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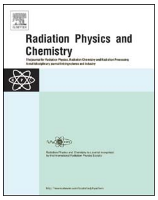

Core level photoelectron spectroscopy probed heterogeneous xenon/neon clusters

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ABSTRACT

Binary rare gas clusters; xenon and neon which have a significant contrariety between sizes, produced by a co-expansion set up and have been studied using synchrotron radiation based x-ray photoelectron spectroscopy. Concentration ratios of the heterogeneous clusters; 1%, 3%, 5% and 10% were controlled. The core level spectra were used to determine structure of the mixed cluster and analyzed by considering screening mechanisms. Furthermore, electron binding energy shift calculations demonstrated cluster aggregation models which may occur in such process. The results showed that in the case of low mixing ratios of 3% and 5% of xenon in neon, the geometric structures exhibit xenon in the center and xenon/neon interfaced in the outer shells. However, neon cluster vanished when the concentration of xenon was increased to 10%.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful technique for probing matters. It can be used to determine a material's electronic structure, geometry, and chemical properties, such as ionization energy and chemical shift. In various systems, these properties can be controlled by adjusting a material's size or structural arrangement. A cluster is one system in which geometric and electronic structure depends on such parameters.

Recently, several cluster types have been examined using XPS to elucidate the properties water, metal, molecular and rare gas clusters. Surface enrichment is a dominant phenomenon in such systems. Minimizing the surface area of a material tends to minimize the total free energy of the system. Close packed clusters and radially layered structures may form Buck and Krohne (1996). This is an important model system in cluster science and for complex heterogeneous nanoparticles.

Clusters can be produced through a co-expansion process which the bonding strength between monomers is related gas pressure and nozzle temperature. Additionally, the number of elements in multicomponent systems, i.e., mixed clusters, significantly impacts system properties (Laarmann et al., 2002; Kambach et al., 1993). Argon/krypton binary clusters were created by using this technique, the structure showed that krypton molecules formed in the core and argon atoms accumulate at the surface. Moreover, in argon/neon heterogeneous cluster the core full filled with argon atoms and neon comprised the outer shells (Lundwall et al., 2007) whereas argon/xenon clusters exhibited different interfacial areas between argon and xenon atoms depending on mixing ratios (Tchaplyguine et al., 2004).

Generally, clusters formed in an adiabatic expansion are initially in a gaseous state (Farges et al., 1986). Consequently, temperature and atomic radii of the binary species have to be considered. Argon/krypton, argon/neon, and argon/xenon have similar sizes and boiling points. Therefore, formation of these mixed clusters is possible. However, creating mixed xenon/neon clusters is harder due to their very different properties. Therefore, this work concentrated on producing heterogeneous xenon/neon mixed clusters by using a co-expansion setup and probed structural arrangement, based photoelectron spectroscopy.

2. Experimental details

The experiments were performed at the undulator based soft X-ray beamline I411 at the Swedish synchrotron radiation facility, MAX-lab (Bässler et al., 2001). A Scienta R4000 electron spectrometer was used for measurements in two XPS regions, Ne 2s and Xe 4d. Energy calibration was performed using atomic peaks in the spectra. They were 48.48 and 67.55 eV for atomic Ne 2s and Xe $4d_{5/2}$ respectively (Hall et al., 1991). The core spectra of Ne 2s and Xe 4d were obtained with

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photon energies of 88 and 109 eV, respectively. Photon energies in the XPS study were chosen such that the photoelectrons were emitted with approximately equal kinetic energy, 40 eV, for both the xenon and neon measurements. This simplified interpretation of the spectra, since all measured photoelectrons essentially had an equal mean free path length with respect to intra cluster scattering. The total energy resolutions were 80 and 36 meV for neon and xenon XPS spectra, respectively.

A supersonic jet cluster source, based on adiabatic co-expansion of gases, was used to produce mixed clusters. The geometry of the experimental source was similar to that described elsewhere (Laarmann et al., 2002). The mean cluster size < N > produced with this equipment using a pure, expanding gas can be estimated using the Γ^*– formalism (Buck and Krohne, 1996; Hagena and Obert, 1972). It depends upon geometry and nozzle temperature, type of gas used and its pressure. The equipment was mounted with a conical nozzle and a 150 µm orifice and a 20° total opening angle. The nozzle was cooled to a temperature of −138 °C using a system combining liquid nitrogen and Peltier elements. A mixing system allowed preparation of mixtures containing 1%, 3%, 5%, and 10% concentrations of xenon in neon. The primary mixtures filled the stagnation chamber at a pressure of 1.9 bar.

Experiments with argon/xenon clusters revealed additional features between surface and bulk material, i.e., the interface (Tchaplyguine et al., 2004). Therefore, this work also examined the interface. Contributions of atoms to cluster features were seen in XPS analysis. This was done using Voigt profiles with Lorentzian widths corresponding to the natural lifetime of the core ionized states and a Gaussian accounting for the instrumental broadening contributions. Lifetime broadening of atomic Ne 2 s is less than 1 meV, whereas the cluster broadening is considerably larger (Lablanquie et al., 2000). In the case of Xe 4d, atomic and cluster lifetimes are similar. They are 111 and 104 meV for Xe 4d$_{5/2}$ and Xe 4d$_{3/2}$, respectively (Jurvansuu et al., 2001).

3. Results and discussion

3.1. Computer calculation

Since the photoelectrons recorded in both the xenon and neon panels had comparable kinetic energy, and therefore the same mean free path length, measurements were comparable with respect to surface sensitivity. This is important in the analysis of the XPS data. Different sample surroundings are distinguished by binding energy shifts in the spectrum. The origin of the observed change is to a large degree due to polarization screening by the atoms surrounding an ionized atom. Surface and bulk resolution is often achieved in homogeneous clusters, where the surface feature is the component closest to the atomic reference signal and the bulk feature is found shifted further from the atomic peak (Björneholm et al., 1995). In the case of heterogeneous clusters, the chemical shifts also contain information about the atomic mixing and radial distributions in the system. Therefore, we calculated the induced polarization of atoms surrounding the core-ion using the TINKER molecular modeling package (Ponder, 2010) and the polarizable amoeba force field (Halgren, 1992). The calculation details are described elsewhere (Lundwall et al., 2007). Binding energy shifts for sites in the cluster with different co-ordinations, relative to their gas phase counterparts, may be calculated from the electrostatic relaxation of the core ionized cluster, facilitating interpretation of the spectra (Amar et al., 2005; Hatsui et al., 2005). In the current work, electron binding energy shifts were calculated for sites with different arrangements of neon atoms on icosahedral xenon clusters. There were 1415 atoms for large clusters, 55 and 56 for medium clusters, 13 and 14 for small clusters. The binding energy shift calculations are summarized in Table 1 and related to the XPS spectra as illustrated in Fig. 1.

Table 1
The core level binding shift calculations of neon and xenon.

Structure	**ΔE of Ne (eV)**	**ΔE of Xe (eV)**
a) A Xe atom in core shell, 12 Ne atoms on the surface	−0.19	−0.15
b) A Ne atom on the vertex site of 12 Xe atoms	−0.55	−0.42
c) Pure 13 Xe atoms	–	−0.44
d) A Ne atom on the hollow site of 13 Xe atoms	−0.42	−0.45
e) 13 Xe atoms in core shell, 42 Ne atoms on surface with		
1 Xe neighbor	−0.35	−0.52
2 Xe neighbors	−0.46	−0.52
3 Xe neighbors	−0.51	−0.53
f) A Ne atom on the vertex site of 54 Xe atoms	−0.70	−0.56
g) A Ne atom on the hollow site of 55 Xe atoms	−0.41	−0.56
h) Pure 1415 Ne atoms and ionized a Ne atom which in		
Vertex	−0.27	–
Edge	−0.35	–
Face sites	−0.40	–

It was notable that the hollow, vertex, edge, and face sites had 3, 6, 8, and 9 coordinates, respectively. In addition, ΔE represents the core-level binding shift of ionized neon and xenon atoms.

The binding energy shifts of various cluster sizes and conditions are shown in Table 1. In small clusters consisting of 13 atoms, a xenon atom in the core surrounded by 12 neon atoms, the binding energies of both species were shifted lower to 0.19 eV and 0.15 eV, respectively. In contrast, when a neon atom was placed at the core and surrounded by 12 xenon atoms, the binding energy shifts of neon and xenon atoms were 0.55 eV and 0.42 eV, respectively.

For larger clusters (55 atoms to 56 atoms), the energy shifts varied with the position and species of ionized atom. In the case of a neon atom on the vertex and hollow sites with 54 and 55 xenon neighbors, the binding energy shift of neon remained 0.56 eV. However, xenon energy ranged from 0.41eV to 0.70 eV. When less xenon and more neon was present (13 xenon atoms in the core with 42 neon neighbors), the binding energy shift of xenon was 0.52 eV. An ionized neon atom with one, two, or three xenon neighbors had binding energy shifts of 0.35, 0.46, and 0.51 eV, respectively. Large neon clusters had 1415 atoms with energy shifts of 0.27, 0.35, and 0.40 eV when ionized atom were in vertex, edge, and face sites, respectively.

From the calculations, it can be inferred that the geometric structures of xenon/neon showed xenon atoms at the center for all sizes with various species at different surface sites. For small and medium clusters, incomplete neon shells were observed on the surface. Larger clusters have xenon or neon on the incomplete outer shell. The calculation well agrees with mixed Ar-Xe and Kr-Xe Lennard-Jones clusters in (Calvo and Yurtsever, 1988; Clarke et al., 1993; Doye et al., 2005) in which the cluster size from 13 atoms to 55 atoms show a core-surface phase separation behavior.

3.2. Cluster structure

The core-electron spectra of Ne 2s and Xe 4d$_{5/2}$, corresponded to primary mixing ratios of 1%, 3%, 5% and 10% of xenon in neon, are shown in Fig. 1. The left side gives the core spectra of Ne 2s. The center panel features Xe 4d$_{5/2}$ and was obtained with photon energies of 88 eV and 109 eV, respectively. The lower panel gives relative binding energies when the monomer feature is put at 0 eV in all spectra. The structures at lower binding energies are due to clusters. Atomic features in the core level spectra corresponded to cluster signals shifted to lower binding energies due to polarization screening as in water