x$, f_i is the atomic scattering factor of the i-th atom and l_{im} is the root mean-square deviation of the mean interatomic distance, r_{im}. The notation s is the scattering parameter defined by $4\pi\sin\theta/\lambda$ (2θ: scattering angle, λ: wavelength of X-rays). The summation for i is over all the atoms of the central TCE molecule, while the summation for m is over all the atoms in the discrete structure region within the radius R_c. I_c is the contribution from the region where the structure is regarded as a continuum. The expression of I_c is given by:

$$I_c=\sum_{i}f_i\langle F\rangle n\ \frac{3[sR_c\cos(sR_c)-\sin(sR_c)]}{(sR_c)^3}\exp(-l_c{}^2s^2/2) \qquad (2)$$

where $\langle F\rangle$ is the mean scattering amplitude of a molecule given by:

$$\langle F\rangle=\sum_{i}f_i \qquad (3)$$

and n is the number of molecules within the discrete-structure region.[4)] For the mean-square deviation the Prins relation:[2,10)]

$$l_{im}{}^2=2Dr_{im} \qquad (4)$$

was employed.

By the application of the Poisson summation formula,[11)] we can obtain the following expression as the reciprocal space expansion:

$$I(s)=\frac{1}{v}\sum_{\nu}{}'\frac{2\pi Ds}{b_\nu}\left[\frac{1}{(Ds^2)^2+(s-b_\nu)^2}-\frac{1}{(Ds^2)^2+(s+b_\nu)^2}\right]\times$$
$$\sum_{\alpha}\sum_{\beta}f_\alpha f_\beta\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\alpha\beta})+\sum_{\alpha\neq\beta}\sum f_\alpha f_\beta[\exp(-l_{\alpha\beta}{}^2s^2/2)$$
$$-\exp(-Dr_{\alpha\beta}s^2)]j_0(sr_{\alpha\beta}) \qquad (5)$$

where $\boldsymbol{b}_\nu$ is the reciprocal-lattice-point vector. The notation α indicates the α-th atom and $\boldsymbol{a}_{\alpha\beta}$ is the vector between α and β atoms. The summation for α in the first term is carried out over all the atoms in a molecule and the summation for β over all the atoms in a unit cell. The second term in Eq. 5 is the correction term due to the mean-square deviations of intramolecular distances which are not given by the Prins relation. The summation for α and β in the second term is carried out over all the atoms in a molecule. The notation $l_{\alpha\beta}$ is the root mean-square amplitude of the intramolecular distance, $r_{\alpha\beta}$. The details of the derivation of Eq. 5 has been described in the previous papers.[5,7)]

Results and Discussion

The experimental total coherent intensity, $I(s)$, from liquid TCE is shown in Fig. 1 by a solid curve, with the calculated self-scattering intensity shown by a broken curve. The weighted structure function is shown in Fig. 2; it is defined by:

$$si(s)=s(I(s)-\sum_{i}f_i(s)^2). \qquad (6)$$

The weighted structure function for a free TCE

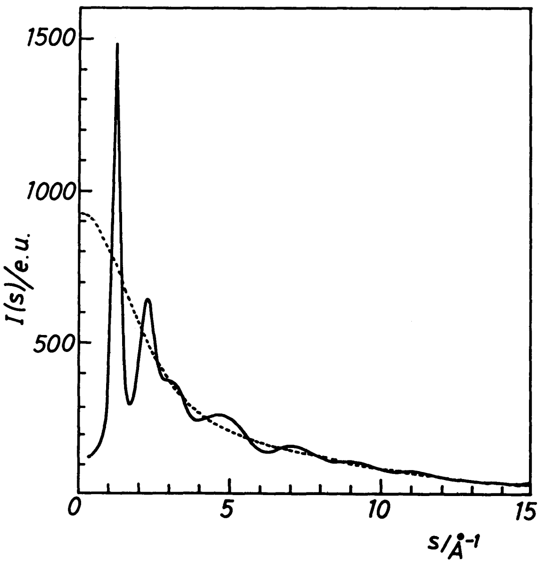

Fig. 1. The observed total coherent intensity $I(s)$ for liquid TCE (solid curve) and the self-scattering intensity from the constituent atoms (dotted curve).

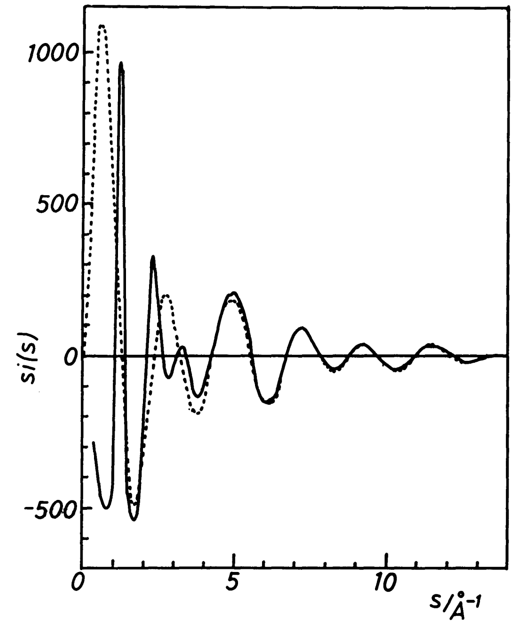

Fig. 2. Observed weighted structure function $si(s)$ for liquid TCE (solid curve) and the calculated one for a free molecule of TCE (dotted curve).

molecule is shown by a broken curve. For the intramolecular parameters, r_{ij} and l_{ij}, the data for a gaseous molecule[12] were utilized. The experimental weighted structure function is in good agreement with the calculated one for the free molecule in the range of $s>6$ Å^{-1}. The pattern of the scattering intensity from liquid TCE is very similar to that from liquid carbon tetrachloride,[3,4,8] i.e., a very sharp peak at $s\approx1.3$ Å^{-1} the successive peak at $s\approx2.3$ Å^{-1} and a small peak at $s\approx3.2$ Å^{-1}. However, the relative intensity of the second peak of TCE at $s\approx2.3$ Å^{-1} is lower.

The Fourier transform of the weighted structure function, $si(s)$, as defined by:

$$4\pi r^2(\rho-\rho_0) = \frac{2r}{\pi\sum_i Z_i^2}\sum si(s)\sin sr\cdot\Delta s \qquad (7)$$

gives the distribution function, including the weight of the electron cloud of each atom. The distribution function is shown in Fig. 3. The peaks at $r\approx1.8$ Å and 2.9 Å are attributed to the intramolecular distances of the carbon and chlorine atoms and of the chlorine and chlorine atoms, respectively. The peak at $r\approx3.9$ Å shows the nearest distance between the atoms belonging to the neighboring molecules. The peaks with respect to the long-range correlation of the molecular arrangement appear at integral multiples of about 5.9 Å; i.e., r=6.3, 11.5, 16.5, and 21.5 Å. This may show that the TCE molecules are arranged linearly. The peak at $r\approx3.9$ Å is a probe to know the distance of the neighboring molecules. When the head-tail head-tail packing is assumed, the distance of the centers of neighboring molecules is obtained as 5.9 Å by using the value of 3.9Å; the second nearest neighbor distance is 6.8 Å, which corresponds to the lattice constant of the bcc lattice. The pile of the first nearest neighbors at 5.9 Å and the second nearest neighbors at 6.8 Å forms a large peak centered at 6.3 Å in the distribution function of Fig. 3.

As has been mentioned above, the most probable packing for the molecules of liquid TCE is the head-tail head-tail packing. In fact, the calculated intensity based on the bcc model with the random orientation of a methyl group has reproduced the experimental intensity well. The intensity calculation for the random orientation of a methyl group was performed as follows; a central molecule was placed on the lattice point of the bcc, four possible arrangements of a methyl group being considered. The first nearest neighbor molecules were put on the next lattice points with the four arrangements of a methyl group in the same way. The intensities for the 16 ways of molecular arrangement were calculated by the use of Eq. 1, and then the total was divided by 16. For molecules farther than the first nearest neighbors, similar calculations were carried out.

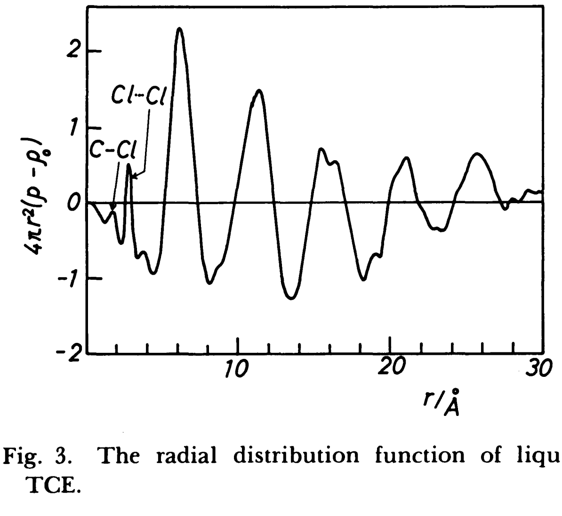

Fig. 3. The radial distribution function of liquid TCE.

Next, the least-squares refinements for the weighted structure function $si(s)$, based on the bcc local-lattice structure with the random orientation of a methyl group were carried out. The refined parameters were as follows; the number of molecules (n) in the discrete structure region, the lattice constant of the bcc cell (a), the Prins parameter (D) which gives the mean-square deviation of the distance of atoms belonging to different molecules (see Eq. 4) and the radius of the discrete-structure region (R_c) and its damping factor (l_c) (see Eq. 2). For the determination of the number n, a trial-and-error method was applied. The other four parameters were refined by the least-squares method. The weighted structure function obtained by the use of the following values showed the best agreement with the experimental values: n is 51, which corresponds to the inclusion up to the fourth nearest neighbors, a=6.78 (0.11) Å, D=0.049 (0.009) Å, R_c= 12.70 (0.48) Å and l_c=1.76 (1.22) Å, where the numerals in the parentheses are the standard deviations. The reliability factor, $\mathscr{R}$, as defined by:

$$\mathscr{R} = \left[\frac{\sum w(s)[si(s)_{\rm exp} - si(s)_{\rm calc}]^2}{\sum w(s)[si(s)_{\rm exp}]^2}\right]^{\frac{1}{2}} \qquad (8)$$

was 0.23, where $w(s)$ was the weight function. The values of $w(s)$ were chosen as 0.1 for $0<s\leqslant1$ Å^{-1} and 1.0 for $s>1$ Å^{-1}. From the refined value of a, the distance of the first nearest neighbors becomes 5.87 Å. The weighted-structure function calculated by the use of these refined values is shown in Fig. 4 by the solid curve together with the experimental one (broken curve). The calculated intensity is in good agreement with the experimental one in the region of $s\geqslant1$ Å^{-1}.

The discrepancy in the region of $s<1$ Å^{-1} originates from the sudden onset of the continuum region to the discrete-structure region.[5,7] In order to overcome the difficulty of the real space expansion, the reciprocal space expansion was carried out. Because it is impossible to simulate the intensity for the random orientation exactly in the case of the reciprocal space expansion, the following approximation was adopted: the bond distance between a centered carbon atom

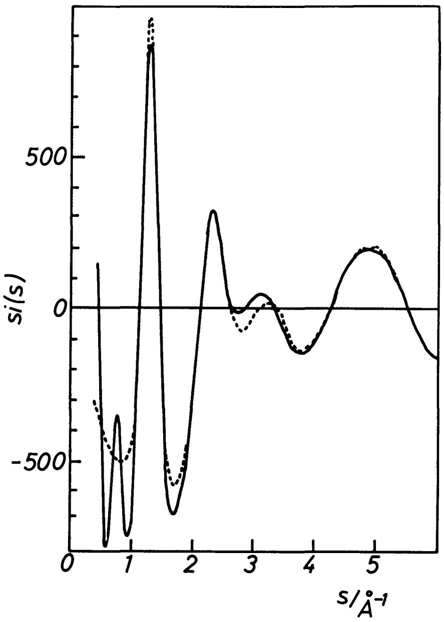

Fig. 4. The weighted structure function $si(s)$ for liquid TCE. The solid curve is the calculated one for the bcc model with the random orientation of the methyl group and the dotted curve is the experimental one.

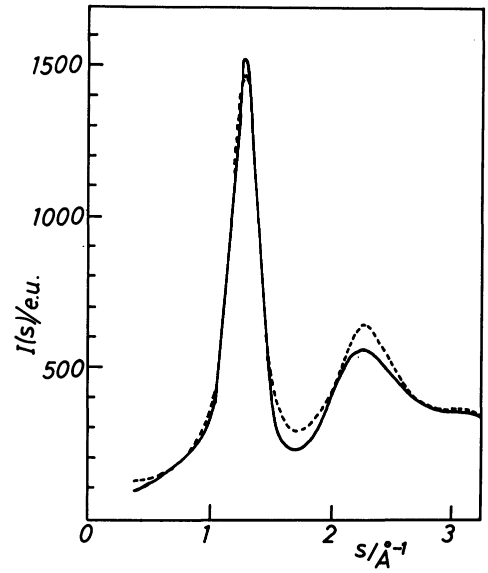

Fig. 5. The total coherent intensity of liquid TCE. The solid curve is the calculated intensity based on the bcc model by the use fo the "reciprocal space expansion." The broken curve is the experimental intensity.

and a methyl group (1.54 Å) was changed to that between the carbon atom and a chlorine atom (1.77 Å) and hypothetical atoms with the scattering factor of $(3f_{\mathrm{Cl}}+f_{\mathrm{Me}})/4$ were equally placed at the positions of chlorine atoms and a methyl group. The other structural parameters used in the reciprocal-space expansion were identical with those obtained by the least-square refinement in the real-space expansion. Reciprocal lattice points up to $\nu=(600)$ $(b_\nu=5.56\ \text{Å}^{-1})$ were included. The results of the application to TCE based on the bcc local-lattice structure shows an excellent agreement of the calculated intensity with the experimental value in the region of s smaller than $2\ \text{Å}^{-1}$ (see Fig. 5). The total coherent intensity is shown in Fig. 5, because it demonstrates the discrepancy between the experimental and the simulated intensities in the small-s region. Contrary to the real space expansion, the convergence becomes worse with an increase in the s. By the use of both the real space and the reciprocal space expansion, the observed scattering intensity of liquid TCE in the whole range of s is satisfactorily accounted for on the basis of the bcc local-lattice model.

Molecules with an octupole moment, such as carbon tetrachloride and neopentane, are highly stabilized by the head-tail head-tail packing.[13] Because a TCE molecule has a dipole moment, the bcc model in the liquid TCE with the random orientation of a methyl group is not consistent with the electrostatic interaction of the molecule. Some of the other orientations of the methyl group were, therefore, attempted in the simulation study. As was shown in the structure study of the plastic crystal of carbon tetrachloride,[14] the calculated intensity curve for packings other than the head-tail head-tail packing has peaks and valleys at entirely different positions from the experimental curve. Therefore, we can restrict the model for liquid TCE to the head-tail head-tail packing. The head-tail head-tail packing with the parallel orientation of a methyl group gives the same pattern, but the first peak at $s\approx1.3\ \text{Å}^{-1}$ becomes much higher than the experimental one and the reliability factor becomes worse. Of course, the parallel orientation of the methyl group can not be permitted physically because of the unstabilization caused by the interaction between the dipole moments. However, the fact mentioned above shows that the height of the first peak in the intensity curve is fairly sensitive to the orientation of the methyl groups. Next, the intensity for another model was calculated, where molecular arrangements with a parallel dipole moment to that of the central molecule are omitted in the arrangements of the first neighbors and molecules farther than the first nearest neighbors have the random orientation for the methyl groups. The intensity curve for this model was in very good agreement with that for the random orientation of the methyl group, and the reliability factor was 0.235 (cf. 0.230 in the random orientation.)

Though the TCE molecules may be arranged so as to stabilize the dipole interaction, the information on the orientation of the methyl group is smeared in the liquid; it may, however, be said that the orientation is random in the liquid on the average. In the case of liquid TCE, the agreement between the experimental intensity and the calculated one based on the bcc model is of the same degree as in liquid carbon tetrachloride or liquid neopentane.

TCE has two plastic crystal phases, i.e., a fcc phase and a rohmbohedral phase,[15] just like carbon tetrachloride. In the structure analysis of Phase Ia (plastic crystal fcc) of carbon tetrachloride, it has been shown that the head–tail head–tail packing is dominant.[14] The simulation study in the plastic crystal is easier than in the liquid, because the nearest neighbor distance of molecules can be determined from the unit-cell dimensions and so only the orientational correlation needs to be investigated. The structure study of plastic crystal of TCE is now under way and it will give further information on the structure of liquid TCE. It will be reported in the near future.

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