Chapter 4

Experimental Details

A model system for investigation and control of molecular phenomena comprises molecules which do not interact with each other. The molecules should also be sufficiently isolated so as to avoid collisions with air particles. A molecular system must also be in a well-defined initial state, usually the ground state, at the starting point of an experiment. This can be accomplished by combining a molecular beam apparatus with a mass spectrometer. For a high versatility of the femtosecond experiments, two femtosecond laser systems were used. In the first section the components of the molecular beam machine will be first described. A detailed description of the two femtosecond laser systems will be included in the second section.

4.1 Molecular Beam Apparatus

The molecules to be investigated are produced in a supersonic molecular beam by adiabatic co-expansion of the hot sample vapor with the carrier gas through a small nozzle into the vacuum.

For the production of the cluster beam a so-called oven (where the adiabatic co-expansion takes place), a vacuum apparatus (in order to study isolated molecules) and a detection device are necessary.

In this work the clusters are produced in the first vacuum chamber (from now on called *oven chamber*). The resulting beam is then skimmed off by a skimmer and carried by an inert carrier gas into the second vacuum chamber (called *detection chamber*). In the detection chamber the interaction with the laser pulses takes place together with the detection of the photo-ions. As a detector a quadrupole mass spectrometer oriented perpendicularly on the cluster beam and the laser beam is used.

4.1.1 Description of the Vacuum Chambers

A schematic of the molecular beam apparatus is shown in Figure 4.1. The vacuum in the oven chamber is produced by an oil diffusion pump[1] with a capacity of 3100 l/s. This allows a pressure in the oven chamber during the experiment of about 5×10^{-4} mbar. A valve is situated between the oven chamber and the oil diffusion pump, in order to isolate the pump and to avoid turning the pump off when the oven chamber is under atmospheric pressure. The detection chamber is differentially evacuated by two turbo molecular pumps[2] of pumping capacity of 2200 l/s and 500 l/s respectively, which evacuate the detection chamber during the measurements to 2–5×10^{-6} mbar. The critical pressure in the detection chamber is 5×10^{-5} mbar; if the vacuum is under this value, the mass spectrometer can be damaged. The first stage of the pumping system consists of a roll piston pump[3] and a rotary vane pump[4] which produce a low vacuum (2×10^{-3} mbar) for the oil diffusion pump and the turbo molecular pumps.

The Oven

The oven is constructed from a 160 mm long cylindrical cartridge with a diameter of 14.1 mm (see Figure 4.2). Recently, the oven construction was developed with exchangeable plates for the nozzle (see Ref. [50]). The oven is made of Chromium-Nickel steel and plates of different materials[5] for the nozzle are welded onto it. In these plates a nozzle is later drilled by using a home-built drill. The quality of the nozzle materials and of the welding process is decisive for the production of e.g. an sodium fluorides molecular jet, since at higher temperatures, the plates might fall off the cartridge.

The plates are made from different types of alloys:

• Stainless steel: the iron based alloy containing at least 10.5 % Chromium-Molybdenum improves the corrosion resistance particulary in chloride containing environments. The lower Carbon content of alloy 316 L gives even better corrosion resistance in welded parts.

• TZM: a Titanium-Zirconium-Molybdenum alloy with a high melting point. Molybdenum increases the resistance of the alloy against corrosion.

• Inconel: a Nickel-Chromium-Iron alloy very stable at high temperatures. It is used for its anti-corrosion and heat-resistance properties as well as for its high strength and excellent weldability.

[1] Pfeiffer Vacuum GmbH, model DIF 400, Asslar, Germany.
[2] Pfeiffer Vacuum GmbH, models TMP 3000 and TMP 500.
[3] Pfeiffer Vacuum GmbH, model DUO 300.
[4] Pfeiffer Vacuum GmbH, model WKP 250 A.
[5] Alfred Rexroth GmbH & Co. KG, Berlin.

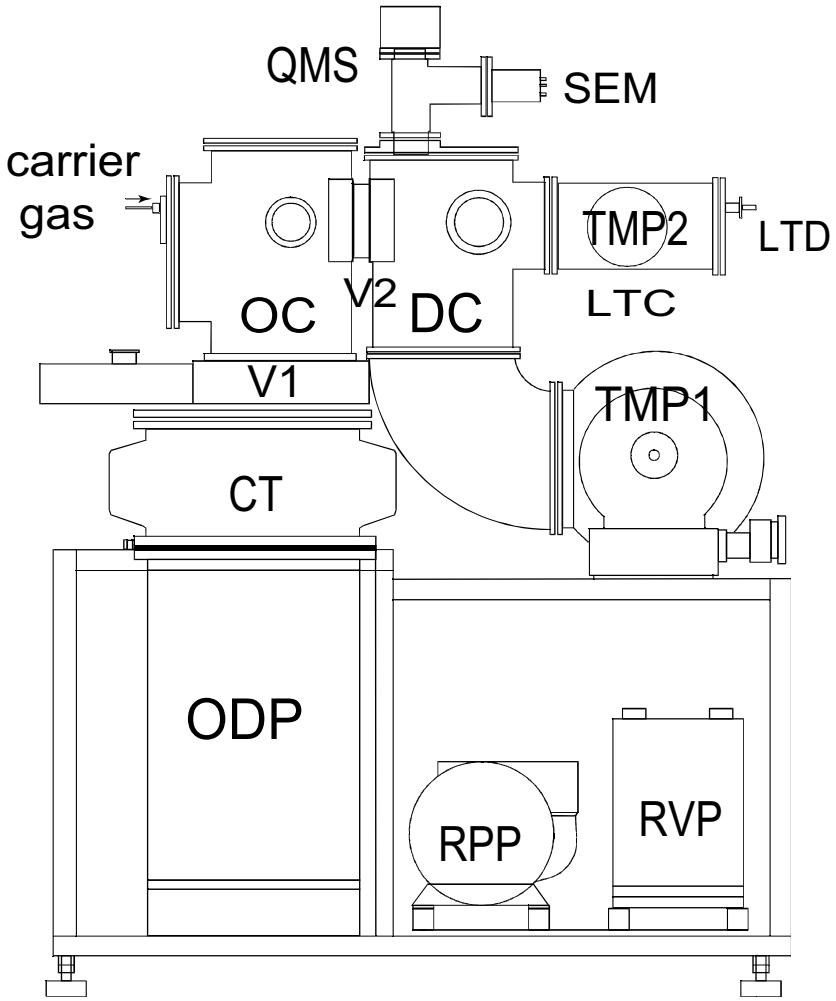

Figure 4.1: The molecular beam apparatus consisting of two differentially pumped vacuum chambers. The evacuation of the oven chamber (OC) is realized by an oil diffusion pump (ODP) together with the cooling trap (CT) up to 1×10^{-6} mbar. The oven chamber is separated from the detection chamber (DC) by the second valve (V2) and from the ODP by the valve (V1). The 4×10^{-8} mbar pressure in the detection chamber is produced by two turbo molecular pumps (TMP1 and TMP2). In the detection chamber the quandrupole mass spectrometer (QMS) is situated perpendicularly on the cluster beam. The ions are deflected towards the secondary electron multiplier (SEM). At the end of the Langmuir-Taylor chamber (LTC), the Langmuir-Taylor (LTD) is situated. The pre-pumps roll piston pump (RPP) and the rotary vane pump (RVP) are connected with the main pumping system in the lower part of the molecular beam machine. The apparatus was built by H. Kühling [49] in 1990 and continuously improved over the past few years.

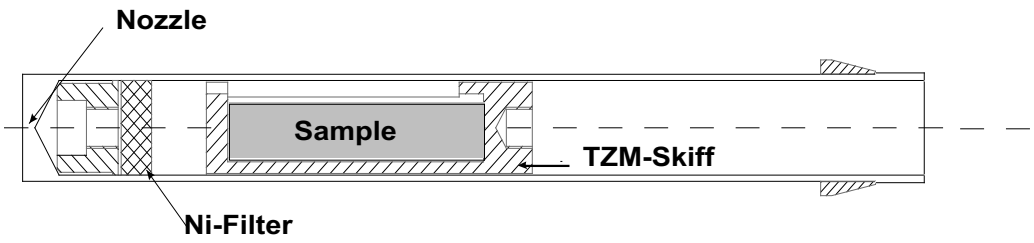

Figure 4.2: The oven cartridge.

• Nimonic: a Nickel-Chromium-Cobalt alloy primarily used for creep resistance, high strength, good weldability and stability at high temperatures.

The oven cartridge position can be manipulated from outside the chamber in the *xyz* direction. This allows a good alignment of the nozzle in front of the skimmer. The skimmer is situated 10 mm downstream from the nozzle. Moreover one can optimize the interaction with the laser pulses between the QMS lenses by monitoring the ion signal on the QMS console. Nevertheless, the temperature gradient in the oven can be also modified by changing the *xyz* position of the cartridge.

The Skimmer

The cluster beam, produced in the oven chamber, enters the detection chamber through a skimmer of 1–2 mm diameter[6]. In this way, the beam quality is improved. In the oven chamber, the beam is very divergent. The almost-conical shape of the skimmer is chosen for blocking diffuse parts of the beam. The Nickel-made skimmer is resistive to alkali vapors, but during the sodium-fluoride measurements was sometimes corroded by the Fluorine vapor.

4.1.2 Detection of the Ion Signal

The molecular beam containing different cluster sizes enters the interaction chamber through the skimmer. Situated 20 cm downstream from the skimmer, the quadrupole mass spectrometer (QMS) is perpendicularly oriented to the molecular beam in order to extract the ionized molecules. In a linear arrangement (perpendicular only to the laser beam but on the same axis as the cluster beam) the electrostatic optics of the QMS would become unclean by the alkali metal flux during every measurement and would require removal and cleaning after only a few hours of exposure to the beam. The device is

[6]Beam Dynamics, Inc., Oneida, WI, U.S.A.

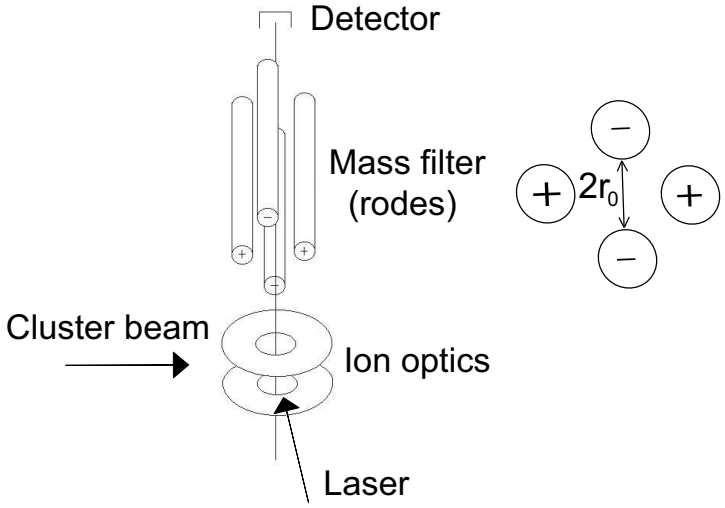

Figure 4.3: The quadrupole mass filter. The laser is shone perpendicular to the cluster beam and to the quadrupole mass spectrometer. The photo-ions are extracted by the electrostatic optics and guided by the quadrupolar field existing between each pair of rods.

commercially available[7], except for the electrostatic optics used for photo-ionization experiments, which were constructed in the institute's workshop.

The working principle of the QMS is displayed in Figure 4.3. The laser beam interacts with the neutral clusters between the electrical lenses of the QMS and ionizes them. The ionized species are focused at the entrance of the mass selector by a system of electrostatic lenses, on which a voltage is applied. The mass selector (or filter) consists of four parallel cylindrical rods. The opposite bars are coupled together. Between each pair there is a potential difference $(U + V\cos\omega t)$ applied, whereby U is a continuous and V is an alternative voltage. The resulting field is now quadrupolar. Here the particles accelerated by a potential just after ionization have either a stable orbital trajectory within the volume determined by the bars and hit the detector, or have an unstable trajectory and are lost. The stability criterium for each ion mass is given by U, the value of the continuous field and V the amplitude of the variation, for a given frequency of ω. The resolution of the mass filter is described by the ratio 2U/V. This is particulary adjusted so that only the trajectory of the selected mass is stable.

The detector inside the QMS is a secondary electron multiplier (SEM), which in principle operates like a photo-multiplier.

The cluster ions are mass-selected with a typical resolving power of $m/\Delta m$

[7]Pfeiffer Vacuum GmbH, model QMA 420.

higher than 200. This is sufficient, for example, to distinguish between $^{39,39}K_2$ and $^{39,41}K_2$ isotopes. The transmitted ion signal is collected by the SEM and further amplified. The amplification factor amounts 10^8 at 3500 V. The signal is sent to a computer by an A/D converter through a standard serial interface. In comparison with a time-of-flight spectrometer, where the ions reach the detector at different times, the QMS allows a continuous record of the ion signal. Therefore lasers with high repetition rates can be used. Moreover since the QMS is situated closer to the nozzle than a time–of–flight would be, high cluster intensities can be measured.

The Langmuir-Taylor Detector

The intensity of the molecular beam in the interaction chamber is monitored by the Langmuir-Taylor Detector (LTD). The neutral alkali clusters are thermo-ionized on the Rhenium filament of the LTD [51]. The ion current is measured by two electrodes. With an active area of $A_d = 0.085$ cm^2, an alkali ion current up to 2 μA can be measured. The LTD signal is used to normalize the mass-filter signal to the cluster beam intensity. This way, one can avoid possible artifacts arriving from the short or long time fluctuations of the cluster beam. The detector is located on the axis of the oven's nozzle, the skimmer and the interaction zone between the laser beam and the clusters.

4.1.3 Production of a Cluster Beam

The supersonic molecular beam is produced in the oven chamber by expanding a sample vapor (or gas mixtures) with an inert carrier gas through a small nozzle of ca. 70 μm into the vacuum. The flow velocity at the nozzle exit is identical with the sonic speed, because the nozzle exit aperture is identical with the minimum cross section area. Outside the nozzle, for a free expansion[8], the molecular beam velocity increases, because the cross section expands. The center part of the expansion consists of (different) molecules in a narrow well-defined jet moving at a constant velocity. The flow process is isentropic since it takes places at constant entropy without exchange of heat between the flowing gas and the surroundings.

The following theoretical considerations concern diatomic molecules. The energy ε_i of a diatomic molecule in a particular quantum state i is described

[8] A free expansion takes place when the pressure outside the nozzle P_c is smaller than the pressure in the oven p'. Sonic speed is obtained at the nozzle exit under the condition $p'/P_c \geq ((k+1)/2)^{k(k+1)}$, where $k = c_p/c_v$ is the specific heat ratio.

by three important quantities: the translational energy ε_t, the rotational energy ε_r and the vibrational energy ε_v [52]:

$$\varepsilon_{\mathrm{i}} = \varepsilon_{\mathrm{t}} + \varepsilon_{\mathrm{r}} + \varepsilon_{\mathrm{v}}. \tag{4.1}$$

The average value of the translational energy ε_t per particle is given by [52]

$$\overline{\varepsilon}_{\mathrm{t}} = \frac{\overline{mv^2}}{2} = \frac{3}{2}\mathrm{k_B T}, \tag{4.2}$$

where $\overline{v} = 1.455 \times 10^4 \sqrt{\frac{\mathrm{T}}{\mathrm{M}}}$ is the average molecular speed (in cm/s), $\mathrm{k_B}$ is the Boltzmann constant, T is the absolute temperature in K and M is the molecular weight. The contribution of the translational energy to the total internal energy of the molecule is

$$\mathrm{E_t} = \frac{3}{2}\mathrm{N k_B T}, \tag{4.3}$$

where N is the total number of particles.

The rotational energy levels of a heteronuclear diatomic molecule are given by [52]

$$\varepsilon_{\mathrm{r}} = \mathrm{hcB}_e\mathrm{J(J{+}1)}, \tag{4.4}$$

where B_e is the rotational constant, h is the Planck's constant, J is the rotational quantum number and c is the velocity of light in vacuum. The fraction of the total internal energy corresponding to the rotational energy of the diatomic molecule at low temperatures ($\mathrm{hcB}_e \geq \mathrm{k_B T}$) is [52]

$$\mathrm{E_r} = 6\mathrm{NhcB}_e \exp\Big(-\frac{2\mathrm{hcB}_e}{\mathrm{k_B T}}\Big). \tag{4.5}$$

Thus the rotational contribution to the internal energy goes toward zero as the temperature decreases. The energies of the vibrational states of a diatomic molecule, in terms of the harmonic oscillator, are

$$\varepsilon_{\mathrm{v}} = \hbar\omega\big(\mathrm{v} + \frac{1}{2}\big), \tag{4.6}$$

where ω is the frequency of the harmonic oscillator, v the vibrational quantum number and $\hbar = h/2\pi$. The vibrational contribution to the internal energy of the diatomic molecule is [52]

$$\mathrm{E_v} = \mathrm{N}\hbar\omega\left(\frac{1}{2} + \frac{1}{\exp\big(\frac{\hbar\omega}{\mathrm{k_B T}}\big) - 1}\right). \tag{4.7}$$

At low temperatures E_v decreases to a minimum value of $N\hbar\omega/2$. At room temperature, the rotation of molecules is generally developed, while almost all molecules are still in the lowest vibrational state [52]. Under our experimental conditions, for K_2, the rotational temperature is $T_r \approx 10$ K and the vibrational temperature is $T_v \approx 50$ K [49, 53].

The oven tube is heated by two separate heatable groups of tungsten filaments of 2 mm diameter to support high intensity currents (of up to 20 A). There are four filaments for the oven heating and three for the nozzle heating. The heating filaments are surrounded by three Tantalum foils which reflect the thermal radiation onto the oven region. The chamber over-heating is prevented by the water cooling system. One end of the oven is screwed into a holder by a cone–over–cone arrangement in order to have a connection with the carrier gas inlet. On the other end a nozzle with 70–80 μm diameter is situated.

The sample is filled in one or two skiffs made of TZM alloy. The skiff is filled in a glove-box under a Nitrogen atmosphere in order reduce the air contact during the filling process. At each side of the skiff, filters made of Nickel wire-net[9] are situated in order to avoid heavy turbulences produced by the inlet of the carrier gas and of the sample vapor, which could clog the nozzle.

During the measurements one can increase independently the oven temperature relative to the nozzle temperature. The current through the two filament groups is adjusted so that the temperature of the nozzle is kept 80–150 °C higher than the oven temperature. This allows one to establish a temperature gradient which ensures a stable beam and avoids the clogging of the nozzle during the supersonic expansion (e.g. by the melted metal). The oven temperature is kept at approximately 450 to 650 °C for the production of K_2 and NaK; around 700 to 750 °C for Na_nF_{n-1} and at 70–80 °C during the $CpMn(CO)_3$ experiments, respectively.

Then the sample cloud expands in the vacuum through the cylindrical nozzle. During this expansion, which occurs at speeds higher than the speed of sound (over 1000 m/s), the vapor saturates and condenses into small clusters. The shape of the nozzle is very important and plays a significant role in determining the cluster size distribution. It increases the formation of clusters because the clusters spend more time in the high pressure region close to the nozzle. The ideal length of the nozzle is three times its diameter (not longer than 400 μm) [54].

In this work Argon is used as carrier gas to transport the molecules to the detection chamber. Set at a few bars over the atmospheric pressure,

[9] Tedra Dahmen GmbH, Wassenberg, Germany.

it ensures a high over-saturation of the sample vapor, which is efficiently cooled down so that the resulting supersonic beam contains very cold small clusters with vibrational and rotational temperatures of $T_{vib} < 50$ K and $T_{rot} < 10$ K [53, 55]. The collision between the clusters and the carrier gas takes off the heat released in the cluster generation. Thus by carrying off the condensation heat, the clusters stabilize against evaporation.

One measurement cycle includes loading of the oven, pumping the oven chamber for an hour, heating the sample for 2–3 hours, the "beam time", cooling down the chamber for 60–90 minutes and cleaning of the oven chamber. During this work, measurements involving a beam time with a duration up to 3 hours for sodium-fluorides, about 20 hours for an alkali beam (NaK, K_2), or 50 hours ($CpMn(CO)_3$) were performed with the present apparatus.

4.2 The Laser Systems

The results presented in this work were obtained by using two different femtosecond laser systems. For convenience, they will be named FS I and FS II.

For the alkali metals measurements the FS I was used. It consists of a commercial femtosecond Ti:sapphire oscillator (Spectra Physics,Tsunami, Model 3960) pumped by a all solid-state diode-pumped Nd:YVO_4 cw laser (Spectra Physics, Millennia X). The oscillator's pulses can be amplified by a regenerative/multipass amplifier system (Quantronix, RGA/MPA Model 4800).

The $CpMn(CO)_3$ and the sodium-fluoride experiments were performed with laser pulses generated by FS II. This system contains a home-built Ti:sapphire oscillator [23] based on Kapteyn-Murnane Laboratories' technique [56]. The outcoming femtosecond pulses seed a commercial multipass amplifier (Quantronix, Odin). The amplified laser output was split in two beams in order to pump two optical parametrical amplifiers (Light Conversion, TOPAS).

The two laser systems are situated on two different optical tables[10], which are vibration-free due to the pressurized air system situated under the table. The laser path was directed onto the experiment by commercial available mirrors, lenses, filters, gratings, mounted on mechanical holders which allow a precise alignment of the laser beam on the xy-axes. Special attention was given to the two laser setups for a good day-to-day operation.

A detailed description of the two laser systems is given in the next sections.

[10] Newport Co., Irvine, CA, U.S.A.

4.2.1 Femtosecond System – FS I

The cw Pump Laser – Spectra Physics Millennia X

The Millennia X is a solid-state, high power, diode-pumped, visible cw laser that provides more than 10 W of 532 nm output. The active medium consists of a Yttrium vanadate crystalline matrix (Nd:YVO_4) doped with Nd^{3+} ions. The two crystals situated in the *Z*-like head are pumped by four fiber-coupled diode bar (FC bar) modules which provide very high cw signal gain. Each module is capable of producing over 20 W of 1064 nm infrared power with a conversion efficiency greater than 50 %. The outputs from the four power supply pump diode modules are coupled with 19 fibers into the dual *Z*-head and focused into the end of each of the Nd:YVO4 laser crystals. The 1064 nm output light is resonated in the Millennia X cavity and amplified through stimulated emission. An LBO crystal doubles the frequency of 1064 nm photons, providing an output wavelength of 532 nm. A brief description of the laser performance is given in Table 4.1. The Millennia X laser serves as pump laser for the Ti:sapphire femtosecond oscillator (Spectra Physics Tsunami).

Output power	>10 W
Wavelength	532 nm
Polarization	vertical
Beam Diameter	2 mm

Table 4.1: Spectra Physics Millennia X specifications [57].

The Ti:Sapphire Oscillator – Spectra Physics Tsunami

The Tsunami is a commercial solid-state femtosecond laser which operates at 80 MHz repetition rate providing high output power. The active medium is a sapphire crystal rod doped with Ti^{3+} ions. In the six-mirror folded cavity there is a combination of four prisms for the GVD compensation. The Tsunami is tunable between 700 and 1000 nm, whereby four sets of each 10 mirrors are required.

For obtaining femtosecond pulses the cavity modes have to be phase mode-locked. The mode locker used in the Tsunami is an acousto-optic device driven by a low-power radio frequency source. The mode-locker insures 80 MHz nominal pulsing action at laser start up and allows the laser to operate for extended periods of time without dropouts or shut downs associated with passive mode-locking systems. The lock of the longitudinal modes takes place due to the Kerr-Lens mode-locking (see Chapter 2, section 2.1.1). The

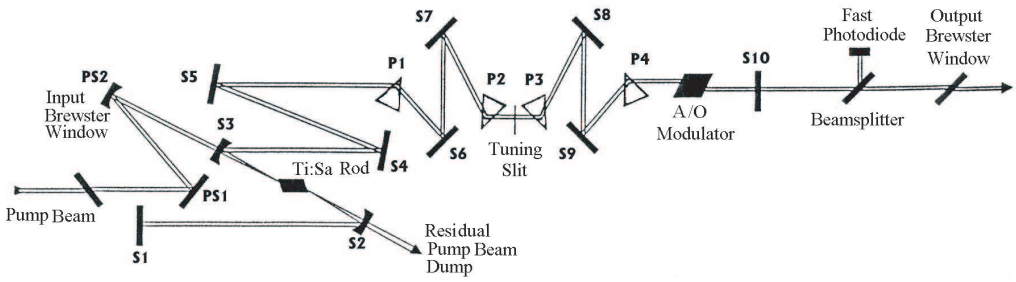

Figure 4.4: Schematic view of the Spectra Physics Tsunami laser head (top view).

Kerr lens effect occurs due to self-focusing of the intense electric field in the crystal, since the intensity distribution is higher in the center than at the wings and the refractive index of the Ti:sapphire crystal becomes intensity dependent. In the resonator cavity (see Figure 4.4) the stronger focused frequencies are more amplified. An algorithm adapts the frequency of the acousto-optic modulator to the instantaneous repetition rate. This concept is also known as regenerative mode-locking [15]. The amplification of different modes[11] in the laser cavity is limited by losses in mirror coatings and polished surfaces and, more importantly, the residual loss in the Ti:sapphire material itself. This loss is proportional to the rod length and varies with the Ti^{3+} concentration, generally increasing as the Ti^{3+} concentration increases.

The laser pulses are later focused by a lens (f = 200 mm focal length) on the molecular beam. In the focusing region the laser beam has a diameter of ca. 100 μm, corresponding to a maximum pulse peak intensity of 1 GW cm^{-2}. Thus the experiments take place in the linear power regime [53].

Average power	1.2–2.4 W
Wavelength range	740–850 nm
Pulse Width	70–100 fs
Polarization	vertical
Beam Diameter	1.5 mm
Repetition Rate	80.3–80.9 MHz

Table 4.2: Spectra Physics Tsunami specifications [13].

[11] Ten million modes for a 200 nm fluorescence band.

The Regenerative/Multipass Amplifier – Quantronix RegA/MPA

The combination of regenerative and multipass amplifiers leads to a higher output pulse energy, up to 1.7 mJ. Experiments requiring higher pulse energies can now be performed (e.g. $CpMn(CO)_3$). The high peak power allows other nonlinear processes, such as optical parametric amplification of superfluorescence or while light generation. The RegA model 4800 [58] is a commercial amplifier system consisting of two separate units: the stretcher/compressor and the amplifier itself. The stretcher and compressor use the same grating to disperse/compress the pulse. For an input of 7 nJ the amplified pulse reaches approximately 350 μJ (uncompressed). After the additional two-path multipass amplifier (MPA) the pulse energy increases up to 1.7 mJ. The pulse duration depends on the oscillator output (usually is slightly longer). The Pockel-cell (Medox) in combination with a thin film polarizer allows the inlet of the pulse to be amplified and the outlet of the amplified pulse at different time delays, D_1 and D_2. The RegA/MPA was used in Ref. [59] for optimizing the ion yield of $CpMn(CO)_3^+$. In the present work the laser system was realigned on the optical table and optimized for seeding a Non-collinear Optical Parametric Amplifier (NOPA).

Average power	1.5–1.7 W
Wavelength	800 nm (depends on the oscillator output)
Polarization	horizontal
Beam Diameter	2 mm
Repetition Rate	1 kHz

Table 4.3: The specifications of the regenerative amplifier Quantronix RegA 4800 [58].

4.2.2 Femtosecond System – FS II

The cw Pump Laser – Coherent Verdi V-5

Similar to Spectra Physics Millennia X (described in 4.2.1), the pump laser used in FS II is also a cw solid-state frequency-doubled Nd^{3+}-doped yttrium vanadate ($Nd:YVO_4$) laser. The central wavelength is 532 nm and the maximum output power is 5.5 W. The main difference is that Coherent Verdi V-5 has only two assemblies of laser diodes, whereas Millennia X possesses four. The size of the Verdi case is smaller, since the laser head has only one crystal for the population inversion. The type I LBO crystal for frequency doubling is non-critically phase matched and is held around 150 °C. The laser head

is hermetically closed and is mounted on a base plate which can be water cooled or heated (depending on the environment). This allows a stable operating temperature by dissipating the accumulating heat in the laser head. The pump laser can be replaced by a Spectra Physics Millennia V. Table 4.4 summarizes a few of the laser's specifications.

Average power	5 W
Wavelength	532 nm
Polarization	vertical
Beam Diameter	2.2 mm

Table 4.4: Coherent Verdi V specifications [60]

The Titanium:Sapphire Oscillator - Kapteyn-Murnane

This femtosecond oscillator was designed in Kapteyn-Murnane Laboratories [56], with the purpose of generating very short laser pulses (sub-20 fs). In our laboratory the commercially available kit was installed by M. Krenz [23]. The specifications are shown in Table 4.5.

As it can be seen in Figure 4.5, the laser is a folded prism oscillator. There are two paths to be distinguished: the short path (which includes the two curved mirrors and the output coupler) and the long one. The longer path consists of the high reflector, the folding mirror and the two prisms, which compensate the GVD of different frequencies inside the resonator.

The use of the folding mirror reduces considerably the size of the setup. The spectrum is dispersed by the first prism and reflected by the folding mirror onto the second prism. After the second prism, where the frequencies are spectrally separated, a high reflector and a slit are situated. The high reflector redirects the beam back into the resonator. By moving the slit one can choose the desired central wavelength, within the 760–840 nm spectral range. The cavity length is 172 cm, corresponding to 87.2 MHz repetition rate. For achieving Fourier-transformed sub-20 fs pulses one needs to compensate the GVD induced by the output coupler. This can be done by a two-prism arrangement situated outside the laser cavity. The pulse duration of 80 fs was measured without using the prism compressor outside the laser cavity. The laser serves as seed laser for the Quantronix multipass amplifier Odin.

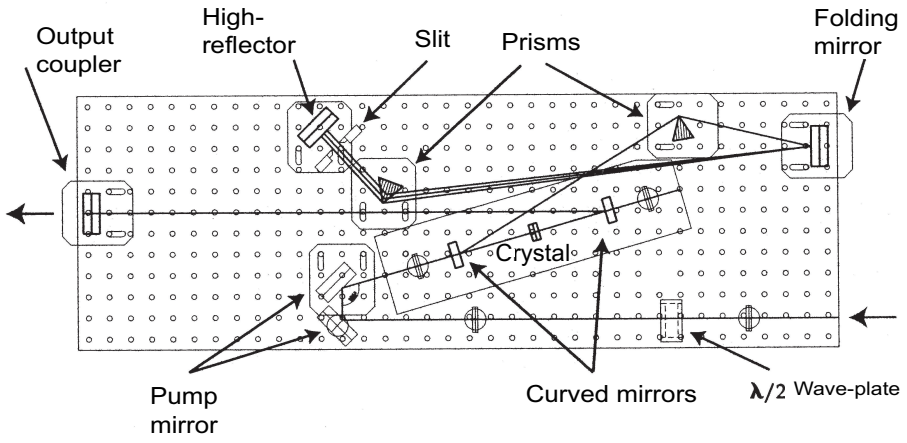

Figure 4.5: The laser head of the home-built Ti:sapphire oscillator based on the Kapteyn-Murnane model (top view).

Average power	600–700 mW
Wavelength	760–840 nm
Polarization	horizontal
Beam Diameter	2 mm
Repetition Rate	87.1-87.3 MHz
Pulse duration	50–80 fs

Table 4.5: The specifications of the Ti:sapphire oscillator used in FS II [61].

The Multipass Amplifier – Quantronix Odin

The femtosecond laser pulses delivered by the previously described Ti:sapphire oscillator are used to seed this multipass amplifier. Odin[12] is commercially available and it has the advantage of providing very short pulses (ca. 40 fs). Compared to the RegA/MPA, there is no cavity resonator in the amplifier. The amplifier crystal is synchronously pumped by a Nd:YLF pulsed laser (Quantronix, YLF 527 DP), which provides pulses of about 120 ns at 1 kHz and maximum 25–27 mJ energy. The Ti:sapphire amplification medium is pumped by only 14–15 mJ.

The incoming beam is first collimated by a telescope. Then the pulses are stretched to approximately 30 ps to avoid damaging the amplifying crystal. The pulse passes through a Faraday rotator consisting of a polarization cube

[12]In Norwegian mythology, Odin is the name of The War God.

and a $\lambda/2$ wave-plate, which hinders any possible reflection back to the oscillator. In this way accidental damage of the oscillator's crystal is excluded. The Pockel-cell (pulse picker) is set to "pick" 1000 pulses from the incoming 87.2 million ones. A photodiode situated between the oscillator and the amplifier sends information about the repetition rate of the oscillator to a frequency divider which is connected to the Pockel-cell driver. This frequency divider reduces the repetition rate to 1 kHz. The operating time window of the Pockel-cell is set, similar to the RegA/MPA amplifier, by two time delays D_1 and D_2. The time window of the Pockel-cell has to be synchronized with the arrival of the pump pulses from the Nd:YLF laser. The pulse is send in the amplification stage, whereby it passes 8 times through the Ti:sapphire crystal. The TEM_{00} mode is spatially filtered by a diaphragm. Then the amplified pulse is recompressed by a set of two diffraction gratings in femtosecond domain.

From an incoming pulse energy of about 7 nJ, after the amplification process the pulse energy is around 1.3 mJ. The output central wavelength of the amplifier can be tuned if the central wavelength of the oscillator is changed, the stretcher does not cut a part of the spectrum and the time delays D_1 and D_2 are adjusted. The multipass amplifier was employed for the measurements on $CpMn(CO)_3$ and its fragment ions, as well as in preliminary adaptive control experiments employing shorter pulses on $CpMn(CO)_2$. The multipass amplifier can serve as pump laser for two optical parametric amplifiers (TOPAS, see the next section).

Average power	1.1–1.3 W
Wavelength	805 nm (depends on the oscillator output)
Polarization	horizontal
Pulse duration	$\leq$40 fs
Beam Diameter	3 mm
Repetition Rate	1 kHz

Table 4.6: Quantronix Odin operating parameters [62].

The Optical Parametric Amplifiers – TOPAS

The name of this laser, reminiscent of the semi-precious stone, is in fact an acronym for T*ravelling-wave* O*ptical* P*arametric* A*mplifier* of S*uperfluorescence*. The principle of optical parametric amplification is described in Chapter 2, section 2.7. A pair of signal and idler waveforms is amplified if the phase matching condition

Output energy	3 μJ (UV); 30 μJ (VIS); 175 μJ (IR)
Wavelength	250–2600 nm
Polarization	depends on the output wavelength
Pulse duration	$<$ 40 fs
Beam Diameter	$\leq$2 mm
Repetition Rate	1 kHz

Table 4.7: TOPAS operating parameters [23, 63].

$$n_{pump} \cdot \omega_{pump} = n_{signal} \cdot \omega_{signal} + n_{idler} \cdot \omega_{idler}, \tag{4.8}$$

is satisfied simultaneously with the energy-matching condition

$$\omega_{pump} = \omega_{signal} + \omega_{idler}. \tag{4.9}$$

Thus the output frequencies ω_{signal} and ω_{idler} can be tuned continuously by changing the refractive indices n_{signal}, n_{idler} and n_{pump}. This is done by controlling the temperature of the crystal, its orientation or the electric field applied on the crystal. As pump laser, the fundamental beam of the previously described multipass amplifier (Quantronix, Odin) is used, but TOPAS can be also pumped by the second- or third-harmonic of Neodymium lasers, as well as second-harmonic of Ti:sapphire lasers.

In TOPAS there are four amplification stages, whereby the beam passes five times through the nonlinear BBO crystal [63]. In the first stage the broad-banded superfluorescence (white light) is generated in the BBO, which serves as seeder for the next passes. The second and the fourth passes (also called pre-amplifiers) shape the laser beam, by acting as a small amplifying aperture. In the first three passes the frequency is selected by a diffraction grating. The parametric amplification (generation of the signal wave and the corresponding idler wave) takes place between the pump pulse and the selected frequency in the fourth trip of the beam through the crystal. The amplification is negligible in the third pass. The highest parametric efficiency is achieved in the fifth pass, whereby the amplified pulse is pumped by a large quantity (90 %) of the rest pump beam. The overall energy conversion into parametric radiation is about 15–20%. A residual (unconverted into parametric generation) pump wave is still available at the laser output, which can be optionally blocked, so that only signal and idler waves leave the laser.

At the laser output one or two optional frequency converters (mixers) are situated. They are nonlinear crystals (BBO type I and II) for frequency doubling/mixing and their role is to generate either second-harmonic of TOPAS

signal (SHS) and/or idler (SHI) or to mix the pump beam with TOPAS signal (SFS) and/or signal (SFI) by generating sum-frequency. Second-harmonic of the sum-frequency of the signal (SHSFS) and/or the idler (SHSFI) or the fourth harmonic generation of the TOPAS signal (SHSHS) and/or idler (SHSHI) are also possible. The mixers are installed on a computer controlled rotation stage, which can be easily operated with the delivered software package (WinTopas for Mixer1 and/or Mixer2) through a parallel interface. Wavelengths in the 250 nm–2.6 μm spectral range can be generated.

There are two TOPAS in our laboratory, both pumped by approximately 500 μJ from Odin. The main difference between them is that on one is only one mixer module installed, whereas the other has two frequency converters.

An interesting feature of TOPAS is that it can be tuned throughout the whole range without replacing the optics. This is because the pump beams are directed by dielectric mirrors and the signal beam path contains metal-coated mirrors.

The two TOPAS were successfully employed in the experimental studies on sodium-fluorides described in Chapter 7. Table 4.7 summarizes the operating parameters of the two optical parametric amplifiers.

4.3 Acquisition of the Experimental Data

During a measurement session the data is acquired by several personal computers (PCs).

1. The $\mathbb{A}$ computer records the pump–probe measurements, mass spectra and the SHG FROG traces. The optical delay table is also controlled. The program was developed by S. Rutz [53] in LabView 4.0. An A/D controller[13] digitalizes the analog signals from the QMS, LT detector, photomultiplier(s) and photodiode(s). The following signals are monitored/recorded for the corresponding experiments:

- QMS ion signal — mass spectra, pump–probe,
- CCD signal — SHG FROG traces,
- LT signal — monitoring of the neutral cluster beam.

2. The $\mathbb{B}$ computer measures the evolution of the optimization algorithm and the cross-correlation signals of the (un)shaped laser pulses. The software which controls the SLM and the implementation of the feedback-loop in the experiment was developed by P. Wetzel [64], and A. Bartelt [20] in LabView 5.1 and later by S. M. Weber [40] in LabView 6.i. The signals mentioned below are monitored/recorded for the corresponding experiments:

[13] Stanford Research Systems, Inc., model SR 245, Sunnyvale, CA, U.S.A.

• QMS ion signal — optimization algorithms,

• LT signal — observation of the neutral cluster beam in the optimization experiments,

• photomultiplier signal — cross-correlation of (un)shaped pulses,

• photomultiplier signal — XFROG traces.

3. The $\mathbb{C}$ computer monitors the spectrum of the Ti:sapphire oscillators and amplifiers and of the two TOPAS. The LabView 5.1 software developed by M. Krenz [23] allows its acquisition. The spectra of the shaped pulses are also measured by the optical fiber spectrometer[14].

4. The motors driving the two TOPAS are software controlled by the $\mathbb{D}$ computer. The software (WinTopas) is commercial.

5. Another PC is used for drilling the nozzles into the oven plates. The software was developed by B. Baptist in LabView 4.0 [50]. The 70 μm diameter drill is mounted on a air-cooled rotation stage and it is driven by a translation unit[15]. The drilling procedure depends on the plate thickness, the drilling speed forwards and backwards. Usually a nozzle is drilled in less than an hour.

[14]Ocean Optics Inc., Dunedin, FL, U.S.A.

[15]Physik Instrumente (PI), Karlsruhe, Germany.