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LETTER TO THE EDITOR

Photo-induced bond breaking in the S₈ ring: an *ab initio* molecular-dynamics simulation

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Abstract. The microscopic mechanism of the recently observed bond breaking in the S₈ ring illuminated by a pulsed laser is investigated by means of an *ab initio* molecular-dynamics simulation. It is found that a bond in the S₈ ring is easily broken immediately after an electron in the highest occupied molecular orbital is excited to the lowest unoccupied molecular orbital. From the time dependence of the eigenvalues and the wave functions obtained by the simulation, it is established that the bond breaks in order to stabilize the anti-bonding states occupied by the excited electron.

It is well known that the S₈ ring is the most common and most stable among the many sulphur rings, and it appears as the main component in the solid and liquid as well as the vapour phases. The ground-state structure of the neutral S₈ ring cluster has the D_{4d} crown-shaped geometry with strong bonds between sulphur atoms [1, 2]. Not only do the neutral clusters have ring structures, but so also do the ionized S₈ clusters. The S₈ clusters do indeed show strongly in the mass spectra [3] as positive ions, which are considered to have ring structure. The stable structure of the negatively charged S₈ cluster is a puckered ring which is similar to the structure of the neutral cluster [4]. It is, therefore, thought that the geometrical shape of the S₈ ring is very stable thanks to the strong σ - and π -like bonds formed by 3s and 3p electrons, and is not significantly affected even when an electron is removed or added.

Recently, Sakaguchi and Tamura [5] measured the transient absorption spectra of liquid sulphur after illuminating it with the third harmonics (355 nm) of a Nd:YAG pulsed laser below and above the polymerization temperature $T_p = 432$ K. Below T_p , where the liquid sulphur consists of S₈ rings, they found that the transmittance increases abruptly just after the illumination with a pulsed laser, and that this is followed by long-time relaxation processes. They asserted that this change in the transmittance is caused by the photo-induced polymerization in the liquid sulphur below T_p . Before the polymerization, a bond breaking in the S₈ ring has to take place as a result of the illumination by the laser. However, that such a photo-induced bond breaking in the S₈ ring is possible is not obvious, because neutral and ionized S₈ rings are rather stable as stated above.

In this article, we have performed *ab initio* molecular-dynamics (MD) simulations of an isolated S₈ cluster in order to discuss the instability of an S₈ ring which is illuminated by a pulsed laser. We show for the first time that a bond in the S₈ ring is easily broken immediately after an electron in the HOMO (highest occupied molecular orbital) is excited to the LUMO (lowest unoccupied molecular orbital). This result strongly supports the

possibility of photo-induced bond breaking in the S_8 ring followed by polymerization in the liquid sulphur below T_p .

Our calculations have been performed within the framework of density functional theory in the local density approximation (LDA) [6]. We have also performed some calculations using the generalized-gradient approximation (GGA) [7] and confirmed that the conclusion reached in the following does not depend on the approximation chosen. Moreover, we have made sure that the spin polarization has no effect on the results of our calculations. The electronic wave functions were expanded in the plane-wave (PW) basis set. The energy functional was minimized using an iterative scheme based on the preconditioned conjugate-gradient method [8–10]. For the interaction between valence and core electrons, we used the ultrasoft pseudopotential proposed by Vanderbilt [11]. The PW cut-off energy is 15 Ryd, which gives the total energy with an accuracy of 1 mRyd/atom. A fcc supercell with the lattice constant $a = 15.9 \text{ \AA}$ was used, and periodic boundary conditions were imposed. This supercell is large enough for the adjacent clusters to be separated.

First, to check the accuracy of our method, we applied it to an S_2 dimer. The bond length r_e and the vibrational frequency ω_e were obtained as 1.91 \AA and 702 cm^{-1} , respectively, which are in good agreement with the experimental values [12], $r_e = 1.8892 \text{ \AA}$ and $\omega_e = 725.65 \text{ cm}^{-1}$, and with the previous theoretical calculations [1, 2]. Then we calculated the geometrical parameters for the optimized S_8 ring, such as the bond length ($r = 2.05 \text{ \AA}$), the bond angle ($\theta = 108.8^\circ$) and the dihedral angle ($\phi = 97.8^\circ$), which are also in good agreement with the experimental values [13], $r = 2.055 \text{ \AA}$, $\theta = 108.2^\circ$ and $\phi = 98.5^\circ$.

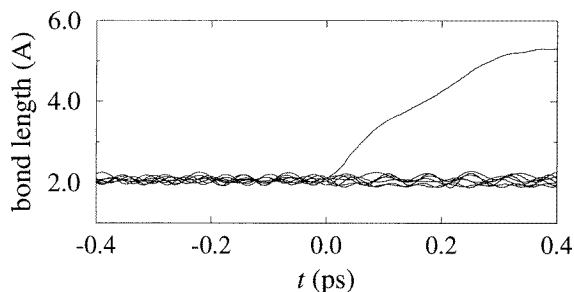


Figure 1. The time dependence of the S–S bond lengths in the S_8 cluster. The bond lengths for eight S–S bonds are displayed. The origin of time ($t = 0$) is the time at which an electron in the HOMO is excited to the LUMO.

In dynamic simulations, the equations of motion were solved by the velocity Verlet algorithm using the Nosé–Hoover thermostat technique [14, 15], with the time step $\Delta t = 1.68 \text{ fs}$. The equilibrium temperature of the S_8 cluster was chosen to be 400 K which is lower than T_p . The initial charge density at each MD step was estimated by extrapolating the charge densities for the previous steps [9], and the initial wave functions were estimated from the wave functions for the previous steps by a subspace diagonalization [16].

First, we carried out an *ab initio* MD simulation of the S_8 cluster with the ground-state geometry as the initial configuration. The S_8 cluster shows a vibrating motion, while retaining the ring structure. The vibrational frequencies calculated by the present MD simulation are in good agreement with the experimental values [17].

When a photon is absorbed by an S_8 ring, an electron is excited to one of unoccupied states. To simulate the dynamic process of structural change in the S_8 ring illuminated by a pulsed laser, the electron in the HOMO was excited to the LUMO at a certain MD step,

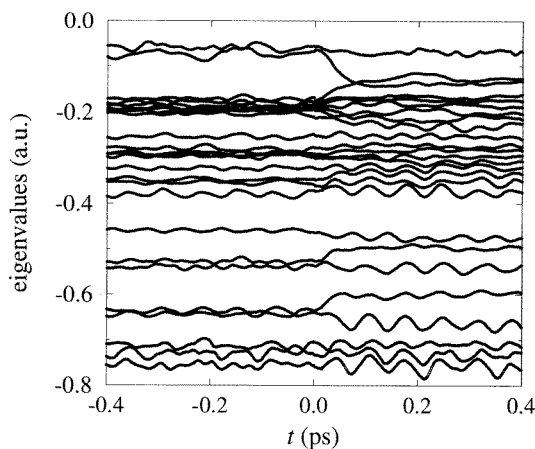


Figure 2. The evolution of the single-electron eigenvalues as a function of time.

and after that the electron configuration was fixed. Note that, although the LUMO is now occupied by one electron and is not literally the ‘unoccupied’ orbital and the HOMO is not the ‘highest occupied’ orbital any more, we continue to use these expressions to refer to these orbitals for convenience. Several MD simulations have been performed with various initial atomic configurations, which were generated by the MD simulation without excited electrons.

In figure 1 we show a typical example of the time dependence of the S–S bond lengths in the S_8 cluster, where the bond lengths for eight S–S bonds are displayed. The origin of time ($t = 0$) is the time at which an electron in the HOMO is excited to the LUMO. Before that ($t < 0$), the S–S bond lengths oscillate around their equilibrium distances (2.05 Å), and the ring structure is retained. After the excitation ($t > 0$), where the LUMO as well as the HOMO are occupied by one electron, one of the bond lengths increases suddenly, as shown in figure 1, which means that the bond breaking occurs in the S_8 ring. Figure 2 shows the evolution of the single-electron eigenvalues as a function of time. The electronic states below and above -0.4 au are characterized mainly as 3s and 3p orbitals, respectively. For $t < 0$, the electronic states below -0.17 au are occupied by electrons, and there is a gap of about 0.1 au between the HOMO and the LUMO. This large gap is related to the stability of the S_8 ring. After the electron is excited, the electronic structure is changed. At $t = 0$, the eigenvalue of the HOMO starts to increase, while that of the LUMO starts to decrease. They intersect at around 0.07 ps. It is considered that this change in electronic structure induces the bond breaking, i.e. the bond breaking occurs to release the high electronic energy due to the electron occupation of the LUMO. Since the formation of an S–S bond in the S_8 cluster is related not only to the HOMO and the LUMO but also to almost all states, it was not obvious whether or not the bond breaking occurs after only one electron is excited. However, it is found, from our calculations, that the bond always breaks in the S_8 ring with the excitation of one electron, which suggests that photo-induced bond breaking occurs in real liquid sulphur.

In order to investigate the mechanism of the bond breaking in more detail, we have traced the evolution of the spatial distributions of wavefunctions for the HOMO and the LUMO as shown in figures 3 and 4, respectively. The origin of time in these figures is the same as that in figures 1 and 2. At 0 fs, both wave functions spread over the whole cluster. It can be seen that the HOMO has bonding and lone-pair characters, while the LUMO has

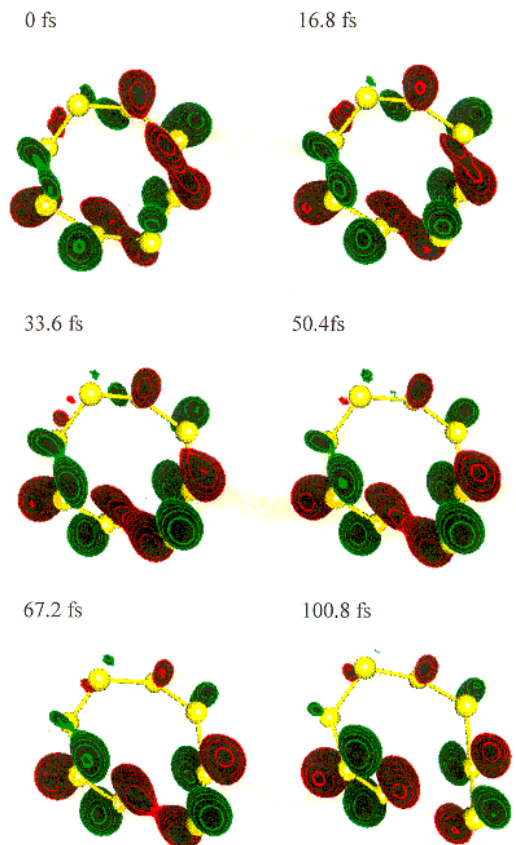


Figure 3. The time evolution of the spatial distributions of the wave functions for the HOMO. The yellow circles show the sulphur ions. The green and the red contour curves show the wave functions with different signs.

mainly anti-bonding character. At 16.8 fs, the distribution of the wave function for the LUMO starts to change in the way that the amplitude of the wave function increases around the S–S bond which will be broken, and decreases around other S–S bonds of the S_8 ring. Accompanying this change, the wave function for the HOMO changes its amplitude in the same way as that for the LUMO does. It is clearly seen that the HOMO and the LUMO form bonding and anti-bonding orbitals, respectively, at the S–S bond to be broken. These facts are crucially important for the bond breaking in the S_8 ring; that is, as is seen from the figures which show the time evolution of the wave functions, the bond breaking occurs so as to stabilize the anti-bonding LUMO.

It should be noted that, as shown in figure 2, with the bond breaking, some eigenvalues increase, and some eigenvalues decrease. The electronic states corresponding to the former have bonding characters at the S–S bond which will be broken as the HOMO does, while the electronic states corresponding to the latter have anti-bonding characters at the S–S bond as the LUMO does.

Here, we should comment on our calculations. In our electronic structure calculations, an electron was always excited from the HOMO to the LUMO, and so the electronic states

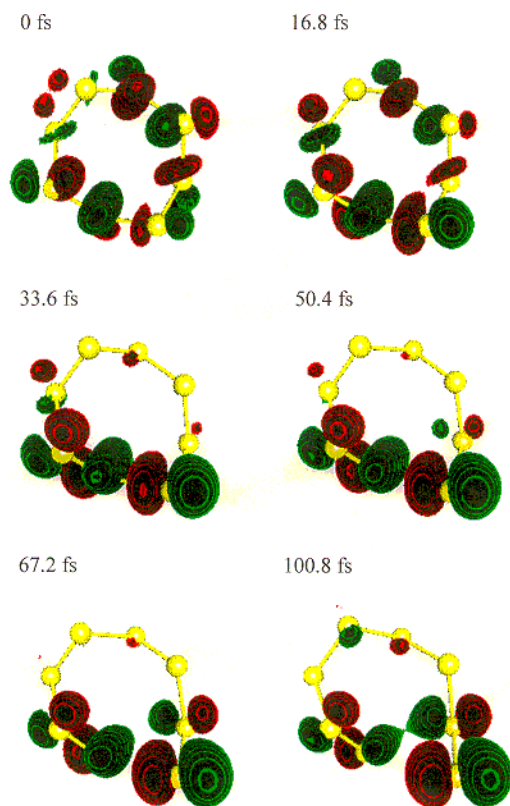


Figure 4. The time evolution of the spatial distributions of the wave functions for the LUMO. The yellow circles show the sulphur ions. The green and the red contour curves show the wave functions with different signs.

that we are concerned with are not the ground states. Therefore, strictly speaking, there is a fundamental problem in the use of the density functional theory (DFT), since the DFT is valid only for the ground state [18]. Moreover, it may be claimed that the trajectory obtained by the MD simulation is not on the Born–Oppenheimer surface. Despite these problems, we can justify our study by considering that our electronic structure calculations are equivalent to the calculation utilizing the finite-temperature DFT with fractional occupations, which has already been widely used. Our main assertion is based on the characters, i.e. the bonding or the anti-bonding characters, of the wave functions in the S_8 cluster, which never depend on the methods of calculation.

In this article, we have detailed our investigations into the microscopic mechanism of bond breaking in the S_8 ring illuminated by a pulsed laser using an *ab initio* molecular-dynamics simulation. We have found that a bond in the S_8 ring is easily broken immediately after an electron in the HOMO is excited to the LUMO. Since the unoccupied states of the puckered S_8 ring are basically characterized by anti-bonding states, they are stabilized by the bond breaking. Furthermore, since the occupied states have basically bonding character, S–S bonds become weak if electrons are removed from the occupied states. These are the reasons for which the bond breaking in the S_8 ring occurs. These results strongly support the possibility of photo-induced bond breaking in the S_8 ring followed by polymerization in the liquid sulphur below the polymerization temperature.

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