Tender:

Vibrationally-Resolved Photodissociation Spectroscopy and Franck-Condon Simulations of Cu_2^+ and Ag_2^+

TECHNISCHE UNIVERSITÄT DARMSTADT

M.Sc. Thesis / B.Sc. Thesis / Internship

Motivation

Dimers of metal clusters are ideal test systems for probing not only the electronic structure of the smallest cluster aggregates, but especially for investigating their vibrational and rotational fine structure. In contrast to larger clusters where the large manifold of excited states close in energy together with numerous direct dissociation pathways impedes the resolution of vibronic states, diatomic clusters further play an important role in examining high-level quantum chemical concepts.

Methods that reveal corresponding spectroscopic information are, i.e., the multiphoton ionization (MPI) and laser-induced fluorescence (LIF) technique. However, due to excited state lifetimes becoming inaccessibly short for clusters with more than three atoms, these types of spectroscopy fail in exploring the absorption behavior although many four- and five-atom clusters show at least a vibrational fine structure. In this regard the photodissociation spectroscopy (PD), as an indirect action spectroscopy, has been proven a fruitful method for investigating the electronic structure of larger clusters.

In this project the PD will be applied to small cationic metal dimers, Cu_2^+ and/or Ag_2^+, where information on the absorption spectrum is partially available. This study follows the objective to pave the way for probing Jahn-Teller active trimer and tetramer metal clusters by PD in combination with quantum chemistry.

Physical Solid-State Chemistry
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Laser Spectroscopy

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Project Description

In the context of this project the following goals should be achieved:

- **Experiment:** Recording photodissociation spectra of ultracold cationic cluster dimers [*Internship*]
- **Experiment:** Determining the cluster's vibrational (and rotational) temperature from hot band excitations (and highly-resolved 0-0 vibrational band) [*Internship*]
- **Theory:** Simulating Franck-Condon spectra for cationic cluster dimers [*Internship*]
- **Experiment and Theory:** See above [*Thesis*]

Requirements

- Understanding the contents of the basic lectures in physical chemistry
- Fundamentals of vibrational and optical spectroscopy
- The willingness to familiarize oneself with a new, diverse subject area

Recommended Literature

J. L. Gole, J. H. English, and V. E. Bondybey, *Laser Spectroscopy of the Cooled Metal Clusters: Copper Dimer*, J. Phys. Chem. **1982**, *86*, 2560-2563.

K. Egashira, C. Bartels, T. Kondow, and A. Terasaki, *Optical Absorption Spectrum of the Silver Dimer Ion: Temperature Dependence Measured by Photodissociation and Photon-Trap Spectroscopy*, Eur. Phys. J. D **2011**, *63*, 183-187.

P. Y. Cheng, and M. A. Duncan, *Vibronic Spectroscopy and Dynamics in the Jet-Cooled Silver Trimer*, Chem. Phys. Lett. **1988**, *152*, 341-346.

A. Shayeghi, R. L. Johnston, and R. Schäfer, *Evaluation of Photodissociation Spectroscopy as a Structure Elucidation Tool for Isolated Clusters: A Case Study of Ag_4^+ and Au_4^+*, Phys. Chem. Chem. Phys. **2013**, *15*, 19715-19723.

M. F. Jarrold, and K. M. Creegan, *Optical Spectroscopy of Metal Clusters: Cu_4^+*, Chem. Phys. Lett. **1990**, *166*, 116-122.

M. F. Jarrold, and K. M. Creegan, *Photodissociation of Copper Clusters, Cu_n^+ ($n = 3-8$), in the 370-710 nm Wavelength Region*, Int. J. Mass Spectrom. Ion Process. **1990**, *102*, 161-181.

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