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Time-resolved studies of neutral and ionized Na_n clusters with femtosecond light pulses

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Abstract. The real-time dynamics of Na_n (n=3-21) cluster multiphoton ionization and fragmentation has been studied in beam experiments applying femtosecond pump-probe techniques in combination with ion and electron spectroscopy. Three dimensional wave packet motions in the trimer Na_3 ground state X and excited state B have been observed. We report the first study of cluster properties (energy, bandwidth and lifetime of intermediate resonances Na_n^*) with femtosecond laser pulses. The observation of four absorption resonances for the cluster Na_8 with different energy widths and different decay patterns is more difficult to interpret by surface plasmon like resonances than by molecular structure and dynamics. Time-resolved fragmentation of cluster ions Na_n^+ indicates that direct photo-induced fragmentation processes are more important at short times than the statistical unimolecular decay.

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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]. Clusters and in particular metal-clusters have been the subject of many experimental and theoretical studies, because they form the link between solid state physics and molecular physics. There are yet no studies of cluster-size dependent properties employing ultrashort laser pulses. In this contribution we report on first experiments in cluster physics applying ultrashort laser pulses to time resolved studies of Na_n-cluster ionization and fragmentation. We studied the three dimensional wave packet motion in the trimer Na_3 B- and X-states as well as the lifetime of the Na_3 D-state. Furthermore we measured energies, widths and lifetimes of the various Na_8-resonances as well as the fragmentation dynamics of metal cluster ions Na_n^+.

2. Experiment

Fig. 1 shows the femtosecond laser system. Femtosecond laser pulses of 50-100fs time duration and of 0.1-50μJ energy in the wavelength range 400nm to 800nm are generated in a home-built colliding-pulse mode-locked 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 laser pulses are employed to induce and to probe cluster transitions in order to investigate the time evolution of the ionization and fragmentation processes. The final continuum states are analyzed by time-of-flight (TOF) photoelectron and ion spectroscopy. Sodium clusters are generated in a

seeded beam expansion where sodium vapor is coexpanded with the carrier gas argon. Details of the experimental arrangement are given elsewhere [3].

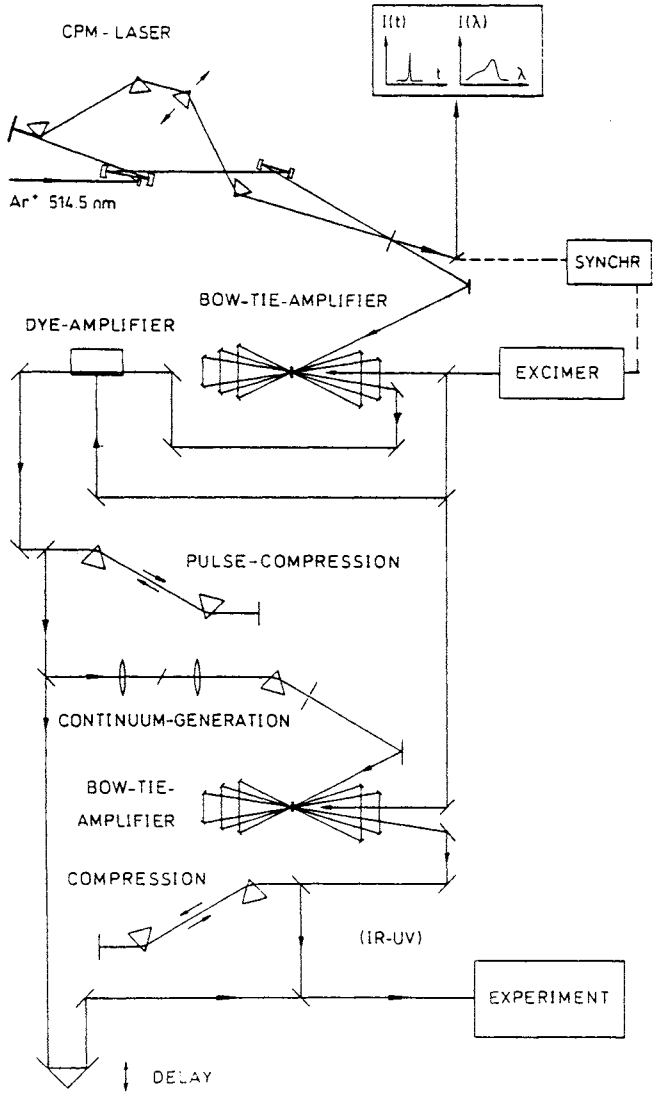

Fig.1: Femtosecond laser system

3. Results and Discussion

We have recently reported the femtosecond time-resolved multiphoton ionization- and fragmentation dynamics of the molecule Na_2. From the real time observation of vibrational wave packet motions it was concluded, that two different physical processes determine the time evolution of the multiphoton ionization and fragmentation processes [4].
Fig.2 shows the transient Na_3^+-spectrum obtained at the wavelength 623nm. This time domain spectrum is much more complex than that

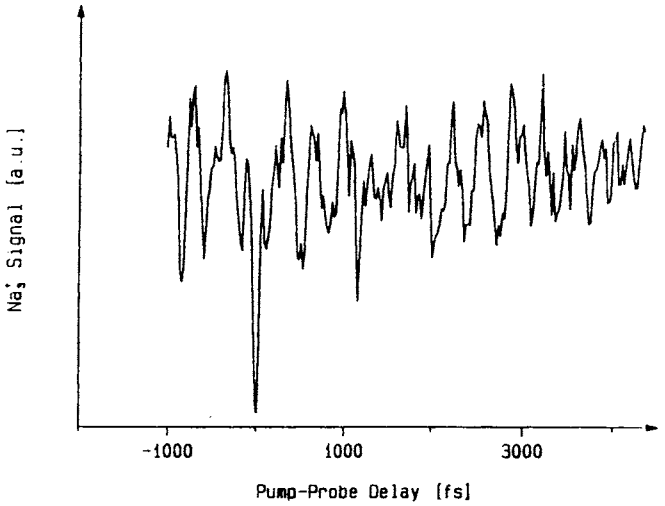

Fig.2: Pump-probe ionization spectrum of Na_3 at 623nm

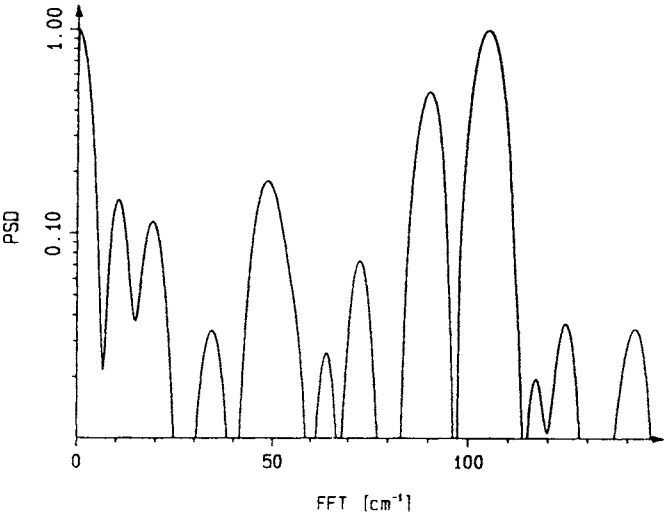

Fig.3: Fast Fourier Transformation spectrum of Fig.2

observed for Na_2. As the Fourier spectrum in Fig.3 shows, the dynamics of the two photon ionization process is determined by the three dimensional wave packet motions in the Na_3 B-and the Na_3 X-state. At the applied laser intensity both states are involved. The pump laser generates a wave packet in the intermediate B-state and simultaneously a wave packet in the X-ground state through stimulated emission pumping during the pump pulse. Both wave packet motions are transferred to the ionization continuum by the delayed probe laser pulse. Fig.3 gives the Fast Fourier Transformation (FFT) spectrum of the pump-probe spectrum shown in Fig.2 The contributions near $50cm^{-1}$, $90cm^{-1}$ and $140cm^{-1}$ are attributed to the bending, to the asymmetric stretch and to the sym-

metric stretch mode in the Na_3 electronic ground state. The wave packet dynamics in the excited B-state is dominated by the symmetric stretch mode with frequencies close to $105cm^{-1}$. Furthermore we observed frequencies $12cm^{-1}$, $19cm^{-1}$ and $35cm^{-1}$. On the basis of a pure Jahn-Teller distortion of the excited Na_3 B-state these frequencies can be assigned to a free pseudorotational wave packet motion in the Jahn-Teller distorted potential surface of the Na_3 B-state. However, it is remarkable that the corresponding radial component of the pseudorotational motion plays no role in the transient spectrum, whereas high resolution measurements of the Na_3 B-X-system exhibit a strong contribution of the radial pseudorotational component [5]. On the other hand theoretical studies of Meiswinkel and Köppel [6] showed, that the observed high resolution spectrum could also be explained taking into account a Pseudo-Jahn-Teller (PJT) model. In that model the vibronic coupling of the accidentally degenerate (D_{3h})-states $3^2E'$ (B) and $2^2A_1'$ is responsible for the observed vibronic structure. So far it is not yet clear, which of the two models is more appropriate to explain the observed femtosecond dynamics. Further experiments are in progress.

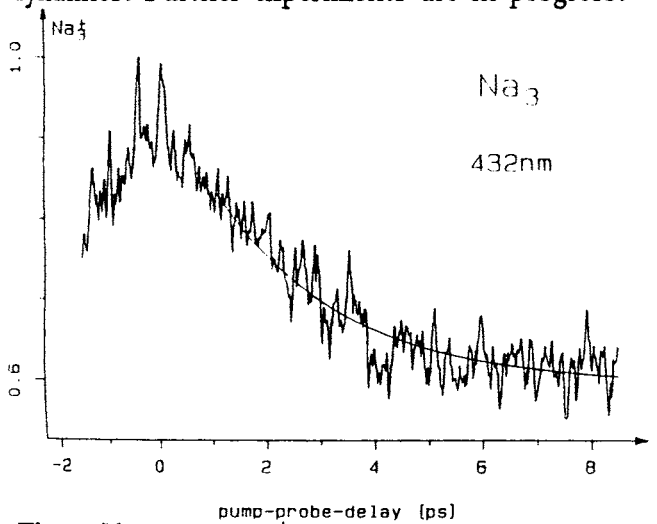

Fig.4: Transient Na_3^+ spectrum at 432nm

Within the measured delay-time of 10ps we did not observe a decay of the Na_3 B-state, which is quite remarkable, since we found that all other known electronic states of Na_3 (A',A,B',B'' and D) decay on ultrashort time scales [7]. Fig.4 shows a pump-probe experiment at 432nm, where the Na_3 D-state is excited by the pump laser and ionized by the delayed probe laser. In that case the transient ion signal decreases with increasing pump-probe delay time. The observed fast decay (τ=2.3ps) is due to the decay of the D-state population after the excitation. Rutz et.al. [8] observed with ps laser pulses also a fast decay of the Na_3 D-state.

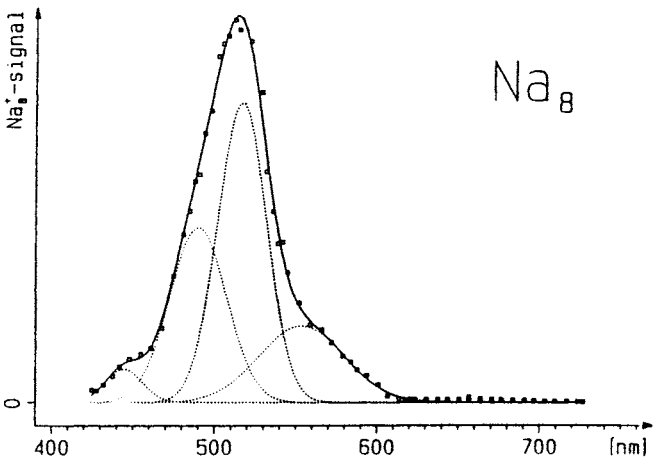

Fig.5 Femtosecond two photon ionization spectrum of Na_8

The photoabsorption spectra of larger clusters Na_n with n≥4 are yet not observed in two photon ionization using nanosecond laser pulses

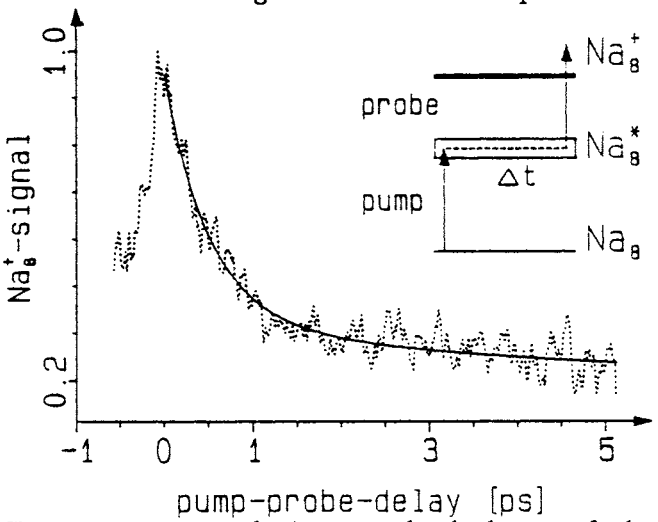

Fig.6: Femtosecond time resolved decay of the Na_8^* resonance at 518nm

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 the bandwidth of these resonances from Na_3 to Na_{21} by femtosecond two-photon ionization in the range 430nm to 750nm [9]. 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 metal cluster a single intense band corresponding to a classical surface-plasma oscillation. Fig. 5 shows the two-photon ionization spectrum of Na_8 measured with a femtosecond laser pulse. The spectrum clearly shows four resonances at 445nm,490nm,518nm and 555nm. No 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. The transient Na_8^+ spectrum obtained at the center of the 518nm transition is shown in Fig.6. The observed fast decay of the resonance (τ=0.45ps) does not correspond to its observed bandwidth. This is also true for the other three resonances. The observed four Na_8 resonances with their different widths and decay times are difficult to interprete within the picture of a single surface plasmon like resonance. The transient ionization 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 [9].

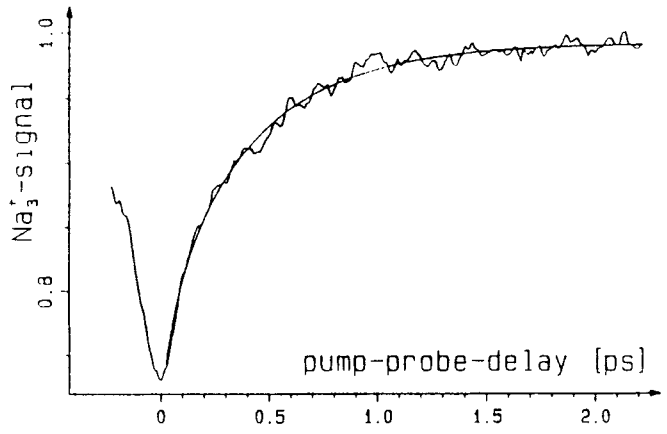

Fig.7: Transient cluster ion fragmentation spectrum of ejected neutral Na_3

In an other experiment, we studied the dynamics of Na_n clusters during and immediately following the photoionization process by applying femtosecond pump-probe laser spectroscopy. Na_n clusters are ionized by the pump pulse. After the ionization the ejected neutral fragments (Na_2,Na_3) are ionized by the delayed probe pulse. We used recompressed laser pulses of 60fs duration and a central wavelength of 618nm. We found neutral dimer Na_2 and, for the first time, trimer Na_3 ejection (Fig.7) on ultrashort time scales of 2.5ps and 0.4ps respectively [10]. This and the abscence of cluster heating during the femtosecond laser pulse reveals that photo-induced fragmentation processes are important at short times rather than the statistical unimolecular decay.

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