Photodissociation and photon-trap spectroscopy of metal cluster ions

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A quantitative understanding of the electronic structure of clusters is of fundamental importance for the development of nanoscience. Although most anticipated applications are expected to rely on deposited clusters with less well-defined size distribution, experiments on very small clusters in the gas phase are essential for establishing and testing new models for this difficult size regime \[1\]. Our approach is to investigate size-selected cluster ions by laser spectroscopy. In order to achieve sufficient ion densities, clusters are accumulated in a trap. As many features of the electronic structure appear broadened and are thus more difficult to understand at room temperature, we use buffer-gas cooling to lower the thermal energy of the clusters. At a temperature of 10 K, the thermal energy per degree of freedom is less than 1 meV or 8 cm\(^{-1}\), and consequently vibrational excitation can be neglected in small clusters. Moreover, we present a novel technique for the direct measurement of the absorption of clusters by combining the ion trap with cavity ring-down or photon-trap spectroscopy \[2,3\]. The extinction of light is converted to a characteristic change of the photon lifetime in the cavity, which provides sensitivity of up to 1 ppm absorbance per round-trip, depending on the reflectivity of the cavity mirrors. All experiments can also be performed under magnetic fields of up to 5 T, created by a superconducting magnet around the trap, which makes it possible to probe magnetic properties by magneto-optical effects \[2\].

The experimental setup is shown in Figure 1. Cluster ions are produced in a magnetron sputter source and then guided through the machine using RF octopole ion guides. A quadrupole mass filter is used to select a single cluster size. The ion trap itself is surrounded by two stages of cooling cells, which can be cooled by liquid nitrogen and liquid helium, respectively. Pre-cooled helium buffer gas is injected into the inner cooling cell, and clusters are thermalized by buffer-gas cooling. The laser system consists of a frequency-tripled 10 Hz...
Nd:YAG and an optical parametric oscillator/amplifier that can be tuned over a broad range of wavelengths. Typical pulse energies are in the range of 1 to 10 μJ, and pulse duration is around 7 ns. For photodissociation spectroscopy, the cluster ions are irradiated by a fixed number of laser pulses, extracted from the trap and mass-analyzed in a second quadrupole mass filter. For photon-trap spectroscopy, the ring-down signal is measured for alternating cycles of empty and loaded ion trap, and the difference is taken to be proportional to the clusters’ absorption.

We investigated the absorption of the silver dimer cation Ag$_2^+$ by photodissociation spectroscopy. A strong absorption peak at around 3.0 eV shows a pronounced temperature dependence (Figure 2). For the room-temperature data, this peak is very broad with FWHM > 0.1 eV and clearly asymmetric with a longer tail towards the low-energy side. While this shape seems to suggest to be a reflection of the thermal population of ro-vibrational states, the width is not consistent with a temperature of 300 K. The data taken at a temperature of 10 K show considerable narrowing, but part of the asymmetry persists, and no detailed structure can be observed. Theoretical calculations predict the vibrational spacing of the Ag$_2^+$ ground state to be 128.2 cm$^{-1}$ [4], so we expect any occupation of higher vibrational states to be completely negligible at 10 K. Analysis of the spectra is in progress for understanding the temperature dependence of the absorption profile by calculating Franck-Condon overlap factors between the vibrational levels of the ground and excited electronic states.

Figure 2: Absorption of Ag$_2^+$ at 10 K (solid symbols) and 300 K (open symbols).

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