molecules and clusters

A new method for the size-selective EXAFS of neutral free clusters

Makoto Yao,[a]* Tetsuichiro Hayakawa,[a] Kiyonobu Nagaya,[a] Koichi Hamada,[a] Yoshinori Ohmasa[a] and Masaharu Nomura[b]

[a]*Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan, and* [b]*Photon Factory, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan. E-mail: yao@scphys.kyoto-u.ac.jp*

Recently we have measured Photoelectron Photoion Coincidence (PEPICO) spectra for selenium dimer Se_2 and larger species such as Se_5 at the beamline BL-12C in Photon Factory. The PEPICO spectra reveal that the multiply charged ions, Se^{z+}, are produced as a result of de-excitation processes following the inner-shell excitation and fragmented to atomic ions owing to the Coulomb explosion. The branching ratios from the parent clusters to the daughter ions exhibit clear dependence on the size of the parent clusters. In particular, the branching ratios in the non-resonant absorption region are well reproduced by assuming that the charges are randomly distributed within the clusters before the Coulomb explosion. Based upon these findings, we propose a new method for the size-selective EXAFS of neutral free clusters by utilizing the PEPICO measurements.

**Keywords: size-selective EXAFS, selenium, cluster, PEPICO, de-excitation process**

1. Introduction

Clusters have attracted great interest, because they are considered to be intermediate states between atomic and condensed states of matter, and tremendous efforts have been done to study their properties as a function of the cluster size (Haberland, 1994). Although various experimental methods have been used to investigate atomic arrangement in the clusters, general methods for the size-selective structural analysis of neutral clusters have not been established so far. Recently XAFS (X-ray Absorption Fine Structure) spectroscopy has been applied to several clusters produced in the free space (Rühl *et al.,* 1993; Kakar *et al.,* 1997; Yao *et al.,* 1999). In these experiments the conditions under which the clusters are produced were controlled to vary the cluster size distribution. By this method, however, many experiments under different conditions are needed to be performed to get precise information on the size-dependent structural properties.

In this paper, based upon our recent Photoelectron-Photoion-Coincidence (PEPICO) measurements for selenium clusters (Hayakawa *et al.,* 2000a; Hayakawa *et al.,* 2000b), we suggest a new XAFS method that could provide size-selective information from a single experiment. In the next section a brief review is given on our recent PEPICO measurements for selenium clusters (Hayakawa *et al.,* 2000a; Hayakawa *et al.,* 2000b). Then in the last section the suggested method is tested for the selenium clusters.

2. PEPICO Measurements

The PEPICO measurements were carried out by utilizing the synchrotron radiation at the BL-12C station in Photon Factory, KEK (Nomura & Koyama, 1995). The neutral cluster beam were produced by a supersonic jet expansion method, intersected with the X-ray at right angle in the horizontal. 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 electron signal provides a start pulse for a time-amplitude-converter (TAC) and the ion signal provides a stop pulse, which gives the ratio z/n of the charge z to the number of atoms, n, for the detected selenium ion (Se_n^{z+}). The PEPICO measurements were performed under two different conditions (A) and (B): under the condition (A) the temperature of the cluster source was kept at $570\pm2°C$ and it was kept at $361\pm1°C$ under (B). The size distribution in the cluster beam was mass-spectrometrically studied in advance, which revealed that the major constituents were Se_2, Se_5, Se_6 and Se_7 (Yao *et al.,* 1999) and that the ratio of Se_5, Se_6 and Se_7 remained nearly constant (i.e. 7:4:2) irrespective of the cluster source temperature. Hence, hereafter we refer to Se_5, Se_6 and Se_7 simply as "Se_5", and we regard the cluster beams as two-component systems of Se_2 and "Se_5". The probability that a Se atom in the cluster beam is included in the Se_2 was about 62% under (A) and 10% under (B), and the rest of atoms were considered to be included in "Se_5". Thus the PEPICO spectra of Se_2 and "Se_5" were deduced from the raw PEPICO spectra taken under the conditions (A) and (B). Further experimental details were described elsewhere (Hayakawa *et al.,* 2000a).
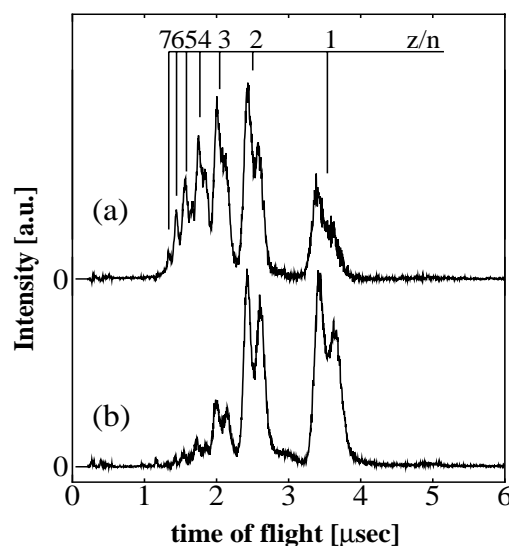
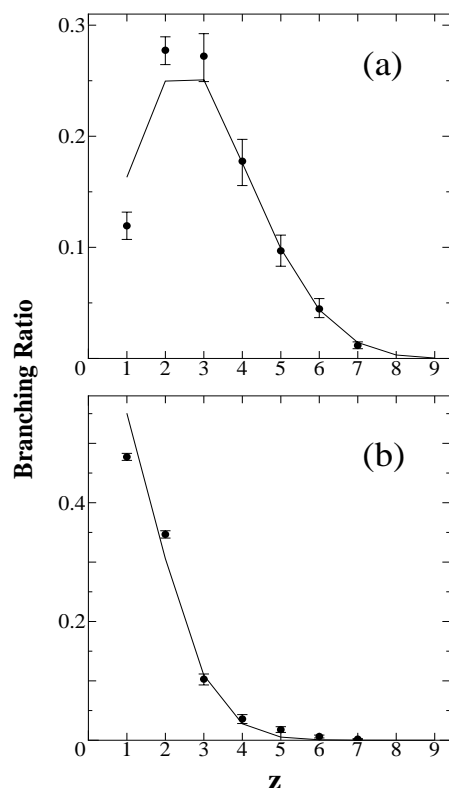**Figure 1**
PEPICO spectra of Se_2 (a) and "Se_5" (b) taken at 12.68keV.

Figs.1(a) and 1(b) show the PEPICO spectra taken at the X-ray photon energy of 12.68keV for Se_2 and "Se_5", respectively. Each peak in the PEPICO spectrum corresponds to a multiply charged ion, Se_n^{z+}. The value of z/n is indicated in the Figure. For Se_2, broad peaks corresponding to $z/n = 1$ to 7 were observed. No clear peaks

were seen at the half-integers of z/n, indicating that $n = 1$. Moreover most of the peaks were split into asymmetric doublets owing to the Coulomb explosion (Hayakawa *et al.,* 2000a).

In the present paper, we are interested in the branching ratio $B_N(h\nu, z)$ from neutral parent clusters with N atoms (i.e. $N = 2$ or 5) to daughter atomic ions with z charges. Here $h\nu$ is the photon energy. $B_N(h\nu, z)$ is defined by

$$B_N(h\nu, z) = I_N(h\nu, z) \left/ \sum_{z'=1} I_N(h\nu, z') \right. , \qquad (1)$$

where $I_N(h\nu, z)$ is the integrated intensity of each PEPICO peak.

Figure 2
 Experimental (closed circles) and theoretical (solid lines) branching ratios for Se$_2$ (a) and "Se$_5$" (b) at the photon energy of 12.68keV.

In Fig.2, the branching ratio at 12.68keV is plotted by the closed circles for Se$_2$ (a) and "Se$_5$" (b). It should be noted that $B_N(h\nu, z)$ for Se$_2$ (a) exhibits a maximum near $z = 2$ or 3 while that for "Se$_5$" decreases monotonously with increasing z. The solid lines in the Figures denote the results of our simple calculations, where we have asuumed that the de-excitation following the non-resonant absorption can be regarded as a two-step process (Hayakawa *et al.,* 2000a). In this case the branching ratio may be written as

$$B_N(h\nu, z) = A \sum_{z_0} f_N(h\nu, z_0) p_N(z_0, z). \qquad (2)$$

Here $f_N(h\nu, z_0)$ is the probability that a neutral cluster with N atoms is changed into a z_0 charged cluster ion by the photoabsorption and subsequent vacancy cascades. As $f_N(h\nu, z_0)$ experimental data for atomic krypton (Krause & Carlson, 1967) are used

because Kr has the same inner shell configuration as Se. $p_N(z_0, z)$ is the conditional probability that a z charged atomic ion (=daughter ion) is fragmented from the z_0 charged parent cluster ion. As $p_N(z_0, z)$ the binomial distribution is adopted because the statistical distribution may be favored from entropic consideration in isolated systems. A is a normalization constant. It should be noticed that the experimental resulrs of $B_N(h\nu, z)$ are well reproduced by our theoretical curves for both Se$_2$ and "Se$_5$". This implies that the branching ratio may serve as a finger-print of the parent clusters.

In Figs.3(a) and 3(b) the branching ratios $B_2(h\nu, z)$ and $B_5(h\nu, z)$ for $z = 1$ are plotted as a function of the photon energy (Hayakawa *et al.,* 2000b). Near 12.653keV, which corresponds to 1s-σ^* resonance energy, the branching ratios exhibit a prominent maximum. Kosugi (Kosugi, 2000) has determined the resonance positions for Se$_2$ theoretically by the multi-reference single and double configuration interaction (MR-SDCI) method. The energy levels of π^*, σ^*(quartet) and σ^*(doublet) are located at -8.04, -5.36 and -4.26eV, respectively, below the 1s-ionization potential (1s-IP) in accordance with the experimental XANES spectrum (Hayakawa *et al.,* 2000b) (see also Figs.3(a)).
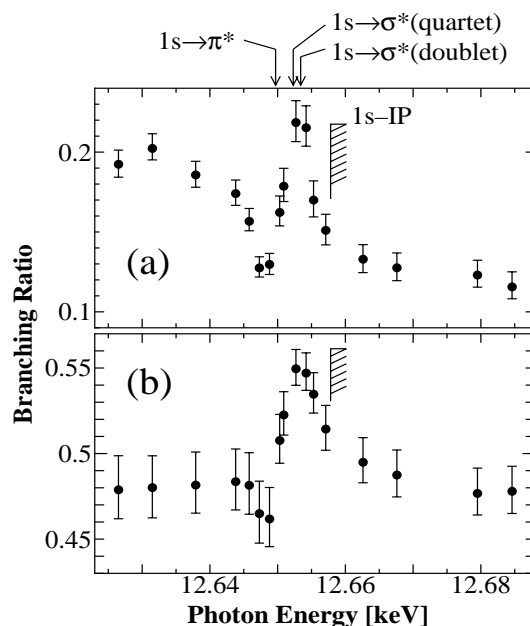
Figure 3
 The branching ratios of Se$^+$ from Se$_2$ (a) and "Se$_5$" (b) are shown as a function of the photon energy. The the 1s-π^* and 1s-σ^* resonance levels calculated by Kosugi (2000) are indicated by the arrows as well as the 1s-ionization potential (1s-IP).

Above 12.66keV, however, the branching ratio $B_2(h\nu, z = 1)$ seems to converge to 0.12, which coincides with the observed value at 12.80keV. Below 12.64keV, on the other hand, it approaches 0.19, which is an observed value at 12.50keV. The branching ratio $B_5(h\nu, z = 1)$ also becomes flat above 12.66keV and below 12.64keV. For higher z the energy dependence of the branching ratio is also small in the energy ranges below 12.64keV and above 12.66keV (Hayakawa *et al.,* 2000b). Thus the energy range under the present investigation can be devided into three regions: (i) below 12.64keV, (ii) 12.64-12.66keV and (iii) above 12.66keV. Here the region (ii) is the resonant absorption range and the regions (i) and (iii) are the non-resonant absorption ranges. Very recently we

have confirmed that the branching ratios remain nearly constant in the energy range (iii) up to 13.35keV, which covers the EXAFS range for Se K-edge absorption (Nagaya *et al.,* 2000). We may conclude that, in the de-excitation processes following the inner-shell excitation in the energy ranges (i) and (iii), the core-hole states are completely relaxed before the molecular (or cluster) dessociation. In the energy range (ii), however, the fast dessociation, which was first pointed out for HBr by Morin and Nenner (Morin & Nenner, 1986), is expected to occur in the Se clusters analogous to the molecular oxygen (Schaphorst *et al.,* 1993).

3. Size-Selective EXAFS

When the EXAFS measurements are carried out for mixed cluster beam, the observed TIY, $T_{obs}(h\nu)$, is expressed as

$$T_{obs}(h\nu, \{p\}) = \sum_N A_N(\{p\})N\alpha_N(h\nu). \qquad (3)$$

Here $\{p\}$ stands for the condition under which the cluster beam is produced and $A_N(\{p\})$ is the abundance of various clusters which can be measured by mass-spectroscopy. Conventionally, TIY spectra were measured under different conditions and the size-selective EXAFS was deduced by solving the simultaneous equations (i.e. eq.(3)) parametrized by $\{p\}$ (Rühl *et al.,* 1993; Kakar *et al.,* 1997; Yao *et al.,* 1999). In Figs.4(a) and 4(b), the solid lines denote $\alpha_N(h\nu)$ for $N = 2$ and 5, respectively, which were deduced from the TIY spectra measured under the conditions (A) and (B) (Yao *et al.,* 1999). In this case the method was successfully applied because the cluster beams could be regarded as two-component systems.

However, in more general case, where many different clusters are mixed in the beam, tremendous amounts of measurements are required to extract $\alpha_N(h\nu)$. Here we propose an alternative method for the size-selective EXAFS, in which the PEPICO spectra are measured as a function of photon energy. The integrated intensity of the observed PEPICO, $I_{obs}(h\nu, z, \{p\})$, can be written as

$$I_{obs}(h\nu, z, \{p\}) = \sum_N A_N(\{p\})N\alpha_N(h\nu)B_N(h\nu, z). \qquad (4)$$

As mentioned in Sec.2., the branching ratios of selenium small clusters depend very little on the photon energy above 12.66keV. Then $B_N(h\nu, z)$ can be replaced simply by $B_N(z)$ and eq.(4) may be treated as simultaneous equations of $\alpha_N(h\nu)$ parametrized by z. Thus $\alpha_N(h\nu)$ will be estimated from PEPICO measurements in a single condition $\{p_0\}$. The circles in Figs.4(a) and 4(b) denote $\alpha_N(h\nu)$ for $N = 2$ and 5, respectively, which are obtained from the PEPICO spectra measured under the condition (A) and by using eq.(4). It is noted that at energies above 12.66keV (i.e. in the energy range (iii)) the results of $\alpha_N(h\nu)$ agree well with those deduced from eq.(3). It is interesting to investigate whether our new method is applicable to other clusters.
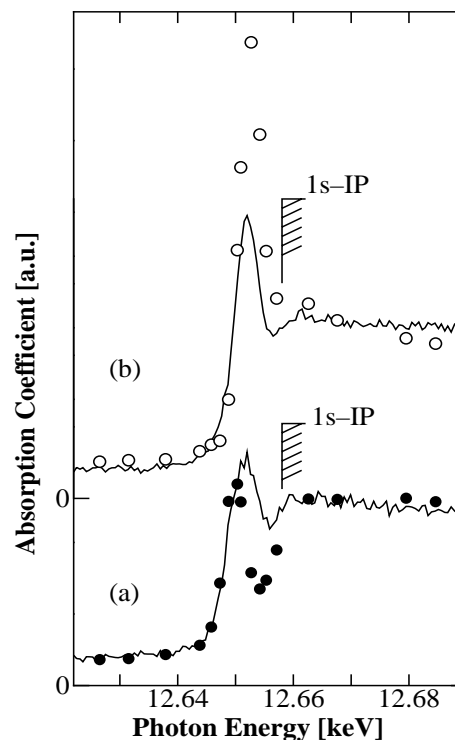
Figure 4

The absorption spectra for Se$_2$ (a) and "Se$_5$" (b) obtained from the PEPICO spectra under the condition (A) by using eq.(4) are denoted by the circles, and those obtained from the TIY spectra taken under two different conditions (A) and (B) by using eq.(3) are denoted by the solid lines. The agreement between these two kinds of spectra is fairly good in the energy range above 12.66keV. The 1s-IP is also shown in the Figures.

References

Haberland, H. *Clusters of Atoms and Molecules,* (Springer, Berlin, 1994).
Hayakawa, T., Nagaya, K., Yamamoto, I., Ohmasa, Y., Yao, M. & Nomura, M. (2000a) *J. Phys. Soc. Jpn.* **69**, 2039–2048.
Hayakawa, T., Nagaya, K., Hamada, K., Ohmasa, Y. & Yao, M. (2000b) *J. Phys. Soc. Jpn.* **69**, 2850–2858.
Kakar, S., Björneholm, O., Weigelt, J., de Castro, A. R. B., Tröger, L., Frahm, R., Möller, T., Knop, A. & Rühl, E. (1997) *Phys. Rev. Lett.* **78**, 1675–1678.
Kosugi, N. (2000) *private communication.*
Krause, M. O. & Carlson, T. A. (1967) *Phys. Rev.* **158**, 18–24.
Morin, P. & Nenner, I. (1986) *Phys. Rev. Lett.* **56**, 1913–1916.
Nagaya, K., Hayakawa, T. & Yao, M. *unpublished data.*
Nomura, M. & Koyama, A. (1995) *KEK Report* **95-15.**
Rühl, E., Heinzel, C., Hitchcock, A. P., Schmelz, H., Reynaud, C., Baumgärtel, H., Drube, W. & Frahm, R. (1993) *J. Chem. Phys.* **98**, 6820–6826.
Schaphorst, S. J., Caldwell, C. D., Krause, M. O. & Jiménez-Mier, J. (1993) *Chem. Phys. Lett.* **213**, 315–320.
Yao, M., Hayakawa, T., Nagaya, K., Ohmasa, Y., Hamada, K., Tai, M., Yamamoto, I. & Nomura, M. (1999) *Jpn. J. Appl. Phys.* suppl.**38-1**, 564–567.