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Photo-induced structural change in liquid sulphur

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Abstract. The structure of liquid sulphur at 400 K, below the polymerization temperature $T_p = 432$ K, is investigated by first-principles molecular-dynamics simulations. The calculated structure factor is in excellent agreement with the experimental data. To investigate the microscopic mechanism of the photo-induced structural change in liquid sulphur below T_p , simulations are performed by exciting electrons in the valence band to the conduction band. It is found that a bond in one of the S_8 rings is easily broken and consequently the S_8 ring turns out to be the S_8 chain after an electron excitation, in the same way as was seen for an isolated S_8 ring. After the electron excitation is stopped, the S_8 chain does not reconstruct the S_8 ring; instead a ‘tadpole’ structure is formed. Since the tadpole structure persists for a long time, it is considered that the tadpole is one of possible structures for the experimentally observed long-lived product in the relaxation process. We have shown that photo-induced polymerization occurs in liquid sulphur when the S_8 chains or the S_8 tadpoles are close to each other at their ends.

1. Introduction

Liquid sulphur consists of eight-membered rings S_8 near its melting point, 386 K. When a polymerization transition occurs at the temperature of $T_p = 432$ K, the liquid sulphur becomes a mixture of long chains and S_8 rings. To gain an understanding of the elementary process of the polymerization of liquid sulphur, Sakaguchi and Tamura [1] illuminated liquid sulphur with a pulsed laser below and above T_p and measured the transient absorption spectra. They found two kinds of relaxation, which suggests that a photo-induced polymerization occurs below T_p . From their experimental results they proposed the following scenario for the polymerization and the relaxation: due to the laser illumination, the S_8 rings break and become S_8 chains. On increasing the power of the pulsed laser, the number of broken S_8 rings increases and finally polymerization occurs when the density of the broken S_8 rings has reached a critical value. In the relaxation process after the illumination is stopped, first the broken S_8 ring turns into a long-lived product, whose structure is not known, and then there is a return to the original S_8 ring structure after about forty minutes.

To investigate the possibility of photo-induced bond breaking of the S_8 ring, Shimojo *et al* [2] have performed a first-principles molecular-dynamics (MD) simulation for an isolated S_8 ring. They have shown that a bond of the isolated S_8 ring breaks immediately after an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). From their analysis of the time dependence of the eigenvalues and

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the wave functions, it is established that the bond breaks in order to stabilize the anti-bonding states occupied by the excited electron. It was also shown by Hoshino *et al* [3] using first-principles MD simulation that a similar bond breaking occurs for an infinite Se chain as well as an Se₈ ring on exciting an electron from the HOMO to the LUMO.

Recently Tse and Klug [4] carried out a Car–Parrinello first-principles MD simulation for liquid sulphur and showed that the S₈ rings begin to break up at temperatures higher than 1200 K. They also performed calculations for excited states at temperatures higher than 800 K and showed that an S–S bond in one of the S₈ rings breaks on exciting an electron.

In this paper we apply first-principles MD simulation to liquid sulphur at 400 K, below T_p , and investigate its microscopic structures for the ground state and also for the relaxation process after electron excitation. The purposes of this paper are as follows:

- (i) to investigate the possibility of photo-induced bond breaking in liquid sulphur below T_p ;
- (ii) to clarify the microscopic structure of the experimentally observed long-lived product in the relaxation process; and
- (iii) to investigate how the photo-induced polymerization occurs.

2. Method

Our calculation is based on density functional theory with the generalized-gradient approximation (GGA) [5]. For the electron–ion interaction, we employ the ultrasoft pseudopotential proposed by Vanderbilt [6], which is derived from the calculation for the atomic electron configuration $3s^23p^43d^0$. The electronic wave functions are expanded in terms of a plane-wave basis set with a cut-off energy of 14 Ryd. The Γ point is used to sample the Brillouin zone of the supercell. The Kohn–Sham energy functional is minimized by the preconditioned conjugate-gradient method [7–9]. The forces on the ions are calculated using the Hellmann–Feynman theorem. The constant-temperature MD simulation is performed using the Nosé–Hoover thermostat [10, 11]. The equations of motion are integrated by the velocity Verlet algorithm with the time step $80 \text{ au} = 1.944 \text{ fs}$. In our MD simulation, a system of 80 atoms, i.e. ten S₈ molecules, is used. The mass and the number densities of the system are 1.79 g cm^{-3} and 0.0336 \AA^{-3} , respectively, and the length of the side of the cubic supercell is 13.4 \AA . The initial atomic configuration was generated by a Monte Carlo simulation with the Stillinger–Weber potential [12] which is composed of parametrized two-body and three-body potentials. The electron excitation is carried out by exciting an electron from the highest occupied level to the lowest unoccupied level and the excited electron is forced to stay at this level during the excitation. Then, to investigate the relaxation process, the electronic states are calculated without the electron excitation. There have been several studies for sulphur [2, 4], silicon [13, 14] and selenium [3, 15, 16] in their liquid states with excited states of electrons using the density functional theory.

3. Results and discussion

3.1. Ground state

In figure 1, we show a snapshot of the atomic configuration in liquid sulphur at 400 K, where bonds are drawn when the separation of two atoms is less than 2.3 \AA . We confirm that liquid sulphur consists of S₈ molecules with the shape of a puckered ring. The S₈ rings are very stable and no S–S bond broke at this temperature during our simulation. The structure of the S₈ ring in this system is almost the same as that of the isolated S₈ ring. The averaged bond length r_e and bond angle θ in the liquid are 2.08 \AA and 108.3° , respectively, while for the calculated

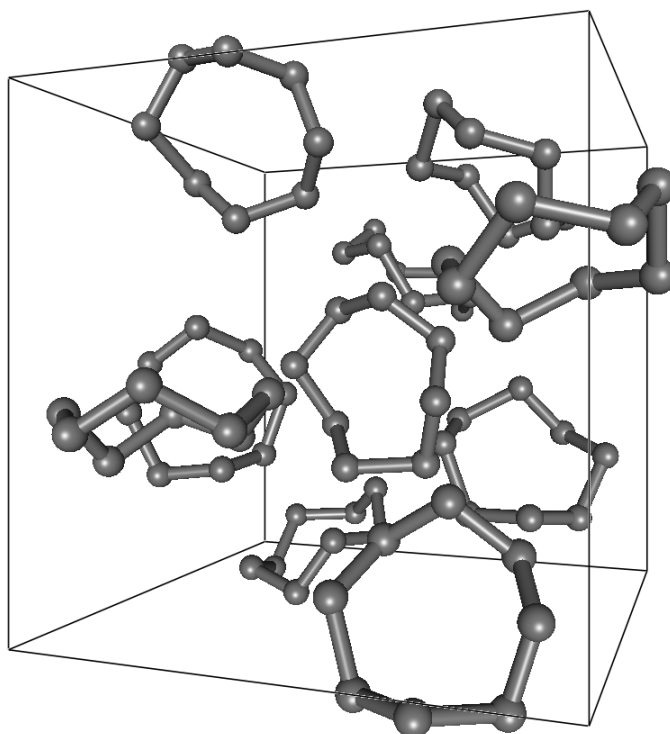


Figure 1. A snapshot of liquid sulphur for the ground state at 400 K. Bonds are connected when the separation of two atoms is less than 2.3 Å.

optimized structure of the isolated S_8 ring, r_e and θ are 2.075 Å and 109.0° , respectively. These quantities are in good agreement with the observed values of $r_e = 2.06$ Å and $\theta = 108.2^\circ$ for the isolated S_8 ring [17].

The structure factors $S(k)$ of liquid sulphur are shown in figure 2. The line shows the result of the present study, which is obtained by averaging over the atomic configurations for 800 steps after the equilibration. The solid circles show the experimental data at 403 K obtained by Winter *et al* using neutron scattering [18]. The calculated $S(k)$ is in excellent agreement with the experimental result and this verifies the accuracy of our calculation.

The radial distribution functions $g(r)$ of liquid sulphur at 400 K are shown in figure 3. The solid line shows the total $g(r)$. The intermolecular and intramolecular $g(r)$ s are also shown, by the dashed line and the long-dashed line, respectively. From this figure the positions of the first, second and third peaks of the total $g(r)$ correspond to the distances between the first-, second- and third-neighbour atoms within the S_8 molecule, respectively. No distinct structure can be seen in the intermolecular $g(r)$. While the S–S bond distance is in the range of 1.9–2.3 Å, the closest-approach distance between the atoms of the different molecules is 2.8 Å. This feature shows that the S_8 ring is very stable in liquid sulphur at 400 K.

3.2. Excitation of an electron

To investigate the photo-induced bond breaking in liquid sulphur, an electron is excited from the highest level of the occupied states to the lowest level of the unoccupied states at a certain

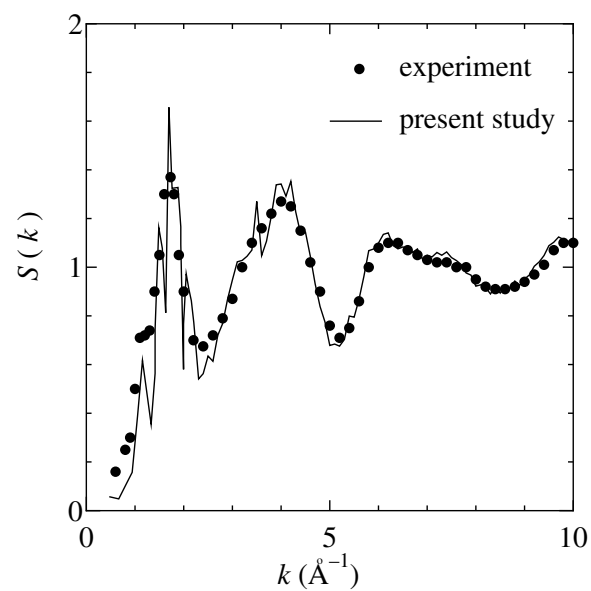


Figure 2. The structure factors $S(k)$ of liquid sulphur at 400 K. The calculated result is shown by the line and the neutron experimental data [18] are also shown, by the solid circles.

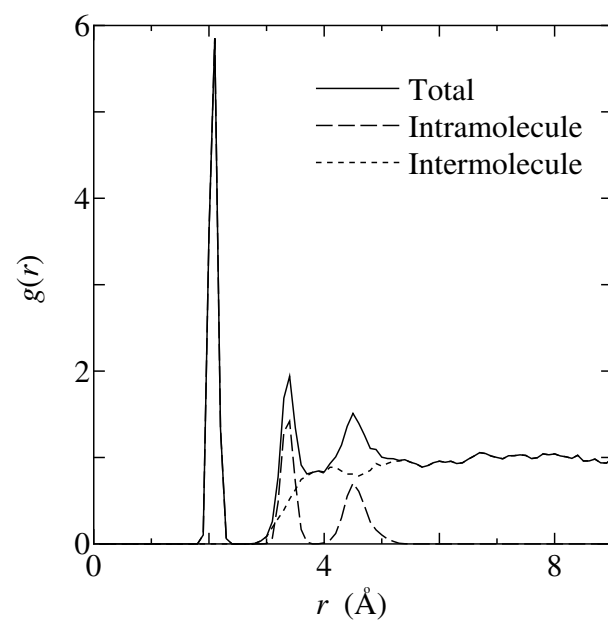


Figure 3. The radial distribution function $g(r)$ of liquid sulphur at 400 K. The solid line shows the total radial correlation function. The intermolecular and the intramolecular correlation functions are also shown by the dashed line and the long-dashed line, respectively.

MD step. It is found that one of the S_8 rings breaks immediately after the excitation in the same way as was seen for an isolated S_8 ring [2]. In figure 4, we show the time dependence of the S–S bond lengths in the S_8 molecule, which will break upon electron excitation. The

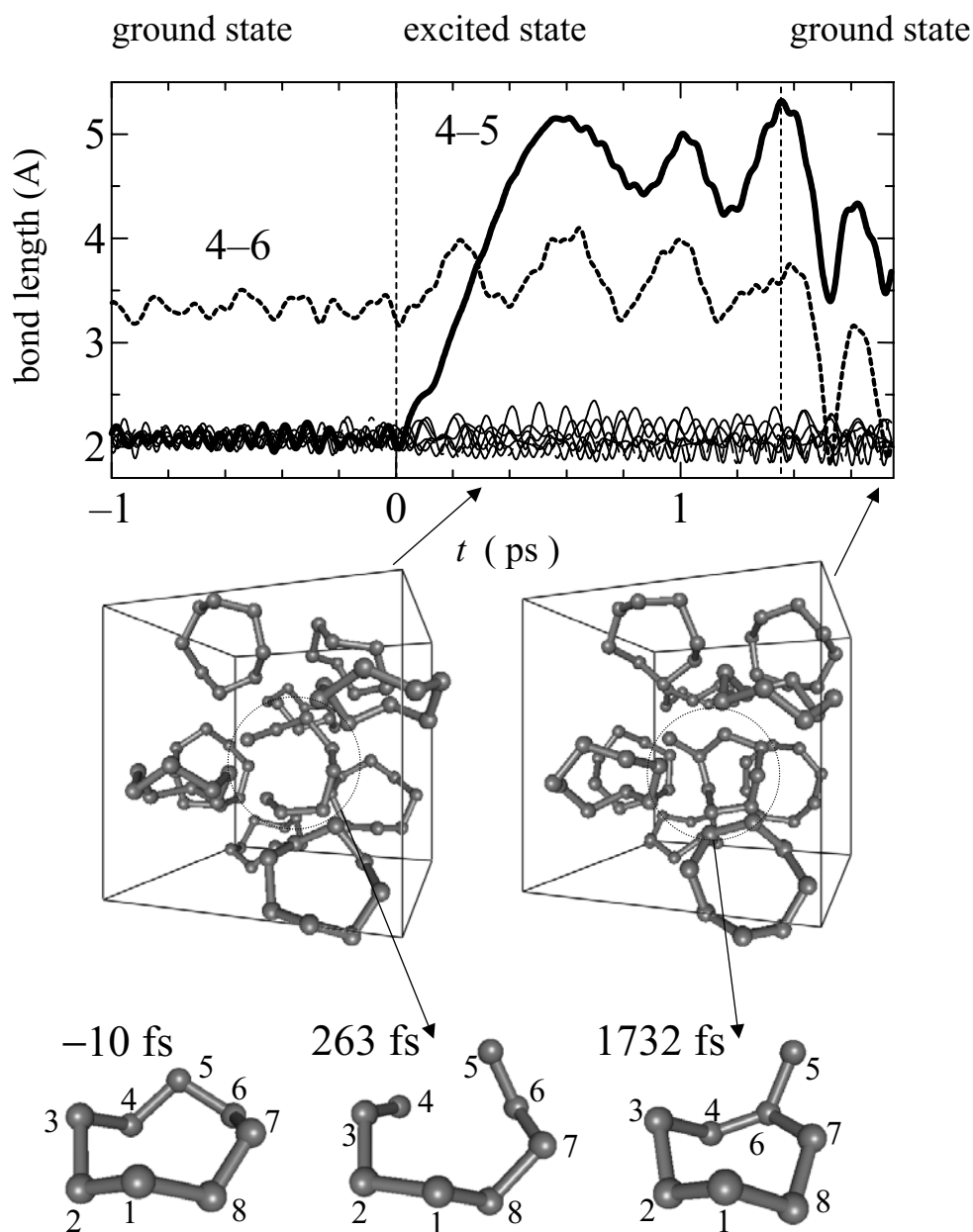


Figure 4. The time dependence of eight S-S bond lengths on the S_8 molecule, which will break upon electron excitation. The origin of time is the instant when an electron is excited. Snapshots of the structure during the excitation and after stopping the excitation are also shown for the S_8 molecule. Two atoms whose distance apart is smaller than 2.5 \AA are connected by a bond.

origin of time is the instant when an electron is excited. Each atom is numbered as shown in the bottom insets. The distance between atoms number 4 and number 6 as well as the bond lengths of the eight S-S bonds between adjacent atoms in the S_8 ring are shown. Though the eight bond lengths oscillate around their average value of 2.08 \AA when the system is in the

ground state for $t < 0$, the bond between atoms number 4 and number 5 increases suddenly upon the electron excitation.

Snapshots of the atomic configuration during and after the excitation are also shown in figure 4. It is clearly seen that, upon excitation, a bond in the S_8 ring breaks. Compared with the snapshot at -10 fs, before the excitation (see figure 1), it is found that the S_8 ring whose bond will be broken changes its structure very rapidly upon the excitation, while the other S_8 rings are in almost the same position, maintaining the shape of the puckered ring.

To simulate the relaxation process after the laser illumination, the electron excitation is discontinued at $t = 1.36$ ps. As shown in figure 4, upon stopping the excitation, the fourth and sixth atoms, which are originally second-neighbour atoms, approach each other and finally these two atoms are connected by a new bond. That is, the S_8 chain does not reconstruct the original S_8 ring but forms a 'tadpole-shaped structure' in the relaxation process.

3.3. Further excitations

Next, following the first electron excitation, the second-highest-energy electron is excited from the valence band to the conduction band instead of the electron excitation being stopped, i.e. two electrons are excited at the same time. As we have shown, when an electron is excited from the highest energy level to the lowest unoccupied level, a bond in one of the S_8 rings is broken. However, we cannot specify in advance which bond will be broken. There are two possible structural changes due to the excitation of the second electron: one is that where a bond in the already broken S_8 ring breaks, i.e. the molecule breaks up into two parts, and the other is that where one of the other S_8 rings breaks and turn into an S_8 chain. By detecting this second excitation, we observed that it was the latter change that actually occurred; that is, another S_8 ring is broken in the same way as the first one. While the system is in the excited state, the two S_8 chains neither attack the other S_8 rings nor change their own structures, maintaining the S_8 chain structure.

After the electron excitation was stopped, the simulation was continued for about 1 ps. In the same way as for the relaxation process with one electron excitation, each of the two chains does not reconstruct the original S_8 ring but forms a tadpole structure. Since the two tadpoles are surrounded by S_8 rings and do not approach each other during the simulation, we did not observe a structural change caused by interaction between the two tadpoles. To look at the stability of the tadpole structure, we investigate the time evolution of one of the broken S_8 rings as shown in figure 5. The time is measured from the instant when the electron excitation is stopped. At 21 fs (just after the electron excitation is stopped), we can see that the S_8 molecule has the chain structure. The bond between the fourth and fifth atoms is broken. At 79 fs, the fifth atom is connected with the third atom (not with the fourth atom), and the tadpole structure is formed as was already shown in figure 4. Since the bond between the third and fifth atoms is not the *correct* bond, its bond distance sometimes becomes large as displayed in the atomic configurations at 166 and 584 fs. At 933 fs, the bond between the fourth and sixth atoms is formed, and consequently another type of tadpole structure is constructed. Thus we find that the rearrangement of the bondings in the tadpole structure occurs in the relaxation process. From figure 5, it is also found that, though the tadpole changes its structure with time, it survives for a long time. These structural properties in the relaxation process are consistent with the experimental suggestion; when the power of the laser is weak, the S_8 ring does not polymerize but turns out to be a long-lived product. From these facts, we suggest that the tadpole is one of the possible structures for the experimentally observed long-lived product.

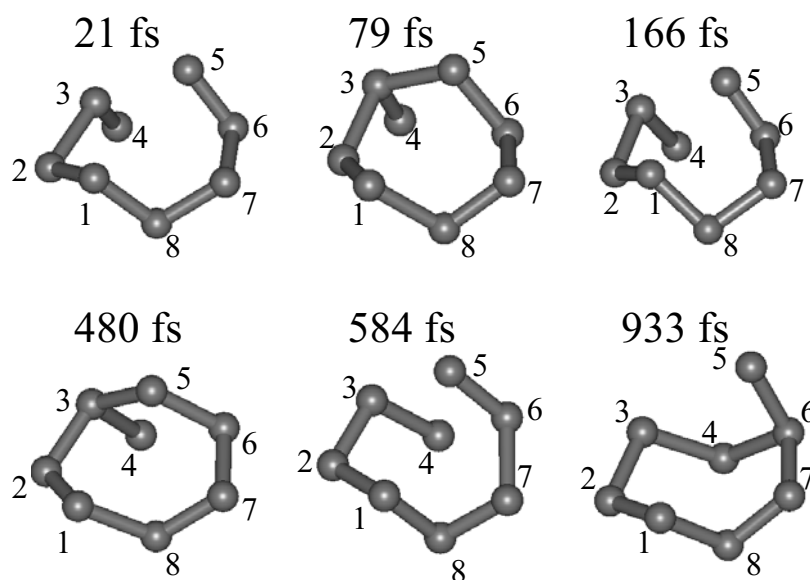


Figure 5. The time evolution of a broken S_8 molecule during the relaxation process. The origin of time is the instant when the electron excitation is stopped. Two atoms whose distance apart is smaller than 2.5 \AA are connected by a bond.

3.4. Polymerization

As mentioned above, the S_8 chain or S_8 tadpole does not interact with other S_8 rings during the simulation with a run time of about 3 ps. However, it is expected that, if two or more broken S_8 rings were closely positioned, they might interact with each other and eventually polymerize. Since it takes a long time for a broken S_8 ring to approach another one, we tried to make a configuration in which the polymerization may occur by increasing the number of broken S_8 rings; following the second excitation, a third electron was excited at a certain moment. As a result, a bond in one of the S_8 chains broke and that chain broke up into two parts. Although it is considered that this type of bond breaking occurs due to laser illumination, it is not desirable for the present purpose. Therefore, we positioned the four S_8 chains closely on purpose by hand and performed the simulation by exciting four electrons to investigate the possibilities of photo-induced polymerization. To reduce the artificial effects on the atomic configuration, the MD simulation was performed for about 0.4 ps, keeping the four electrons in the excited states. After the electron excitation was ceased, the simulation was continued for about 1.4 ps and we found that two S_{16} chains are formed by the four S_8 chains. In figure 6 we show the two processes of polymerization observed in this simulation. In process (a), the two S_8 chains are connected by the edge atoms and turn into a long S_{16} chain. On the other hand, in process (b), one of the S_8 chains becomes a tadpole at once. When the other S_8 chain approaches that tadpole at one edge, the tadpole turns out to be an S_8 chain, and finally the two S_8 chains are connected. The newly formed bonds are very stable and the two S_{16} chains survive throughout the simulation.

Thus we have demonstrated photo-induced polymerization by means of first-principles MD simulation. From the results of our simulations we conclude that

- (i) when a broken S_8 ring is surrounded by S_8 rings and is isolated from other broken S_8 rings, it tends to form a tadpole structure, and

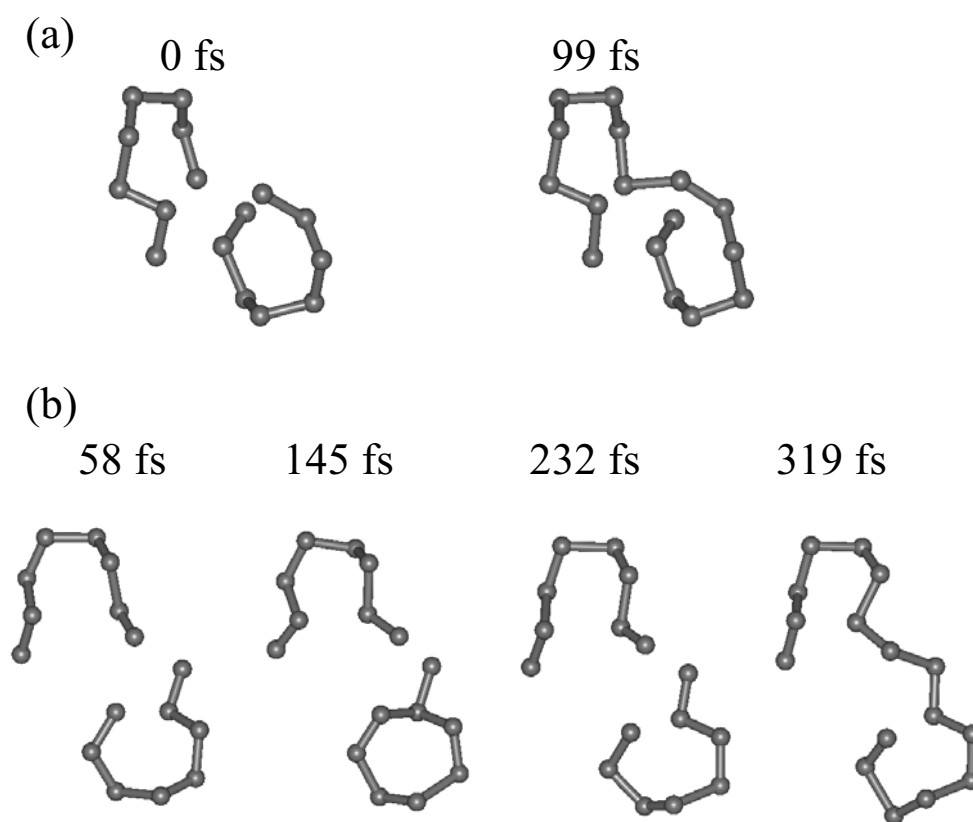


Figure 6. The two types of polymerization process in liquid sulphur during the relaxation: (a) the two S_8 chains among the four chains form an S_{16} chain; (b) one S_8 chain becomes tadpole at once; then the tadpole turns out to be an S_8 chain when the other S_8 chain approaches it, and finally the two S_8 chains form another S_{16} chain. The origin of time is the instant when the electron excitation is stopped. Two atoms whose distance apart is smaller than 2.5 \AA are connected by a bond.

- (ii) when the edge atoms of the broken S_8 rings approach each other, the broken rings form a long chain rather than forming tadpoles.

3.5. Mean square displacements

Figure 7 shows the mean square displacement for the atoms in the liquid sulphur. The solid curve shows the result for the liquid at 400 K, before the polymerization. The self-diffusion coefficient D calculated from the gradient of this curve is $3.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This result is in reasonable agreement with the experiment [19]. The dotted line shows the results for after the polymerization and the calculated value of D is $2.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. It is shown that the diffusion coefficient becomes smaller when polymeric chains are formed, as is expected.

4. Summary

In this paper we have investigated photo-induced bond breaking, the subsequent relaxation and polymerization in liquid sulphur by first-principles MD simulation. When an electron on the

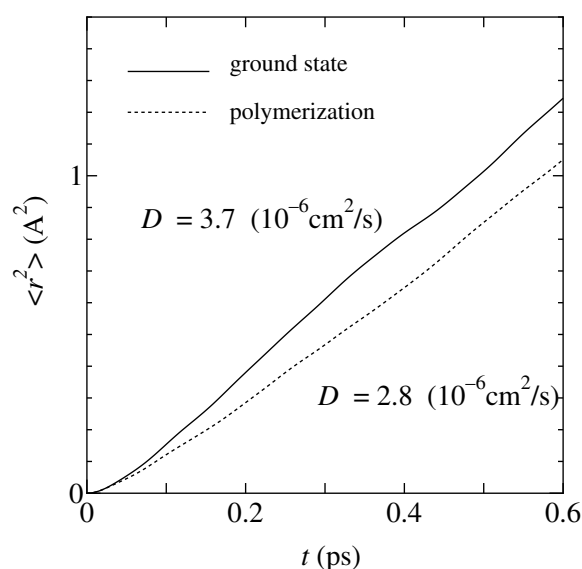


Figure 7. The mean square displacement of the atoms in liquid sulphur. The solid and the dashed lines show the result for the liquid at 400 K and that following the polymerization process, respectively.

highest orbital in the valence band is excited, a bond in one of the S_8 rings is broken and the S_8 ring turns out to be an S_8 chain. In the relaxation process the S_8 chain does not reconstruct the original S_8 ring structure but forms a tadpole structure. We suggest that the S_8 tadpole structure is one of the possible structures for the experimentally observed long-lived products. We have shown that photo-induced polymerization occurs in liquid sulphur when the S_8 chains or the S_8 tadpoles are close to each other at their ends.

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