Optical absorption spectra of size-selected silver cluster cations: Size and temperature dependence

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Optical properties of metal particles change dramatically with their size. Nanometer-scale particles exhibit broad absorption spectra due to collective excitation of electrons, whereas small clusters show relatively sharp spectra originating from electronic transitions between molecular orbitals. We measured size and temperature dependence of optical absorption spectra of silver cluster cations (Ag_N^+) to characterize their optical responses quantitatively.

Silver cluster cations were generated in a magnetron-sputter ion source, and were size-selected by a quadrupole mass filter. They were stored in a linear radio-frequency ion trap and irradiated with a UV laser tunable between 285 and 335 nm. Absorption spectra were measured by photodissociation and photon-trap (a generalized scheme of cavity ringdown) spectroscopy [1]. Measurement was performed both at room temperature and at a lower temperature by cooling with liquid nitrogen.

One-photon absorption led to dissociation of clusters with $N \leq 14$, whereas two photons were required for $N \geq 15$ due to an increasing number of vibrational modes and to a cooling effect by buffer He gas. Figure 1 shows optical absorption spectra of Ag_N^+. The photodissociation cross section is nearly equal to the absorption cross section for $N \leq 14$. Therefore, photodissociation action spectra for $N \leq 14$ is regarded to be equivalent to optical absorption spectra. As for $N \geq 15$, spectral profiles were measured by two-photon dissociation, while absorption cross sections were determined by photon-trap spectroscopy, which does not rely on dissociation of the cluster. Structure-rich spectra were observed for $N < 25$, where the peaks became narrower at a lower temperature. In contrast, spectral profiles for $N \geq 25$ showed a single broad peak with almost no temperature dependence. The oscillator strength per 5s-electron evaluated for $N \geq 25$ increased with size and reached 0.3 at $N = 35$, which is comparable with those of silver nanoparticles exhibiting surface plasmon resonance.

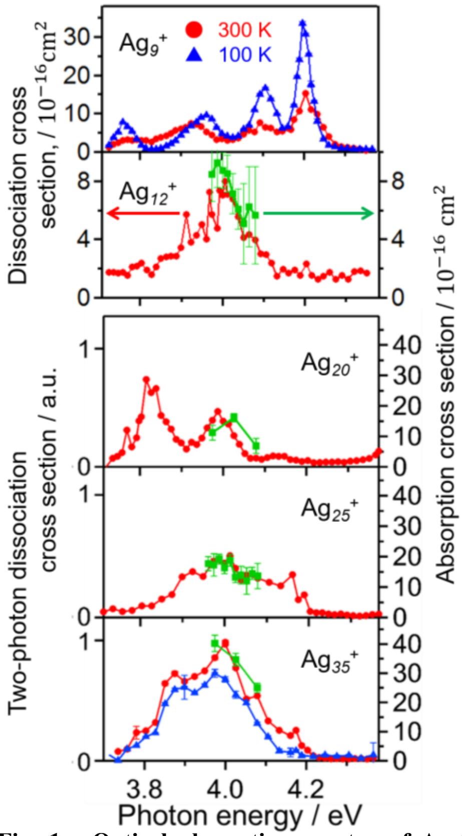

Fig. 1. Optical absorption spectra of Ag_N^+ measured by photodissociation (red circles: 300 K, blue triangles: 100 K) and photon-trap techniques (green squares).

[1] A. Terasaki, T. Majima, C. Kasai, and T. Kondow, *Eur. Phys. J. D* **52**, 43 (2009).