Extending the pump energy range for a pump-probe system using High Harmonics Generation

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May 2015

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ABSTRACT

The presented project takes place in the field of Molecular and Condensed Matter Physics in which knowing more about the microscopic behavior of matter is of great interest. Probing matter is however barely achievable with classical techniques since the smaller the scale is, the finer the probing technique needs to be. When dealing with physical phenomena of the order of nanometers, the only suitable tool is light which has the advantage to be adaptable to different wavelengths. Laser pump-probe is a widely successful technique used to understand small and complex systems at ultra-fast time scales. Helios, standing for High Energy Laser Induced Overtone Source [1], is a versatile facility designed for time resolved spectroscopy experiments using high harmonics generation as a probe source. In more concrete terms, this means that high energy photons are produced and their microscopic interaction with matter can be recorded as a function of time. The physical idea behind the pump-probe technique is quite simple. As an illustration, consider a sample of which the transmission properties at a microscopic scale need to be explored. In order to get any information, the sample must be perturbed and analyzed according to the light it transmits when this perturbation occurs. Photons are used for both perturbation and probing. There are then two laser beams involved in the experiment, a pump beam for perturbing (exciting from the ground state) and a probe beam that sweeps the system in the perturbed state and then makes it possible to notice any change in its transmission. Helios is based on this pump-probe beam configuration.

Figure 1: Pump-probe experiment [2]

The project was focused on second harmonic generation (SHG) and third harmonic generation (THG) on the Helios’ pump beam. This process allows the conversion from the fundamental frequency (800 nm) into another pulse of two and three times the frequency of that fundamental. Ti:Sapphire lasers are centered at 800 nm, second and third harmonics are then 400 nm and 266 nm respectively. Those lower wavelengths are useful because a smaller wavelength has a higher energy and the wavelength is chosen based on the sample’s energy needs to be perturbed in the experiment. 800 nm laser beams are sometimes sufficient but for higher energy demanding experiments, for instance when band gaps in materials are large, SHG and THG are a solution.
CONTENTS

1 Aim of the project 3
2 Overview of Helios 4

3 Notions and optical effects to be considered 6
  3.1 Short laser pulse 6
  3.2 Signal amplification 8
  3.3 High Harmonic Generation 8
    3.3.1 Second Harmonic Generation 9
    3.3.2 Third Harmonic Generation 11
  3.4 Group Velocity Mismatch 11
    3.4.1 Sellmeier equation 12
  3.5 Cross and auto-correlation 12

4 Design of the Second and Third Harmonic Generation setup 14
  4.1 Femtokit 14
  4.2 Beam de-expander 14
  4.3 Auto-correlator 15
  4.4 Global setup 16

5 Settings and measurements 19

6 Applications 21
1 Aim of the Project

The project’s goal was to extend the range of wavelengths of the pump beam by using a second harmonic crystal to produce the second harmonic of the laser and then to produce the third harmonic by frequency summation of the second harmonic with the remaining fundamental wavelength. The pulse duration had to be measured to figure out how much it is altered by those processes. The whole system had to be easy to insert and non invasive. The project involved purchasing mounts and crystals in order to construct the tripler system and to design a telescope system to achieve power densities suitable for the non-linear processes involved. The properties and consequences of the choice of optics are discussed in the report.
An overview of Helios features will be given in this paragraph which will be referred to in the report. The whole device can be approximately broken into five parts incorporating the laser pulse generation, its amplification, the pump beam, the probe beam and the sample itself.

![Schematic of Helios’ setup](image)

The photon source is a Titanium-Sapphire laser (Coherent Mantis oscillator) which generates pulses centered at 800 nm and a time width of the order of 35 fs which changes depending on the repetition rate of the laser. A Coherent Legend Elite Duo amplifier amplifies the signal up to a maximum of 2.5 mJ. The amplification process is explained in Section 3.2. Both signal generation and signal amplification are denoted A on Figure 2.1. The amplified laser beam is then divided into two beam lines in the area B on Figure 2.1 which form the pump beam (0.1 mJ) and the probe beam (0.516 mJ).

The **probe beam** is focused into a gas cell where a HHG (High Harmonic Generation) process takes place. Most of the fundamental wavelength remains unconverted to XUV and is present in the output of the gas cell and input of the monochromater. The monochromater is used for filtering the 800 nm component and for spectrally selecting one desired wavelength from the produced harmonics using a diffraction grating and slit combination. Without going into detail, it is important to mention that the monochromater was designed from the perspective of pulse duration conservation, high transmission and fine wavelength selection. The selected pulse is reflected into the final beam routing chamber where it is directed to the sample. There exist two beam lines leading to two end-stations; one for ultra-high vacuum (UHV) required experiments and one for non UHV experiments.

The **pump beam** passes through a delay stage which is an element of great importance in the setup since it makes it possible to control the delay between the pump and the probe pulses. It is then possible to know the sample’s state at any time (before, while and after perturbation). This is a common technique in research used for time resolved experiments. The pump beam is then reflected into one of the two end stations.
The trippler system was made on the UHV pump beam line between the flip mirror and the entrance to the beam routing chamber (area C on Figure 2.1). After generation, there are three out coming beams with wavelengths 800 nm, 400 nm and 266 nm. In the case of lenses, optics were chosen to transmit at all three wavelengths and in the case of mirrors, combinations of different mirrors and beam splitters were chosen to reflect particular wavelengths while absorbing or transmitting others (see Section 4) and to make pulse duration measurements possible. The pulse duration measurement uses an auto-correlator that requires wavelength combination to operate. More details are given in Sections 3.5 and 4.

References to the different elements of Helios will be brought in the following sections to illustrate the physical phenomena taken into account when developing the setup for SHG, THG and pulse time width measurement. Some examples of Helios application made possible by an extended range of wavelengths will be given in the last section.
3 NOTIONS AND OPTICAL EFFECTS TO BE CONSIDERED

3.1 Short laser pulse

Pump-probe time resolved experiments make reference to fine control of the delay between pump and probe pulses but also to the pulse time width itself. Generating very short pulses requires a particular treatment of light [3] [4]. The main thing to remember is the relation between spectral and time widths of a pulse. The spectral width is obtained from a spectroscopic measurement of the laser pulse and is related to the minimum temporal pulse width achievable according to Heisenberg uncertainty principle \( \Delta E \Delta t = 1.82 \text{ eV}.\text{fs} \) [5] meaning that the shorter a pulse, the broader its spectrum.

This is of great importance not only for the short pulse generation but also for its conservation along the different paths in Helios. Such pulses are obtained with the so-called mode locking method. How photons are created in a laser will not be detailed, only a simple overview of what mode locked lasers do will be given. The photon source originates from a gain medium which amplifies the signal. This medium is mounted in between two mirrors with reflections of 100% and about 99.9%. This makes a cavity up of length \( L \). As for a Fabry-Perot cavity, the resonance condition imposed by the length \( L \) gives the allowed modes. The mode locking method is based on the arrangement of those modes in phase which leads to constructive interferences at the mirror boundaries.

Amplification will occur when the modes resonate with the gain medium. Once maximum gain occurs in the system, the laser will operate with a single mode configuration called CW operation. The laser
can be made to operate in a multi-mode configuration by slightly changing the length of the cavity. This allows multiple modes to resonate with the gain medium and increase the bandwidth of the laser. As said previously about the pulse duration, the shorter time, the broader spectrum. Consequently, the pulse time width depends on the number of modes interfering.

![Figure 3.3: Time width dependence on the number of modes][2]

Once short pulses are generated, they must be preserved through the different optics because their frequency can vary in time. This effect is called chirping. A pulse of which the frequency increases in time is called positively chirped pulse and negatively chirped when the frequency decreases. Most materials introduce negative chirp.

![Figure 3.4: Two types of chirps][2] (a) Positive chirp (b) Negative chirp

As for the time width depending on the number of modes, a modification of the frequency also alters the pulse duration.

![Figure 3.5: Chirp effect][2]

If the out coming beam is broader than that incoming, the pulse duration is left with being lengthened. The chirping is due to the frequency dependence of a medium’s refractive index. It has to be kept in mind that any medium chirps a pulse, therefore the aim is to limit this effect by choosing optics that have as small as possible a variation of refractive index with frequency.
3.2 Signal amplification

This section was not of greatest importance for the project but the beam path in the amplifier had to be realigned and the trick in the amplification process makes it an interesting component of Helios. At the output of the laser, the constraints are to amplify the mode locked signal and preserve its pulses duration. This cannot be achieved with common amplification techniques because the power of the beam with short pulses would damage the optics during the process. The way to get round the problem is to use the so called chirp pulse amplification (CPA) technique [7] [3] which is based on the dispersion of a pulse’s spectrum in time, its amplification and its compression.

![Chirp Pulse Amplification](image)

3.3 High Harmonic Generation

High harmonic generation is a non linear optical process that occurs in gases and plasmas [3] [4] [7]. In concrete terms, such a material inserted in a beam path transforms the incoming beam of frequency $\omega_0$ in an out going beam of frequency $n\omega_0$ with n an integer. The material has to be subjected to high enough beam intensity. This differs to linear optics in which the incoming frequency equals the out going frequency. To understand what non linear effects are due to and how they differ to linear ones, light matter interaction at small scales needs to be considered. Recall that electrons are bound to atoms through the Coulomb potential.
When electromagnetic radiation reaches matter, its electric field may interact with that of the atoms. This interaction essentially depends on the radiation intensity. For weak intensities, the radiation is only absorbed by atoms and re-emitted during their de-excitation. The wavelength remains the same since the emission energy is equal to the absorption energy which is equal to incoming photon energy. The potential itself does not change during those steps. For intense enough radiation, the Coulomb potential shape is altered which results in a modification of the electrons behavior. If now the oscillating characteristic of a strong incoming radiation is taken into account, one gets an oscillating response of the Coulomb potential which gives rise to an oscillating electron dipole. Electromagnetic field theory states that an oscillating charge emits radiation; a photon of which the wavelength is driven by the amount of released energy during the potential relaxation is then emitted. This directly depends on how much it has been perturbed that is to say on the incoming radiation intensity. This process is called three-step model of tunnel ionization, acceleration and recombination and it is responsible for generation of high harmonics of the incoming beam.

As mentioned before, HHG is a non linear intensity dependent process which means that the induced polarization in the material contains high terms in electric field, not only one as it would be with a linear process.

\[ P = \epsilon_0(\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + ...) \]  

### 3.3.1 Second Harmonic Generation

The polarization shows an electric field component up to \( E^2 \) which means that the second order term holds a frequency of \( 2\omega \) hence second harmonic.

\[ P_{\text{SHG}} = \epsilon_0(\chi_1 E + \chi_2 E^2) \]  

SHG process can be illustrated as follow as caption:
For strong electric field, the population in low excited levels can play the role of ground state for higher excited levels. De-excitation provides photons of $2\omega$ while excitation was made by photons of $\omega$ as shown in the Figure 3.10. In this process, two photons of frequency $\omega$ are annihilated and one photon of frequency $2\omega$ is created. It is important to mention that harmonic generation is not a full conversion process; there is always a major amount of fundamental mode transmitted without being converted.

Generating such photons is however subjected to some constraints. Refractive indices in matter are frequency dependent and given by the dispersion relation. Without going into detail, a phase matching condition between the incoming and produced photons which states that $n(\omega) = n(2\omega)$ must be satisfied. This is achievable in birefringent crystals. A birefringent crystal has the property to show different refractive indices according to the direction it is observed. This results in a split of light polarizations along two axes. The fundamental mode (incoming beam) will then propagate along a so called extraordinary axis and the second harmonic along a so called ordinary axis. Rotating the crystal can make both refractive indices equal. This is called critical phase matching. When both polarizations of the incoming beam are in the directions of the crystal axes, there is no need to rotate the crystal and it is called non critical phase matching. When the incoming beam polarization is perpendicular to that of the second harmonic, the phase mismatch is zero. The latter is called Type 1 phase matching and was used in the setup. The second harmonic is generated at the crystal’s entrance and travels a different path to the fundamental.
3.3.2 Third Harmonic Generation

THG calls on similar rules to SHG. The polarization shows now an electric field up to the power three.

\[ P_{\text{THG}} = \varepsilon_0 (\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + ... ) \]  \hspace{1cm} (3.3)

THG can be achieved by tripling the incoming radiation frequency as it was doubled for SHG process or a combination of two incoming beams. The combination process is called Sum or Difference Frequency Generation (SFG or DFG). Those processes can be illustrated as follow as caption.

![Figure 3.12: Third Harmonic Generation](image)

![Figure 3.13: THG through Sum Frequency Generation](image)

THG is weaker than SFG and DFG so the third harmonic is usually generated using SHG followed by SFG rather than by direct THG. This configuration was then used. The phase matching condition for SFG is achieved by using the previous Type 1 mismatch technique.

3.4 Group Velocity Mismatch

Harmonics generation process itself is bad for the pulse duration conservation. When the phase matching condition is reached, it usually works for the central wavelength of the signal but not for the edge (see Section 3.1). Since the bandwidth is large for short pulses, extreme wavelengths see a different refractive index to that central. According to the refractive index definition \[ n = \frac{c}{v} \], the large bandwidth leads to different traveling speeds for each wavelength and consequently lengthens the pulse duration. This effect is called group-velocity mismatch [7] [3] and the signal is chirped (see Section 3.1).

![Figure 3.14: Group velocity mismatch](image)

A dazzler is used to compensate the group velocity mismatch. This is a device that makes it possible to chirp positively or negatively a signal. The idea is then to use a dazzler at the beginning of the setup to overchirp a signal positively by taking into account that optics will chirp it negatively further on. The combination of the dazzler positive chirp and optics negative chirp cancels each other out and re-establishes the initial unchirped signal. It is important to notice that group velocity mismatch and phase matching are two different things. Phase matching concerns the waves relative phases whereas group velocities concerns the speed of one given wavelength in the crystal. The group velocities are generally not matched even when the phase matching is achieved.
3.4.1 Sellmeier equation

In order to estimate how the group velocities evolve in a medium, it is necessary to know how the refractive index behaves with respect to the different wavelengths making the pulse up. This behaviour is given by the Sellmeier equation.

\[ n^2(\lambda) = 1 + \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} + \frac{B_3\lambda^2}{\lambda^2 - C_3} \]  

(3.4)

\( B_{1,2,3} \) and \( C_{1,2,3} \) are usually given with the optical properties of the crystal of interest and they are experimentally measured. Curves of refractive indices calculated from the Sellmeier equation for Fused-Silica and BK7 are given in Figures 3.15.

![Figure 3.15: Refractive indices calculated from the Sellmeier equation (a) Fused-Silica (b) BK7](image)

3.5 Cross and auto-correlation

Measuring events duration requires the measurement device to have a higher time resolution than the event itself. The challenge in measuring femto-second events is that there is nothing available with a higher time resolution at this scale. The trick to measure a pulse duration is to use it and make it interfere with itself. Interference enables one to get a more intense signal and to use non-linear optical properties to partially measure the temporal pulse. To do so, the beam of interest is divided
into two; one of them goes through a delay stage and meets the other in a SHG crystal. The latter transmits pulses that do not overlap (SHG is an intensity dependent process) and generates a second harmonic for constructive interferences that can be seen by a detector. The resulted signal is then analyzed in terms of its intensity plot against the introduced delay. This gives the shape of the pulse and its temporal width. The process is called auto-correlation and can be illustrated by the following schematic.

![Figure 3.16: Auto-correlation process [2]](image)

The same process is feasible with using sum frequency generation with two beams of different wavelengths. This is a cross-correlation process [3].

![Figure 3.17: Cross-correlation process [2]](image)
4 **DESIGN OF THE SECOND AND THIRD HARMONIC GENERATION SETUP**

The technical specifications were to build a SHG and THG system and measure their pulse time width without any heavy intervention in the setup. The main difficulty was to be able to treat three different wavelengths at a time without disturbing their relative phase and their time widths. Initially, the idea was to build one general setup and make it adaptable for SHG or THG by only changing the crystal. This implies that they both had to present the same phase matching conditions and be suitable for a femto-second pulse at a fundamental wavelength of 800 nm (i.e. second harmonic at 400 nm and third harmonic at 266 nm) with a bandwidth of about 40 nm. Such crystals should consequently not absorb at 800 nm and chirp the signal the least as possible (see Sections 3.1 and 3.4). This means that the refractive indices for all the wavelengths in the bandwidth had to be the same or very close and the transmission at 800 nm had to be as high as possible. Refractive indices were worked out with the Sellmeier equation and transmission curves were provided with the crystals. It turned out as mentioned in Section 3.3.2 that THG is not an efficient process and can be replaced by a combination of SHG and SFG which perfectly matches the technical specifications. A kit specially built up for femto-second pulses centered at 800 nm called Femtokit [9] has then been used. Also, all the additional optics are uncoated to preserve the pulse duration.

4.1 **Femtokit**

![Femtokit diagram](image)

SHG and SFG crystals are of Type 1 phase matching and polarization conditions are fulfilled thanks to half wave plates. SFG requires the 400 nm pulse to be in phase and of the same polarization as the 800 nm which is fixed by a group delay compensation plate and a half wave plate. Physical properties of the crystals insure that the group velocity mismatch is close to zero so that pulses are not chirped. Transmissions also match the beams wavelengths. A selection of wavelengths for experiments is made possible with harmonic separators.

4.2 **Beam de-expander**

The Femtokit requires an incoming beam of 2.6 mm diameter; the beam size has then been reduced by using a telescope in front of the Femtokit. This was done by using a plano-convex and a plano-concave lens of which the focal lengths fulfilled the magnification formula:

\[
M = \frac{\text{exit diameter}}{\text{input diameter}} = -\frac{f_2}{f_1} \quad (4.1)
\]

where the exit diameter is 2.6 mm, the input diameter is 13 mm, \(f_1\) is 150.5 mm and \(f_2\) is ~30 mm.
Some information on the beam’s power density and the crystals’ damage threshold is given in the following table.

<table>
<thead>
<tr>
<th>Energy (J)</th>
<th>Pulse duration (s)</th>
<th>Diameter (m)</th>
<th>Radius (m)</th>
<th>Area (m²)</th>
<th>Power density (W/m²)</th>
<th>Eksma quote of damage threshold (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>3.4 × 10¹⁴</td>
<td>0.002159468</td>
<td>0.001079734</td>
<td>3.66255 × 10⁻⁶</td>
<td>8.03041 × 10¹⁴</td>
<td>2.00 × 10¹⁵</td>
</tr>
</tbody>
</table>

Figure 4.2: Characteristics of the beam

The used power density is lower than the damage threshold.

![Figure 4.2: Characteristics of the beam](image)

Figure 4.3: Telescope

The mounted telescope’s features looks like the following caption.

![Figure 4.3: Telescope](image)

Figure 4.4: Telescope setup

4.3 Auto-correlator

Temporal pulse duration measurements of the second and third harmonics are needed for experimental applications. The auto-correlator on which the rest of the setup is totally dependent is used to measure this. Some settings would have to be changed on it according to which wavelength one wants to measure.
**800nm pulse:** No modification on the auto-correlator and only the 800 nm pulse is needed (case on Figure 3.16). The mirrors to guide the signal from the Femtokit to the auto-correlator must reflect only 800 nm. This could be done with a 800 nm mirror provided with the Femtokit and with an Aluminum mirror which reflects a broad band of wavelengths (see Figure 4.7).

**400nm pulse:** One extra component (cross 1) would have to be added to the auto-correlator and both 400 nm and 800 nm pulses are needed for the measurement (case on Figure 3.17). Silver mirrors could be used to guide the two wavelengths to the auto-correlator. Silver mirrors do not reflect 266 nm but do reflect 400 nm and 800 nm (Figure 4.8).

**266nm pulse:** Another extra component (cross 2 different to cross 1) would be needed for the auto-correlator and both 266 nm and 800 nm pulses are needed for the measurement (Figure 3.17). It turned out that the 400 nm component would have to be removed from the input of the auto-correlator because it would have interacted with the beam generated by SFG. Depending on the SHG and THG efficiencies, the amounts of IR, blue and UV at the output of the Femtokit are different. A measurement of the spectrum would inform about those amounts. There are two possibilities to achieve the wavelength selection.

- If the amount of blue is insignificant, an Argon Ion mirror can be used as is. Argon Ion mirrors reflect UV very well and about the same small amount of IR and blue.
- If the amount of blue is significant, the trick could be to use an Argon Ion mirror coated with Aluminum. The coating should be $\frac{\lambda}{4}$ thick with $\lambda = 400$ nm. That would give rise to destructive interferences of 400nm waves.

![Figure 4.5: Argon Ion mirror with Aluminum coating](image)

4.4 Global setup

There are several possible setup configurations due to the different available wavelengths and the different use one can make of them. They are summarized in the following schematics.
Figure 4.6: Selection of one out of three available wavelengths

Figure 4.7: Configuration of fundamental pulse duration measurement

Figure 4.8: Configuration of Second Harmonic pulse duration measurement
After the Femtokit, mirrors are mounted on magnetic bases which allow the configurations to be switched easily.

![Mirror mounts schematic](image)

**Figure 4.9: Mirror mounts schematic**

The apparatus is illustrated by the following pictures.

![Picture of the global setup](image)

**Figure 4.10: Picture of the global setup with the telescope at the bottom and the Femtokit at the top**
5 SETTINGS AND MEASUREMENTS

First of all, it is worth mentioning that the Femtokit presents an orientation dependence that the optics must respect. The crystals are unidirectional and so have to be mounted with a particular side facing the incoming beam. Also, a change in the setup of Helios has been done to allow more power at the input of the Femtokit. The beam splitter in the region B on Figure 2.1 has been changed for a mirror on a magnetic basis to make the switch pump/probe beam easy. The measurements of the harmonics pulses durations have not been possible due to long delivery time and unexpected constraints on the auto-correlator. Spectra of the harmonics have however been recorded.

Figure 5.1: Spectrogram of the signal at the output of the Femtokit

Figure 5.2: Selection of the 266nm and 800nm beams using second and third harmonic separators

Figure 5.3: Selection of the 266nm and 800nm beams using the Al mirror and the second harmonic separator

Figure 5.4: Selection of the 400nm beam using the second harmonic separator

It has to be noticed that the reflectivity of the third harmonic separator is much better than the reflectivity of the Aluminium mirror as seen on Figures 5.2 and 5.4. The Aluminium mirror should reflect all the wavelengths, the amount of UV in Figure 5.4 should then be much higher than what it is.
An anomaly can also be noted from Figures 5.5 and 5.6. The Silver mirror reflects more UV than the Aluminium mirror which should be the opposite. However, there is still a clarification to make on how these spectrograms are recorded since the detector (Toshiba TCD1304) of the spectrometer shows a wavelength dependent sensitivity.

The formula of the sensitivity (see Figure 5.7) would make it possible to correct the previous spectrograms.
6 APPLICATIONS

"Probing molecular systems at a defined delay after an optical excitation with a second laser pulse constitutes the most eminent tool of femtochemistry" [10]

The main idea of using a pump probe configuration is to change the energy of a sample and probe it. Heating the sample with a 800 nm beam can be sufficient as a perturbation but for higher energy excitations, a wavelength in the UV such as 266 nm can be relevant. Generating third harmonics is made through the processes previously discussed. It would have been possible to use an OPA (Optical Parametric Amplifier) as shown on Figure 2.1 to change the wavelength however too much intensity would have been required and too little intensity would have been left for the experiment. 266 nm usually correspond to the energy gap between the valence band and the excited level of interest in the probed material. Most of the time, the studied phenomena by pump-probe experiments occur in a very short period of time after excitation which justifies the use of femto-second pulses. A few examples of what this technique using very short UV pulses can be applied on are given in the next paragraphs.

Dynamics and Reactivity of Trapped Electrons on Supported Ice Crystallites [11]
Excess electrons in low-dimensional water and ice structures are of general importance in atmospheric science, chemistry, biology and astrophysics since electron-driven excitations and relaxation processes can induce reactions spanning a wide range of energy and time scales.
The aim of the experiment is to study how electrons behave in an environment surrounded by water. This is done at the interface between a metal and ice crystallites. Electrons are pumped out of the metal with UV pulses and travel to trapping sites at the interface metal-ice. It is made possible thanks to a spacial overlap between the metal and the conduction band of ice. The UV pulses then excite electrons from the conduction band of the metal to the conduction band of ice. Those de-excite in the trapping sites where the life time is long (up to one minute) so their behaviour in aqueous environment can be studied. They finally travel back to the metal thanks to a second pump excitation out of the traps.

Figure 6.1: Elementary process of the experiment

Ultrafast Evolution of the Excited-State Potential Energy Surface of TiO2 Single Crystals Induced by Carrier Cooling [12]
TiO$_2$ is widely used as a photocatalyst in processes like decomposition of organic contaminants in water purification or as a part in water-splitting set-ups (water to hydrogen gas and oxygen gas). Its band gap is of about 3 eV which makes UV light suitable for band gaps excitation. This motivates time-resolved studies of UV excited states in TiO$_2$ with and without adsorbed molecules.
In this experiment, a TiO$_2$ sample is subjected to ultra short UV excitation. The energy of the pulse
corresponds to the energy gap between the valence band of TiO$_2$ and the excited-state along the A$_{1g}$ optical phonon coordinate. It has been observed that the reflected probe beam shows a shift in its phase after excitation. This is explained by a shift in the potential energy surface minimum induced by the cooling of electron-hole plasma. During excitation, electrons leave the valence band for the conduction band. ”Holes” remain at their original location. The combination electron-hole forms a plasma thanks to the free character of electrons in that conduction band. The cooling of this plasma explains the aforementioned observations.

**Photoinduced Reconfiguration Cycle in a Molecular Adsorbate Layer Studied by Femtosecond Inner-Shell Photoelectron Spectroscopy [10]**

Electronic and structural reorganizations of electrons in molecules during chemical reactions are fast multiple-steps processes. Studying their dynamics requires short pulses and higher or lower energy according to the electrons’ energy levels of interest. UV light induces a change in the molecular structure and consequently in the electronic structure. In this case, 4d electrons of Iodine are investigated, their reorganization occurs and is observable within 50 ps after excitation before relaxing back to the ground state. Such systems can then be used as ”photoswitches” at very fast time scale.

![Figure 6.2: Experimental setup](image-url)
CONCLUSION

The aim of the project was to generate the third harmonic (266 nm) of Helios’ pump beam (800 nm). This was done using high harmonic generation; a small system was then built for that purpose combining the generations of second and third harmonics. Different concepts of non-linear optics were discussed to preserve the pump beam’s pulses duration. Harmonics were well generated and recorded but no pulse duration measurement has been done.
BIBLIOGRAPHY


