Ab initio Molecular-Dynamics Study of Dissociation Mechanism of Highly Charged Molecules

Satoshi Ohmura1, Kiyonobu Nagaya1, Fuyuki Shimojo2 and Makoto Yao1

1 Department of Physics, Kyoto University, Kyoto 606-8502, Japan
2 Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan
E-mail: ohmura@scphys.kyoto-u.ac.jp

Abstract. Charge state dependence of dissociation mechanisms of the highly charged bromophenol (C6H5OHBr)n+ (n≤10) is studied by ab initio molecular dynamics simulations based on density functional theory. When the charge state n is 6 or 7, one or two hydrogen atoms dissociate in the first stage (at times shorter than 20 fs) while all hydrogen atoms dissociate when the charge state is over 7. After hydrogen dissociation, the carbon ring breaks at about 150 fs. There is also a difference on the mechanism of the ring breaking depending on charge states, in which the ring breaks with expanding (n = 6, 7) or shrink (n ≥ 8).

1. Introduction
With the advent of free electron laser (FEL) such as Extreme Ultraviolet FEL and X-Ray FEL, many interesting phenomena in which atoms or molecules are highly excited due to the strong laser fields are observed. When a molecule is irradiated by hard x-ray, holes are proliferated through the Auger cascade and the molecule takes high charge. The highly charged molecular ions are quite unstable due to the Coulomb repulsive force and typically destroyed on a subpicosecond time scale (Coulomb explosion). The fragment ions may convey information about molecular shape because they reflect geometric structure of the parent molecule just before dissociation. Recently, dissociation of several highly-charged aromatic molecules has been investigated by position-sensitive time-of-flight measurements [1, 2]. Sugishima et al. investigated the momenta of ejected ions from highly charged benzene and fluorobenzene molecules by using position-sensitive time-of-flight mass spectrometer [1]. They found that there exists clear angular correlation between the momenta of H+-H+ and H+-F+ fragment ions which reflects the structure of the parent molecules even for the dissociation channels for which the dissociations are not described by the simple Coulomb explosion model. In addition, Nagaya et al. have tried to investigate the conductivity properties of single molecules with using Coulomb explosion [2]. They determined the conductance of bromo aromatic molecules by ionizing the Br atom and detecting an opposite O+ ion after the Coulomb explosion. Although many studies about Coulomb explosion have been reported, details of the Coulomb explosion are still unknown. In this paper, we investigate the dissociation mechanisms from highly charged bromophenol by ab initio molecular-dynamics simulations based on density functional theory (DFT) to clarify the atomic mechanisms of Coulomb explosion. Generally, relaxation of electron system is much...
faster than that of ionic (atomic) system. Therefore, we suppose that the dissociation of the charged molecules occurs on the ground state.

2. Methodology

2.1. Method of calculation or charged system

To calculate charged molecular system in reciprocal space, we used cluster boundary conditions imposed with the method of Martyna and Tuckerman [3], which rigorously corrects for the error resulting from artificial repetitions of an aperiodic system by a screening function in the reciprocal space. In a fully periodic system, the potential described by the electron density \( n(r) \) and the potential \( \phi(r-r') \) is given by

\[
\langle \phi \rangle = \frac{1}{2V} \sum |\bar{n}(\mathbf{g})|^2 \tilde{\phi}(-\mathbf{g}),
\]

where \( \bar{n}(\mathbf{g}) \) and \( \tilde{\phi}(-\mathbf{g}) \) are the Fourier transform of the density and potential, respectively. For systems with fewer than three periodic dimensions,

\[
\langle \phi \rangle^{(1)} = \frac{1}{2V} \sum_{\mathbf{g}} |\bar{n}(\mathbf{g})|^2 \tilde{\phi}(-\mathbf{g}).
\]

where \( \bar{\phi}(\mathbf{g}) \) and \( \bar{n}(\mathbf{g}) \) denote a Fourier expansion coefficient of the potential and density, respectively in the non-periodic dimensions. In determining the form of \( \bar{\phi}(\mathbf{g}) \), we need to consider two functions \( \phi^{\text{long}}(r) \) and \( \phi^{\text{short}}(r) \), which are assumed to be the long and short range contributions to the total potential.

\[
\phi(r) = \phi^{\text{long}}(r) + \phi^{\text{short}}(r).
\]

Assuming that the simulation cell is large enough so that \( \tilde{\phi}^{\text{short}}(\mathbf{g}) \simeq \tilde{\phi}^{\text{short}}(\mathbf{g}) \), the desired Fourier transform is expressed as

\[
\bar{\phi}(\mathbf{g}) = \bar{\phi}^{\text{long}}(\mathbf{g}) + \bar{\phi}^{\text{short}}(\mathbf{g})
\approx \bar{\phi}^{\text{long}}(\mathbf{g}) + \bar{\phi}^{\text{short}}(\mathbf{g})
= \bar{\phi}^{\text{long}}(\mathbf{g}) - \bar{\phi}^{\text{long}}(\mathbf{g}) + \bar{\phi}^{\text{short}}(\mathbf{g}) + \bar{\phi}^{\text{long}}(\mathbf{g})
= \hat{\phi}^{\text{screen}}(\mathbf{g}) + \bar{\phi}(\mathbf{g})
\]

where \( \hat{\phi}(\mathbf{g}) = \tilde{\phi}^{\text{short}}(\mathbf{g}) + \tilde{\phi}^{\text{long}}(\mathbf{g}) \) is the Fourier transform of the full potential \( \phi(\mathbf{g}) = \phi^{\text{short}}(\mathbf{g}) + \phi^{\text{long}}(\mathbf{g}) \) and

\[
\hat{\phi}^{\text{screen}}(\mathbf{g}) = \bar{\phi}^{\text{long}}(\mathbf{g}) - \bar{\phi}^{\text{long}}(\mathbf{g}).
\]

Eq. (4) demonstrates that this formalism is equivalent to augmenting \( \hat{\phi}^{\text{screen}}(\mathbf{g}) \) with a “screening potential” \( \hat{\phi}(\mathbf{g}) \) which cuts off the interactions from the periodic images of the simulation cell. This result leads to

\[
\langle \phi \rangle = \frac{1}{2V} \sum_{\mathbf{g}} |\bar{n}(\mathbf{g})|^2 [\bar{\phi}(-\mathbf{g}) + \hat{\phi}^{\text{screen}}(-\mathbf{g})].
\]

Now, we consider the Coulomb potential, \( \phi^{(\text{Coul})}(r) = 1/r \). Using an identity commonly employed in Ewald summation, the Coulomb potential can be written as

\[
\frac{1}{r} = \frac{\text{erf}(\alpha r)}{r} + \frac{\text{erfc}(\alpha r)}{r} = \phi^{(\text{long,Coul})}(r) + \phi^{(\text{short,Coul})}(r).
\]
where $\alpha$ is a convergence parameter which determines the region where the transition from short to long-range terms takes place.

The Coulomb potential for cluster systems in reciprocal space given by Eq. (4):

$$\bar{\phi}^{\text{Coul}}(\mathbf{g}) = \hat{\phi}^{\text{(screen,Coul)}}(\mathbf{g}) + \tilde{\phi}^{(\text{Coul})}(\mathbf{g}).$$

The Hartree and local-pseudopotential terms in the DFT energy functional are of long-range nature. The Hartree term is given by

$$E_H[n] = \frac{e^2}{2} \int_{D(V)} d\mathbf{r} \int_{D(V)} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \sum_{g} \tilde{n}(\mathbf{g}) \left[ \frac{4\pi}{g^2} + \hat{\phi}^{\text{(screen,Coul)}}(\mathbf{g}) \right] + \frac{e^2}{V} \tilde{\phi}^{\text{(screen,Coul)}}(0)\tilde{n}(0) \tag{9}$$

In a similar way, the local-pseudopotential term is obtained:

$$E_{\text{local}}[n] = \sum_{I=1}^{N} \int_{D(V)} d\mathbf{r} V_{\text{loc},I}(\mathbf{r} - \mathbf{R}_I)n(\mathbf{r})$$

$$= \frac{1}{V} \sum_{g} \tilde{n}(\mathbf{g}) \exp(-i\mathbf{g} \cdot \mathbf{R}_I)[\bar{V}_{\text{loc},I}(\mathbf{g}) - e q_I \hat{\phi}^{\text{(screen,Coul)}}(\mathbf{g})]$$

$$+ \frac{1}{V} \sum_{I=1}^{N} \tilde{n}(0)[\bar{V}_{\text{loc},I}^{(0)} - e q_I \hat{\phi}^{\text{(screen,Coul)}}(0)] \tag{10}$$

Here, the prime indicates that the $\mathbf{g} = 0$ term is eliminated and the term, $V_{\text{loc},I}^{(0)}$ is the nonsingular part of the local pseudopotential at $\mathbf{g} = 0$ and $q_I$ is the charge of atom $I$. The long-range term $\bar{\phi}^{(\text{long,Coul})}(\mathbf{g})$ is calculated with using a different supercell from that for the other terms (dual grid method) [4].

2.2. Numerical details

In our simulation, we used 4-bromophenol as a target system, in which a bromine atom and a hydroxyl group are located on the opposite sides of the carbon ring. Electronic states are obtained by using the projector-augmented-wave (PAW) method [5, 6], which is an all-electron electronic-structure-calculation method within the frozen-core approximation in the framework DFT. The generalized gradient approximation (GGA) [7] was used for the exchange-correlation function. The cutoff energies of plane waves were 30 and 250 Ry for the electronic pseudo-wave functions and pseudo-charge density, respectively. The energy functional was minimized using an iterative scheme [8, 9]. Projector functions were generated for the $2s$ and $2p$ orbitals of C and O, $1s$ of H and $4s$, $4p$ and $4d$ of Br. The equations of motion were integrated numerically using an explicit reversible integrator [10] with time step of 0.048 fs (hydrogen dissociation process) and 0.24 fs (carbon-ring breaking process). Initially, we began with carrying out an ab initio MD simulation of neutral molecule in the canonical ensemble using the Nosé-Hoover thermostat techniques [11, 12] for about 6 ps at 300 K. Then we picked several configurations from the MD simulation as initial configurations for MD simulations of the charged systems. The charge distribution within the molecule were determined by the self-consistent calculation in each MD step. Then the time evolution of the structure was obtained in the micro canonical ensemble.
3. Result and discussion

When the charge state \( n \) is more than 5, the molecule begins to break immediately after the molecule takes charges. From the simulation, it is found that the dissociation in this charge state region \( (6 \leq n \leq 10) \) occurs through a sequential process in a sense that the molecular dissociation occurs through the several-stage fragmentation. The first stage is hydrogen dissociation and the second stage is carbon-ring breaking. This dissociation process does not depend on initial configurations (we calculate each charge state with three different initial configurations); the molecular dissociation in all simulations occurs through hydrogen dissociation process and carbon-ring breaking process. However, we observed a sharp contrast in each process between the charge state is not more than 7 and over 7. The typical examples of dissociation mechanisms of the +6 and +8 charged bromophenol molecules are shown as representatives in the following sections.

3.1. Hydrogen dissociation

At times shorter than 20 fs after the molecule takes charges, Hydrogen dissociate from the molecule. In order to clarify the mechanism of this dissociation, we investigate the time evolution of the bonding and atomic charge nature by utilizing the population analysis [13, 14]. The gross charge \( Q_i \) on the \( i \)th atom and the bond overlap population \( O_{ij} \) for a pair of \( i \)th and \( j \)th atoms are given by

\[
Q_i = Z_i - \sum_n \sum_{\mu \in i} \sum_\nu C_{\mu i}^{n} S_{\nu i} C_{\nu i},
\]

\[
O_{ij} = \sum_n \sum_{\mu \in i} \sum_{\nu \in j} \frac{1}{2} \left[ C_{\mu i}^{n} S_{\nu j} C_{\nu j} + C_{\nu j}^{n} S_{\mu j} C_{\mu j} \right],
\]
where \( Z_i \) is the total number of valence electrons in the ground state of the free neutral atom and

\[
S_{\mu\nu} = \langle \varphi_\mu | \varphi_\nu \rangle.
\]  

(13)

In this expression, \( \varphi_\mu \) is the atomic wave function used as basis for the projection of the wave function of the interest \( \chi_n \), and \( C_{\mu n} \) is the coefficient of the projection, that is,

\[
| \chi_n \rangle = \sum_\mu | \varphi_\mu \rangle C_{\mu n}
\]

(14)

Figure 1 shows (a) the time evolution of the gross charge \( Q_i(t) \) and (b) the bond overlap population \( O_{ij}(t) \) with snapshots of atomic configurations when the charge state \( n \) is 6. As displayed in the snapshot at \( t = 12.0 \) fs, a hydrogen atom in the hydroxyl group dissociates from the molecule. As shown in Fig. 1(b) \( O_{O-H1} \) (black solid line) becomes almost zero at \( t = 20 \) fs. During this dissociation, \( Q_{H1} \) (purple solid line) increases and becomes 1 at about \( t = 20 \) fs while \( Q_{Br} \) (magenta solid line) decreases with time till \( t = 20 \) fs. After this dissociation (\( t > 20 \) fs), \( O_{C4-C3} \) (green solid line) and \( O_{C4-C5} \) (cyan solid line) decrease while \( O_{C2-C3} \) (purple dashed line) and \( O_{C5-C6} \) (blue dashed line) increase with time. \( O_{O-C4} \) (red dashed line) also increases during this dissociation process.

When the charge state is 8, all hydrogen atoms dissociate from the molecule at the same time. This mechanism is shown in Fig. 2. \( O_{ij} \) for all C-H bonds decrease with time and becomes almost zero at less than 20 fs. During this ejection, \( Q_{Br} \) (magenta solid line) decreases drastically with time. \( Q_{O} \) (red dashed line) also slightly decreases with time.

\[ \textbf{Figure 2.} \text{(Left panel) Time evolution of the gross charge (a) and bond overlap population for n=8 (b) (Right panel) Atomic configurations at t=0.0, 4.0 and 12.0 fs.} \]

3.2. Carbon-ring breaking

After the Hydrogen dissociation, the carbon ring breaks up into two fragments. In the case of \( n=6 \), C3-C4 and C1-C6 bonds break at about \( t = 70 \) fs and \( t = 125 \) fs, respectively, and the
carbon ring splits into two fragments. These longer time behavior is shown in Fig. 3. The ionic charge of C4 (black dashed line) bonding to O becomes 0.75 after C3-C4 bond breaks. This value is the second largest after Br. This leads to a large Coulomb repulsive interaction between Br and C4. Therefore, Br atom is never located on the same fragment of O atom bonding to C4. After this fragmentation, the ionic charge of C2 (blue solid line) which does not have H atom and that of C6 (green solid line) which is the end of O-fragment have positive value. In the molecules with \( n = 8 \), fragmentation occurs with a different mechanism from that for \( n = 6 \). This mechanism is shown in Fig. 4. During this fragmentation mechanism, some bond switching are observed. After C1-C6 bond breaks, new covalent bonds (C2-C6, C1-C3) are formed as displayed in the snapshot at \( t = 70 \) fs, and immediately after that, C1-C2 bond breaks. Through the bond switching process, the carbon ring becomes a chain-like structure as displayed in the snapshot at \( t = 136.8 \) fs. The Coulomb repulsive energy in the molecule is stronger than the covalent like interaction, the one of C-C or C-Br bonds is broken as seen in snapshot at 190 fs.

In order to clarify quantitatively the charge state dependence of the dissociation mechanism in the process of carbon-ring breaking, we calculate the time evolution of the areas of carbon ring \( S_n \) at each initial charge state \( n \), shown in Fig. 5. Here, we suppose that the area of carbon ring is equal to area of hexagon made of six carbon atoms. The residual charges after hydrogen ejection are noted in parentheses. The area of the carbon ring increases with time when \( n = 6 \) or 7. Since +5 charges are left on the molecule in these charge states, the ring expands due to the Coulomb repulsive force. On the other hand, \( S_n \) decrease when \( n \) is more than 7. Even though the residual charges of the molecule with \( n = 10 \) are the same of that with \( n = 6 \) or 7, the area decreases with time while \( S_6 \) and \( S_7 \) increase. This fact is attributed to the absence of C-H bonds in the molecule with \( n \geq 8 \). It is found from this figure that the carbon ring in lower charge state \( (n < 8) \) exhibits more Coulombic dissociation in a sense that the carbon ring breaks with simply expanding.
Figure 4. (Left panel) Time evolution of the bond overlap population for $n=8$ (Right panel) Atomic configurations at $t=30.0$, $70.0$, $136.8$ and $190.8$ fs.

Figure 5. The time evolution of the area of aromatic ring $S_n$ after hydrogen ejection, where $n$ is the initial charge state.

4. Conclusion
We have investigated the dissociation mechanisms from highly charged bromophenol by $ab$ initio MD simulations based on density functional theory with the cluster boundary condition method of Martyna and Tuckerman. It is found that dissociation mechanisms have clear charge state dependences. In the hydrogen dissociation at times shorter than 20 fs, hydrogen atom of OH group dissociates from the molecule with $n=6$ while all hydrogen atoms dissociate from the molecule $n=8$. In the process of carbon ring breaking, the charge state dependence is also observed. When the charge state is 6 or 7, the ring breaks with molecular expanding. On the other hand, molecular shrink during the ring breaking when the charge state is over 7.

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