X-ray diffraction measurements of expanded fluid sulfur up to the supercritical region

M. Inui1, Y. Azumi1, S. Hosokawa2, Y. Kajihara1, K. Matsuda3 and K. Tamura3
1Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan
2Center for Materials Research using Third-Generation Synchrotron Radiation Facilities, Hiroshima Institute of Technology, Hiroshima 731-5193, Japan
3Graduate School of Engineering, Kyoto University, Kyoto, 606-8501, Japan
E-mail: inui@mls.ias.hiroshima-u.ac.jp

Abstract. The structure factor, $S(Q)$, of fluid sulfur was measured up to 1573 K and 30 MPa using synchrotron radiation at SPring-8 in Japan. The pair distribution function, $g(r)$, deduced from $S(Q)$ exhibits the first peak well separated from higher coordination shells in the entire density region from liquid to dense vapour. At 0.6 g cm$^{-3}$ near the critical density the coordination number of the first peak is one but the bond length remains approximately 2 Å, longer than that of an isolated S$_2$ molecule. These results hint a strong intermolecular interaction between S$_2$ molecules in the dense vapour phase near the critical density in the supercritical region.

1. Introduction
Elemental sulfur (S) exhibits many species of molecular forms in the solid [1], liquid and gaseous states. The most stable one at the ambient conditions may be an eight-membered ring (S$_8$) molecule and they are main components in the liquid near the melting temperature of 388 K. However the S$_8$ molecules are unstable at 432 K where the polymerization transition occurs. When temperature is elevated, liquid S becomes a mixture of ring- and chain-molecules. The fraction of chain molecules increases with increasing temperature while small molecules such as S$_2$ and S$_8$ become dominant in the vapour phase above the boiling point.

Studies on fluid S in a wide density range are attractive subjects because large variation of the molecular forms is expected in the fluid phase. To do them, experiments at high temperature and high pressure are needed because a continuous volume expansion from the liquid to the dense vapour is possible only by surrounding the liquid-vapour critical point (the critical temperature, pressure and density of fluid S are $T_C = 1313$ K, $P_C = 20.3$ MPa and $\rho_C = 0.58$ g cm$^{-3}$, respectively [2]). As for the properties of the supercritical fluid S, optical absorption [3] and reflection [4, 5] measurements at high temperature and high pressure were reported and the results indicate that there appear several absorption bands in the supercritical region, which suggests molecular species like S$_2$, S$_3$, S$_4$, S$_6$, S$_8$ and so on. However the real structure in the supercritical fluid S is unknown. We carried out X-ray diffraction measurements for expanded fluid S using synchrotron radiation and high-pressure and high-temperature apparatus of our
Figure 1. (a) The structure factor \( S(Q) \) of expanded fluid S at temperatures and densities indicated in the figure. (b) The pair distribution function \( g(r) \) obtained from the Fourier transform of \( S(Q) \) shown in (a). \( g(r) \) at 0.03 g cm\(^{-3}\) is reduced by the factor of 0.1 as indicated in the figure. In both (a) and (b) each curve is displaced for clarity.

own design. In this article we report the density dependence of the local structure in fluid S, focusing on the covalent bonds.

2. Experimental
We have performed energy-dispersive X-ray diffraction measurements for expanded fluid S using synchrotron radiation at BL28B2/SPRING-8 in Japan. We used an internally-heated high-pressure vessel made of a super-high-tension steel, which permits measurements up to 2000 K and 196 MPa. The high-pressure vessel had Be windows for incident and scattered X-ray beams. The latter windows were located at the scattering angles of \( 2\theta \) of 4, 7, 11.5, 15, 20, 25 and 33 degrees, to cover a wide range of the modulus of the scattering vector \( Q \), \( Q = 4\pi E \sin \theta / hc \), where \( h \) is Planck’s constant, \( c \) is the velocity of light and \( E \) is the energy of the X-ray). The S sample (99.999 %) was contained in a single-crystalline sapphire cell with the sample thickness of 1.3 mm. The measurements were done from 403 K to 1573 K at 30 MPa and from 30 MPa to 5 MPa at 1573 K. The density of fluid S was determined from the temperature and pressure data using the density data [2]. Details of the high-pressure gas apparatus for X-ray diffraction experiments and the data processing were described in the literature [6].

3. Results and discussion
Figure 1 (a) shows the structure factor \( S(Q) \) of fluid S at 30 MPa except for the top spectrum at 15 MPa and at selected temperatures. The temperature and weight density \( \rho \) are indicated in the figure. \( S(Q) \) at 403 K and 473 K agrees with that obtained from neutron scattering
Figure 2. The coordination number of the first shell $N_1$ (the upper panel) the nearest neighbour distance $r_1$ (the lower panel) as a function of density $\rho$. Each solid curve is a guide for the reader’s eyes.

measurements [7, 8]. We could obtain $S(Q)$ above 773 K for the first time (the boiling temperature of liquid S at the normal pressure is 718 K). Below 473 K $S(Q)$ exhibits a clear first peak at 2 Å$^{-1}$. With increasing temperature, the peak at 2 Å$^{-1}$ becomes broader and broader while the shoulder at 1.5 Å$^{-1}$ develops and becomes the first peak. The oscillations in $S(Q)$ from 403 K to 1423 K remain nearly the same phase for $Q > 3$ Å$^{-1}$ while the oscillations slightly damps with increasing temperature. This behaviour may indicate that $S(Q)$ at large $Q (> 3$ Å$^{-1}$) represents the short range correlation probably up to the second neighbours in the real space.

Figure 1 (b) shows the pair distribution function $g(r)$ obtained from the Fourier transform of $S(Q)$ shown in Fig.1 (a). The first peak which clearly separated from the second coordination shell is observable at all densities. The present $g(r)$ exhibits several spurious peaks due to a termination error because the $Q$ maximum of approximately 15 Å$^{-1}$ in the present data is much smaller than the neutron scattering data [7, 8]. However the density dependence of the first peak in $g(r)$ is obviously detected.

We determined the covalent bond length $r_1$ as the first peak position in $g(r)$, and deduced the coordination number of the first peak $N_1$ from the integration of $4\pi n r^2 g(r)$ for the first peak region, where $n$ is the number density. Figure 2 shows $N_1$ and $r_1$ as a function of $\rho$. Below the boiling temperature at the normal pressure ($\rho > 1.6$ g cm$^{-3}$), $N_1$ and $r_1$ are approximately 2 and 2.1 Å, which suggests that the liquid is constituted from ring- and chain-molecules. With decreasing $\rho$, $N_1$ decreases monotonically while $r_1$ is approximately constant. It is noteworthy that at 0.6 g cm$^{-3}$ near the critical density $N_1$ becomes approximately 1, corresponding to $N_1$ of a $S_2$ molecule, but $r_1$ remains more than 2.0 Å longer than the bond length of an isolated $S_2$. This result suggest a strong intermolecular interaction between $S_2$ molecules in the dense vapour phase near the critical density. At the lowest density, $r_1$ becomes 1.9 Å, suggesting that $S_2$ molecules are really isolated in the rarefied vapour phase.

For further investigation, theoretical calculations for several S clusters [9, 10] may be useful. The first possibility is that if the population of $S_3$ molecules giving $N_1 = 1.3$ is significant but not so large, the average $r_1$ may be larger than that of the isolated $S_2$ molecule. As the second
possibility, $S_4$ clusters with $D_{2h}$ and $C_{2v}$ symmetries have the structure where two $S_2$ units are combined with each other. Although the simulation gives the same bond length of the $S_2$ unit in the isolated $S_4$ clusters and the isolated $S_2$ molecule, the covalent bond of the $S_2$ unit may be slightly longer in the dense vapour phase. Meanwhile the bond bridging two $S_2$ units in the isolated clusters is approximately 2.7 Å, which is located in the tail region of the second peak in the observed $g(r)$. Consequently we speculate that such $S_4$ clusters are formed in the dense vapour phase around the critical density in the supercritical fluid $S$.

Acknowledgments
The authors are grateful to K. Kato and Y. Imai for their valuable discussions. This work is supported by Grant-in-Aids for Scientific Research from the Ministry of Education, Science and Culture of Japan. The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No.2006A1067).

References
[1] Donohue J *The structure of the elements* (John Wiley and Sons, Inc., 1974).
[2] Fischer R, Schmutzler R W and Hensel F 1982 *Ber. Bunsenges. Phys. Chem.* 86 546.
[3] Weser G, Hensel F and Warren Jr W W 1978 *Ber. Bunsenges. Phys. Chem.* 82 588.
[4] Tamura K, Seyer H P and Hensel F 1986 *Ber. Bunsenges. Phys. Chem.* 90 581.
[5] Ikemoto H, Yamamoto I, Yao M and Endo H 1994 *J. Phys. Soc. Jpn.* 63 1611.
[6] Tamura K and Inui M 2001 *J. Phys.: Condens. Matter* 13 R337.
[7] Winter R, Szornel C, Pilgrim W-C, Howells W S and Egolstaff P A 1990 *J. Phys.: Condens. Matter* 2 8427.
[8] Winter R, Egolstaff P A, Pilgrim W-C and Howells W S 1990 *J. Phys.: Condens. Matter* 2 SA215.
[9] Hohl D, Jones R O, Car R and Parrinello M 1988 *J. Chem. Phys.* 89 6823.
[10] Jones R O and Ballone P 2003 *J. Chem. Phys.* 118 9257.