Effects of electron-impact ionization on the damage to biomolecules irradiated by XFEL

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Abstract. The damage to biomolecules irradiated by an X-ray free electron laser is investigated with time-dependent rate equations, considering photoionization, Compton scattering, Auger decay and electron-impact ionization of the C atom and its ions. Averaged energies of secondary electrons, which are produced by electron-impact ionization, are calculated with the binary encounter dipole model (Kim Y-K. and Rudd M. E., 1994 Phys. Rev. A, 50 3954) to study electron-energy distribution in the biomolecule. We found that those energies for the C atom, C\(^{1+}\) and C\(^{2+}\) ions are about 20, 60 and 150 eV, respectively, at an incident electron energy of 12 keV, while those energies are in the order of tens of electronvolts when the incident electron energy is about 250 eV. We also found that the importance of electron-impact ionization increases as the X-ray flux decreases.

1. Introduction
In X-ray free electron laser (XFEL) applications, the analysis of three-dimensional structures of single biomolecules is a critical issue [1, 2]. When the biomolecule is irradiated by the XFEL, the electron density distribution of the biomolecule (three-dimensional structure) is obtained from the diffraction patterns of elastic-scattered photons. It is important to estimate intensities of the diffraction patterns, since a large number of X-ray photons will be needed for this measurement. The target samples, however, are damaged by photoionization, Auger decay, Compton scattering and electron-impact ionization processes. Therefore, we need to investigate the damage caused by those processes that influence the diffraction patterns.

Here, we concentrate on a description of the atomic processes leading to damage in the previous reports [1, 2]. The electron-impact ionization was not considered in Neutze’s paper [1]. On the other hand, the Compton scattering was not considered in Hau-Riege’s paper [2]. In the present study, photoionization, Auger decay, Compton scattering and electron-impact ionization are all taken into account. In addition, we also address here the electron-impact ionization, and study energy distribution of free electrons in the biomolecules. When a biomolecule is irradiated by the XFEL with a photon energy of 12 keV (or wavelength of \(\sim 0.1\) nm), the free electrons in the biomolecules have different energy components (\(\sim 12\) keV for photoelectrons, \(\sim 250\) eV for Auger electrons [1] and \(\sim 270\) eV for Compton recoil electrons). Moreover, to describe the damage, the energies of the secondary (or ejected) electrons produced by the processes listed above should also be estimated to describe the damage.

Time-dependent rate equations are solved with the atomic processes of the C atom and its ions. The population dynamics of the C atom and its ions, and the contributions of the
previously mentioned atomic processes to ionization, are investigated at the X-ray flux from 1 × 10^{19} to 1 × 10^{22} photons/pulse/mm^2.

2. Atomic data and model simulation
For our model simulation, we assumed that the target biomolecules can be treated as non-bonded carbon clusters with radius \( r [2, 4, 5] \). Photoionization cross sections were calculated using the Flexible Atomic Code (FAC) [6]. Auger rates were taken from previous results [5]. Compton cross sections and Compton recoil electrons energies are calculated by the Klein-Nishina formula.

For the electron-impact ionization process, the energy distributions and averaged energies of secondary electrons were obtained to calculate the single differential cross section (SDCS). The SDCS of the C atom and its ions are calculated by BED model [3] given by

\[
\frac{d\sigma}{dW} = \frac{S}{B(t+u+1)} \left\{ \frac{N_i/N}{t+1} \left( \frac{1}{w+1} + \frac{1}{t-w} \right) \right. \\
\left. + \left[ 2 - \frac{N_i}{N} \right] \frac{1}{(w+1)^2} + \frac{1}{(t-w)^2} \right\} \ln \frac{t}{(w+1)} \frac{df(w)}{dw},
\]

with

\[ t = T/B, \quad w = W/B, \quad u = U/B, \quad S = 4\pi a_0^2 N(R/B)^2, \quad N_i = \int_0^\infty \frac{df(w)}{dw} dw, \]

where \( B \) is the binding energy of the ejected electron, \( T \) is the nonrelativistic kinetic energy of the incident electron, \( W \) is the kinetic energy of the ejected electron, \( U = \langle p^2/2m \rangle \) is the orbital-electron-kinetic energy with the target electron momentum \( \vec{p} \) and the electron mass \( m \), \( a_0 \) is the Bohr radius and \( R \) is the Rydberg energy. In equation (1), \( df(w)/dw \) is the differential oscillator strength as a function of \( w \). Hartree-Fock wavefunctions of the C atom and its ions [7] were used to calculate the orbital electron kinetic energy \( U \). The differential oscillator strengths of the C atom and its ions were calculated with the FAC [6]. The integral cross section (ICS) \( \sigma \) and averaged energy of secondary electron \( \langle W \rangle \) are given by

\[
\sigma = \int_0^{(T-B)/2} \frac{d\sigma}{dW} dW, \quad \langle W \rangle = \frac{\int_0^{(T-B)/2} W \frac{d\sigma}{dW} dW}{\int_0^{(T-B)/2} d\sigma/dW dW}.
\]

The treatment of free electrons in this model simulation can be described as follows:. The Compton recoil electrons and the Auger electrons are trapped in a target sample because those kinetic energies are sufficiently low. The photoelectrons, however, escape from the target sample after \( \sim 0.15 \) fs in the case of \( r = 10 \) nm since these have high kinetic energies. Therefore, the target sample is ionized by the photoelectrons when these are within a target sample of radius \( r \). The time-dependent rate equation is solved by applying this atomic model. A pulse X-ray flux with the energy of 12 keV was employed. The pulse had Gaussian distribution and a width of 10 fs.

3. Results and Discussion
To verify the results of the energies of the secondary electrons, we present the integral cross section (ICS) of a C atom for the BED calculation. Figure 1 shows the comparison of our calculated results with the recommended data [8] for a C atom from the ionization energy to 20 keV. Our result is in good agreement with the recommended data [8]. Note that our results for C ions for the BED calculation are also in good agreement with the recommended data [8].
Figure 1. Ionization cross section of C atom from the ground state to all the 1s²2s²2p and 1s²2s²p² states. ——, Present; ---, Recommended data [8].

Figure 2. Averaged energies of secondary electron of C atom, C¹⁺ and C²⁺ ions. ——, C atom (2p-orbital ionized); ---, C¹⁺ ion (2p-orbital ionized); ——, C²⁺ ion (2s-orbital ionized).

Figure 3. Normalized populations of C atom and ions at 1 × 10²² photons/pulse/mm², pulse width 10 fs, target radius 10 nm. ---, Normalized X-ray flux.

Figure 4. The contributions from the different atomic processes to ionization at 1 × 10²² photons/pulse/mm², pulse width 10 fs, target radius 10 nm.

Figure 2 shows the results of the averaged energies of secondary electrons for the C atom, C¹⁺ and C²⁺ ions. Those energies for the C atom, C¹⁺ and C²⁺ ions are about 20, 60 and 150 eV, respectively, at the incident electron energy of 12 keV (photoelectron impact). Those energies are in the order of tens of electronvolts from figure 2 when the incident electron energy is about 250 eV (Compton recoil and Auger electron impact). Those results suggest that the ionization effects of the secondary electrons, which are produced by Compton recoil electrons and Auger electrons impact, are minor because those cross sections are small in this energy region.

Time-dependent rate equations were solved to investigate the population dynamics of the C atom and its ions. Figure 3 shows the resulting populations as a function of time (femtosecond). In this simulation, we chose a pulse width of 10 fs, and an X-ray flux of 1 × 10²² photons/pulse/mm² and a target radius of 10 nm. The results show that the populations of C⁵⁺ become dominant at the peak intensity of the X-ray flux. It is clear that the damage to the biomolecule is severe under these conditions. Figure 4 shows the contributions from the different atomic processes involved in ionization under the same conditions, as in figure 3. We found that the photoionization becomes dominant at an X-ray flux of 1 × 10²² photons/pulse/mm², and
Table 1. The contributions of the each atomic processes to ionization at the peak intensity of X-ray flux (%).

| photons/pulse/mm² | (A) | (B) | (C) | (D) | (E) |
|-------------------|-----|-----|-----|-----|-----|
| $1 \times 10^{22}$ | 42.8| 17.4| 10.2| 8.50| 79.0|
| $1 \times 10^{21}$ | 13.4| 12.1| 1.67| 2.80| 29.9|
| $1 \times 10^{20}$ | 1.61| 1.78| 0.16| 0.28| 3.86|
| $1 \times 10^{19}$ | 0.16| 0.18| 0.02| 0.03| 0.39|

(A) Photo-ionization. (B) Electron-impact ionization. (C) Compton scattering. (D) Auger decay. (E) Total.

electron-impact ionization becomes a more important process in the investigation of the damage when the X-ray flux decreases, see table 1.

4. Conclusions
The atomic data of the photoionization, electron-impact ionization and Compton scattering of the C atom and its ions were calculated using the FAC, BED model and Klein-Nishina formula, respectively. We found that the averaged energies of secondary electrons for C atom, C$^{1+}$ and C$^{2+}$ ions were about 20, 60 and 150 eV, respectively, at an incident electron energy of 12keV, while those energies were in the order of tens of electronvolts when the incident electron energy was about 250 eV. The time-dependent rate equations were solved to investigate the damage to the target sample. We also found that the electron-impact ionization became a more important process as the X-ray flux decreased. To understand the damage evaluation, it is necessary to evaluate the damage as well as the intensities of the diffraction patterns at the same time. In the future, we will investigate the intensities of diffraction patterns in connection with the damage to the biomolecules for the various XFEL parameters.

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