

# Surface-sensitive measurements of excitonic processes in rare gas clusters by electron energy loss spectroscopy

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**Abstract.** We present the electron energy loss spectra of Ar clusters as a function of cluster size ranging from 120 to 3500 atoms/cluster. The intensity of the bulk excitation peak decreases for cluster sizes larger than 500 atoms/cluster. This characteristic feature can be explained based on a simple calculation that takes into account the mean free path of the incident electrons. The present study demonstrates the promise of surface-sensitive measurements of the excitation processes of clusters.

## 1. Introduction

The physics of clusters has attracted significant interest, because they not only bridge the gap between atoms and solids, but also have specific physical properties [1]. One unique aspect of clusters is their large surface-to-volume ratio, which enables sensitive measurements of surface processes. In addition, clusters traveling through a vacuum have very clean surfaces, as opposed to solid-substrate surfaces; this is especially true for condensed solids such as rare-gas solids [2]. This property is important because small amounts of impurities may affect dynamic processes on the surface [3].

In a previous paper [4], we published electron energy loss spectra of Ar clusters as a function of both incident electron energy and cluster size (average cluster size,  $\langle N \rangle = 120 \sim 270$  atoms/cluster). These results clearly showed the surface and bulk excitation peaks, and the appearance cluster size of the bulk excitation peak was found to be dependent on the incident electron energy. This characteristic feature was qualitatively explained by a simple model that takes into account the mean free path,  $\lambda$ , of the incident electrons in Ar clusters.

Here, we report experimental results for larger clusters up to  $\langle N \rangle = 3500$  atoms/cluster. We show that the bulk excitation peak decreases for larger clusters and discuss the promise of surface-sensitive measurements.

## 2. Experiments

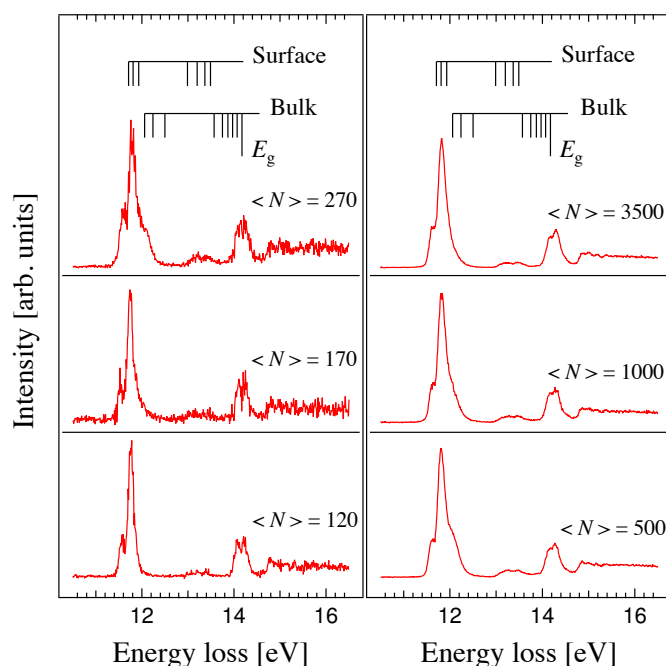
Details of the experimental apparatus and procedure have been described elsewhere [4]. Briefly, a pulsed cluster beam is generated by adiabatic expansion through a conical nozzle attached to a pulse valve (General Valve Co.). The average cluster size is controlled by changing the stagnation pressure and nozzle temperature. The size distribution is determined experimentally by measuring the kinetic energy of the ionized cluster beam [5].

A mono-energetic electron beam is generated using a simulated hemispherical energy selector [6]. The electron beam is deflected by 90° by a set of parallel plates and subsequently merges with the cluster beam. The length of the merging region is approximately 200 mm. After passing through the merging region, the electrons are analyzed in terms of their energy and detected by a channel electron multiplier. The overall energy resolution of our setup is 150–180 meV.

Under the present experimental conditions (typical duration and frequency of the cluster beam pulse of 10 ms and 2–4 Hz, respectively), the acquisition time of one spectrum is about 50 hours. The merging-beam geometry is essential to obtain energy loss spectra with adequate statistics, because of the low target (cluster) density.

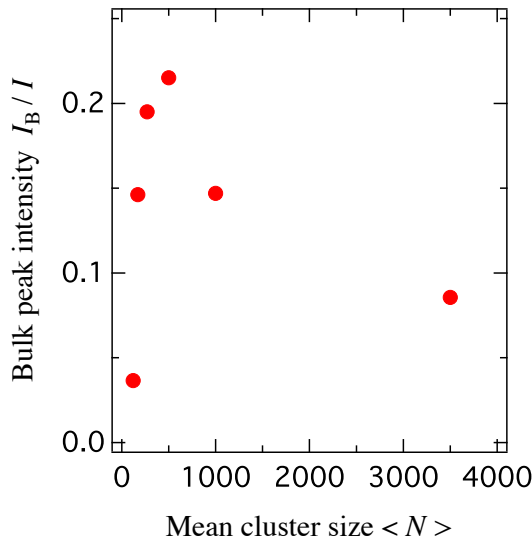
## 3. Experimental results

Figure 1 shows electron energy loss spectra of Ar clusters for average cluster sizes,  $\langle N \rangle$ , ranging from 120 to 3500 atoms/cluster at an incident electron energy  $E_0 = 100$  eV. The observation angle is 0° with respect to the direction of the incident electron beam. Vertical lines indicate the energy positions of surface and bulk excitons and the band gap energy,  $E_g$ , in solid Ar [7].



**Figure 1.** Electron energy loss spectra of Ar clusters with  $\langle N \rangle$  ranging from 120 to 3500 atoms/cluster. The incident electron energy is 100 eV and the observation angle is 0°. Vertical lines show the energy positions of surface and bulk excitons and the band gap energy,  $E_g$ , in solid Ar [7].

The peak (shoulder) of the  $3p^54s$  bulk excitation at 12.1 eV is found in the spectrum for a cluster size of  $\langle N \rangle = 170$  atoms/cluster, indicating that bulk excitation can occur in clusters with diameters corresponding to approximately five atoms [4]. We also find that the intensity of the bulk peak relative to the surface peak increases with cluster size up to  $\langle N \rangle = 500$  atoms/cluster, but decreases for sizes larger than 500 atoms/cluster, as shown in Fig. 2. This characteristic feature is discussed in the following section.



**Figure 2.** Dependence of the  $3p^54s$  bulk peak intensity,  $I_B$ , at 12.1 eV on mean cluster size,  $\langle N \rangle$ . The bulk peak intensity is normalized to  $I = I_B + I_S$ , where  $I_S$  is  $3p^54s$  surface peak intensity.

#### 4. Discussion

We now discuss the dependence of the surface and bulk excitation peak intensities on cluster size (cf. our previous work [4]). The ratio of the number of surface atoms,  $N_S$ , to the total number of atoms,  $N$ , in a cluster is given by [8]

$$\frac{N_S}{N} = \frac{4\pi R^2/\pi r^2}{(4\pi R^3/3)/(4\pi r^3/3)} = 4\frac{r}{R} = 4N^{-1/3} \quad (1)$$

and

$$\frac{N_S}{N} N^{1/3} = 4, \quad (2)$$

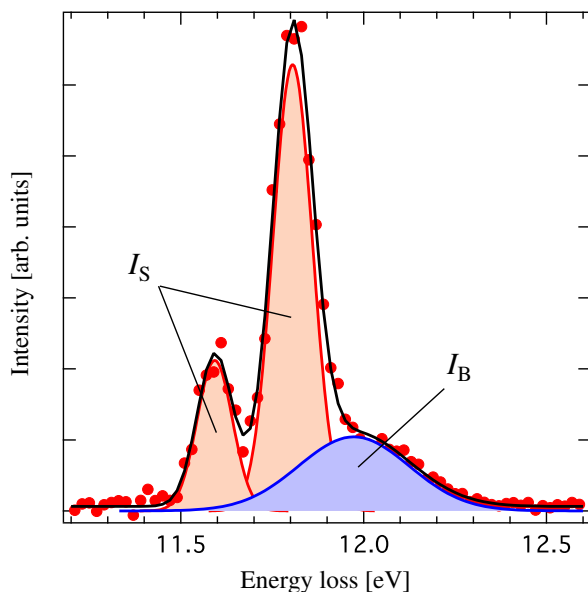
where  $r$  and  $R$  are the radii of a single atom and a cluster, respectively. Assuming that the intensity of surface excitation,  $I_S$ , is proportional to the number of surface atoms,  $N_S$ , and that the total intensity,  $I = I_S + I_B$ , is proportional to the experimentally determined cluster size  $\langle N \rangle$ , we can write Eq. (2) as

$$\frac{I_S}{I_S + I_B} \langle N \rangle^{1/3} = 4. \quad (3)$$

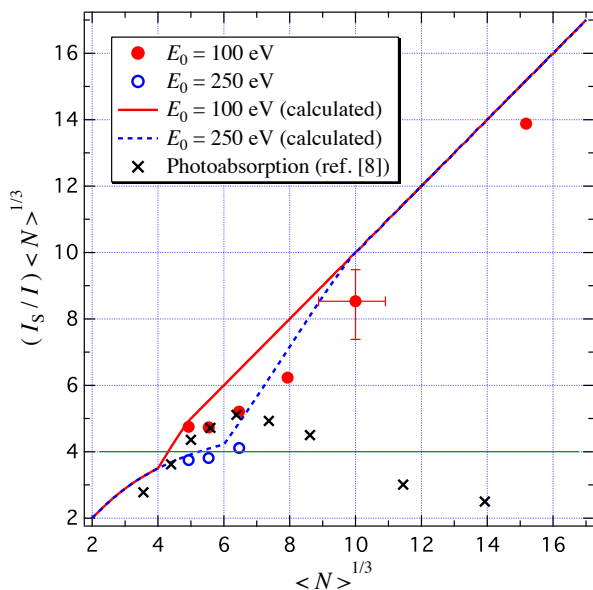
The peak intensities of the surface excitation  $I_S$  and those of the bulk excitation  $I_B$  are obtained by fitting the measured spectra to three Gaussian peaks, as shown in Fig. 3.

Figure 4 shows a plot of  $(I_S/I) \langle N \rangle^{1/3}$  versus  $\langle N \rangle^{1/3}$ . The experimental results for  $E_0 = 100$  and 250 eV (spectra not shown) show a value around 4 for smaller cluster sizes, but this increases with increasing cluster size. We attribute this characteristic feature to the fact that the mean free path of the incident electrons in Ar clusters is smaller than the cluster diameter and that  $\lambda$  varies with the incident electron energy. In other words, the numbers of surface atoms,  $N'_S$ , and bulk atoms,  $N'_B$ , that can be excited by an incident electron and detected by our  $0^\circ$  spectrometer are smaller than the numbers of surface and bulk atoms in a cluster.

We calculate  $N'_S$  and  $N'_B$  using the following simple model. We assume that the electron cannot be detected by our spectrometer if the length of its trajectory within a cluster is longer than  $2\lambda$ ; i.e., an electron excites an atom at a depth of  $\lambda$  in the cluster and it can then pass through the cluster without exciting another atom in the cluster within a distance of  $\lambda$ . Figure 5 shows the model schematically. An electron coming from the left passes through the cluster



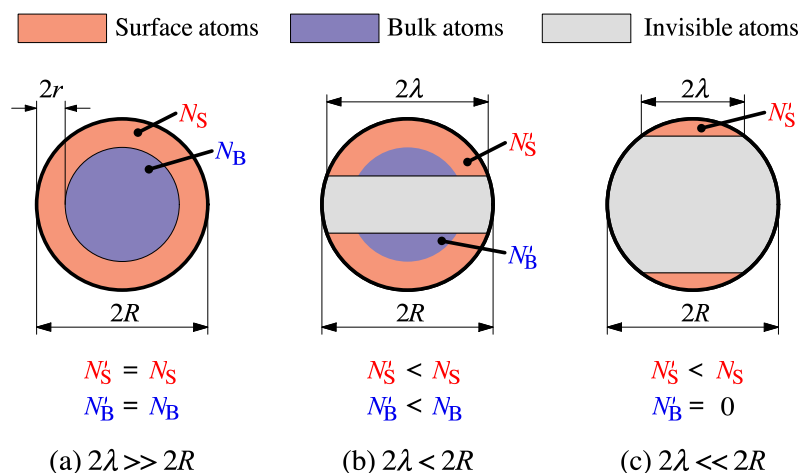
**Figure 3.** Electron energy loss spectrum of Ar clusters from 11 eV to 13 eV.  $I_S$  and  $I_B$  are the intensities of surface and bulk excitations, respectively. See text for details.



**Figure 4.**  $(I_S/I) \langle N \rangle^{1/3}$  for incident electron energy  $E_0 = 100$  eV ( $\bullet$ ) and 250 eV ( $\circ$ ). Also shown are  $[N'_S / (N'_S + N'_B)] \langle N \rangle^{1/3}$ , calculated using the model taking into account the mean free path of incident electrons for electron energies of 100 eV (—) and 250 eV (---). Photoabsorption results ( $\times$ ) [8] are also plotted for comparison. See text for details.

and is detected by the  $0^\circ$  detector on the right-hand side of the cluster. If the mean free path is much longer than the cluster radius, as shown in Fig. 5(a), all surface and bulk atoms can contribute to the electron energy loss spectra; i.e., electrons scattered by any atom within the cluster can be detected by our spectrometer ( $N'_S = N_S$  and  $N'_B = N_B$ ). In the case shown in Fig. 5(b), where  $\lambda$  is slightly smaller than  $R$ , some of the surface and bulk atoms can be invisible to our spectrometer; i.e.,  $N'_S < N_S$  and  $N'_B < N_B$ , because multiple collision may occur in the cluster. Finally, for  $\lambda \ll R$ , as in Fig. 5(c), all of the bulk atoms are invisible and only some of the surface atoms are visible; i.e.,  $N'_S < N_S$  and  $N'_B = 0$ . In the latter case, it is expected that the spectrum is composed of the surface excitation peaks only.

The solid and dashed lines in Fig. 4 show the calculated results for incident electron energies,  $E_0$ , of 100 and 250 eV, respectively. The calculation has been done in a similar manner described



**Figure 5.** Schematic of the model used in our calculation.  $R$ ,  $r$ , and  $\lambda$  are the radii of a cluster and a single atom, and the mean free path of an electron in a cluster, respectively.  $N_S$  and  $N_B$  are the numbers of surface and bulk atoms in a cluster, respectively, and  $N'_S$  and  $N'_B$  are the numbers of surface and bulk atoms visible to the spectrometer, respectively. See text for details.

in [4]. It should be noted that in the present calculation, we have estimated both  $N'_S$  and  $N'_B$ , while only  $N'_B$  has been estimated in our previous work. We use the fact that the nearest-neighbor distance in solid Ar is 0.376 nm [9] and that the mean free paths of incident electrons with  $E_0 = 100$  and 250 eV in solid Ar are approximately 0.7 and 1.2 nm, respectively [7]. As shown in the figure, the model calculation qualitatively reproduces the trend in the experimental results.

For cluster sizes larger than 1000 atoms/cluster, the slope of the experimental results approaches unity, which is well reproduced by the calculation. This finding indicates that most of the bulk atoms are invisible to our spectrometer, as shown schematically in Fig. 5(c). In turn, this suggests that surface excitation can be observed effectively by selecting the cluster size and the incident electron energy even for very large clusters. Note that this is not the case in the photo-absorption study, because the penetration depth of a VUV photon into the cluster is generally longer than the electrons' mean free path, resulting in a surface-to-bulk intensity ratio similar to the geometrically calculated ratio. Therefore, the photo-absorption results [8] in Fig. 2 show a roughly constant value of 4 for cluster sizes between 50 and 3000 atoms/cluster. It can be expected that the surface sensitivity will be higher for heavier rare gases (such as Kr and Xe) because of their longer nearest-neighbor distances and shorter mean free paths.

Surface-sensitive measurements are currently underway. Electron energy loss spectra of Ar clusters are measured with a small amount of gaseous Ne simultaneously introduced into the main chamber. The peak at 16.848 eV of the Ne ( $2p^53s\ ^1P_1$ ) atomic line is used for energy calibration. The blue shift of approximately 30 meV was observed in our preliminary results of surface excitation for Ar clusters with sizes from 120 to 3500 atoms/cluster. This shift is consistent with previously reported values [10, 11]. Systematic measurements are in progress.

## 5. Summary

We have studied electron energy loss spectra of Ar clusters as a function of cluster size. The intensity of the bulk excitation peak decreases for larger clusters. This characteristic feature has been qualitatively reproduced based on a simple calculation, taking into account the mean free

path of the incident electrons in Ar clusters. We have shown that the surface-excitation process can be effectively observed with an appropriate choice of cluster size and incident electron energy.

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