Femtosecond Dynamics of Molecular and Cluster Ionization and Fragmentation

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Abstract. The real-time dynamics of molecular (Na_2 , Na_3) and cluster Na_n (n=4-21) multiphoton ionization and -fragmentation has been studied in beam experiments applying femtosecond pump-probe techniques in combination with ion and electron spectroscopy. Wave packet motion in the dimer Na_2 reveals two independent multiphoton ionization processes while the higher dimensional motion in the trimer Na_3 reflects the chaotic vibrational motion in this floppy system. The first studies of cluster properties (energy, bandwidth and lifetime of intermediate resonances Na_n^*) with femtosecond laser pulses give a striking illustration of the transition from "molecule-like" excitations to "surface-plasma"-like resonances for increasing cluster sizes. Time-resolved fragmentation of cluster ions Na_n^+ indicate that direct photo-induced fragmentation processes are more important at short times than the statistical unimolecular decay.

1. Introduction

Femtosecond techniques have been advanced in recent years to directly probe molecular motions in real time. The time evolution of the induced coherences has been studied either by measuring the total fluorescence emitted from excited electronic states [1] or by ionizing the molecule and measuring the transient ionization spectrum as a function of the pump-probe time delay [2]. Molecular vibrational wave packet motion has been observed for a number of systems. The spreading and full recurrence of the wave packet is seen in the I_2-fluorescence signal [3] and in the Na_2-ionization signal [4].
Clusters and in particular metal-clusters have been the subject of many experimental and theoretical studies. They form the link between surface chemistry and molecular physics. Clusters show for different sizes very distinct features ranging from molecule-like properties for small particles to solid-like properties seen in large aggregates. Until now there have been no studies of cluster size-dependent phenomena and the dynamics of metal-cluster ionization and fragmentation employing femtosecond laser pulses. Two major issues in cluster physics which are adressed in this contribution are i) energy,width and lifetime of Na_n^* (molecular or surface plasmon-like) resonances and ii) stability and fragmentation dynamics of metal cluster ions Na_n^+ .

2. Experimental

Femtosecond laser pulses of 50-100fs time duration and of 0.1-50 μJ energy in the wavelength range 400nm to 800nm are generated in a home-built colliding-pulse mode-locked (CPM) ring dye laser. The pulses are amplified in a bow-tie amplifier, which is pumped by an excimer laser at 308nm, pulse compressed, selected from a white light continuum, amplified again and compressed before entering the molecular/cluster beam-laser interaction region. A Michelson arrangement was used to delay the probe laser relative to the pump laser. The tunable ultrashort pulses are employed to induce and to probe molecular transitions and cluster plasmon resonances in order to study the time evolution of the different ionization and fragmentation processes. Sodium molecules and clusters are produced by

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a seeded beam expansion in which sodium vapor is co-expanded with the argon carrier gas. This technique provides efficiently cooled clusters. The final molecular and cluster continuum states are analyzed by time-of-flight (TOF) photoelectron and ion spectroscopy, and by measuring the kinetic energy of the formed ionic fragments. Details of the experimental arrangement are given elsewhere [5].

3. Results and Discussion

Femtosecond time-resolved multiphoton ionization of Na_2 reveals unexpected features of the dynamics of the absorption of many photons by a diatomic molecule [2]. The wave packet motions in different bound molecular potentials show that incoherent contributions from direct photoionization of a singly excited electronic state and from excitation and autoionization of a bound doubly excited molecular state determine the time evolution of the multiphoton ionization. Electronic autoionization of Na_2^{**} (n'l',nl) leads to ground state molecular ions Na_2^+ and to ionic and neutral fragments $Na^+ + Na(3s) + e^-$. Figure 1 shows the transient Na_2-photoionization signal as well as the transient Na^+ photofragmentation spectrum. The transient Na_3-photoionization spectrum, shown in Fig.2, is more complex due to the more complicated three-dimensional wave packet motions in the excited B-state and in the electronic ground state . The observed chaotic vibrational motion is a signature of the floppy Na_3 system. Surprisingly enough, spectroscopic data like vibrational eigenfrequencies and pseudorotation energies can still be obtained from the Fourier Transformation of the time domain measurement.
The photoabsorption spectra of larger clusters Na_n with $n \geq 4$ are yet not observed in two-

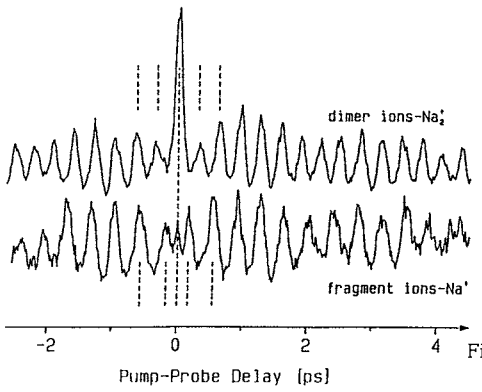

Fig.1 Transient ionization -Na_2^+- and photofragmentation -Na^+- spectra

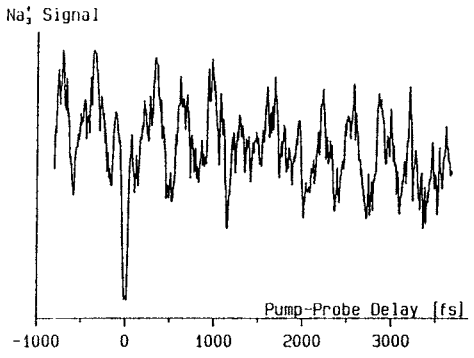

Fig.2 Transient Na_3^+ spectrum

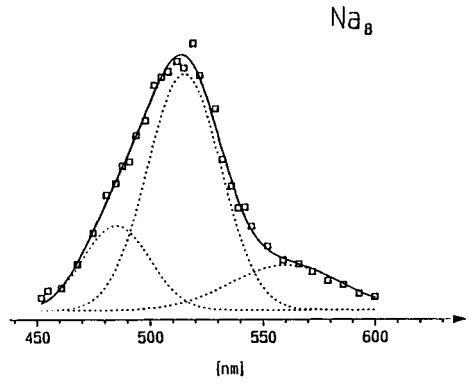

Fig.3 fs two-photon ionization spectrum of Na_8

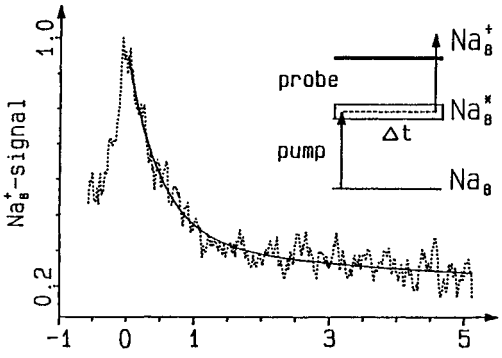

Fig.4 fs time-resolved decay of the Na_8^* resonance at 515nm

photon ionization using nanosecond laser pulses because of the fast decay of the intermediate Na_n^* states. These states are of primary interest in view of the size-dependent transition from molecule-like absorption to collective excitation of valence electrons. We have measured the energy and bandwidth of these resonances for Na_3 to Na_{21} by femtosecond two-photon ionization in the range 450nm to 750nm. The most striking result is obtained for the cluster Na_8 . On the basis of the Mie-Drude model theory predicts for this spherically symmetric metallic cluster a single intense band corresponding to a classical surface-plasma oscillation. Figure 3 shows the two-photon ionization spectrum of Na_8 measured with a femtosecond pulse. The spectrum clearly shows three resonances at 485nm, 515nm and 560nm with different widths. No direct measurements of the intermediate resonance lifetime(s) have been reported so far. Employing femtosecond pump-probe techniques we have measured the decay time(s) for the observed Na_8^* resonances . A pump laser excites the resonance and a time delayed probe laser probes the population by ionizing the excited neutral cluster. The transient Na_8^+ spectrum obtained at the center of the 515nm transition is shown in Fig. 4 . The observed fast decay (τ=0.45ps) of the resonance does not correspond to the measured bandwidth. For Na_8 therefore, the observation of three absorption bands with different widths and different decay dynamics is difficult to interpret within the classical picture of a single "surface-plasmon" like resonance. The transient Na_n^+ spectra obtained for the cluster sizes n=3-21 show a variety of different decay patterns and lifetimes ranging from 0.3ps to several ps. The absorption spectra and the lifetimes measured for the clusters Na_3 to Na_{21} give a striking illustration of the transition from molecular excited states to collective electronic oscillations in larger clusters.

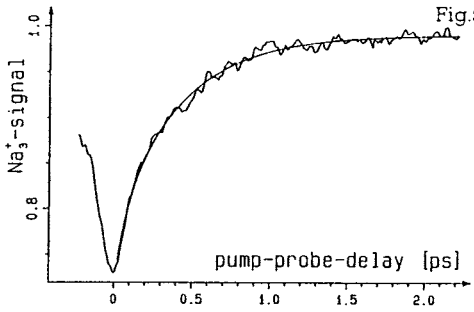

Fig.5 Transient cluster fragmentation spectrum of ejected neutral Na_3 ; τ=0.4ps

Time-resolved fragmentation of small cluster ions Na_n^+ show that ejection of neutral dimer Na_2 and trimer Na_3 photofragments occur on ultrashort time scales of 2.5ps and 0.4ps, respectively. This and the absence of cluster heating reveals that photo-induced fragmentation processes are important at short times rather than the statistical unimolecular decay.

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