X-ray Absorption Fine Structure of Free Selenium Clusters

Although clusters have attracted great interest as intermediate states between atomic and condensed states of matter [1], general methods for the size-selective structural analysis of neutral clusters have not been established so far. Recently we measured the Photoelectron Photoion Coincidence (PEPICO) spectra for selenium dimer Se_2 and larger species such as Se_5 [2,3]. The PEPICO spectra reveal that the multiply charged ions are produced as a result of de-excitation processes following the *K*-shell excitation and fragmented to atomic ions with z charges, Se^{z+}, owing to the Coulomb explosion (see Fig. 1). The branching ratios from the parent cluster to the daughter ions exhibit clear dependence on the size *N* of the parent clusters. In particular, the branching ratios in the non-resonant absorption region are well reproduced considering that the charges were randomly distributed within the clusters before the Coulomb explosion. Based upon these findings, we proposed a new method for the size-selective EXAFS of neutral free clusters by utilizing the PEPICO measurements [3].

The basic relations we have suggested are the simultaneous equations of the X-ray absorption coefficients per atom, $\alpha(h\nu)$, parameterized by z, as follows:

$$I(h\nu, z) = \sum N A_N B_N(z) \alpha(h\nu) \qquad (1),$$

where $I(h\nu, z)$ is the integrated PEPICO intensity for the z charged ion, A_N is the abundance of parent clusters consisting of N atoms and $B_N(z)$ is the branching ratio. Since A_N and $B_N(z)$ can be estimated either from experiments or calculations, $\alpha(h\nu)$ was deduced by solving eq. (1) from the PEPICO measurements.

In order to verify eq. (1) experimentally, we have carried out synchronous XAFS-PEPICO measurements for an Se cluster beam at the X-ray undulator beamline **BL10XU**. The neutral cluster beams were produced by a supersonic jet expansion method, intersected with the X-rays at right angles in the horizontal plane. The photoions produced by absorbing an X-ray photon were extracted upward by a constant electric field to a detector, while the photoelectrons were extracted downward. The procedures of the synchronous measurements are summarized in a flow chart (see Fig. 2). The XAFS spectrum was measured by the host computer that also controls the multi-channel-
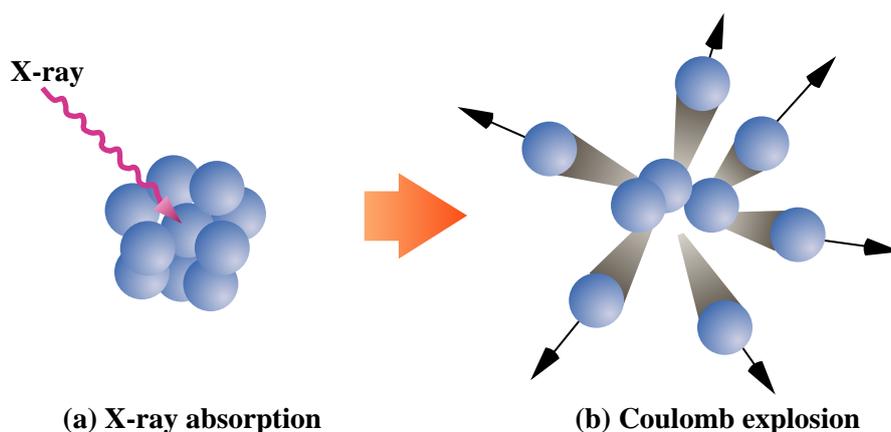
X-ray

(a) X-ray absorption   **(b) Coulomb explosion**

*Fig. 1. Schematic illustration of the X-ray absorption (**a**) and the Coulomb explosion (**b**) taking place in a cluster.*

analyzer, by which PEPICO spectra are taken, as well as the angle of the X-ray monochromators and the gap of the undulator.

In our experiment, Se_2, Se_5, Se_6 and Se_7 were produced and their relative abundances were 66:16:11:7, respectively. In Fig. 3 EXAFS spectrum $\chi(k)$ for "Se_5" deduced from eq. (1) is shown by circles. Here "Se_5" includes Se_5, Se_6 and Se_7, as in previous studies [2-5]. Although the number density of Se atoms in the cluster beam is smaller than that in the bulk Se samples by more than ten orders of magnitude, the EXAFS oscillation is clearly seen. The line denotes the smoothed variation $\chi(k)$ for Se_2 in the cluster beam, which is in good agreement with $\chi(k)$ for Se_2 in the vapor phase [6] except for the scaling factor. The spacing of the EXAFS oscillation clearly demonstrates that the bond length of "Se_5" is longer than that of Se_2. More precisely, the former proves to be 2.35 Å and the latter 2.16 Å [7], which is fully consistent with a pile of EXAFS data for various forms of Se [8]. Therefore, we conclude that the proposed size-selective XAFS is a reliable and realistic method.
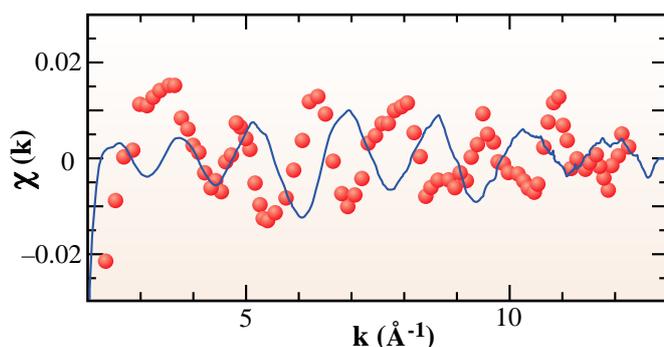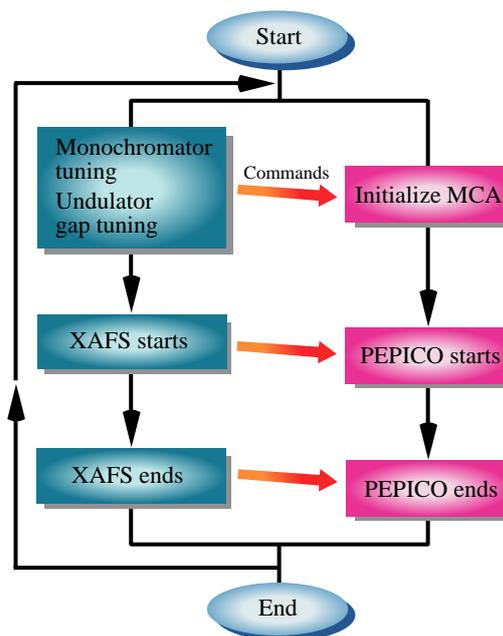

Fig. 2. A flow chart of the XAFS-PEPICO synchronous measurements. Procedures by the host computer are shown on the left and those by the multi-channel-analyzer on the right.

Fig. 3. EXAFS spectra $\chi(k)$ for Se_2 (line) and "Se_5" (circles).

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