

Selective Chemical Bond Breaking Induced by Resonant Inner-Shell Excitation of Acetone Molecule on the Ar Clusters

Active control of chemical reaction using photoexcitation is one of the main issues of photochemistry [1]. Inner-shell photoexcitation is a notable phenomenon associated with selective chemical bond breaking, and it has been a topic of considerable interest to many researchers [1,2]. The following is a scenario of selective chemical bond breaking. An inner-shell electron is generally localized around a specific atom in a molecule. When an inner-shell electron is ionized or excited in a molecule, the electronic relaxation of the core hole occurs at the initially excited atomic site, and final positive charges in valence orbitals, which are produced via Auger decay, are expected to be localized around the excited sites. Consequently, selective bond scission can be expected depending on the excitation of different atomic site. This concept is called “site-specific fragmentation” and it offers possibilities of controlling chemical reactions through selective bond breaking.

Since the pioneering work by Eberhardt *et al.* in 1983 [2], a number of investigations have been carried out to show the site-specific fragmentation. However, less prominent site selectivity has been reported for the fragmentation of isolated molecules. On the other hand, a remarkable site selectivity has been observed in the photostimulated desorption of some thin polymer films on a metal surface [1]. In order to interpret the different ionic fragmentation processes, the following model has been proposed (Fig. 1). In an isolated molecule, the excess energy afforded at a core-excited site is dissipated over the molecule ahead of the fragmentation. The excited molecule loses the memory of the excited site, and nonspecific

fragmentation, i.e., statistical fragmentation, becomes dominant. On the other hand, for a molecule deposited on the surface, the excess energy rapidly flows into the substrate. As a result, the statistical fragmentation is suppressed and specific fragmentation becomes dominant. According to this model, a substrate that absorbs excess energy is indispensable for the occurrence of specific fragmentation induced by inner-shell excitation.

Under these circumstances, we have focused on the fragmentation processes of a small molecule adsorbed on clusters [3]. Nanoclusters are regarded as an intermediate state between an isolated species and a condensed phase, and easily controlled in size and constituent atoms. In this study, inner-shell photoexcitation and fragmentation of acetone-argon heteroclusters, $[(\text{CH}_3)_2\text{CO}]\text{Ar}_n$, have been investigated. In the photofragmentation of molecules on the clusters, the clusters are expected to behave like a substrate that releases the excess energy from the excited molecule and produces the specific fragmentation even under the isolated condition. Experiments were carried out at the soft X-ray photochemistry beamline **BL27SU**. The experimental setup is illustrated in Fig. 2. The heteroclusters were produced by a “pickup technique.” The cluster beam was crossed with a soft X-ray beam in the ionization region and the ions produced were mass-analyzed using a time-of-flight mass spectrometer.

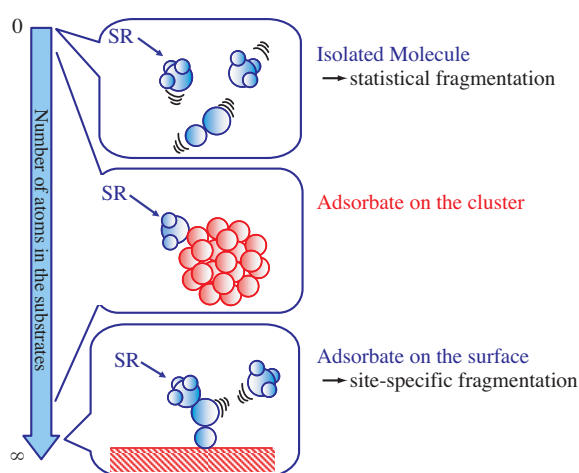


Fig. 1. Illustration of the substrate size dependence on the ionic fragmentation processes.

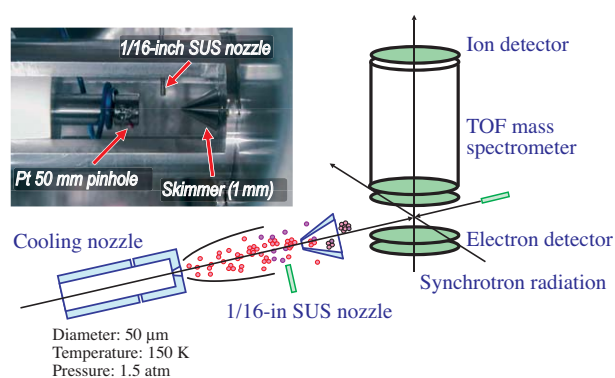


Fig. 2. Schematic layout of the experimental setup.

Figure 3 shows the yield curves of various fragment ions of (a) acetone molecule and (b) $[(\text{CH}_3)_2\text{CO}]\text{Ar}_n$, in the O *K*-edge region. The total ion yield (TIY) curve is also indicated on the top of each spectrum. A clear resonance peak observed at 531 eV can be assigned to the O $1s \rightarrow \pi^*(\text{C}=\text{O})$ resonant excitation, and a small hump observed at

~544 eV is assigned to the σ^* shape resonance [4]. A remarkable difference can be seen between the spectra of the isolated acetone molecule and those on the argon clusters. All the partial ion yield (PIY) curves of the acetone molecule mimic that of the photoabsorption spectrum, and it is suggested that the statistical fragmentation processes are dominant. On the other hand, in the case of heteroclusters, the selective enhancement of the O^+ formation can be observed at the $O\ 1s \rightarrow \pi^*(C=O)$ resonance excitation, while the PIY curves of other fragment ions show only weak resonance features.

A selective C=O bond scission is expected at the $O\ 1s \rightarrow \pi^*(C=O)$ resonance, because of a strong repulsive character of the Auger final state. Following inner-shell electron excitation, a resonantly excited molecule emits an electron through resonant Auger transitions, and spectator Auger decay, which produces a two-hole one-electron (2h-1e) state, usually gains most of the intensity [5]. The resonant Auger decay following the $O\ 1s$ excitation is considered to preferentially create two holes in the molecular orbitals that have a high population near the O atom. The vacant C=O bonding orbital and the spectator electron in the $\pi^*(C=O)$ orbital are expected

to weaken the C=O bond and result in the selective C=O bond scission.

Furthermore, the selective O^+ formation only on the argon clusters should be interpreted by the suppression of statistical fragmentation channels [1]. For the inner-shell-excited acetone molecule, both statistical and specific fragmentations are possible. Because the energy dissipation within the molecule is very rapid and all dissipation processes lead to statistical fragmentations, the former is dominant in the isolated molecule (Fig. 3(a)). On the other hand, when the excited molecule is an adsorbate on the substrate, the substrate can act as an excess energy buffer against the statistical fragmentation of the excited molecule. In the $[(CH_3)_2CO]Ar_n$ clusters, the argon cluster can absorb the excess energy from the excited acetone molecule, and a major part of the clusters causes the evaporation of neutral Ar atoms instead of molecular fragmentation. The selective O^+ formation suggests that either the nonspecific fragmentation is suppressed or the suppression of the specific fragmentation is nonessential. The present results demonstrate that the small cluster is likely to play the role of an excess energy buffer and it produces the selective ionic fragmentation.

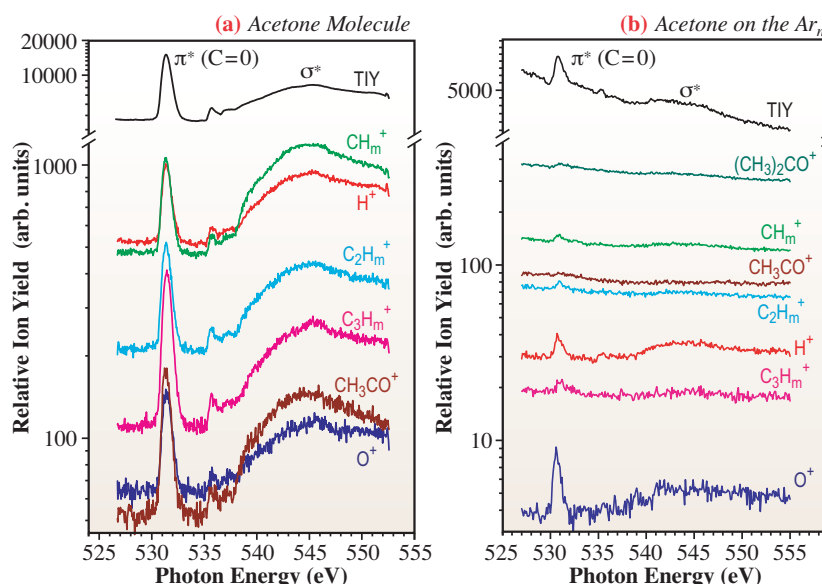


Fig. 3. TIY and PIY spectra of various fragment ions formed by the photoionization of (a) an isolated acetone molecule and (b) heteroclusters in the O K -edge region.

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References

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