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Femtosecond pump-probe experiments on non-stoichiometric sodium-fluoride clusters

I. First direct observation of periodical structural changes in Na_2F

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Abstract. In this paper we present two-color pump and probe spectroscopy on Na_2F, the smallest of the non-stoichiometric sodium-fluoride clusters (Na_nF_{n-1}), in molecular beams by employing femtosecond laser pulses. The molecules were pumped into the first excited state by one photonic transition and consecutively ionized from there by the second photon. We resolved the wavepacket oscillatory motion involving periodical structural rearrangements in the first excited state of Na_2F with a period of $\sim$ 185 fs. The time-resolved experiments show that sodium fluoride clusters provide interesting features which can be manipulated in optimal control experiments.

PACS. 36.40.Vz Optical properties of clusters – 33.80.-b Photon interactions with molecules – 36.40.Mr Spectroscopy and geometrical structure of clusters – 33.15.Ta Mass spectra

1 Introduction

Clusters of atoms and molecules exhibit in many cases size-dependent physical and chemical properties which can differ from the respective bulk materials. Among them, the alkali halide clusters represent the finite size components of certain transparent crystals. Their investigation gives the opportunity to study the microscopic insight into the characteristics of macroscopic systems in order to emphasize how the properties of the cluster differ from the well-known bulk. The non-stoichiometric alkali halide clusters are characterized by a strong ionic bond and one excess electron, localized either in the halide vacancy or attached to the alkali atom which forms the ionic subunit [1,2]. In order to obtain information about the molecular processes, the photo-ionization mass spectrometry combined with the supersonic molecular beam expansion has been proved to be a very efficient technique. The interest to study the real time dynamics in molecular clusters rose after tunable femtosecond laser sources have been developed. Such time-resolved processes can be studied by means of femtosecond pump and probe spectroscopy [3]. This allows, for example, to resolve vibrational frequencies, to observe periodical structural rearrangements, wave-packet dynamics, internal vibrational redistribution of energy (IVR) and to study fragmentation processes, which occur on an electronically excited state [4].

Recently, theoretical [1,2,5] and experimental [6–8] investigations on sodium fluoride clusters have been reported. Starting from *ab initio* considerations, Hartmann *et al.* have investigated the adiabatic dynamics which involve low excited states of several Na_nF_{n-1}. According to their first simulations of pump-probe signals using *ab initio* Wigner distribution approach [1], the Na_2F trimer shows a fast geometric relaxation due to the breaking of the Na–Na bond. This leads to a periodical structural change from triangular-to linear-to triangular in its first electronic excited state 1^2B_2 (see also [9]). The *ab initio* electronic structure calculations for 16 electronic states of Na_2F was done by Cai *et al.* They have also determined the equilibrium geometries and excitation energies for three of the lowest-lying electronic excited states. For the 1^2B_2 state, which is investigated in this work, the predicted transition energy is about 0.98 eV [5]. Poncharal and co-workers have reported resonant two-photon spectroscopy of Na_nF_{n-1} clusters in a wide spectral range, from 290 to 1000 nm, by employing 15 ns pulses and using a time-of-flight spectrometer for the detection [6]. They have measured the ionization potentials and absorption spectra of several non-stoichiometric sodium-fluorides up to $Na_{42}F_{41}$ and correlated these results with the predicted geometry, completing the classification they have started for the visible absorption spectra [7]. The optical

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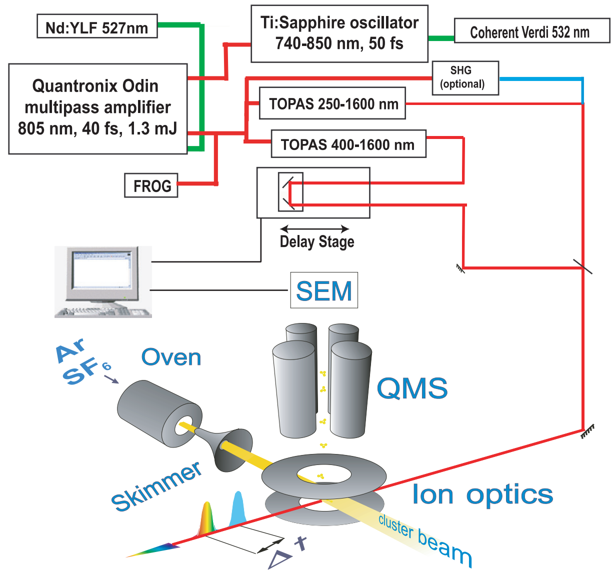

Fig. 1. The experimental setup consisting of a femtosecond laser system and a molecular beam apparatus.

absorption and photo-ionization of Na_2F was studied in the group of Ernst, as well [8]. Motivated by the theoretical simulations, we have selected the non-stoichiometric sodium fluoride molecules as possible test species for optimal control of molecular motion involving different photo-induced processes. This contribution contains the method of producing a supersonic beam of sodium-fluoride clusters, followed by a description of femtosecond nuclear dynamics and periodical structural changes by means of two-color femtosecond time-resolved analysis on the smallest cluster of the Na_nF_{n-1} series: Na_2F.

2 Experiment

The basic components of our experimental setup are the femtosecond laser system and the molecular beam apparatus (see Fig. 1). The laser setup consists of a home-built Kapteyn-Murnane Ti:sapphire oscillator (730−840 nm, 87 MHz, 8 nJ) pumped by a Coherent Verdi diode-pumped laser (5 W). The outcoming pulses are used to seed a commercial multipass amplifier (Quantronix Odin), which provides short pulses of 1.2 mJ energy/pulse centered at 805 nm. The 1 kHz repetition rate was maintained when the amplified pulses were split in three beams: two were used to pump two travelling-wave optical parametrical amplifiers (Light Conversion, TOPAS) which can be tuned in the 250−2580 nm spectral range, whereas the third beam was used to frequency-double the fundamental wavelength in order to produce fs pulses centered at 402.5 nm. The two TOPAS were operated in the wavelength region of 1200−1208 nm for the excitation and 400−415 nm for the ionization, respectively, in order to find the optimal energy of the pump and probe photons. In our setup, the pump pulse was send through a fixed optical path whereas the probe pulse was retarded in an optical time delay, which consists of a retroreflector mounted on a 30 cm computer controlled translation stage (Physics Instruments). The two pulses were then recombined in a Mach-Zehnder-like interferometer.

The supersonic beam of sodium fluoride clusters was prepared in a stainless steel cartridge (oven) by adiabatic co-expansion of sodium metal vapor with argon (Ar) carrier gas seeded with sulfur hexa-fluoride (SF_6) through a 80 μm nozzle into the vacuum. Three to five grams of pure sodium metal were enough to produce a neutral beam for 8 hours. Sodium fluoride clusters were produced *via* a chemical reaction between the sodium vapor and SF_6. The oven was heated to 700−750 °C, while the nozzle was kept at a 150 K higher temperature in order to avoid its clogging. Due to the electronic gas flow controllers present in the setup, it was feasible to maintain a constant Ar–SF_6 flow ratio in the carrier gas, hence to produce a stable beam of cold Na_nF_m aggregates. Depending on the oven temperature, the carrier gas pressure and the Ar–SF_6 ratio, it was possible to manipulate the beam composition. For example, the increase of the SF_6 flow leads to the production of multiple combinations of Na_nF_m clusters ($n > m$). The distribution of the recorded sodium-fluoride cluster ion signal in the supersonic jet depends also on the pulse intensity and laser wavelength. The preparation chamber was pumped by an oil diffusion system (Balzers, Model DIF 400, suction capability of 4000 l/s). Entering the interaction chamber, the molecular beam was skimmed off by a 2 mm Ni skimmer. After the interaction with the ultrashort laser pulses, the resulting photo-ion current was measured by a quadrupole mass filter (Balzers, QMG 420), oriented perpendicular on the laser and cluster beams. The detection chamber was evacuated by two turbo molecular pumps (Balzers, 2200 l/s and 500 l/s, respectively).

3 Results

A typical set of mass spectra (see Fig. 2 was recorded with a single laser pulse in the UV, VIS and IR spectral region using laser multiphoton ionization. The observed cluster size distribution reveals Na_nF_m up to $n = 7$. The intensities of the individual ion peaks change significantly with the ionization wavelength, as already mentioned in the experimental section. The mass spectra show only the molecules which were effectively ionized by a multiphoton process and not the exact composition of the molecular beam. This is illustrated in the case of Na_2F, Na_3F_2 and Na_4F_3, where the amplitudes of the mass peaks vary by tuning the laser wavelength from the UV to IR. The intensities of the Na_3F_2 and Na_4F_3 cluster ion peaks decrease with the reduction of the laser energy from 405 nm to 600 nm. At 405 nm the laser pulse ionizes very effective the Na_nF_m clusters, while on the contrary the ionization process at 600 nm has been proved to be less effective. (The additionally existing sodium cluster peaks show an enhancement at about 532 nm which can be explained by a 2-photon ionization process at this energy.) When an infrared laser pulse centered at 1200 nm is intersecting the

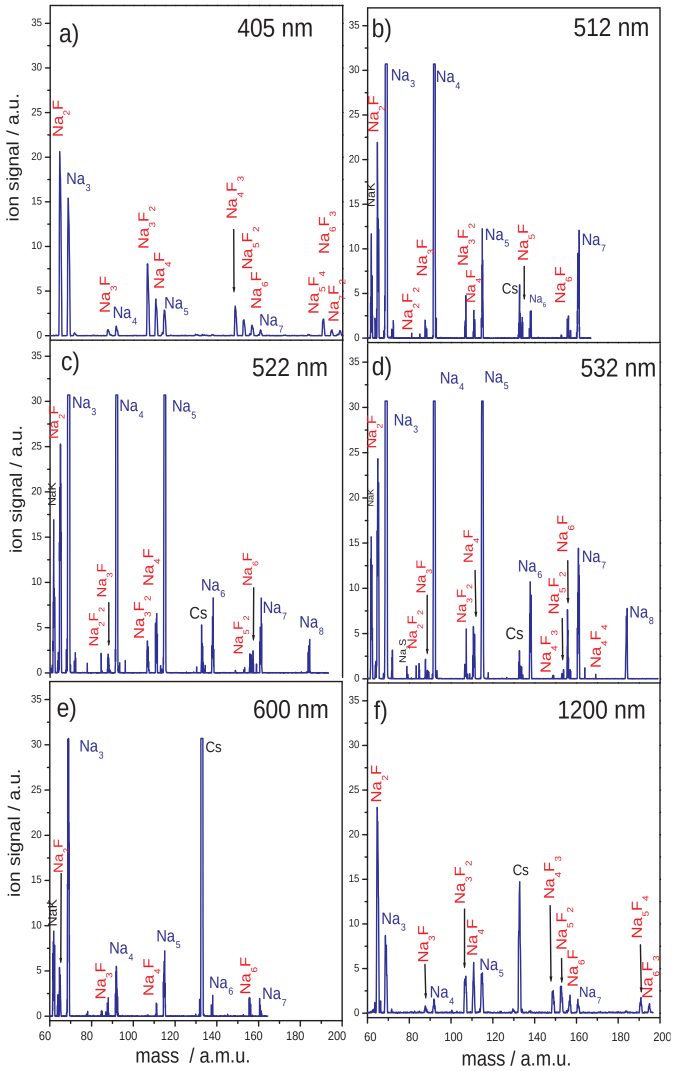

Fig. 2. Typical mass spectra of a Na_nF_m molecular beam recorded using multi-photon ionization by tuning the laser wavelength in the UV, VIS and IR spectral regions: 405 nm (a), 512 nm (b), 522 nm (c), 532 nm (d), 600 nm (e) and 1200 nm (d). The presence of NaK and Cs traces didn't alter the quality of the supersonic beam.

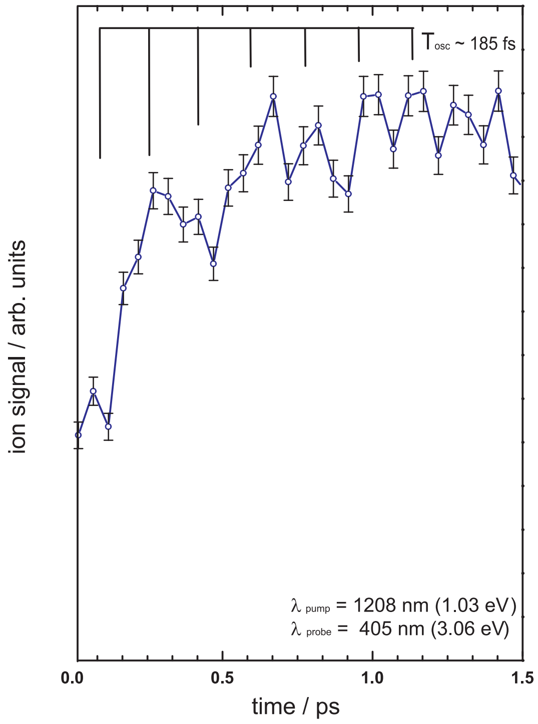

Fig. 3. Pump and probe spectrum of the Na_2F^+ ion signal.

molecular beam the sodium-fluoride cluster ion signal increases substantially compared to the 600 nm spectrum. This can be understood since the 1200 nm photon energy is known to be close to resonant transitions for these clusters, respectively, leading to the obtained higher peak intensities. At this wavelength, the highest amount of Na_2F ions was measured, which we found to be close to the resonant wavelength of the trimer, as already predicted by the theory. For this reason we have selected this spectral region for the pump pulse. Time-resolved spectra (not shown here) were measured by centering the pump wavelength at 1200 nm, whereas the probe pulse was centered at 402.5 nm (second harmonic of the amplifier). The recorded ion signal showed an increase of the Na_2F ion yield upon arrival of the probe pulse and remained constant up to 9 ps. The recorded transient showed the population of first electronic excited state, which confirmed that the first femtosecond experiment was performed close to the wavelength region suggested by the theory [1]. Figure 3 shows a typical time-resolved spectrum measured with pump and probe pulses of 40 fs and 50 fs time duration, respectively. The two optical parametrical amplifiers were tuned to 1.03 eV (1208 nm) for the excitation process and to 3.06 eV (405 nm) for reaching the ionic ground state. At these frequencies the Na_2F^+ signal exhibits an oscillatory behavior with a period of $\sim$ 185 fs. The error bars show that the overall fluctuations of the laser beam and of the supersonic jet are not larger than 2−3%. The pump pulse populates the first excited state (1^2B_2) of the Na_2F cluster by one infrared photon, whereby the molecule has a triangular configuration. Subsequent to the excitation, the molecule relaxes and the Na–Na bond breaks. This is followed by the passage of the fluorine atom between the two metal atoms leading to a linear structure, which has the minimum energy in the excited state. The motion of the system continues until the molecule reaches again the triangular geometry. This triangular-linear-triangular periodical dynamic is attributed to the bending mode. Due to the anharmonicities of the bending mode, the periodicity is perturbed at larger times. We don't expect to observe any IVR since the breaking of the metallic bond excludes the coupling between the bending and the stretching modes. The agreement between the experimentally found internal periodical structural changes with the *ab initio* calculations of the pump and probe ion signal is excellent [9].

4 Summary and outlook

We have described the production of a Na_nF_m supersonic molecular beam and its detection using laser multi-photon ionization in a wide wavelength range. We have investigated the dynamics of Na_2F involving internal structural rearrangements (from triangular-to linear-to triangular geometry) on the 1^2B_2 excited state by means of two-color two-photon time-resolved spectroscopy. Due to the breaking of the metallic bond, no coupling between bending and stretching mode is allowed, which leads to the absence of IVR. To the best of our knowledge, this study is the first successful experimental investigation of real-time analysis in electronically excited states of sodium fluoride clusters. The observed nuclear dynamics in Na_2F makes us believe that the non-stoichiometric sodium fluoride clusters can be the new candidates for femtosecond laser induced experiments. Since they involve relaxation *via* different channels including conical intersections, periodical structural changes, IVR and fragmentation processes, active coherent control experiments can be performed, by employing shaped laser pulses. Future experiments will focus on the investigation of larger Na_nF_{n-1} clusters, with $3 \leq n \leq 5$, by employing ultrafast pump and probe spectroscopy combined with mass spectrometry.

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