

Femtosecond Probing of Sodium Cluster Ion Na_n^+ Fragmentation

T. Baumert, C. Röttgermann, C. Rothenfusser, R. Thalweiser, V. Weiss, and G. Gerber

Fakultät für Physik, Universität Freiburg, W-7800 Freiburg, Federal Republic of Germany

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We report on the first femtosecond time-resolved experiments in cluster physics. The photofragmentation dynamics of small sodium cluster ions Na_n^+ have been studied with pump-probe techniques. Ultrashort laser pulses of 60-fs duration are employed to photoionize the sodium clusters and to probe the photofragments. We find that the ejection of neutral dimer Na_2 and, observed for the first time, neutral trimer Na_3 photofragments occur on ultrashort time scales of 2.5 and 0.4 ps, respectively. This and the absence of cluster heating reveals that direct photoinduced fragmentation processes are important at short times rather than the statistical unimolecular decay.

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The stability and fragmentation dynamics of metal cluster ions formed through laser photoionization is a major issue in cluster physics and has been discussed in many experimental and theoretical publications [1]. Experiments with mass-selected cluster ion beams have shown evidence that fragmentation proceeds by evaporative processes in time regimes ranging from nanoseconds to microseconds [2]. In the discussion of the stability of metal cluster ions against fragmentation and their inherent time scales, it is often assumed that photon-induced electronic excitation is strongly coupled and relaxed to the internal cluster modes. In this model the excess energy from successive absorption of photons in photoionization with nanosecond lasers is quickly redistributed between the vibrational modes of the cluster ion, so that the resulting total energy is above the fragmentation threshold. Since the probability of localizing sufficient energy in a particular fragmentation coordinate is low, this leads to the nanosecond-microsecond fragmentation times observed in the unimolecular decay.

In particular for sodium and potassium cluster ions, Bréchnignac *et al.* [3] have reported that the predominant fragmentation channels, the evaporation of neutral monomers and/or neutral dimers for even and odd numbered cluster ions, respectively, are associated with microsecond fragmentation times. They also found evidence for sequential evaporation of monomers or dimers and for a change of cluster size distribution toward lower masses with increasing laser power due to cluster heating and evaporative cooling.

Time-resolved studies of cluster dynamics are rare. Lineberger and co-workers [4] reported on studies of the photodissociation and recombination dynamics of I_2^- in mass selected $\text{I}_2^-(\text{CO}_2)_n$ clusters with picosecond pump-probe techniques. Studies of the proton transfer dynamics in finite-size molecular clusters as well as fragmentation dynamics of van der Waals clusters using picosecond pump-probe techniques have been reported by Zewail and co-workers [5]. Lifetimes and relaxation processes in electronically excited states of Na_3 have been measured by Broyer *et al.* [6] using nanosecond-time-delayed two-photon ionization techniques.

We report here on the first time-resolved studies of the dynamics of metal clusters during and immediately following the photoionization process by applying femtosecond pump-probe laser techniques. Ultrashort laser pulses are employed to ionize the sodium clusters and to probe the formed fragments. Sodium clusters are generated by a seeded beam expansion in which sodium va-

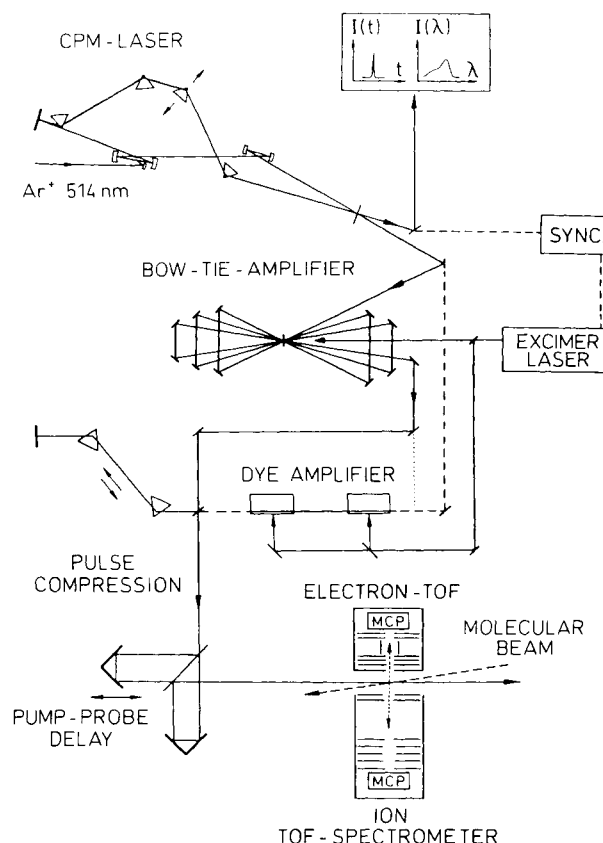


FIG. 1. Femtosecond pump-probe laser system and molecular beam arrangement. Femtosecond pulses ($t = 60$ fs) are generated by a colliding-pulse mode-locked (CPM) ring dye laser, amplified in dye amplifiers, pulse compressed, and split into identical pump and probe pulses. Pump and probe laser beams are collinear and perpendicular to the molecular beam and the TOF spectrometers.

por is coexpanded with the argon carrier gas. The high seeding ratio used in the expansion provides efficiently cooled clusters ($T_{\text{vib}} \approx 30$ K for Na_3 and Na_4) as inferred from zero kinetic energy (ZEKE) photoelectron spectroscopy of small sodium clusters [7]. Time-of-flight (TOF) spectroscopy is used to determine the mass of the cluster ions and the initial kinetic energy of the ionic fragments. The laser system and the schematic experimental arrangement of the molecular beam and the TOF spectrometers are shown in Fig. 1. Femtosecond pulses were generated in a home-built colliding-pulse mode-locked (CPM) ring dye laser. The output of the CPM dye laser was amplified either in a multipass dye amplifier or in a two-stage dye amplifier, both pumped by a 308-nm excimer laser synchronized to the CPM. A Michelson arrangement was used to accurately set the time delay of the probe laser relative to the pump laser. Both pump and probe laser beams enter the interaction region collinearly with the same polarization and perpendicular to the cluster beam. We used recompressed laser pulses of 60-fs duration, of about 100-Å spectral width centered at 618 nm and of 1 μJ energy, for the pump and the probe. Details of the femtosecond laser system and the experimental setup are given elsewhere [8].

The cluster ion time-of-flight spectrum displayed in Fig. 2(a) is obtained when a femtosecond laser pulse of 60-fs duration, 1- μJ pulse energy, and $\lambda_{\text{max}} = 618$ nm interacts with the sodium cluster beam. The spectrum shows Na_n^+ clusters up to $n=21$, with strong Na^+ and Na_2^+ signals, weaker signals of Na_3^+ to Na_9^+ , and much weaker signals of Na_{10}^+ to Na_{21}^+ . Note that a cluster ion mass spectrum produced by a femtosecond laser pulse shows only parent ions and ionic fragments and is free of photoionized neutral fragments [9]. This is because the 60-fs pulse duration is much shorter than the cluster fragment separation time. The spectrum in Fig. 2(a) shows an intensity variation for even and odd numbered cluster ions. This variation is often attributed to the alternation of the ionization potentials for even and odd numbered clusters. In the case of sodium [10], three 618-nm photons are necessary to ionize Na_2 , Na_4 , Na_6 , or Na_8 but only two such photons are needed to ionize Na_3 , Na_5 , Na_7 , Na_9 , and all Na_n clusters with $n \geq 10$. We find that even with 100 times higher laser pulse energy the relative intensities of the even and odd numbered clusters (for $n > 3$) in the ion mass spectrum do not change. A mass spectrum like the one shown in Fig. 2(a) is often taken to support the shell closing effects at masses Na_9^+ and Na_{21}^+ . However, as Fig. 2(b) clearly shows, the alternation and the individual cluster ion intensities for $n \leq 9$ drastically change for wavelengths close to strong absorption resonances like the one for the Na_4 or Na_8 clusters near 500 nm. These findings and the resonances for Na_3 – Na_{21} will be the subject of a detailed discussion in a forthcoming publication [11]. The spectrum in Fig. 2(b) is obtained with femtosecond light

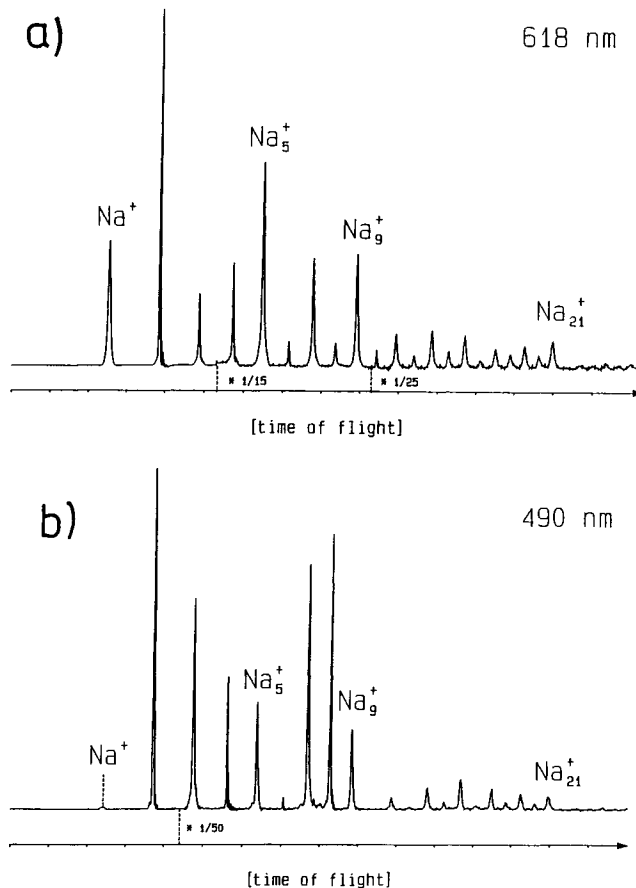


FIG. 2. Sodium cluster ion Na_n^+ mass spectra resulting from the interaction of a femtosecond laser pulse of 60-fs duration and of a 1- μJ pulse energy with a sodium cluster beam. The spectra (a) $\lambda_{\text{max}} = 618$ nm and (b) $\lambda_{\text{max}} = 490$ nm are obtained under the same conditions. The individual cluster ion intensities for $n \leq 9$ strongly depend upon the wavelengths used, whereas they do not for $n = 10$ –21.

pulses at 490 nm from a white-light continuum and is taken under the same experimental conditions as the spectrum at 618 nm. In the 490-nm spectrum, the Na_8^+ signal is much stronger than that for Na_9^+ . Therefore it is difficult to draw any conclusion about shell closing effects and cluster ion stability from mass spectra up to Na_9^+ . We believe the data for Na_{10}^+ to Na_{21}^+ indicate that the even-odd alternation of individual ion intensities is mainly due to the electron pairing effect [12].

Another interesting experimental result contrary to the findings in nanosecond experiments [3] is that we do not observe a shift of the cluster ion mass distribution toward lower masses for increasing laser intensities. On the basis of these findings it is questionable whether cluster heating in femtosecond photoionization plays any role and whether the subsequent sequential evaporative cooling occurs. Note that for the laser pulse duration of 60 fs, which is considerably shorter than the cluster vibrational periods of a few hundred femtoseconds, the clusters are nearly frozen.

Experimental results on the fragmentation of small sodium cluster ions were reported by Bréchnignac *et al.* in a number of recent publications [13]. These authors find the ejection of a monomer Na for even-numbered clusters, whereas they report two fragmentation pathways for odd-numbered clusters: the ejection of a neutral monomer Na or the ejection of a neutral dimer Na₂. In such processes fragments are formed with initial kinetic energy [14]. We photoionized the "fast" dimers and separated them from the parent dimers by time of flight. Observation of the ejected monomers failed because of the strong signal of ionic fragments Na⁺ from photofragmentation of parent Na₂⁺ (Ref. [9]).

To improve the understanding of the stability and fragmentation of metal clusters and to find the dominant time scales and fragmentation channels we performed the first pump-probe experiments in cluster physics with femtosecond time resolution. We employed 60-fs pump laser pulses to ionize the neutral clusters in the beam and to induce the fragmentation, and time-delayed identical probe laser pulses to photoionize the neutral fragments ejected by the sodium cluster ions.

Figure 3 shows the observed transient Na₂ photofragmentation spectrum. The buildup of the Na₂⁺ probe signal strongly depends on the pump-probe delay time and displays a rise time of 2.5 ps. Because pump and probe are identical, the signal is symmetric around zero time delay. The total Na₂⁺ signal doubles within 10 ps indicating strong fragmentation of cluster ions. For lower carrier gas pressure, the probe signal drops and finally reaches for molecular beam conditions (0.1 bar) the delay-time-independent signal level at $t=0$. Since no particular cluster ion is selected in this experiment, the 2.5-ps time constant is probably an average value of cluster ion fragmentation times (mainly from $n=3-9$) rather than the decay time of a single cluster ion. The oscillatory structure in the Na₂⁺ pump-probe spectrum [15],

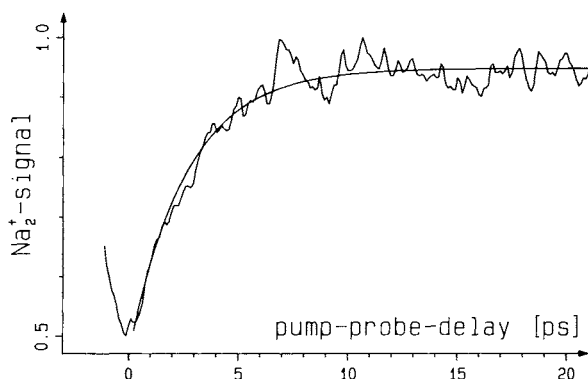


FIG. 3. Transient cluster photofragmentation spectrum showing the buildup of "fast" neutral dimer fragments Na₂ photoionized by the probe laser. The corresponding time constant is 2.5 ps. The strong photoinduced fragmentation doubles the total Na₂⁺ signal within 10 ps.

reflecting the wave packet motion in bound potentials of Na₂, is not seen in this experiment, because (i) the modulation depth of the oscillations is reduced for higher laser intensity and (ii) the oscillations are diminished by the superimposed strong Na₂⁺ probe signal. With the technique applied for probing the neutral fragments, we cannot distinguish between the fragmentation of neutral clusters and of ionic clusters because, in principle, both channels are open. The two-photoionization spectra of neutral sodium clusters Na_n measured with fs-laser pulses [11] and the depletion spectra obtained with ns-laser pulses [16] show no strong resonances for wavelengths around 620 nm, except for the B state of Na₃ whose lifetime is 14 ns [6]. This and the strength of the Na₂⁺ probe signal lead us to the conclusion that the observed fast fragmentation has to occur in the cluster ions Na_n⁺. An estimate on the basis of the Na₂⁺ probe signal and of the total signal of all other observed cluster ions Na_n⁺ ($n=3-21$), for zero delay time and for longer delay times, shows that about every second sodium cluster ion decays by ejection of a neutral dimer Na₂ within the first 10 ps after the photoionization event. A similar result was reported by Bloomfield, Freeman, and Brown [17] who found in their ns-laser studies of Si_n⁺ cluster fragmentation that substantial photofragmentation is likely to occur during the photoionization process.

In an additional pump-probe experiment we measured the time-resolved formation of neutral trimer fragments Na₃. Here again, the pump laser photoionizes the clusters while the delayed probe laser photoionizes the ejected neutral fragment Na₃. The pump-probe Na₃⁺ spectrum displayed in Fig. 4 shows that neutral trimer fragments Na₃ are formed through fragmentation of cluster ions. From an analysis of the signal buildup time, we obtain a single decay component of 0.4 ps. Since the Na₃⁺ probe signal increases by about 30% of the total Na₃⁺ signal within 2 ps, the precursor cluster ion(s) Na_n⁺ must be in

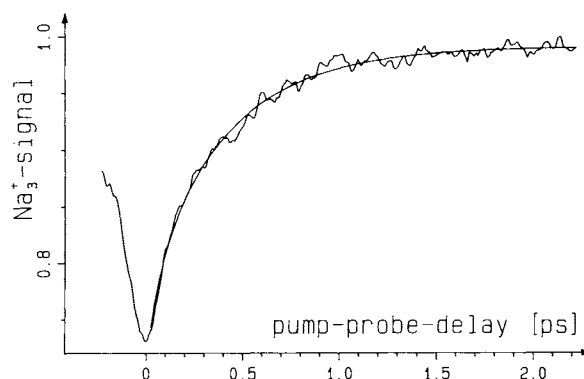


FIG. 4. Pump-probe delay spectrum of the ejected neutral trimer fragments Na₃. The probe signal Na₃⁺ buildup time constant of 0.4 ps indicates a direct photoinduced fragmentation of sodium cluster ions rather than a statistical unimolecular decay.

the range $n=4-9$ due to the low intensities for $n=10-21$. The individual signals of Na_4^+ , Na_5^+ , Na_7^+ , and Na_9^+ are too strong to account for the required increase of the Na_3^+ signal. Moreover, scattering experiments with size selected clusters show that $\text{Na}_2^+ + \text{Na}_2$ is the dominant fragmentation channel for Na_4^+ (Ref. [18]), while Na_5^+ and Na_7^+ mainly decay into $\text{Na}_3^+ + \text{Na}_2$ and $\text{Na}_5^+ + \text{Na}_2$, respectively [19]. The very small signal of Na_6^+ precludes Na_9^+ to be the precursor. To our knowledge there are no theoretical predictions of Na_3 fragments. Since a symmetric decay of Na_6^+ is rather unlikely, we tentatively assign the observed 0.4-ps time constant to the fragmentation of Na_8^+ . We believe the fragmentation process $\text{Na}_8^+ \rightarrow \text{Na}_5^+ + \text{Na}_3$ is mainly responsible for the formation of the neutral trimer fragment Na_3 . This conclusion is supported by results obtained by the Hertel group from scattering experiments with size selected sodium clusters [19].

From ZEKE photoelectron spectroscopy [7] the vibrational frequencies of Na_3^+ and Na_4^+ clusters are determined to be of the order of $50-140 \text{ cm}^{-1}$, corresponding to vibrational periods of about $250-650 \text{ fs}$. The phonon frequency of the sodium solid, $3.1 \times 10^{12} \text{ Hz}$ or $1/(320 \text{ fs})$ deduced from the Debye temperature [20], is only slightly different from the Na_2 ground-state vibrational frequency $1/(210 \text{ fs})$ and the Na_3^+ , Na_4^+ frequencies. This suggests minor frequency variation with cluster mass. The estimated time for the neutral fragments Na_2 and Na_3 to separate along a fragmentation coordinate is about $1-2 \text{ ps}$. This time is too short for an efficient redistribution of the photon energy in the ionized cluster and a statistically dominated fragmentation. In a detailed theoretical investigation of the collision complex $\text{H}^+ + \text{H}_2$, Schlier and Brass [21] found that it takes many vibrational periods to form a microcanonical energy distribution in the H_3^+ complex and a statistically dominated fragmentation. On the basis of the time constants for the observed fragmentation processes we therefore conclude that in femtosecond photoionization of sodium clusters photoinduced fragmentation processes dominate and that cluster heating and sequential evaporation of neutral dimers or trimers are very unlikely.

In conclusion, we have presented the first femtosecond time-resolved study of metal cluster photofragmentation employing pump-probe techniques in combination with ion time-of-flight spectroscopy. Our results show that photofragmentation of sodium cluster ions Na_n^+ ($n \leq 21$) by neutral dimer ejection occurs on an ultrashort 2.5-ps time scale. A substantial part of the sodium cluster ions decay through this photoinduced fragmentation. In addition, we prove by probing the neutral trimer fragments Na_3 that this fragmentation channel exists and that the corresponding time constant is 0.4 ps. We believe the fragmentation of Na_8^+ into $\text{Na}_5^+ + \text{Na}_3$ is mainly responsible for the observed Na_3 probe signal. Cluster heating by electron-phonon coupling is unlikely to occur in femtosecond laser photoionization because (i)

pump and probe laser pulse durations of 60 fs and the fragmentation times of 0.4 and 2.5 ps are too short for an efficient electron-phonon coupling, and (ii) the observation that the femtosecond-laser-induced cluster ion mass distribution up to Na_9^+ is strongly wavelength dependent and that the relative intensities for Na_4^+ to Na_{21}^+ do not change over a wide range of laser intensities do not support sequential processes. The fast photoinduced fragmentation processes, ejection of a neutral dimer or a neutral trimer, play an important role in the decay of sodium cluster ions. These processes are different from the sequential evaporative cooling seen in ns-laser photoionization [3].

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