Femtosecond Time-Resolved Studies of Na_n and Hg_n Metal Clusters

T. Baumert, R. Thalweiser, V. Weiss, E. Wiedenmann, and G. Gerber
Fakultät für Physik, Universität Freiburg, D-79104 Freiburg, Germany

The real-time dynamics of multiphoton ionization and fragmentation of sodium and mercury clusters have been studied in femtosecond pump-probe molecular beam experiments. A major result of our femtosecond experiments is that the conventional view of the optical response of small ($n \leq 20$) metal clusters, e.g. absorption, ionisation and decay processes as well as the relevant time scales had to be changed. For Na_n clusters we find that for cluster sizes $n \leq 21$ molecular structure, excitations and properties are more important than collective excitations and surface plasmon-like resonances. In the case of Hg_n the prompt formation of singly and doubly charged cluster are observed. The dynamics of both show chromophore and cage-effect type behaviour.

Clusters and in particular metal clusters have been the fascinating subject of many studies, because they bridge the gap between atomic/molecular physics and solid state physics. Metal clusters exhibit distinct features ranging from molecular properties seen in small particles to solid state like behaviour of larger aggregates. We report cluster size dependent studies of absorption resonances, lifetimes, decay channels and ionisation processes of the one- and two electron metal clusters Na_n and Hg_n.

For these studies we introduced the combination of cluster beam, ion- and electron spectroscopy and pump-probe techniques with tunable femtosecond laser pulses. Femtosecond pump-probe techniques are used to study cluster transitions and the evolution of coherences and populations in real-time. A seeded supersonic beam provides cold Na_n and Hg_n clusters. Time-of-Flight (TOF) spectroscopy is used to measure the cluster-size distributions and the released kinetic energy of the ionic fragments. Tunable femtosecond pulses of 50-100fs time duration in the wavelength range 420nm to 750nm are generated in a system based on a CPM laser whose output pulses are amplified, pulse compressed and used to generate a white light continuum. Wavelength selected pump and probe light pulses are amplified again. A Michelson arrangement was used to delay the probe laser relative to the pump laser. The home-built Ti:Sapphire

Springer Series in Chemical Physics, Vol. 60 **Ultrafast Phenomena IX**
Editors: P. F. Barbara · W. H. Knox · G. A. Mourou · A. H. Zewail

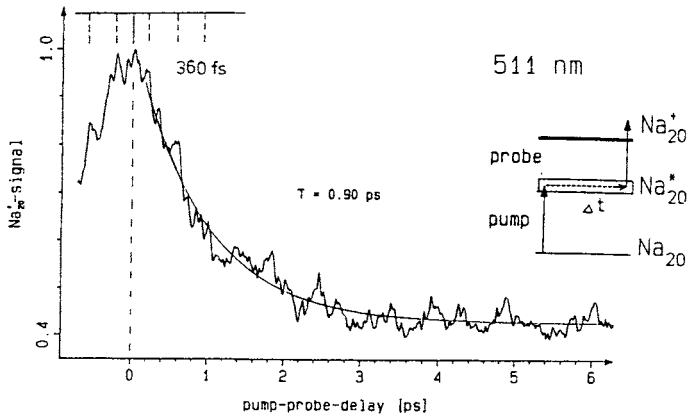

Fig. 1 Femtosecond time-resolved decay of the strongest Na_{20}^{*} resonance

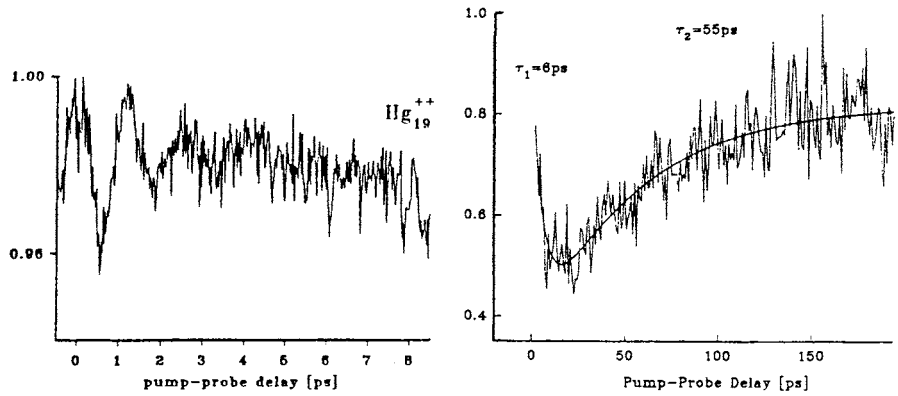

Fig. 2 Transient multiphoton ionization spectra of doubly charged Hg_{19} cluster.

laser generates light pulses of 20fs-80fs time duration in the wavelength range 700nm-850nm, which are amplified in bow-tie and Bethune cell amplifiers. The transient ionization spectrum of Na_{20} obtained with fs-laser pulses tuned to the λ=511nm resonance is shown in Fig.1. A pump pulse of about 100fs duration excites the Na_{20} cluster while a time delayed identical pulse probes the residual population by photoionizing Na_{20}^{*}, the intermediate excited electronic resonance(s). The decay time from a fit with a single exponential is 0.9ps. The superimposed oscillatory structure (360fs) is due to vibrational wave packet motions in the potential surfaces of this cluster. Time-resolved measurements in the cluster size range n=4-21 show ultrashort lifetimes (0.3-1.4ps) and very different decay patterns leading to the conclusion that only for larger cluster sizes collective features become important.

Mercury clusters are interesting species because of the possibility to study the nonmetal-metal transition. Fig.2 shows pump-probe spectra of Hg_{19}^{++}. The chromophore (Hg_2^*) wave packet motion at short delay times and the decay and recovery due to fragmentation and recombination (cage-effect) is clearly seen for longer delay times.