Structural Features in the Growth of Silver Cluster Cations Observed by Photodissociation/Absorption Spectroscopy

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A silver nanoparticle shows optical absorption originating from collective excitation of free electrons, so-called surface plasmon resonance, which attracts much attention due to an enhanced electric field inherent in the optical process that allows various applications. This optical response of a nanoparticle should be contrasted with that of a silver atom, where only one electron participates in the transition between atomic orbitals. Therefore, it is expected that the collective excitation emerges in the cluster regime of several to several hundreds of atoms. We have been tackling this basic problem by spectroscopic studies on size-selected free silver cluster cations, Ag_N^+. Here we extend our previous experiments[1] on $N = 2$–70 to even larger sizes. The series of photodissociation/absorption spectra reveals systematic changes in the geometry of silver clusters as a function of size.

Size-selected Ag_N^+ clusters, which were produced by a magnetron-sputter cluster-ion source coupled with a quadrupole mass filter, were introduced into a linear ion trap to prepare high-density sample clusters. The trapped clusters were irradiated with a pulsed OPO laser to induce dissociation upon photoabsorption. The dissociation yield, as monitored by a second quadrupole mass filter, was normalized by the photon flux of the incident laser. The measurement was performed as a function of photon energy between 3.5 and 4.1 eV (355–302 nm in wavelength) to obtain a photodissociation spectrum.

A part of the results is shown in Fig. 1. A double-peak profile is observed at $N = 71$, implying an ellipsoidal structure; the higher-energy peak is attributed to an oscillation of electrons along the two shorter axes of the cluster, while the other peak corresponds to the longer axis. In contrast, only one peak shows up at $N = 92$, indicating a spherical symmetry. Spectral features similar to those of nanoparticles/nanorods thus appeared at these sizes in the cluster regime. We will present complete results of photodissociation up to $N = 92$ along with photoabsorption measurement performed by a cavity-enhanced technique that is in progress.

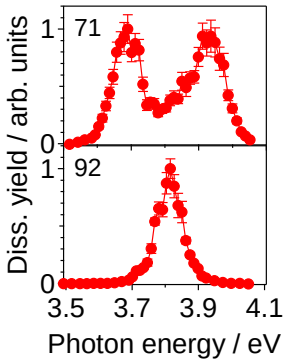

Fig. 1. Photodissociation spectra of Ag_N^+ ($N = 71$ and 92).

1) Fujimoto, Kono, Arakawa, Horio, Yasuike, Terasaki, The 99th CSJ Annual Meeting, 2D3-31 (2019); Kono, Arakawa, Horio, Terasaki, The 100th CSJ Annual Meeting, 1D2-39 (2020).