Chapter 7

Femtosecond Time-Resolved Spectroscopy of Na$_2$F

Clusters of atoms and molecules exhibit in many cases size-dependent physical and chemical properties which can differ from the respective bulk materials [135]. 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 understand 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 [136, 137].

Furthermore, alkali halides can serve as active media for color-center[1] lasers. These type of lasers cover a broad spectral range (0.8–3 μm) and can operate in both cw-mode or pulsed mode. Their energy levels are associated with defects in the alkali-halide crystals, which can be filled either with electrons or alkali ion impurities. Common color-center active media are: NaF, NaCl, KCl:Li, KCl:Na, KCl:Tl, NaCl:OH$^-$, etc. More information about color-center lasers can be found in Ref. [138].

In this chapter the spectroscopic investigations by means of femtosecond laser pulses are presented for the Na$_2$F, which is the smallest species from the non-stoichiometric sodium fluoride family. A description of previous theoretical and experimental studies is given, followed by details regarding the production of these clusters in a molecular beam under our laboratory conditions. Mass spectra recorded at different laser wavelengths are presented in the next section. The femtosecond pump–probe experiments on Na$_2$F are

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[1]Color centers are imperfections in crystals that cause color after absorption of light.

discussed in section 7.4. The measurements are then compared with theoretical calculations. The time-resolved experiments show that sodium fluoride clusters provide interesting features which can be manipulated in optimal control experiments.

7.1 Choice of the System

Recently, theoretical [136, 137, 139, 140] and experimental [141–144] investigations on sodium fluoride clusters have been reported. Starting from *ab initio* considerations, Hartmann and co-workers have investigated the adiabatic dynamics which involve low excited states of several Na$_n$F$_{n-1}$. They have also calculated the real-time behavior of some of these species. According to their first simulations of pump and probe signals using the *ab initio* Wigner distribution approach, the Na$_2$F 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 configurations in its first electronic excited state 1^2B_2 (see also Ref. [144]). In the case of Na$_4$F$_3$, which can serve as prototype system for surface F–center[2] bulk materials, the geometric relaxation leaves the bonds intact. Nevertheless, the structural relaxation gives rise to cage-type oscillations from the cuboidal, going through the open cage configuration to the almost planar structure, so that different types of IVR could have been identified, due to the 15 degrees of freedom [136]. The photo-isomerization mechanism through conical intersection was investigated by the group of Bonačić-Koutecký and illustrated on the Na$_3$F$_2$ example [137]. Here the time scales for the breaking of the metallic and ionic bonds, for the isomerization through the conical intersection, and for the IVR have been established, using the *ab initio* Wigner distribution approach for non-adiabatic dynamics occurring on the $2^2A'$ excited state.

The *ab initio* electronic structure calculations for 16 electronic states of Na$_2$F was done by Cai and co-workers in 1995. 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 from the electronic ground state is about 0.98 eV (see Ref. [139]).

In 1997 Ph. Poncharal and co-workers reported resonant two-photon spectroscopy of Na$_n$F$_{n-1}$ clusters in a wide spectral range, from 290 to 1000 nm, by employing 15 ns pulses and using a time-of-flight spectrometer for detection. They measured the ionization potentials and absorption spectra of se-

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[2]F-center is another name for the color-center materials, originating from the german word *Farbe* (color).

veral non-stoichiometric sodium-fluorides up to $Na_{42}F_{41}$ and correlated these results [141] with the predicted geometry, completing the classification they had already begun for the visible absorption spectra [142]. Furthermore in collaboration with G. Durand and F. Spiegelmann, they have calculated the excited states of these species, up to n = 29. Using an one-electron pseudo-potential model they have calculated that the transition energy from the electronic ground state to the 1^2B_2 excited state for Na_2F amounts 0.95 eV [140]. The optical absorption of Na_2F was studied in the group of Ernst as well [143].

Motivated by the theoretical simulations, the non-stoichiometric sodium fluoride molecules are selected as possible test species for optimal control of molecular motion involving different photo-induced processes. By increasing the cluster size, the higher number of the degrees of freedom will increase the complexity of the intramolecular processes. The first step in understanding the control mechanism is to perform a detailed pump–probe analysis of the investigated system. A method for generating sodium-fluoride clusters in a molecular beam was developed as well. The smallest species, Na_2F, was investigated by means of ultrafast pump–probe technique.

7.2   Experimental Preparations

An illustration of the experimental setup can be seen in Figure 7.1. The laser system FS II was described in Chapter 4, section 4.2.2.

Briefly, the Ti:sapphire oscillator (Kapteyn) seeded the multipass amplifier (Quantronix Odin) with femtosecond pulses centered around 805 nm. The amplifier produced pulses of 40 fs duration and 1.3 mJ energy. The output laser beam was split in three rays: two beams pumped the two TOPAS, with an energy of 500 μJ each and the third one was sent onto the molecular beam in order to excite and ionize the sodium-fluoride clusters (the third pulse can be optionally frequency-doubled in order to obtain photons of 3.1 eV energy, corresponding to 402.5 nm). The amplifier pulses were measured by employing the SHG FROG technique. The TOPAS pulses were measured by auto-correlation and had a time duration of approximately 40 fs. In the pump–probe spectroscopic studies (see section 7.4) the pump pulse duration was 40 fs, whereas the probe pulse had a time duration of 50 fs.

The supersonic beam of sodium fluoride clusters was prepared in a stainless steel cartridge (see Chapter 4, section 4.1.1) by adiabatic co-expansion of sodium metal vapor with argon (Ar) carrier gas seeded with sulfur hexafluoride (SF_6) through a 80 μm nozzle into the vacuum. The sodium-fluoride clusters were produced via a chemical reaction between the sodium vapor and SF_6. The oven cartridge was heated to 700–750 °C, while the nozzle was kept
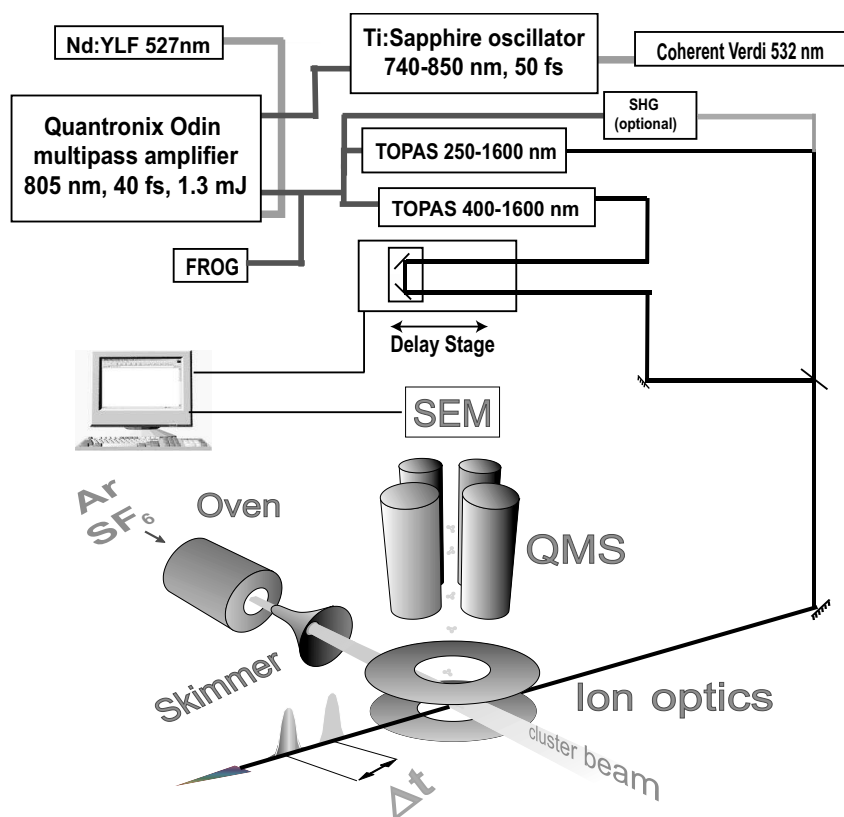
Figure 7.1: The setup used for the sodium-fluorides experiments consisting of a femtosecond laser system and a molecular beam apparatus. The employed laser system, FS II, is described in detail in Chapter 4, section 4.2.2. The femtosecond pulses are analyzed with the FROG technique. The pump and the probe pulse were delivered by the two optical parametric amplifiers (TOPAS). The Na_nF_m molecules were prepared in the molecular beam, by co-expanding Na vapor with Ar and SF_6 into vacuum. The molecules pass through the skimmer and are hit by the laser light between the ion optics of the quadrupole mass spectrometer (QMS). The resulting photo-ions were collected by a secondary electron multiplier (SEM) and the signal was recorded by a PC.

at a 150 degrees higher temperature in order to avoid its clogging. Due to the electronic gas flow controllers and a premixing reservoir present in the setup, the maintenance of a constant Ar–SF_6 ratio in the carrier gas was guaranteed. This allowed the production of a stable beam of cold Na_nF_m aggregates for up to 3 hours. 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 would lead 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 ionization probability (i.e. pulse intensity and laser wavelength).

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 the quadrupole mass filter (see Chapter 4, section 4.1.2). The quadrupole bars were oriented perpendicular on the laser and cluster beams. The ion signal was amplified by a secondary electron multiplier (SEM) and detected by a computer.

7.3 Mass-spectrometric Studies

A set of mass spectra by using a single laser pulse in the UV, VIS and/or IR spectral regions is displayed in Figure 7.2. The clusters are ionized by multi-photon ionization. The observed size distribution reveals sodium-fluoride species up to Na_7F_2.

The intensities of the individual ion peaks change significantly with the ionization wavelength, as already mentioned before. Thus mass spectra show only the molecules which were effectively ionized by a multi-photon 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 wavelength from 405 nm to 600 nm. (The additionally existing sodium cluster peaks show an enhancement at about 532 nm which can be explained by a non-resonant two-photon ionization process at this energy.)

When an infrared laser pulse centered at 1200 nm is intersecting the molecular beam, the sodium-fluoride cluster ion signal increases substantially compared to the 600 nm spectrum. This can be understood since the 1200 nm (1.03 eV) photon energy is known to be close to resonant transitions for these clusters leading to the obtained higher peak intensities. This wavelength, where the amount of detected Na_2F ions was significant, is found to be close to the resonant wavelength of the trimer for the first electronic excited state, as already predicted by the theory. For this reason we have selected this spectral region for the pump pulse and 405 nm for the probe pulse. The theoretical calculations predicted also the wavelength interval for the probe pulse to be between 3.06 and 3.3 eV. The pump–probe experiments are presented in the following section.
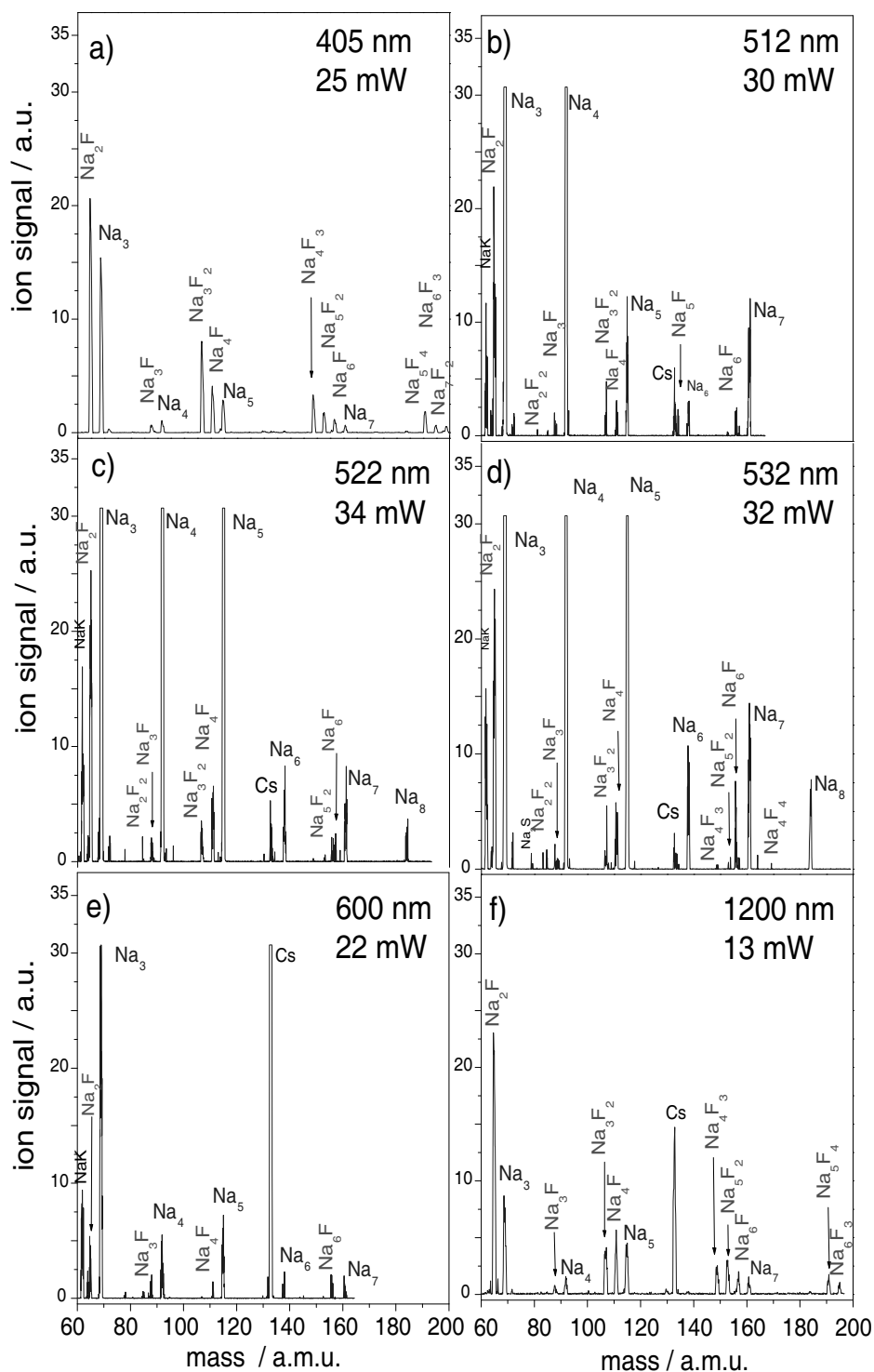
Figure 7.2: Typical mass spectra of a Na$_n$F$_m$ molecular beam recorded by multi-photon ionization. The laser wavelength is tuned in the UV, VIS and IR spectral regions: 405 nm (a), 512 nm (b), 522 nm (c), 532 nm (d), 600 nm (e) and 1200 nm (f). The average laser power is displayed as well. The presence of NaK and Cs traces does not alter the quality of the supersonic beam [145].
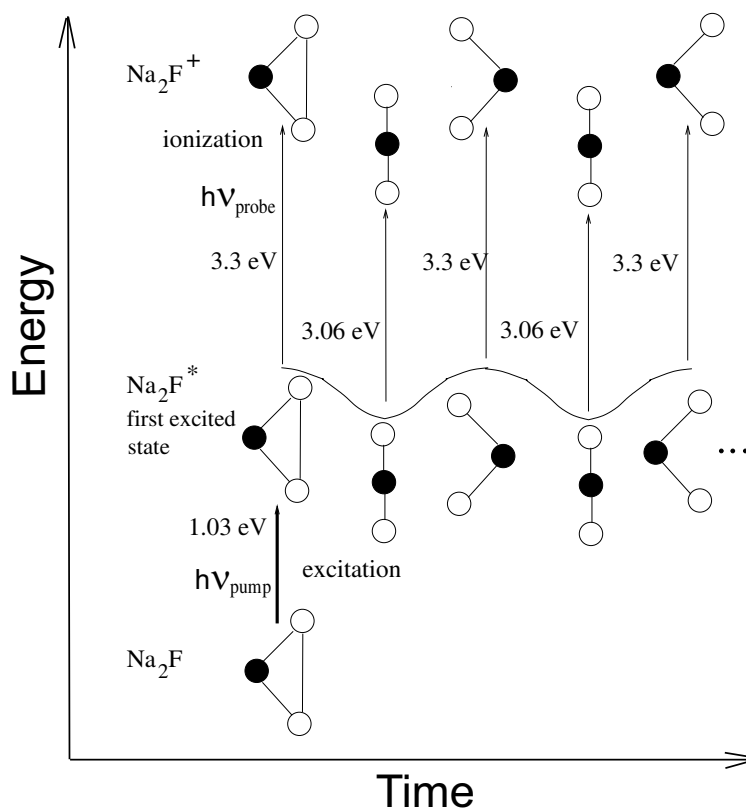
Figure 7.3: The scheme of the femtosecond dynamics of Na_2F in the first excited state 1^2B_2 in the framework of pump-probe spectroscopy [144].

7.4   Pump–Probe Experiments on Na_2F

The pump–probe scheme, containing the required energies for probing the structural features of the ground and the first excited electronic state (1^2B_2) of Na_2F, obtained from *ab initio* [136,144] calculations is given in Figure 7.3.

In order to resolve the dynamics of the 1^2B_2 electronic excited state in Na_2F, the pump–probe experimental scheme requires excitation wavelengths at 1208 nm (1.03 eV) and ionization pulses between 400 and 415 nm (3.06 and 3.3 eV, respectively). This corresponds to the probing window in which the butterfly-like relaxation involving triangular and linear structures can be monitored.

Following the scheme in Figure 7.3 the experimental femtosecond pump-probe setup has been developed. If the ionization energy is 3.06 eV, then the periodical structural changes can be sensitively detected through the Franck-Condon window. Thus the two TOPAS were tuned between 1200–1260 nm
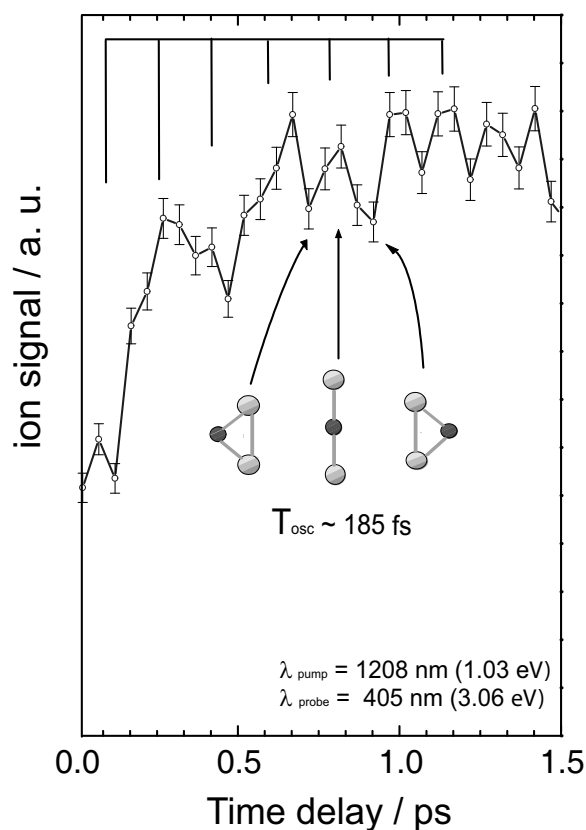
Figure 7.4: Typical pump-probe spectrum revealing the fs dynamics for Na$_2$F cluster on the 1^2B_2 excited state [144,145]. The involved geometries are displayed as well.

and 400–425 nm, respectively. The duration of the pump and probe pulses, measured by auto-correlation technique, were 40 fs and 50 fs, respectively.

For a pump pulse centered at 1208 nm (1.03 eV) and a probe wavelength of 405 nm (3.06 eV), the transient shows an increase of the Na$_2$F ion signal after the arrival of the probe pulse (see Figure 7.4). The Na$_2$F$^+$ signal exhibits an oscillatory behavior with a period of T$_{osc} \sim 185$ fs. The transient spectrum shows undoubtedly that the experiment confirmed the wavelength region for the pump and probe pulses suggested by the theory.

The pump pulse populates the first excited state (1^2B_2) of the Na$_2$F cluster by one-photon transition, when the molecule has a triangular configuration. The spectrum confirms the population of a bound-bound state in concordance with the already predicted stability of the electronic excited state [136].
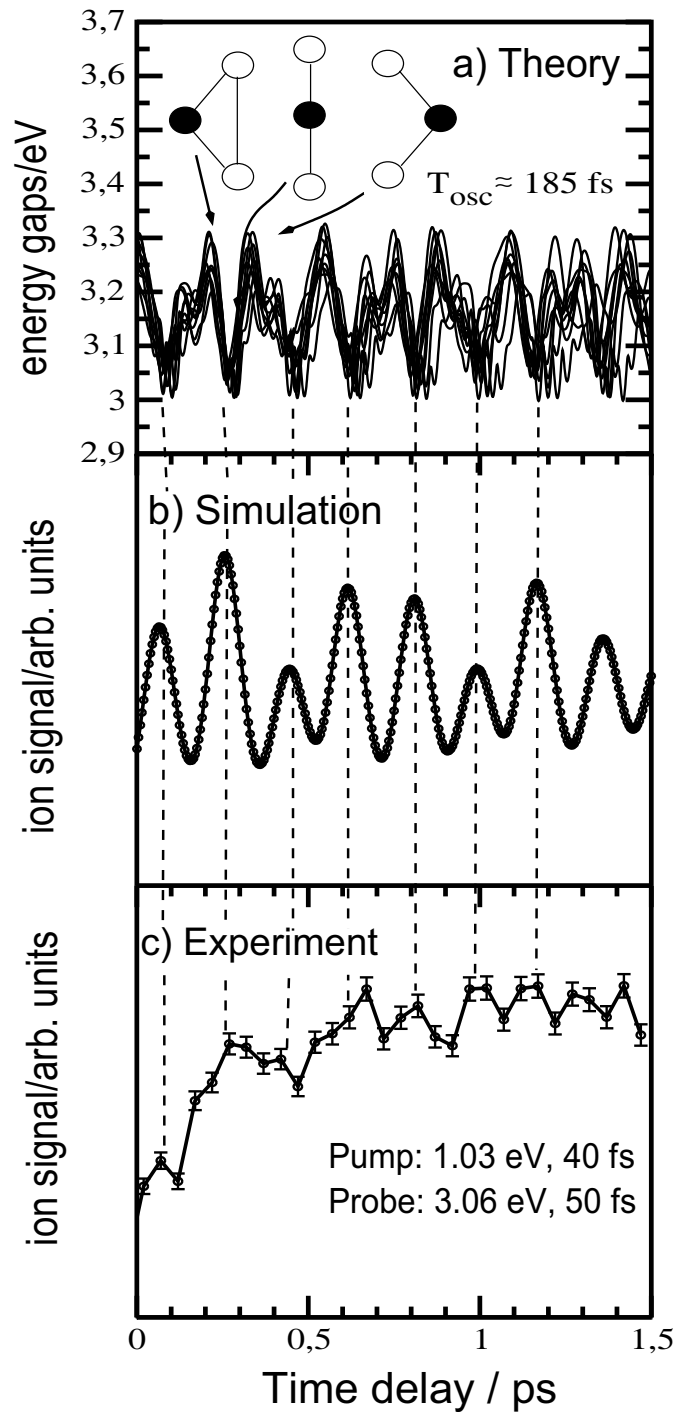
Figure 7.5: Comparison between theoretical and experimental results in the case of Na$_2$F: (a) bunch of energy gaps between the first electronic excited state and the ionic ground state during the dynamics on the excited state; (b) simulation of the pump–probe signal; (c) experimentally recorded transient ion signal as a function of the time delay between the pump–probe laser pulses [144].

After the excitation, the molecule begins to relax. The Na–Na bond breaking is followed by the passage of the fluorine atom between the two metal atoms leading the molecule towards a linear structure. The linear configuration corresponds to the minimum energy geometry in the excited state. The motion of the system continues until the molecule reaches again its initial triangular geometry. Nevertheless, the Na–Na bond remains broken, but no fragmentation occurs since the two Na–F bonds remain intact. The triangular-linear-triangular periodical dynamics are attributed to the bending mode. The asymmetric stretch mode is not excited during the dynamics. Furthermore no signature of IVR was observed. The reason is that the breaking of the metallic bond excludes the coupling between the bending and the stretching modes, hence the internal energy of the molecule can not be redistributed. On a larger time scale the periodicity is disturbed by anharmonicities existing in the bending mode.

The result agrees very well with the theoretical calculations [144]. Figure 7.5a depicts a bunch of energy gaps between the 1^2B_2 excited state and the cationic ground state [136, 144] compared with the simulated pump-probe spectrum (depicted in Figure 7.5b) and the experimentally measured transient ion signal (see Figure 7.5c). The involved geometries of the molecule are shown in the top part.

The calculations performed by Heitz and co-workers revealed not only the same oscillatory pattern ($\sim$ 180 fs) of the Na$_2$F, but also another interesting feature [146]. They state as well that the asymmetric stretch mode does not play a role in the dynamical process. According to their calculations, the bending motion leads to a slight excitation of the symmetric stretch. Although the coupling between the two modes is very weak, a transfer of the kinetic energy from the bending mode into the stretching mode is observed. This process is reversible and it takes place around 355 fs, 1067 fs and 1780 fs after the arrival of the probe pulse. Their calculated photo-electron spectrum shows both the excitation of the bending mode and of the symmetric stretch [146].

In the recorded Na$_2$F$^+$ transient pronounced minima are observed at around 480 fs and 920 fs. They could be associated to the times at which the calculated energy transfer to the stretching mode due to the kinetic couplings (centrifugal acceleration) occurs. Yet this is not claimed because of the 130 fs time shift with respect to the calculated values. The spectrum in Figure 7.5c was recorded for the total Na$_2$F$^+$ ion signal and not for photo-electrons.

7.5   Summary and Outlook

In this chapter the production of a Na_nF_m supersonic molecular beam and its detection using laser multi-photon ionization in a wide wavelength range was described. The dynamics of Na_2F cluster involving internal structural rearrangements (from triangular-to linear-to triangular geometry) on the 1^2B_2 excited state was investigated by means of two-color two-photon time-resolved spectroscopy. Due to the breaking of the metallic bond, no coupling between bending and stretching modes was detected, which leads to the absence of IVR. This study was the first successful experimental investigation of real-time analysis in electronically excited states of sodium fluoride clusters [144, 145]. The periodicity of the bending motion has been observed in the calculations of two theoretical groups [136, 146]. The observed nuclear dynamics in Na_2F shows that the non-stoichiometric sodium fluoride cluster family can be 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 with shaped laser pulses can be performed.

Future experiments will focus on the investigation of larger Na_nF_{n-1} clusters, with $3 \leq n \leq 5$, by employing ultrafast pump–probe spectroscopy combined with mass spectrometry. With the present experimental setup, these clusters were observed in the mass spectra. In the case of Na_3F_2, the group of Bonačić-Koutecký has performed *ab initio* calculation involving nonadiabatic dynamics through the conical intersection [137]. According to their calculations, one could pump the Na_3F_2 molecule from the ground state (where the molecule possess a C_s symmetry) to the first excited state ($2^2A'$), by one-photon of 1.33 eV (931 nm). The relaxation of the cluster begins after the excitation and takes place towards the linear structure, which corresponds to the conical intersection. The relaxation process continues from the linear structure to the ground state where the molecule has two isomers: the C_s one (isomer I) and a pyramidal one, having a C_{2v} symmetry (isomer II). The latter isomer lies 0.1 eV above the ground state energy of isomer I. If the ionization energy is carefully chosen, one could detect different geometries of the Na_3F_2 cation: 2.77 eV (447 nm) for the linear structure in the excited state, 2.93 eV (422.5 nm) for the C_s symmetry and 3.1 eV (400 nm) for the pyramidal structure in the excited state. In order to perform these experiments a pump-probe setup using the laser radiation of two Non-collinear Optical Parametric Amplifiers (NOPA) or of the two existing TOPAS is necessary.

An interesting control experiment would be to use the pulse shaper in order to design a laser pulse sequence, which prepares the Na_3F_2 molecule in the $2^2A'$ excited state (C_s symmetry), waits until the wave packet arrives

before conical intersection (linear structure) when it dumps the cluster into the pyramidal ground state structure (C$_{2v}$ symmetry). In this way conical intersections can be intelligently avoided. The theoretical predictions have been already published in Ref. [105].

Another approach would be to carry out laser control of the isomerization process through an intermediate target by employing the feedback loop experiment. By employing the feedback-loop experiment, the previous experiment can also be performed. The evolution algorithm should deliver an optimal pulse with similar characteristics as the theoretically predicted one. Moreover controlling the population in such a bimodal system might be a pioneering work in molecular switches, which can be used in data storage industry. Luty and co-workers have shown the bi-directional holographic information storage based on optical reorientation of dichroic F$_A$ centers in KCl:Na [147]. (The recording medium was a KCl single crystal doped with Na$^+$ and the orientable absorbing defect is a F$_A$ center.)

The Na$_4$F$_3$ also has interesting features, which can be studied in femtosecond time-resolved experiments. Based on the theoretical approach from Hartmann and co-workers [136], the system has a cuboidal geometry in the ground state and the excess electron is located in the halide vacancy. The dynamics on the first excited state 1^{2}E from the initial cuboidal shape towards the "cage-opening" structure can be monitored by means of pump–dump–probe spectroscopy [148].