

The determination of cluster structures combining infrared spectroscopy and density functional theory calculations

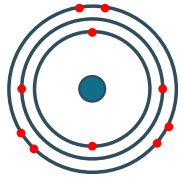
Piero Ferrari

Quantum Solid-State Physics

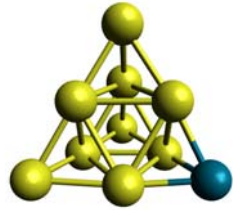
KU Leuven, Belgium

Metal clusters

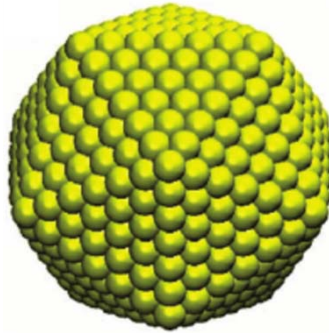
What is a cluster of atoms?



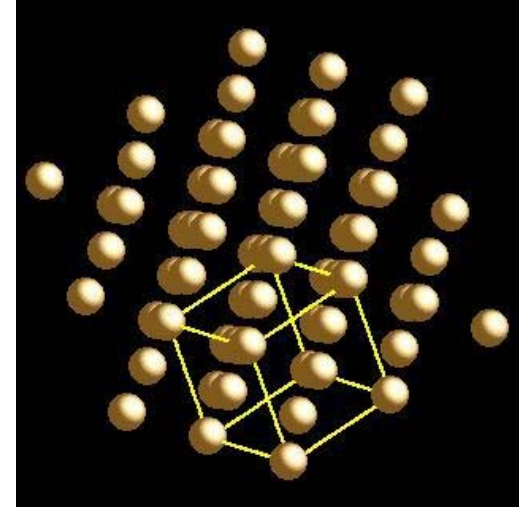
Atom



Cluster



Nanoparticle



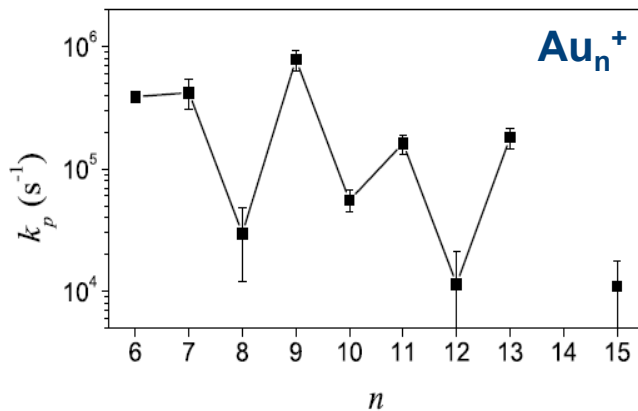
Bulk

A metal cluster is a particle composed of only a **countable number of metal atoms**, ranging from the dimer up to some hundreds of atoms

Size-dependent properties

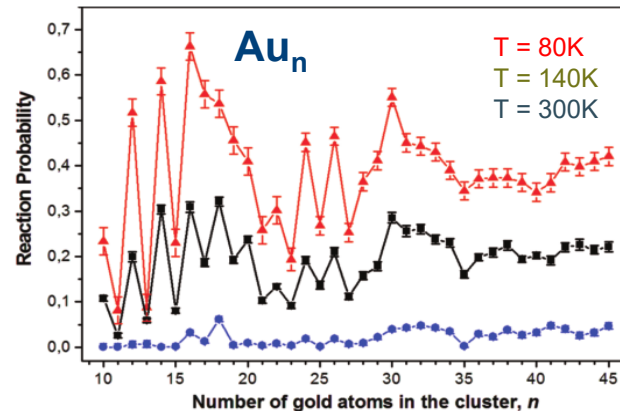
Unlike bulk materials, in clusters most **physical and chemical properties** change drastically **atom-by-atom**

Radiation rates



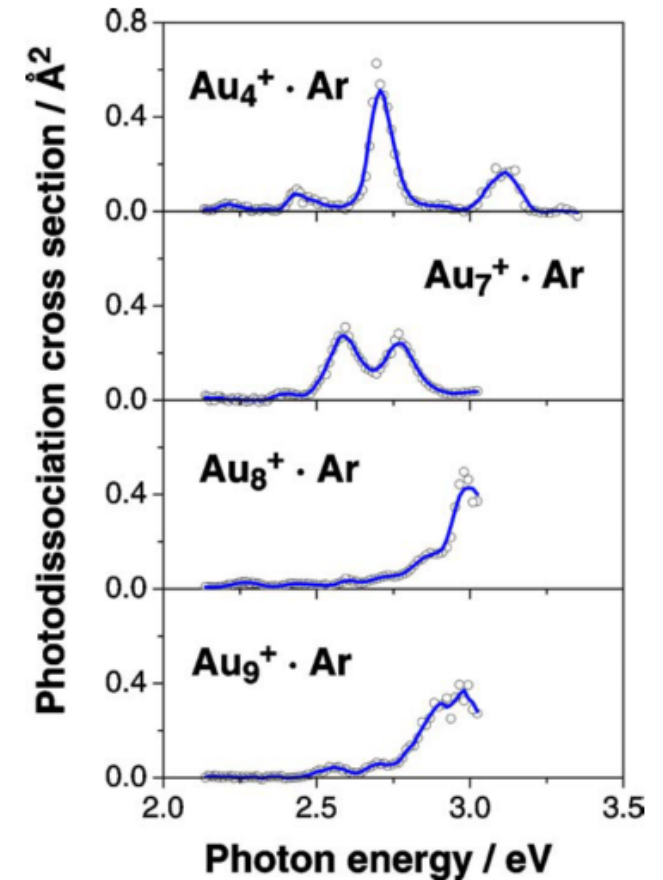
Phys. Rev. A 96, 022511 (2017)

Reactivity towards CO



J. Phys. Chem. A 115, 2103 (2011)

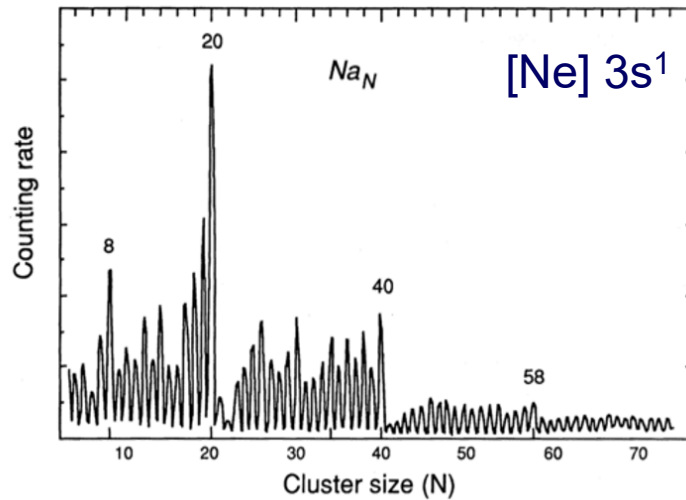
Optical absorption



J. Phys. Chem. 128, 114312 (2008)

Size-dependent electronic structure

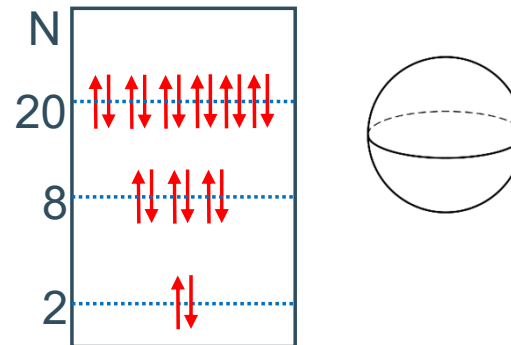
Clusters of specific sizes are produced in higher amounts



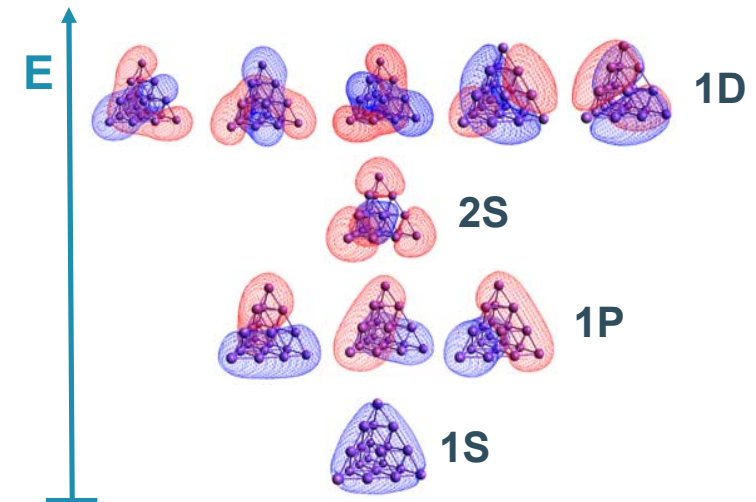
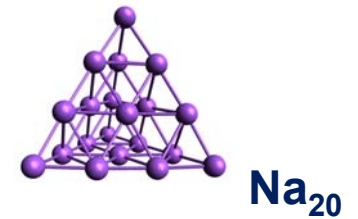
Phys. Rev. Lett. 53, 510 (1984)

Magic sizes: 8, 20, 40, 58, ...

Phenomenological model



Geometry from DFT calculations

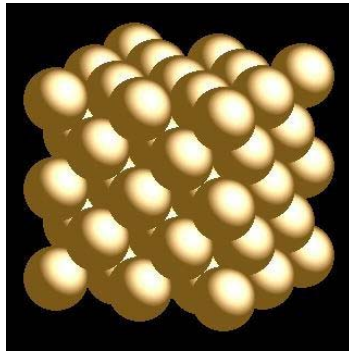


Molecular orbitals

- **Quantum confinement** and electron **delocalization**
- Key ingredients are the **geometry** and the **electronic structure**

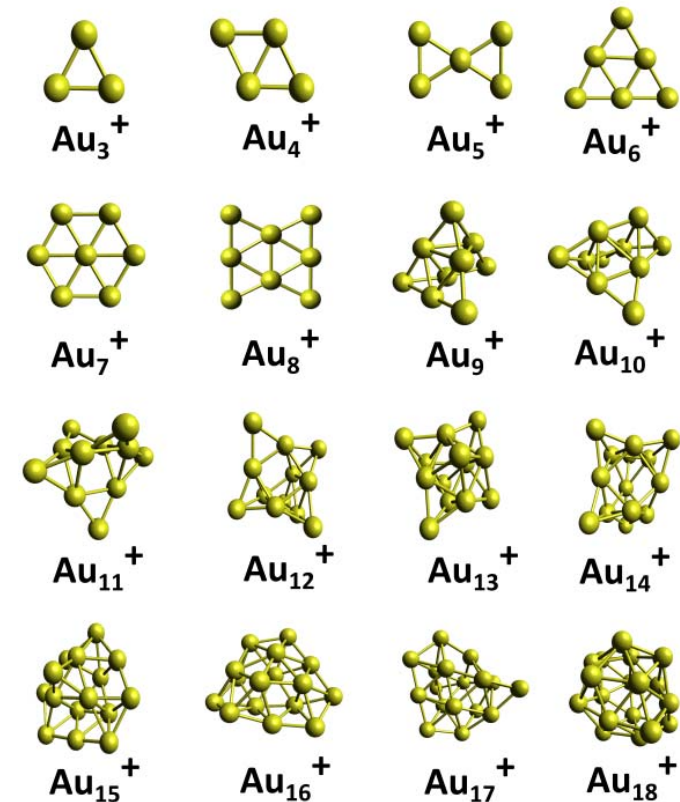
Size-dependent geometries

Bulk gold



The **size-dependency** of cluster properties is a consequence of their **geometry** and **electronic structure**

Gold clusters



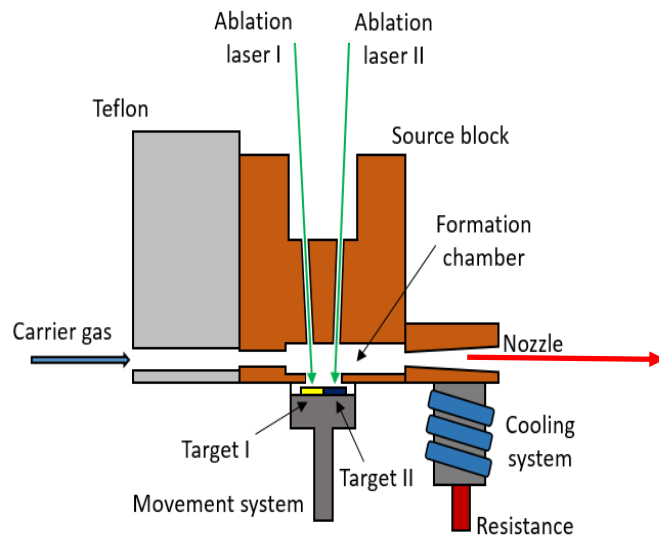
[Phys. Rev. A 2018, 97, 052508](#)

How to determine the precise geometry of an isolated cluster in a molecular beam?

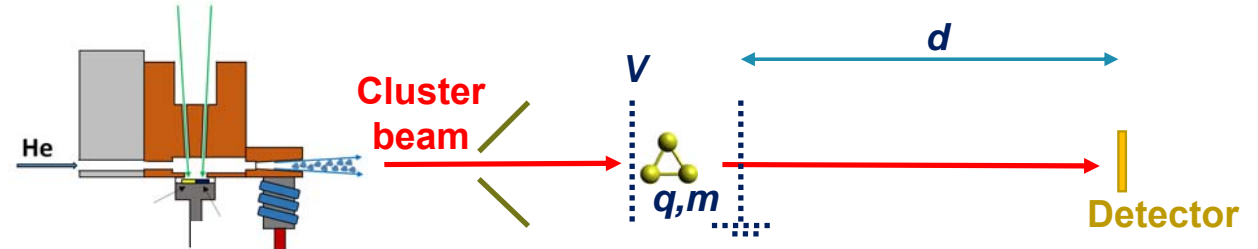
The production of clusters by physical means

Laser ablation and gas condensation

"Modifications of gas aggregation sources: The double laser ablation source approach" Wiley-VCH (2017)

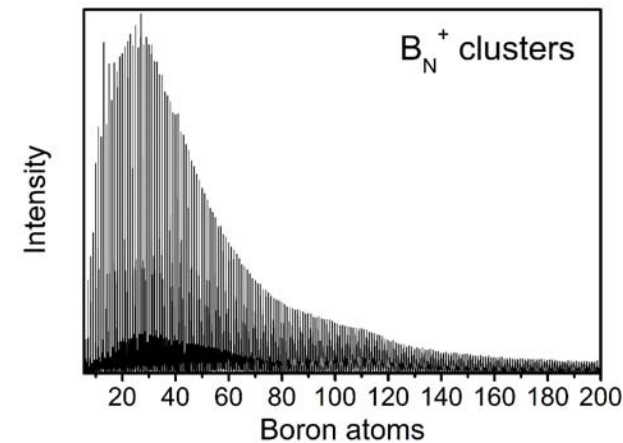


Vaporization lasers



Laser vaporization cluster source

Ion extraction



$$m = \frac{2qV}{d^2} t^2$$

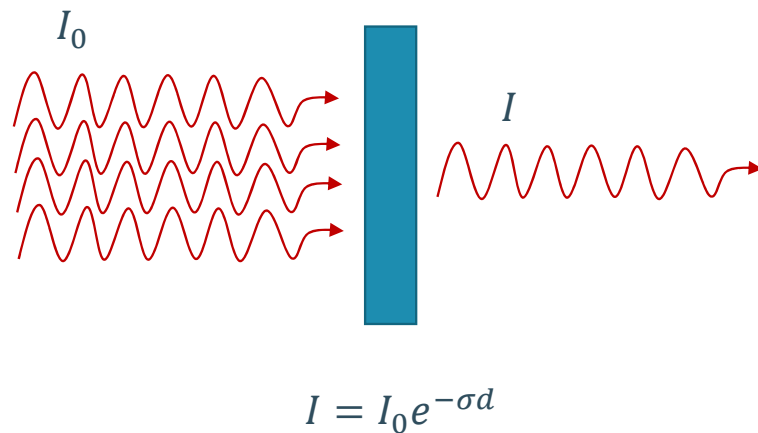
Dual-laser dual-target source for the production of bimetallic clusters

Structural information

The vibrational modes of a cluster are a fingerprint of its geometry

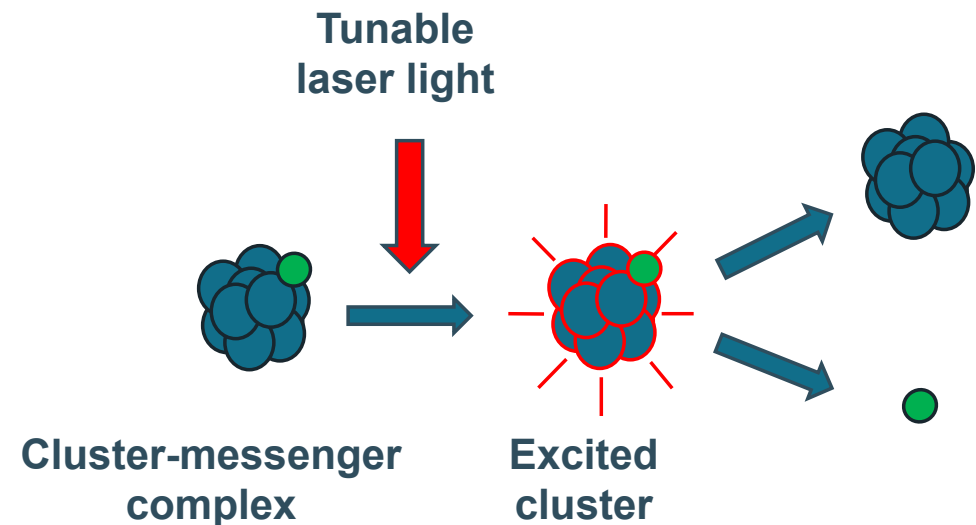
Infrared spectroscopy

In solid-state physics



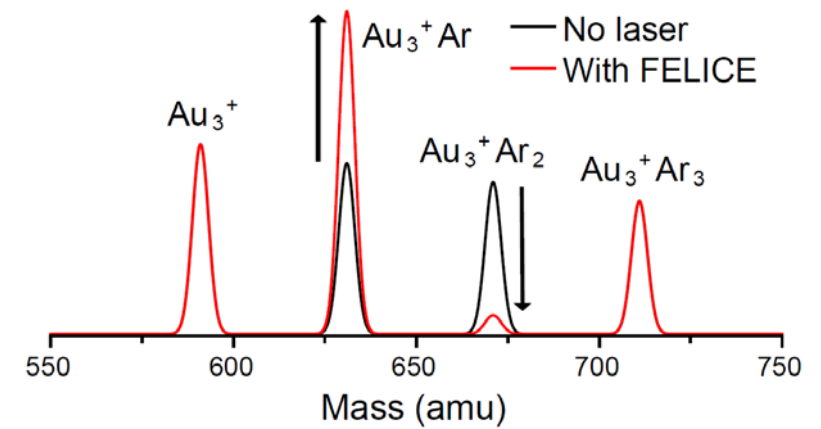
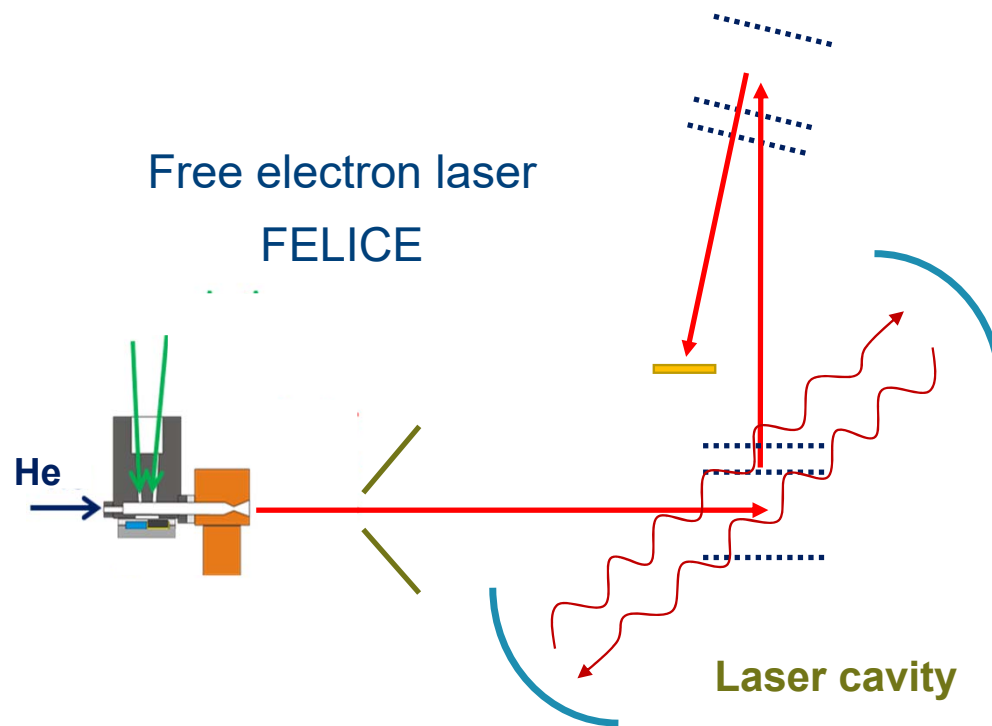
- ✗ Too diluted molecular beam
- ✗ Information won't be size-specific

In the gas phase

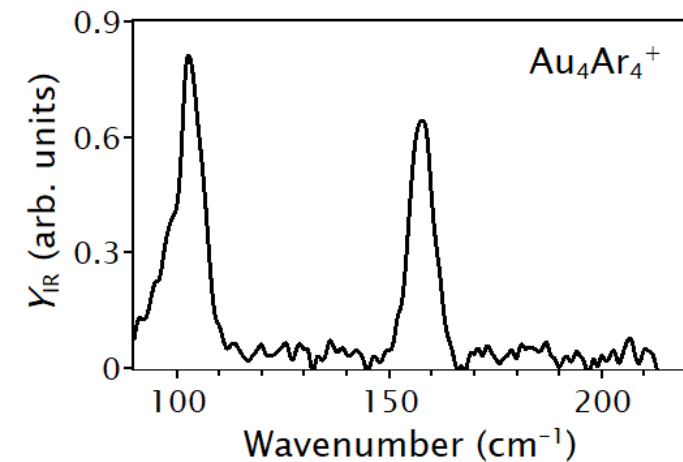


Structural information

Infrared multiple photon dissociation spectroscopy

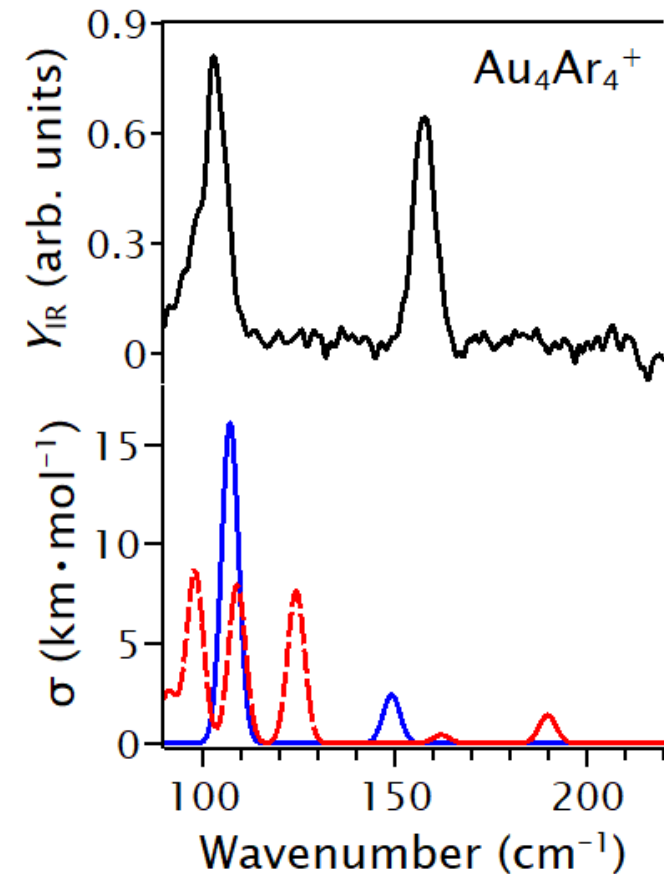
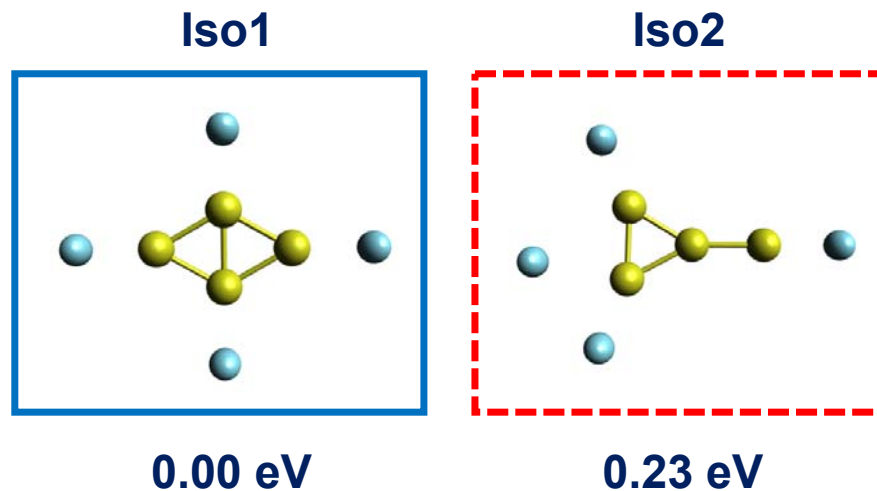


$$Y_{\text{IR}} = -\ln(I/I_0)/E_{\text{IR}}$$

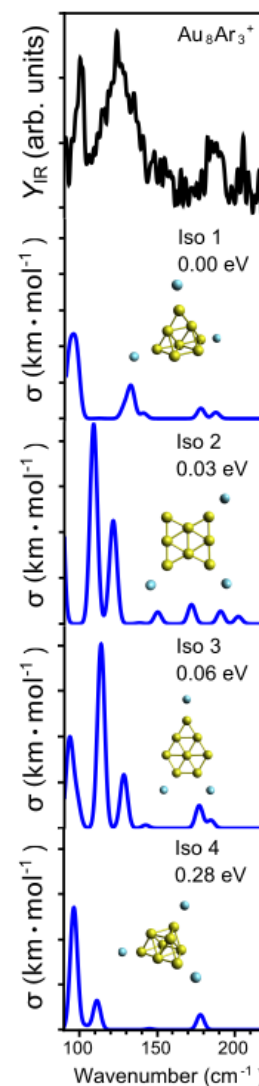
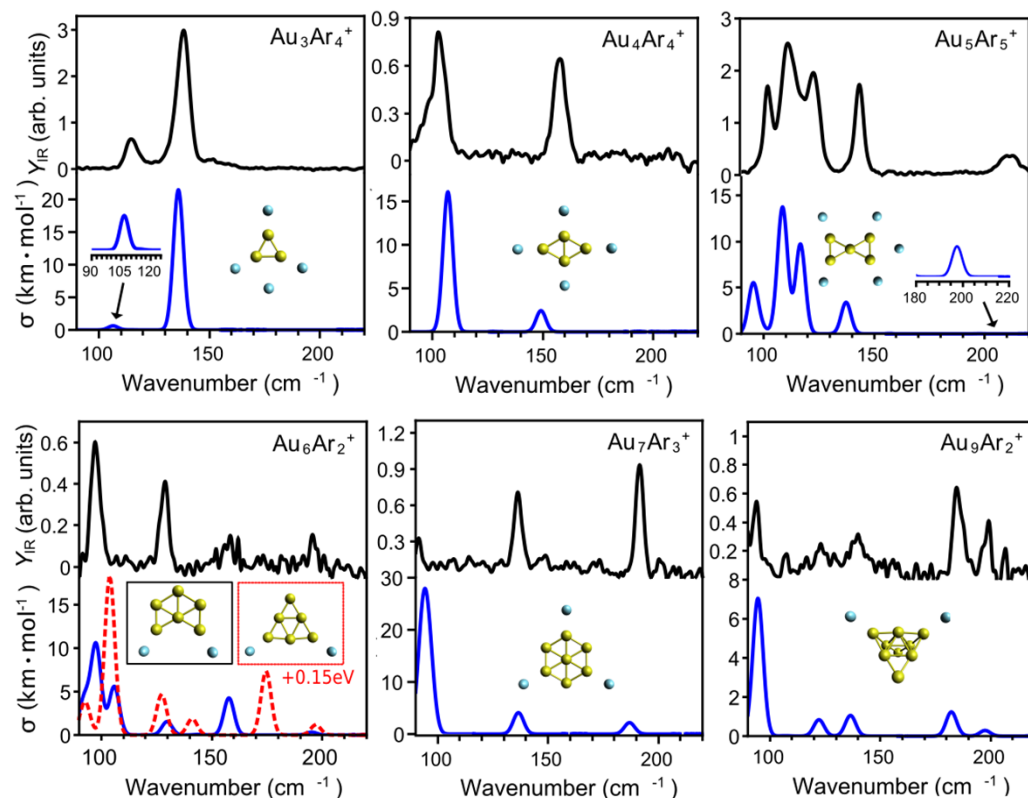


Density functional theory calculations

A **structure is assigned** by comparing the experimental infrared spectrum with the calculated (harmonic) infrared spectrum of **different isomers** calculated by theory



Gold cluster cations

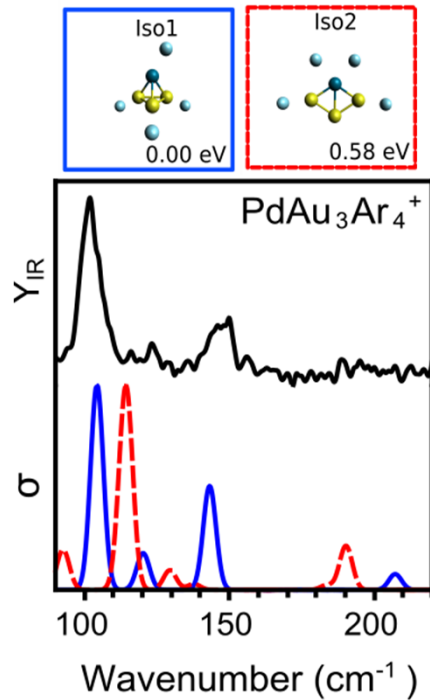


- ✓ IRMPD on $Au_n^+-Ar_m$ complexes
- ✓ Calculations at PBE, Def2-TZVPP level
- ✓ Assigned structures in line with “consensus” in literature
- ✓ 2D-3D transition around $n=8$

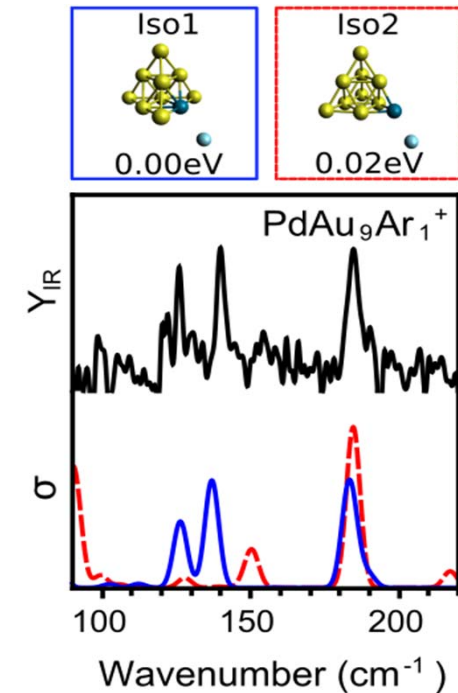
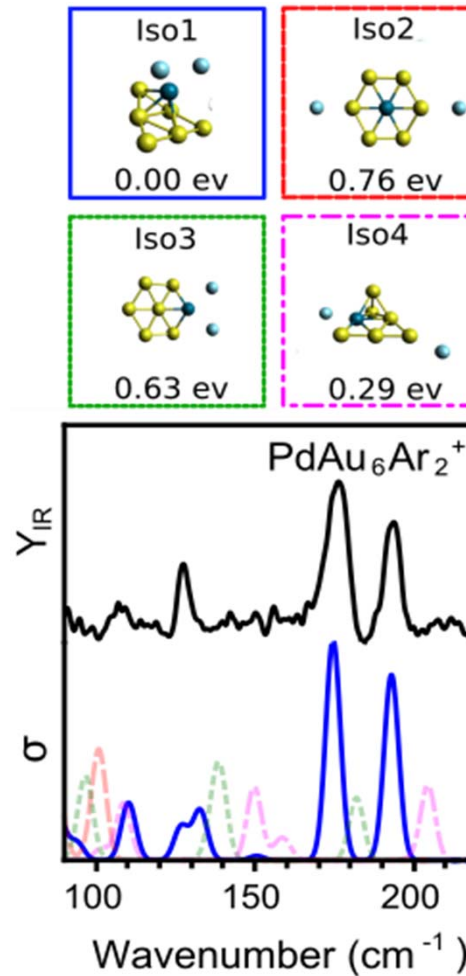
Phys. Chem. Chem. Phys. 2020, DOI: 10.1039/D0CP01613F.

The effect of doping

Pd doped Au clusters



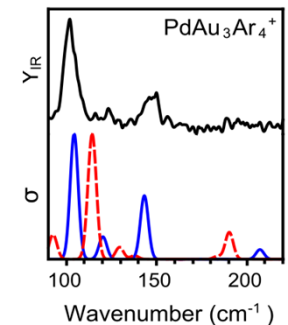
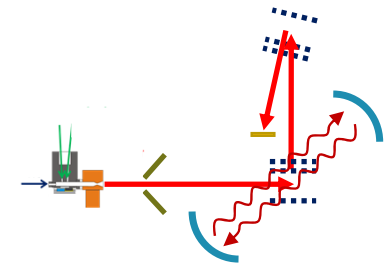
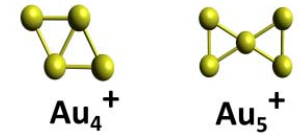
✓ Induced 2D to 3D transition



✓ Magic clusters, with 6 and 8 delocalized electrons

Conclusions

- The size-dependent properties of clusters depend on the precise geometry of the particle
- This geometry can be determined by infrared multiple photon spectroscopy experiments, in combination with theoretical calculations
- The technique has several advantages, as well as weak points, which must be carefully considered
- As a representative case, pure and palladium doped gold clusters have been discussed



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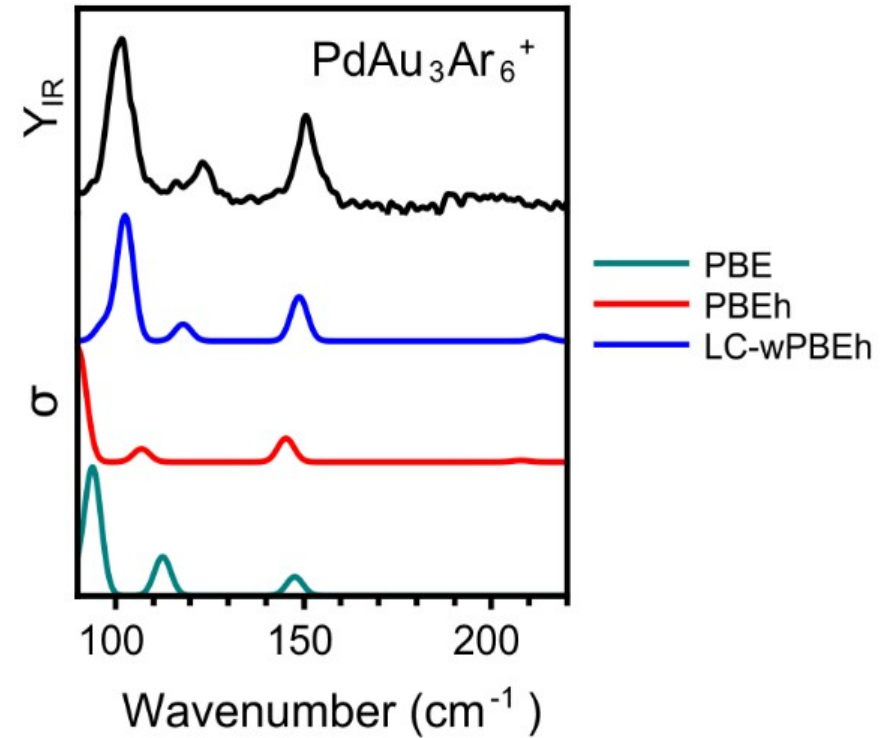
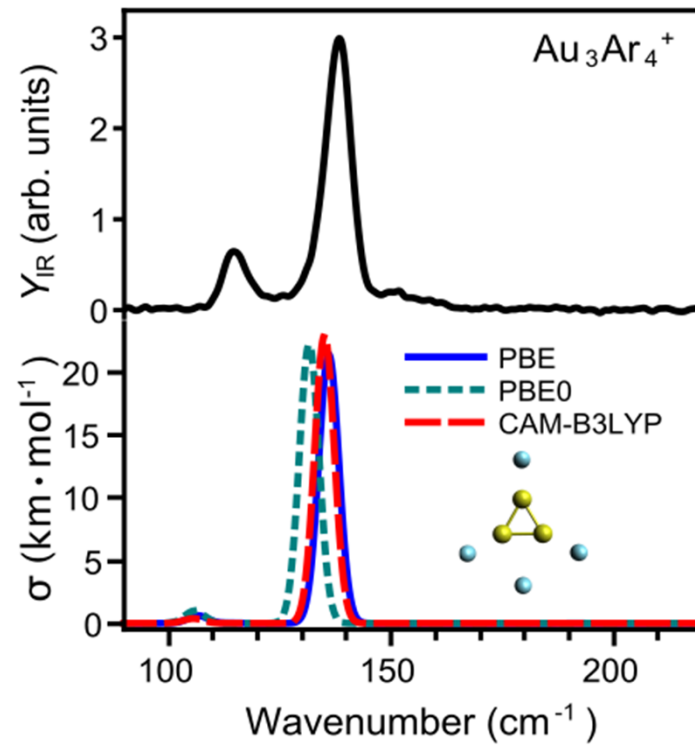
Dr. Francesca Baletto

Laia Delgado Callicó

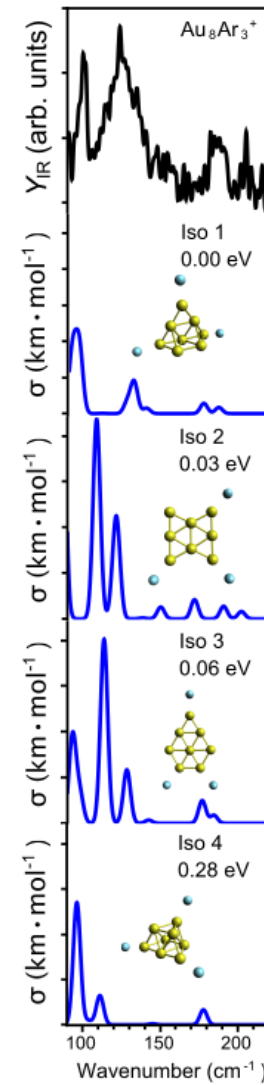
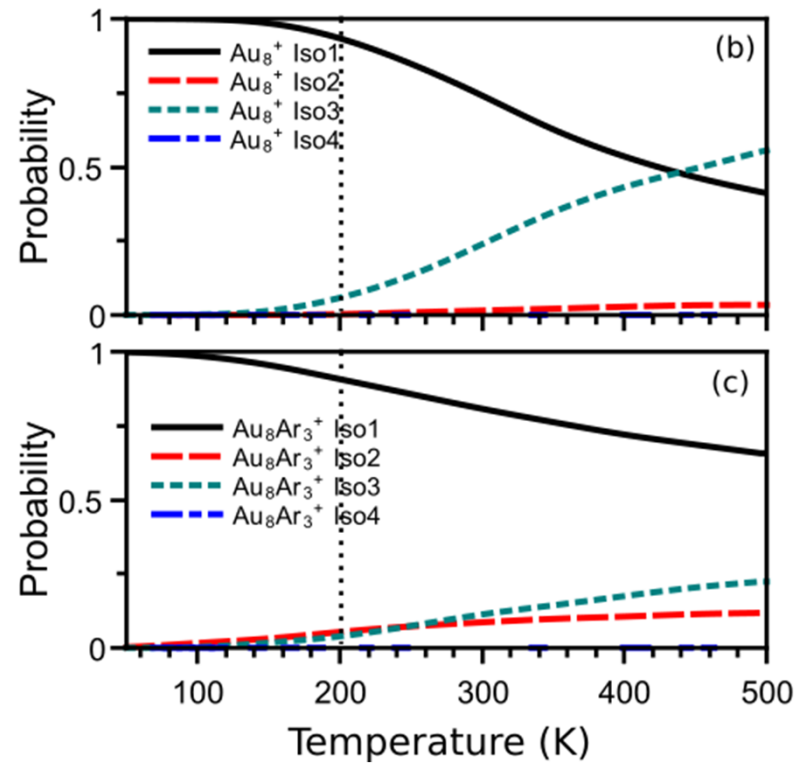


Thanks for your attention

Benchmark analysis



Isomer coexistence



The effect of Ar

