Atomic processes for the damage on bio-molecules irradiated by XFEL

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Abstract. We have calculated the change of the electronic states of C atoms irradiated by an XFEL as a function of time in order to study the damage of bio-molecules. We have treated various parameters such as pulse length, wavelength, flux of an XFEL, and bio-molecule size. This study gives valuable information for experiments of the diffraction patterns of single bio-molecules, which are employed to study their three dimensional structure.

1. Introduction
The analysis of three-dimensional structures of single bio-molecules such as proteins has lately attracted considerable attention as an application of an x-ray free electron lasers (XFEL) [1, 2]. This analysis will come from the diffraction patterns, which are produced from the irradiation of an XFEL onto bio-molecules. As the x-ray flux becomes larger, the better diffraction pattern is produced, however, the bio-molecules become more damaged, that is, the atoms in the bio-molecules become more ionized and more highly charged ions are produced. The highly charged ions lead to destroy the bio-molecules due to a Coulomb explosion. The damage and destroy, which appear as noise for the analysis of the three dimensional structure, depend on the experimental parameters such as flux, pulse length, wavelength of an XFEL, and bio-molecule size. The damage and destroy are studied in Refs. [1, 2] where the changes of the electronic states of atoms or ions as a function of time have been shown by using only one parameter of XFEL for a specific bio-molecule.

In this paper, we have treated various parameters in order to give significant information to the experiments of the diffraction patterns. Further, we employ more accurate atomic data for Auger, radiative transitions and electron impact ionization processes [3-5] which will be mentioned in Sec.2.

2. Models of the calculations
We treat C atoms with a spherical shape at solid density in this paper by the following reasons. (i) for the shapes of bio-molecules, we choose close to spherically shaped bio-molecules because of the lack of data concerning their three dimensional structures. (ii) as for carbon only choosing, the main elements in bio-molecules are carbon, nitrogen, and oxygen atoms. However, we can not see a big difference among their atomic data of cross sections and rates in terms of processes [3, 6]. Among these atoms, the number of carbon atoms is the largest in bio-molecules. (iii) as for density, the density of bio-molecules are almost the same as solid density.

For the calculation of the changes of the electronic states of atoms or ions in a bio-molecule as a function of time, we treat atomic processes such as photo absorption ionization (e.g., C + hν → C⁺ + e⁻), Compton scattering (e.g., C + hν → C⁺ + e⁺ + hν'), Auger (e.g., C⁺ → C²⁺ + e⁻), electron impact ionization (e.g., C + e⁻ → C⁺ + 2e⁻), and radiative transitions (e.g., C⁺⁺ → C⁺ + hν), where hν and C⁺⁺ are an x-ray energy and an inner-shell excited state of the C ion. The atomic data of Auger and radiative transitions are employed given in Ref. [3] where all the electronic states such as 1s² 2s² 2p²,
\[ \frac{dN_0}{dt} = -\beta_0 N_0, \]
\[ \frac{dN_1}{dt} = \alpha_0 N_0 - \beta_1 N_1, \]
\[ \cdot \cdot \cdot \]
\[ \frac{dN_n}{dt} = \alpha_{n-1} N_{n-1} - \beta_n N_n, \]

(1)

where \(N_0, N_1, \ldots, N_n\) are the populations of the ground state of the atoms and ions, singly inner-shell ionized states and hollow atoms of ions, respectively, and \(\alpha_{m,k}\) and \(\beta_k\), which are produced by using the atomic data as mentioned in Refs. \[3, 8-11\], are the transition rate from \(m'\)th to the \(k'\)th state and the decay rate in the \(k'\)th state, respectively.

In our model, bio-molecules are treated as a spherical shape with a radius of \(r\) and the solid density \(\sim 3 \times 10^{22}/\text{cm}^3\). Electrons, in particular, photo-electrons produced due to photo absorption ionization processes give a significant contribution to the effect of bio-molecule size. Just after an XFEL starts to irradiate onto a bio-molecule, the photo-electrons, which have almost the same energy as that of an XFEL, can escape from the bio-molecule. We employ \(r/v\) for the collision time between the photo-electron and the atoms or the ions in the bio-molecules where \(v\) is a velocity of the photo-electron. The secondary and highly order electrons stay in the bio-molecules because their energies are too small to escape from it.

When one electron escapes from a bio-molecule, the charge of the bio-molecule increases. The Coulomb force due to this charge reduces the electron energy \((E_e)\), as a result, the electron cannot escape from the bio-molecule when \(E_e\) becomes 0 in the bio-molecule. We assume that the charge is concentrated at the center of the bio-molecule because of the spherical shape assumed. When the energy of a photo electron produced at the center of the bio-molecule becomes 0 in the bio-molecule, we assume that it cannot escape. For example, when \(\lambda = 0.1 \text{ nm}\), \(r = 10 \text{ nm}\), and \(Q \geq 4 \times 10^{10}\), the photo-electrons cannot escape and stay in the bio-molecule, where \(\lambda\) and \(Q\) are the wavelength of the XFEL and the total charge in a bio-molecule, respectively.

3. Results and discussions

We have been studying the role of atomic processes such as photo-ionization, Auger, radiative transition processes \[3\], and electron impact ionization \[5\] for the damage of bio-molecules irradiated by an XFEL. By considering these roles, we have constructed the models mentioned in Sec.2. Furthermore, we have also proposed measuring the x-ray flux irradiated onto the bio-molecules by using hollow atoms \[3, 9, 11\]. For the measurement, the following property is used. The ratio of the number of fluorescent x-ray photons from the hollow atoms to that from the singly inner-shell ionized atoms is in proportion to the x-ray flux irradiating these atoms. In this paper, we have focused on the relationship of XFEL parameters to the damage. This will benefit future experiments using XFELs.

We have calculated the changes of the electronic states of atoms or ions in a bio-molecule as a function of time. However, the number of the electronic states is too large. Then, for clearer figures, we show the changes of charge determined from the electronic states.

Figures 1 (a - c) show the populations of the charge of C as a function of time for the pulse length \((r)\) and wavelength \((\lambda)\) of an XFEL of 100 fs and 0.1 nm, 10 fs and 0.1 nm and, 10 fs and 0.06 nm, respectively. The x-ray flux of the XFEL and the radius of bio-molecules are \(10^{22}/\text{pulse/mm}^2\) and 10
nm, respectively. A gauss type time function is employed for the intensity of the XFEL (see upper sides of figures 1) and the time of 0 is set when the peak intensity of x-rays is located in the bio-molecule. We have found that a shorter value of $\tau$ produces smaller damage (see figures 1(a) and (b)). This is due to the fact that time scale of Auger processes is about 10 fs. Namely, photo-absorption ionization and Auger processes occur only once in the case of $\tau = 10$ fs and several times in the case of 100 fs, respectively. Auger-electrons also give more significant contribution to the damage in the case of $\tau = 100$ fs. We have also found that a shorter value of $\lambda$ produces smaller damage (see figure 1(c) and (b)). This is caused by the inner-shell photo-ionization cross sections. The photo absorption ionization cross sections for $\lambda = 0.1$ nm is about 10 times larger than that for $\lambda = 0.06$ nm [12].

![Figure 1](image1.png)

**Figure 1.** Population of the changes of the charge of C atom as a function of time for the x-ray flux of an XFEL of $10^{22}$/pulse/mm$^2$, the radius of bio-molecules of 10 nm, and (a) $\tau = 100$ fs, $\lambda = 0.1$ nm, (b) $\tau = 10$ fs, $\lambda = 0.1$ nm, (c) $\tau = 10$ fs, $\lambda = 0.06$ nm, respectively. The numbers written in the figures express charge (Lower figures). Upper figures: the x-ray intensity as a function of time. The time of 0 is set when the peak intensity of x-rays passes through the bio-molecule.

![Figure 2](image2.png)

**Figure 2.** The same as figure 1(b) for the x-ray flux and the radius of a bio-molecule of (a) $10^{22}$/pulse/mm$^2$ and 10 nm, (b) $10^{21}$/pulse/mm$^2$ and 10 nm, (c) $10^{20}$/pulse/mm$^2$ and 10 nm, (d) $10^{22}$/pulse/mm$^2$ and 50 nm, (e) $10^{21}$/pulse/mm$^2$ and 50 nm, and (f) $10^{20}$/pulse/mm$^2$ and 50 nm, respectively.

Figures 2 (a - f) show the population of C with different charge states as a function of time for x-ray fluxes and radiiuses of bio-molecule of $10^{22}$/pulse/mm$^2$ and 10 nm, $10^{21}$/pulse/mm$^2$ and 10 nm, $10^{20}$/pulse/mm$^2$ and 10 nm, $10^{22}$/pulse/mm$^2$ and 50 nm, $10^{21}$/pulse/mm$^2$ and 50 nm, and $10^{20}$/pulse/mm$^2$ and 50 nm, respectively.
$10^{20}$/pulse/mm² and 50 nm, respectively. X-ray fluxes corresponds to the time scale of the photo absorption ionization processes because the rates of photo absorption ionization processes ($R_{ap}$) are in proportion to the x-ray flux. On the other hand, the size dependence comes from electron impact ionization processes because the interaction time of the photo-electron and atoms or ions in a bio-molecule increases according to the the bio-molecule size as mentioned before. The electron impact ionization cross sections decrease as charge numbers become larger [6]. Namely, size effects appear clearly when a lot of neutral atoms exist in the bio-molecule and as the charge number becomes large, the size effect seems to reduce.

Smaller x-ray fluxes and smaller bio-molecule size produce smaller damage. However, the resolution power or the intensities for the diffraction pattern correspond to x-ray fluxes and bio-molecule size. Intensities for the diffraction patterns ($I_o$) are given by

$$I_o = I_{XFEL} \frac{r_c^2 d^2}{R^2} \vert F(\vec{k}) \vert^2,$$

with

$$F(\vec{k}) = \int \rho(\vec{r}) e^{i \vec{k} \cdot \vec{r}} d\vec{r},$$

where $I_{XFEL}$, $r_c$, $d$, $R$, and $\rho(r)$ are the intensity of XFEL, the classical radius for electrons, the distance between the target and detector, the area of the detector, the density of electrons, respectively and $\vec{k}$ is a scattering vector. As a bio-molecule size becomes larger, $F(\vec{k})$ increases because the number of electrons becomes larger. Therefore, we need to study the intensities of the diffraction patterns including the damage in order to propose the best parameter for the experiments in future.

4. Summary
We have studied the damage of a bio-molecule irradiated by an XFEL from the calculation of the changes of the charge of C atoms as a function of time for various parameters of XFELs. We have shown the relationship of the damage with the parameters of pulse length, wavelength, flux of an XFEL and bio-molecule size. We believe that these results become important for the experiment of the three-dimensional structure of a single bio-molecule. In the future, we will study the intensities of the diffraction patterns including the damage.

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