Structural assignment of small silver clusters

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1. ABSTRACT

Silver clusters composed of a few atoms are very interesting for photography and redox catalysis. This is mainly because of their size dependent optical properties and a strong interplay between their geometric and electronic structure, which has a discrete density of states. Despite the wide interest in small silver clusters, there is so far, besides for Ag_3 and Ag_4 [1], no definitive (experimental) assignment of their geometry. Ion-mobility measurements on cationic silver clusters in the gas phase are available [2], but those measurements only provide cross sections. Also, optical absorption spectra of Ag_4 to Ag_{14} have been recorded, mapping their electronic excited states [3].

We have recorded the infrared multiphoton dissociation (IR-MPD) spectra of Ag_3^+ to Ag_{12}^+, by using a Free-electron laser in the far infrared (100-200 cm^{-1} spectroscopic wavenumbers). The silver clusters were produced in a laser vaporization cluster source and tagged with weakly bound argon, with Ar_n up to n=4, which is released after resonant photon absorption.

Comparison of calculated vibrational spectra for different structural isomers by density functional theory with the experimental IR-MPD spectra allows to determine the structures of the silver clusters.

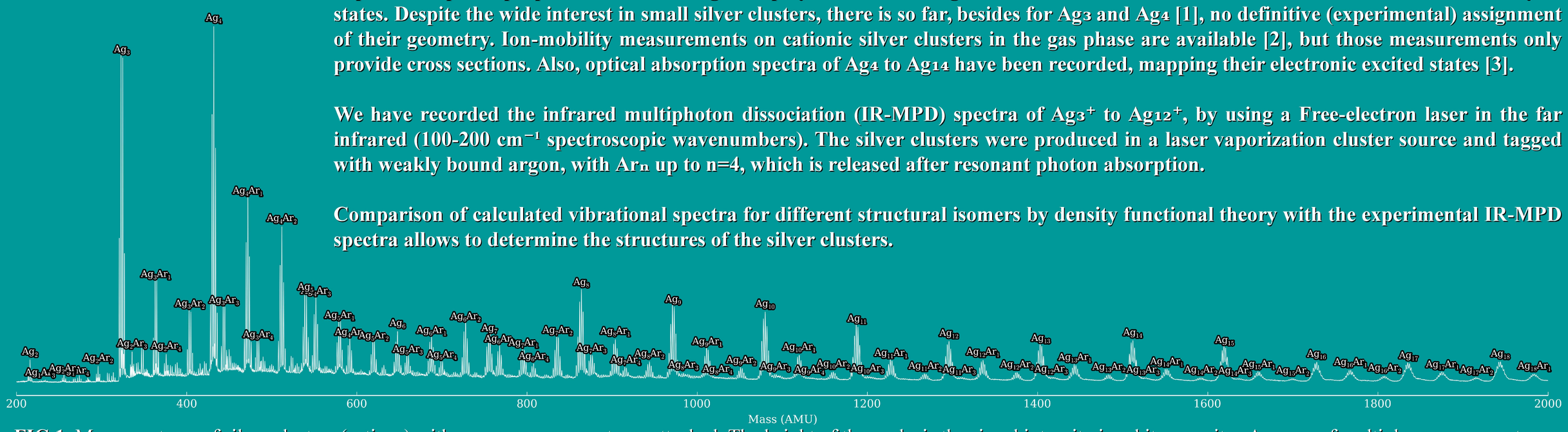


FIG 1. Mass spectrum of silver clusters (cations) with argon messenger atoms attached. The height of the peaks is the signal intensity in arbitrary units. Average of multiple measurements.

2. *PREVIOUS WORK:* ION MOBILITY MEASUREMENTS [2]

P. Weis et al. investigated the structure of cationic silver clusters before by ion mobility measurements. In this type of measurements the silver clusters are first mass selected, and then entered into a drift tube where the clusters collide with helium gas. From the time the clusters take to pass through this tube the collisional cross section can be determined. These are then compared with calculated cross sections. The cross section scales in spherical approximation with $\sim n^{2/3}$, an approximation that becomes better for the larger sizes. Meaning that the cross sections of different structures come closer together, making it difficult to reach a high enough accuracy to uniquely identify the structure. In **FIG 2** the measured cross sections are shown relative to the spherical approximation (squeres), as well as the DFT calculations (circles). **FIG 3** is the legend to this circles.

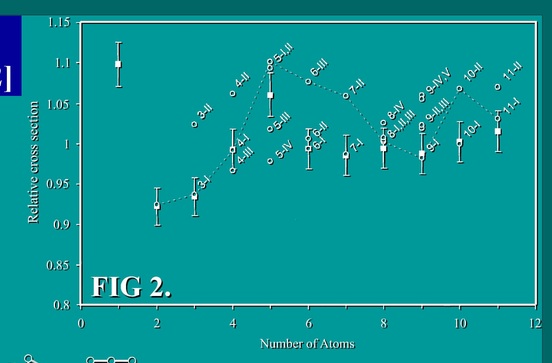


FIG 2.

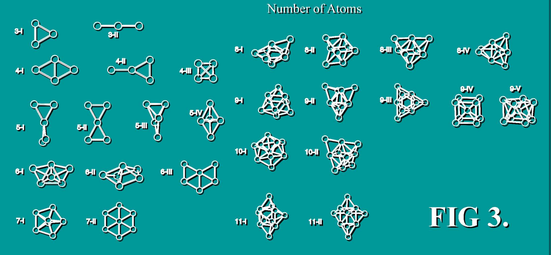


FIG 3.

2. EXPERIMENTAL SETUP

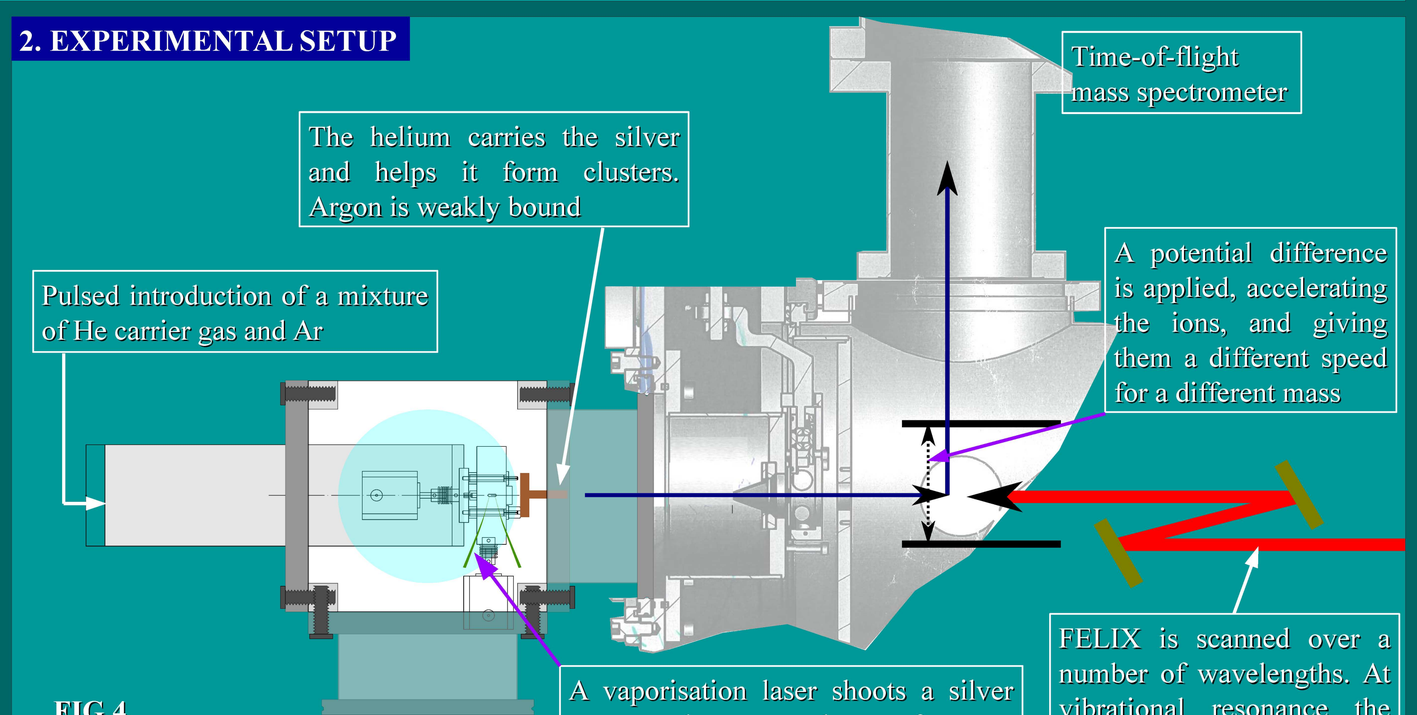
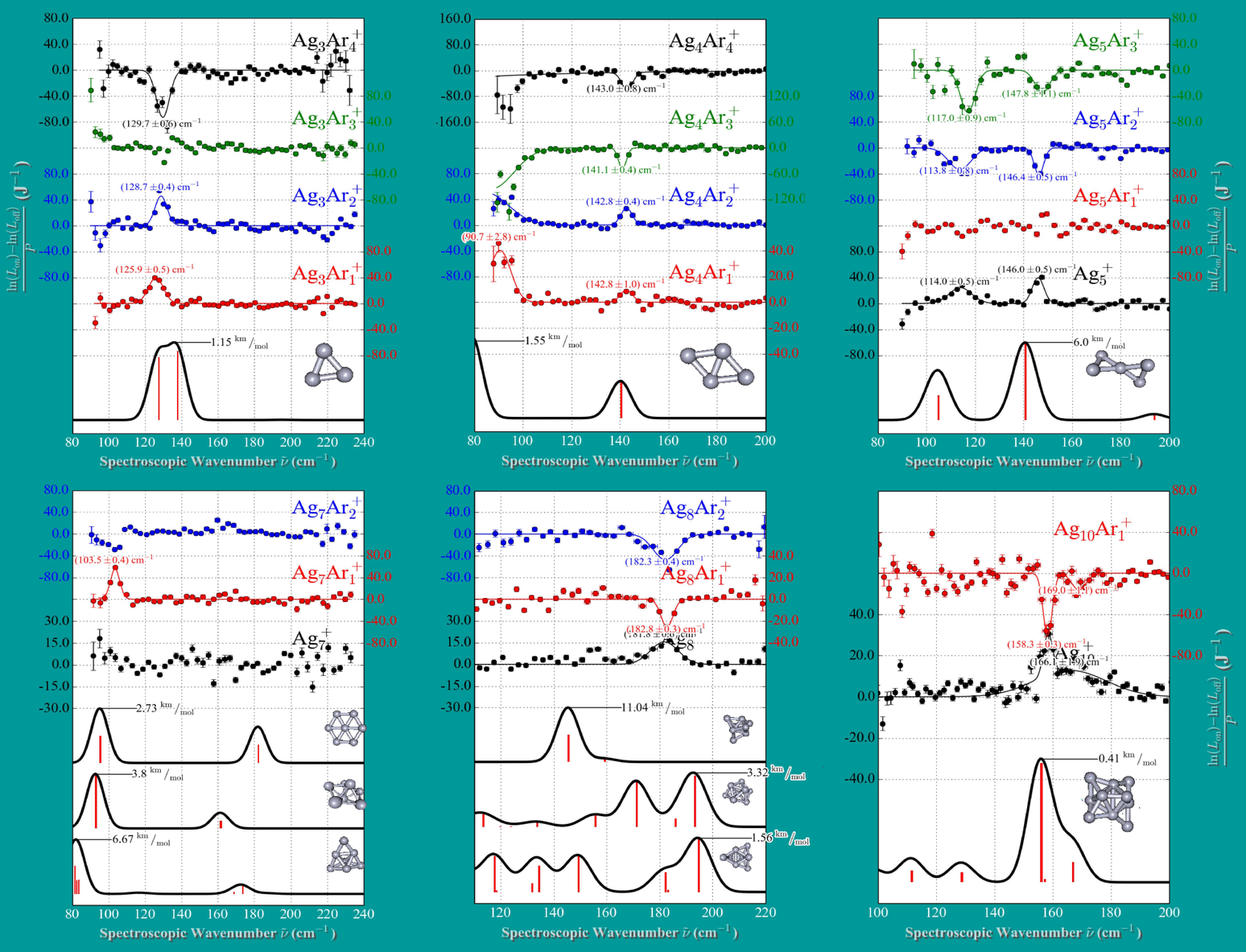


FIG 4.

3. RESULTS

A selection of IRMPD spectra for silver clusters of different sizes. The values on the y-axis scale with the photon-cluster cross section, as a function of wavenumber on the x-axis. One can clearly see depletions if argon atoms are lost, resulting in a growth for the same cluster with less Argon. Lon represents the amount of cluster signal in the mass spectrum with FELIX on, Loff to the situation where FELIX is not on. P is the energy per pulse for FELIX at that wavelength. Uncertainty on the wavelength comes from calibration and binning multiple measurements. A comparison with the harmonic vibrational spectra of the lowest energy isomer as calculated at the DFT/TZVP level is made at the bottom of the figures



4. CONCLUSION & OUTLOOK

We have observed depletion spectra for multiple sizes of $Ag_nAr_m^+$. These occur at the same wavelength for different numbers of argon atoms, this confirms that the argon is weakly bound, and that the influence of the argon is small. By doing DFT calculations on all possible structures we predict the wavenumbers that resonate with the vibrational modes in the cluster, as a function of the structure. By comparing these results with these measurements we will assign unique structures to every different size of silver cluster. The predicted lowest energies are already done and provide good agreement for $Ag_nAr_m^+$ for n=3,4,5,10. For the other size more structures need to be compared.

5. REFERENCES

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FIG 2 & FIG 3 *are taken from* [2]

***BPS** Meeting May 2016, Gent*