UV and IR laser spectroscopy of isolated molecular structural dynamics

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Citation for published version (APA):
Smolarek, S. (2011). UV and IR laser spectroscopy of isolated molecular structural dynamics

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Chapter 2

Experimental details

In this thesis a variety of experimental techniques have been used to study the dynamics of photoactive (bio)molecules by high-resolution spectroscopy. The research presented in Chapters 3 and 6 to 8 on the spectroscopy and dynamics of para-coumaric acid and derivatives, and on diphenylethene uses UV and IR spectroscopic methods in combination with molecular beam techniques. To produce the required wavelength regions in the UV and in the infrared with sufficient output power, various tunable laser systems have been used. The molecular beam set-up serves to produce isolated molecules, and cool them down into their lower vibrational and rotational levels. To obtain well-resolved spectra of medium- to large-sized (bio)molecules, experiments have been performed at ultra-low temperatures by increasing the cooling capabilities. To this purpose, helium nanodroplets have been used that enable one to cool molecules down to ~0.4 K, and record high-resolution UV and IR spectra at this temperature (Chapter 4, 5 and 9). The internal temperatures attained with helium droplets are thus considerably lower than what is possible with molecular beam techniques, but formally the molecule is not isolated.

2.1 Laser systems

The primary tunable light source for the molecular beam experiments is a Nd:YAG-pumped dye laser system (Figure 2.1). The pump laser, a Spectra-Physics Quanta-Ray LAB-190 Nd-YAG laser, produces pulsed radiation at a fixed wavelength of 1064 nm at a repetition rate of 30 Hz and with a pulse duration of 9-12 ns. The Quanta-Ray harmonic generation HG-4B unit is used to produce the second (532 nm) as well as third (355 nm) harmonic with an average pulse energy of 360 mJ and 270 mJ, respectively. The visible and UV radiation of the Nd:YAG laser is used to pump a dye laser (Sirah Precision Scan). Various dye solutions allow for the generation of continuously tunable radiation from 372 nm to 900 nm with pulse energies between 30
and 100 mJ. Depending on the wavelength region of the dye, either the second or third harmonic of the Nd:YAG can be used, resulting in a better efficiency and a longer lifetime of the dye.

The wavelength tunability can be extended to the blue by using the frequency-conversion units integrated in the Sirah laser system. The dye laser output can be frequency-doubled with a conversion efficiency of about 10-15% using either an angle-tuned KDP (63° cut angle) or a BBO (57.4° cut angle) crystal in combination with its corresponding compensation block to minimize beam walk-off resulting from rotation of the crystal used for Second Harmonic Generation (SHG). Both are mounted on synchronously driven rotary posts. The SHG crystals are kept at a constant temperature of 40 °C. The resulting horizontally polarized UV radiation after frequency doubling ranges from 215-280 nm when the BBO crystal is used, and 260-380 nm for the KDP crystal, with pulse energies ranging from 2 to 12 mJ. The correct crystal position required for efficient harmonic generation is obtained by an automatic tuning system, which uses a prior entered table of phase matching angles. To separate the second harmonic beam from the visible dye beam, a set of four Pellin-Broca prisms at Brewster’s angles are used. In this way, both beam displacement and angular beam walk-off are avoided. For experiments where the highest possible output power is required, the separation unit is reduced to two prisms to minimize absorption and quartz-air surface reflection losses. However, the price one has to pay is that now the beam is slightly displaced upon scanning the wavelength.

![Figure 2.1. Schematic overview of the primary laser system in the arrangement for UV generation.](image)

The wavelength can be extended to the near-infrared region by difference frequency mixing (DFM) (Figure 2.2). To generate light at these wavelengths, the dye laser is pumped by the 532 nm beam of the Nd:YAG laser to produce light in the range of 620-900 nm. This beam is further expanded by a telescope, passed through a retarder to obtain the correct polarization, and passed through a dichroic mirror to be frequency-
mixed with the fundamental (1064 nm) of the Nd-YAG pump laser. Temporal overlap is achieved by passing the Nd:YAG fundamental through a delay line. The dye laser and the Nd:YAG fundamental beams are overlapped spatially and mixed in either a LiNbO$_3$ or a MgO:LiNbO$_3$ crystal. In both cases a similar wavelength range can be obtained. However, the LiNbO$_3$ crystal contains water molecules inside its crystal structure, which prevent efficient generation of light in the 2.85-2.90 µm region due to absorption by the OH stretch modes. In the MgO:LiNbO$_3$ crystal this absorption region is slightly blue-shifted towards 2.81-2.84 µm. Interchangeable use of these two complementary crystals allows for generation of IR light in the full range of 1.5-5 µm with pulse energies ranging from 0.5 to 5 mJ. The crystals are kept at 100 °C for temperature stabilization and to avoid water adsorption. The correct phase matching angle is set in the same way as described above for the SHG unit. For the experiments in this thesis it was necessary to have minimal energy losses. We therefore did not use the compensation crystal. As a result, a small walk-off of the IR beam was in principle present. The IR beam is separated from the input beams by a pair of dichroic mirrors. To avoid absorption by water in the air, the IR light was guided to the setup by a system of tubes that are flushed continuously with dry nitrogen gas.

Figure 2.2. The laser system in the arrangement for IR generation.

The second laser system providing tunable UV and visible radiation is based on a dye laser (Lumonics HyperDye 500) pumped by an excimer laser. The excimer laser (Coherent Compex Pro 205) is running on a xenon-chloride (XeCl) gas mixture, emitting 25 ns pulses with a wavelength of 308 nm and a pulse energy ranging from 200 mJ to 400 mJ. Normally, we use pulse energies of 200 mJ to avoid damage of the dye laser optics. The repetition rate can be regulated up to 50 Hz, but for compatibility with the experiments it is set to 30 Hz. The Lumonics HyperDye laser is capable of generating light in the 320-950 nm wavelength region with a pulse energy between 3 and 30 mJ. The shorter wavelength of the excimer pump laser as compared to that of the Nd:YAG pump
laser results in relatively short lifetimes of the dyes. For example, for dyes such as Rhodamine 590, Rhodamine 610, Rhodamine 640 or Coumarin 540A the lifetimes do not exceed 15-20 hours, while in the Nd:YAG-pumped laser system the same dyes last for at least 100 hours before a significant efficiency loss is observed.

To extend for this laser system the wavelength further to the UV, a SHG autotracker was used. This Inrad Autotracker type II equipped with BBO-B and KDP-R6G nonlinear crystals, in combination with their respective walk-off compensation crystals, is capable of producing second harmonic light in the range of 220-285 nm and 282-330 nm, respectively. In contrast to the SHG unit used in the primary laser system, the correct phase matching angle of the nonlinear crystal is tracked automatically via a mechanism that makes use of the beam divergence (Figure 2.3). The resulting second harmonic light has pulse energies in the range of 1-2 mJ and is separated from the fundamental beam by a set of four Pellin-Broca prisms or a Schott UG 5 filter.

A third laser source that is used to produce non-tunable, deep UV light is a Lumonics 700 excimer laser running on an argon-fluoride (ArF) gas mixture and
delivering 20 ns long pulses with a wavelength of 193 nm and pulse energies up to 200 mJ. For compatibility with the rest of the experiments, this laser is operating at a repetition rate of 30 Hz as well, but can in principle work at repetition rates up to 500 Hz. Due to its large beam dimension and its strong divergence only a small part of the produced pulse energy can be coupled into the molecular beam setup. Effectively therefore only 10 mJ is used.

Laser powers are measured with a Spectra-Physics model 407A thermopile detector. The temporal overlap between various laser beams is done by a photodiode coupled to the oscilloscope. To spatially align the IR beam thermo-sensitive liquid crystal sheets (Edmund Optics) are used, even for very low-power beams.

2.2 The molecular beam machine and mass spectrometer

The molecular beam machine used for the experiments described in Chapters 3 and 6 to 8 consists of three chambers: the source chamber, the ionization chamber, and the detection chamber (Figure 2.4).

Figure 2.4. Schematic overview of the molecular beam set-up. To obtain the best vacuum, and for optimal operation, the set-up is divided into three chambers: source, ionization and detection chamber. A bypass line with a valve has been added to avoid damage of the
skimmer due to a possible pressure difference between the ionization and source chambers when the setup is put at atmospheric pressure.

The vacuum is created and sustained by three independent two-stage pump systems. The source chamber is pumped by a 2000 l/s diffusion pump (Edwards Diffstak 250/2000P) backed by a two-stage Edwards E2M40 oil-sealed rotary pump with a pumping speed of 42.5 m$^3$/h (~11.6 l/s). After venting the molecular beam set-up, this backing pump is used to create an initial vacuum at a level of around 10$^{-3}$ mbar in order to avoid the damage of other pumps and contamination of the system with pump oil. In this case the bypass line is used to connect the Edwards E2M40 pump directly to the vacuum chambers. Because diffusion pumps cannot be operated at pressures higher than 10$^{-4}$ mbar because of the risk of oil burn, the setup is equipped with a safety valve that automatically closes off the diffusion pump from the rest of the molecular beam set-up in case of any electrical power failure that could lead to loss of vacuum. The source chamber is connected to the ionization and detection chamber by a skimmer with a 2 mm orifice to select the coldest part of the molecular beam and to maintain a low pressure in the other chambers. Both the position of the skimmer as well as the position of the molecular beam source can be regulated to provide the highest possible density of molecules in the ionization chamber and to reach optimal cooling conditions.

The vacuum in the ionization and detection chamber is sustained by two similar Pfeiffer turbomolecular pumps. The ionization chamber is pumped by a 520 l/s turbo pump (Pfeiffer TMH 521 P) backed by a two-stage rotary pump (Pfeiffer DUO 10, 10 m$^3$/h, ~2.8 l/s), the Time of Flight (TOF) detection chamber by a Pfeiffer TMH 261 P (pumping speed of 210 l/s) turbo pump backed by a DUO 5 (5 m$^3$/h, ~1.4 l/s) rotary pump. The pressure is monitored at key places of the setup by Pfeiffer pressure gauges. Three two-head systems (Pirani and hot cathode) are connected to the main vacuum chambers: model PBR 260 for the TOF chamber and model PKR 251 for the ionization and source chambers (separate gauges). Pirani gauges model TPR 256 are used to monitor pressures between all first and second stage pumps. The pressure is read from a Pfeiffer TPG 256A MaxiGauge controller. Typical pressures with the molecular beam running are 2·10$^{-5}$ mbar for the source chamber, 5·10$^{-7}$ mbar for the ionization chamber and 2·10$^{-7}$ mbar for the detection chamber. Without the molecular beam typical pressures are 2·10$^{-7}$ mbar, 5·10$^{-8}$ mbar and 4·10$^{-8}$ mbar in the source, ionization and detection chamber, respectively.

The detection part of the molecular beam setup closely follows the design reported in ref. [1]. In this setup mass-resolved ion detection is performed with the Jordan Co. D-850 Angular Reflectron Time-Of-Flight mass spectrometer (Figure 2.5). The molecular beam crosses the UV and IR laser beams halfway between the repeller ($V_{A1}$) and extractor ($V_{A2}$) plate. The ions produced in the interaction region are accelerated and steered by deflection plates ($V_{XY}$) into the time-of-flight tube, which in the linear
configuration is 110 cm long. At the end of this time-of-flight tube the ions hit a 18 mm
dual microchannel plate detector (Jordan Co. C-701). To expand the time-of-flight zone
to 190 cm and to compensate for the velocity distribution of ions with the exact same
mass - due to the fact that ionization does not occur in one single point but in a finite
physical space volume, ions are accelerated with different starting velocities - an angular
reflector can be used (Jordan Co. C-852). The C-852 reflector assembly is composed of
an entry grid which normally is grounded or at the potential of the flight tube potential.
Behind this entry grid lies the first repeller grid \((V_{R1})\), followed by several plates resulting
in a uniform repelling field. The last element is a repeller grid that is put at a reflection
potential \((V_{R2})\) or can be grounded to run the set-up in a linear detection mode. After
passing through the reflector and the second time-of-flight region, the ions are detected
by a 40 mm dual microchannel plate (MCP) detector (Jordan Co. C-726) with a gain of
up to \(10^7\). The mass resolution \(\Delta m/m\) of this system lies between 1500 and 4000
depending on the quality of the ion source. Since the mass of the molecular systems
studied in this thesis never exceeded 500 amu, single mass resolution could always be
achieved.

Apart from mass-resolved ion detection, the set-up is also equipped for electron
detection. To this purpose photoelectrons are steered into a \(\mu\)-metal time-of-flight tube of
14.3 cm and detected by an 18 mm dual MCP detector (Jordan Co. C-701). Although it
should be possible to obtain to some extent electron kinetic energy resolved detection,
initial attempts have not been encouraging. For the experiments in this thesis electron
kinetic energy resolved detection is not necessary, and no further efforts have therefore
been made to optimize this aspect.

![Figure 2.5. Overview of the angular reflectron D-850 Time of Flight mass spectrometer
used for both ion and electron detection, showing the flight path of ions when the
reflector is used. The potentials \(V_{A1}\) and \(V_{A2}\) are used to accelerate ions or electrons into
the flight tubes. The distance between the A1 and A2 plates is 13.3 mm, while the distance
between A2 and the first grounded plate is 12.7 mm. The potentials \(V_{XY1}\) and \(V_{XY2}\) are
used to direct the ion beam towards the detector. \(V_{R1}\) and \(V_{R2}\) are used to reflect the ions](image-url)
towards the C-762 MCP detector. The C-701 MCP detector can be placed at either one of two indicated positions.

The signal recorded by the MCP detector is converted into a digital form by a Tektronix TDS 3052 digital oscilloscope and read out by a PC. The time of flight of ions, that is, the time between ionization and arrival of the ions at the detector, is given by the equation:

\[ TOF = a + b \cdot \sqrt{m}, \quad (7) \]

where \( m \) is the mass of the ion in atomic units, and \( a \) and \( b \) are constants determined by the experimental conditions. To calibrate the mass spectrometer, the time of flight of two molecules with known masses are measured. Another way to calibrate is to measure with a fast photodiode the time interval between the moment of the laser pulse arrival at the setup (which is the same as the moment of ionization), and the triggering of the oscilloscope. This directly corresponds to the factor \( a \). The \( b \) factor can then be determined by measuring the time of flight of only one known mass. Values of the factors \( a \) and \( b \) depend on the accelerating potentials, but are typically in the range of 2.75-3.0 \( \mu s/(u)^{1/2} \) for \( b \) and less then 0.5 \( \mu s \) for \( a \).

### 2.3. Supersonic molecular beam sources

To study molecules of interest in the gas phase, two molecular beam sources employing different sample seeding techniques have been used. The first is based on a simple evaporation or sublimation process. The solid or liquid sample is placed into a small glass container that is heated by an electrical coil. A noble gas (normally helium) with a regulated pressure between 0.5-3 bar is mixed with the vapor of the sample and is led towards the vacuum chamber. The mixed carrier gas - sample vapor is expanded into the source chamber by a General Valve nozzle (Parker Series 9 pulsed valve). This system produces a pulsed molecular beam with a pulse duration between 160 to 300 \( \mu s \) and can be heated up to 220 °C. The sample holder and nozzle are heated separately to allow for keeping the valve slightly warmer (usually by 5 °C) than the sample holder to avoid clotting of the sample at the orifice. A simple scheme of the thermal seeding molecular beam source is presented in Figure 2.6.
Figure 2.6. Overview of the thermal seeding molecular beam source. The seed gas passes through the source from the top to the bottom. The magnetic actuator lifts the poppet and in this way opens the orifice to the vacuum.

The nozzle can have different orifice diameters (0.2 mm, 0.5 mm or 1.0 m). A larger opening to the vacuum results in a more efficient transport of the sample to the spectrometer, while for creating and measuring molecular clusters a smaller opening is preferable. These dependencies can be expressed quantitatively by the following equations [2, 3]:

\[ P_{3b} \sim p_0^2 \cdot D \]
\[ M \sim p_0 \cdot D^2, \]  

where \( P_{3b} \) is the probability of three-body collisions in a supersonic molecular beam (clusters can only be created by three or more-body collisions), \( M \) the total mass transported in the supersonic beam, \( p_0 \) the backup pressure, and \( D \) the orifice opening diameter. Assuming two sets of expansion conditions: \((p_{01}, D_1)\) and \((p_{02}, D_2)\) in which the same mass is being transported to the spectrometer:

\[ p_{01} \cdot D_1^2 = p_{02} \cdot D_2^2 \]

one can easily derive the following equation:
\[
\frac{(P_{3b})_2}{(P_{3b})_1} = \frac{(p_{02})^2 \cdot D_2}{(p_{01})^2 \cdot D_1} = \left(\frac{D_1}{D_2}\right)^3.
\]  

Equation (4) shows that when the molecular beam is transporting a constant amount of gas, the probability of cluster creation is inversely proportional to the cube of the orifice diameter.

The supersonic expansion of isolated sample molecules seeded in an inert (mostly noble) gas results in efficient cooling. Due to the collisions inside the supersonic jet, the molecular velocity distribution becomes very narrow, which corresponds to a low translational temperature [4-7]. Additionally, since the expansion occurs isoentropically [8-10], these collisions transfer the cooling effects from translational to rotational and vibrational degrees of freedom [5, 9, 10]. Due to this energy transfer pathway and because of the density of energy levels, the cooling efficiency is highest for translational degrees of freedom, less for rotational degrees of freedom, and the lowest for vibrational degrees of freedom. Since cooling is directly related to the collisions between the sample molecules and the atoms of the seed gas, it is most efficient in the region a few mm from the nozzle opening, where the molecular beam is dense and collisions are numerous. In the end, translational temperatures of the sample molecules well below 1K can be easily obtained [10], while rotational and vibrational temperatures can be expected to be on the order of 2-10 K and over 20 K, respectively [3, 11-13]. Consequently, as compared to non-isolated, room-temperature conditions very high-resolution spectroscopy can be performed where single vibrational levels can easily be distinguished and the linewidth is often only limited by the spectral resolution of the laser source.

Another method to produce isolated sample molecules is based on the process of laser desorption [13-16]. This method can be used for samples which are either non-volatile or would fragment upon heating. The laser desorption source is based on the same General Valve nozzle (Figure 2.7). Here, the sample is grinded and rubbed onto a porous graphite sample bar, which is placed close to the nozzle orifice in the source chamber. The sample is brought into the gas phase by desorbing it from the graphite sample bar with a nanosecond Nd:YAG laser (New Wave model Polaris II 30 Hz) operating at 1064 nm and low energies (about 1-3 mJ). By synchronizing the desorption laser with the opening of the nozzle and aligning the sample bar surface with the nozzle orifice, the sample is produced inside the “high collision number” cooling part of the supersonic molecular beam. The desorbed sample molecules are redirected towards the mass spectrometer and cooled by collisions with noble gas atoms.
Figure 2.7. Schematic representation of the desorption source. The seed gas passes through the nozzle from the top to the bottom. The graphite bar moves in the direction perpendicular to the surface of this figure.

During the measurements the graphite bar is slowly moved perpendicularly to the desorption laser beam to provide a fresh sample at every laser shot. This motion is induced by a PI N-310 NEXTACT miniature piezo motor with an average speed of 0.02 mm/sec at the 30 Hz repetition rate used in the experiments. Since the length of the bar is about 70 mm, a one hour scan with ~$10^5$ acquired data points can be performed before the sample needs to be replaced. A similar piezo motor is also used to align the position of the graphite bar position with respect to nozzle orifice in the direction perpendicular to the travel direction. The sample bar can be removed and replaced without venting the vacuum setup by a small air lock.

The availability of two different sources (thermal and desorption) to produce gas-phase molecules provides a large flexibility in choosing the most efficient way of creating cooled, isolated sample molecules. The heatable source is used for liquid samples or solid state samples with a relatively high room temperature vapor pressure. In most cases this is correlated with the size of the molecule. In general, we can say that for molecules lighter than 300 a.m.u. the heatable source is an easier and completely sufficient choice. Heating the sample to higher temperatures can be achieved for other molecular systems as well, but in many cases this leads to thermal dissociation of the sample before the desired vapor pressure is obtained. Laser desorption is used for thermally unstable and non-volatile samples. Because one has to change the sample every hour, and because of the additional alignment of the sample bar position and the time overlap with the seed beam and excitation/ionization laser, it is a more demanding technique. However, it provides the possibility of measuring a much wider range of samples. The size and complexity of the molecules is more or less unlimited, even
complex molecular systems such as rotaxanes [17], clusters of DNA-bases [16] and large peptides with masses up to 1900 a.m.u. [18] have been measured using this laser desorption technique. However, generally for these large systems the cooling efficiency of the supersonic molecular beam is not sufficient [19, 20], resulting in broad UV excitation spectra that do not allow for conformational distinction.

Different inert gases are used as a seeding gas to produce the molecular beam. Depending on the size of the molecules and the method to bring these molecules in the gas phase, a suitable noble gas is selected [3, 11, 12]. In general, for the small-sized molecules produced by the heatable nozzle helium or neon is used to obtain optimal cooling. For these systems argon or xenon can lead to lower temperatures, but at the price of the formation of noble gas clusters with the sample molecule that interfere with the measurements. In the laser desorption experiments on medium- or large-sized molecules, the plume of desorbed molecules is produced at right angles with the supersonic gas expansion. The desorbed molecules must thus undergo a large change in velocity direction. Normally, one therefore uses argon to acquire sufficient cooling. Moreover, in some cases xenon would be preferred to enhance the cooling conditions.

A simple seed gas supply system consisting of gas lines, pressure regulators and valves provides not only easy control over the type of gas and its pressure, but also allows for the preparation and usage of gas mixtures. A schematic overview of this system is presented in Figure 2.8.

![Figure 2.8. Scheme of the gas supply system for the molecular beam setup.](image)

The inlets for gas bottles 1 and 2 are interchangeably used for helium, neon, or argon. The pressure of the seed gas can be adjusted by a pressure regulator in the range of 0 to 10 bar. Whenever a different type of gas was used, the complete system can be pumped with a vacuum pump to remove the “old” gas after that the pressure is reduced to 1 bar by opening the atmosphere outlet in order to prevent pump damage. A special short
connection is used for xenon with the pressure regulator connected directly to the bottle to minimize the loss of expensive xenon. The gas supply system is also used to create mixtures of noble gasses in order to optimize the cooling capabilities in the supersonic expansion. In this case, the desired gases are first injected at the required pressures one by one into a mixing bottle. Subsequently, the mixture is used with the on-bottle pressure regulator. An external pick-up cell has been incorporated into the gas supply system to form clusters with, for example, water or methanol. To produce these methanol or water clusters, the seed gas of choice passes through the solvent to pick up these molecules and make the appropriate mixture that is used as carrier gas. Collisions with the sample molecules during the expansion then result in the required clusters. This pick-up cell can also be used for samples with high vapor pressures, since in that case heating is not necessary.

The amount of noble gas that is used during the experiments can be estimated using the thermodynamics of ideal gases. According to the ideal gas theory, the number of gas atoms transported via the orifice of a surface $A$ during a time $\Delta t$ is given by

$$x = \frac{A \cdot \Delta t \cdot N_A \cdot P}{2 \sqrt{M \cdot R \cdot T}}.$$  \hspace{1cm} (5)

where $N_A$ is Avogadro’s number, $P$ pressure of the gas, $M$ the molar mass of the used gas, $R$ the gas constant, and $T$ the gas temperature. This can be further converted into the volume of the gas at a pressure of 1 bar:

$$V_{i,\text{bar}} = \frac{A \cdot \Delta t \cdot P}{1 \text{bar}} \frac{R \cdot T}{2 \sqrt{M}}.$$  \hspace{1cm} (6)

For standard experimental conditions, i.e., a nozzle diameter of 0.5 mm ($A \approx 2 \cdot 10^{-7} \text{ m}^2$), $P=2$ bars, $T=300 \text{ K}$ and a gas pulse duration of 220 $\mu$s at a repetition rate of 30 Hz, the use of the different gasses is given in Table 2.1.

**Table 2.1. The use of different carrier gasses under standard experimental conditions.**

<table>
<thead>
<tr>
<th></th>
<th>Helium</th>
<th>Neon</th>
<th>Argon</th>
<th>Xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.6 [l/h]</td>
<td>1.6 [l/h]</td>
<td>1.2 [l/h]</td>
<td>0.6 [l/h]</td>
</tr>
</tbody>
</table>
2.4 Synchronization

To synchronize the laser pulses and the molecular beam, two Stanford (SRS DG535) and one Berkeley Nucleonics (BNC 575) pulse delay generators operating at a 30 Hz repetition rate have been used. Figure 2.9 shows the timing sequence used for a standard three-laser experiment. The lasers are triggered directly by normal TTL pulses. The opening of the nozzle in both beam sources is regulated by the Iota One Valve driver (Parker Hannifin) which also controls the duration of the pulse.

![Diagram of timing sequence](image)

Figure 2.9. Example of a commonly used sequence for triggering the different setup elements in case of a three-laser experiment. Nozzle opening is triggered by $T_0$ pulse.

To ensure optimal overlap between the molecular beam and the UV excitation beam, the delay time $\Delta T_2$ is set such that the arrival time of the sample molecules coincides with the laser pulse. This arrival time is determined by the distance between the molecular beam source and the ionization region (see Figure 2.4), as well as the carrier gas that is used. When the experiments are performed with the laser desorption source, the delay time $\Delta T_1$ can be set to optimize the timing of the desorption pulse with respect to the molecular beam pulse. The optimal values of both $\Delta T_1$ and $\Delta T_2$ depend on various experimental conditions, but are mainly influenced by the carrier gas since the use of lighter carrier gas molecules leads to a beam with a higher velocity and hence the use of shorter delay times. Typical velocities range from 1560 m/s in helium expansions to 600 m/s in argon expansions and 370 m/s in xenon expansions [21]. For the study of clusters longer $\Delta T_2$ times are required as optimal cluster formations occurs later in the expansion. The primary Nd:YAG laser used for pumping the Sirah dye laser requires two trigger pulses, one to trigger the xenon flash lamps and one to open the Q-switch. The use of a single trigger in combination with the internal delay generator of the Nd:YAG laser is theoretically also possible. However, in practice temporal drifts of tens of nanoseconds of the laser pulse are observed when this type of triggering is used, which for the present experiments is unacceptable. When performing a multi-laser experiment, the pump and
probe pulses need to be perfectly synchronized, which can only be achieved by using the delay generators. The optimal intensity of the Nd:YAG laser is observed when a time delay between the flash lamp and Q-switch trigger of $\Delta T_{3}=182 \, \mu s$ is used. To avoid damage of lenses and mirrors in the Sirah dye laser, sometimes the laser power of the Nd:YAG needs to be reduced. This normally is done by using shorter delays between the flash lamp and the Q-switch triggers (down to 140 $\mu s$).

For the double-resonance experiments, the second UV beam ($T_4$) or the ArF laser ($T_5$) need to be synchronized. Therefore, the delay $\Delta T_4$ and $\Delta T_5$ can also be adjusted. Due to the different response times of each laser the values of $\Delta T_4$ and $\Delta T_5$ are not identical, but vary a few hundreds of the nanoseconds. Separate triggering ensures that at the set-up they are synchronized with the rest of the experiment. When Zero Kinetic Energy [22-26] (ZEKE) photoelectron or Mass Analyzed Threshold Ionization (MATI) [27-30] spectroscopy is performed, additional synchronization of electrical field pulses is required. This will be described in more detail in Chapter 2.5.

To obtain background-free measurements in the double-resonance experiments, the delay of every second measuring pulse can be changed by a triggering delay device that has been built at the electronics workshop of the University of Amsterdam. This device shifts every second trigger pulse by a chosen time delay in the range from 10 ns to 1.3 $\mu s$. The laser pulses thus can be moved in and out of synchronization with the other pulse, allowing for correction of the signal for fluctuations in laser fluences and sample concentration.

### 2.5 Capabilities of the molecular beam setup and experimental details

The molecular beam setup described is a very flexible scientific tool. The possibility to detect both ions and electrons opens the door to various spectroscopic techniques such as Resonance Enhanced Multi Photon Ionization [31-33] (REMPI), ZEKE [22-26], or MATI [27-30]. Switching the setup from ion to electron detection requires to change the magnitude and/or polarization of the potentials on the extractor and repeller plates ($V_{A_1}$ and $V_{A_2}$). A detailed scheme is presented in Figure 2.10. The function of most of the plates has been described in Chapter 2.2.
Figure 2.10. A detailed overview of the ionization region indicating the various plates to accelerate and direct the electrons (right side) or ions (left side) to their respective detectors.

To direct the electrons to the MCP detector a field is generated by the potentials $V_{P1}$ and $V_{P2}$, $V_{EFT}$ (Electron Flight Tube) is used to accelerate the electrons further. When working in the ion detection mode, voltages on plates $A1$, $A2$, and the first grounded plate are used to direct the ions into the time-of-flight tube and to the detector. Except for the MATI experiments where a pulsed potential is required, the employed voltages can be approximated by the following empirical equations:

$$V_{A2} = 0.82 \cdot V_{A1} - 580V,$$

$$V_{R2} = 1.62 \cdot V_{R1} - 18V,$$

$$V_{R1} = 0.59 \cdot V_{A1} - 163V.$$

It must be pointed out that we have observed that also other choices for potentials can still lead to a satisfactory functioning of the spectrometer. The empirical dependencies given above result from an optimization aiming at the highest mass resolution and signal level. For $V_{A1}$, we have found that voltages in the range from 1700 to 3850 V lead to quite acceptable signals. However, since the higher values for $V_{A1}$ have been observed to lead to significantly stronger and better time-resolved signal at the MCP detector, we typically have used voltages ranging from 3450 V to 3850 V. Irrespective of the precise voltages, the condition

$$V_{R2} > V_{A2} + \frac{(V_{A1} - V_{A2})}{2}.$$
must be met to ensure that the reflector will have a sufficiently strong field to change the flight direction of the accelerated ions.

For the MATI experiments (see Chapter 2.6) the reflectron was used as a high-pass kinetic energy filter. The scheme of this operation is presented in Figure 2.11.

![Figure 2.11. Scheme for the MATI experiments. Times \( t_1 \) and \( t_2 \) correspond to excitation and ionization by the laser beam, and application of the electric field extraction pulse, respectively. The red line represents the flight path of the ions created directly by the laser pulse. The blue line indicates the flight path of the ions originating from the pulsed-field ionized molecules that initially have been excited to high-\( n \) Rydberg states.](image)

The MATI experiments have been performed in two different ways. The simplest method (Figure 2.11a) uses only one single electric field pulse. Excitation of high-\( n \) Rydberg states is performed in the weak field region generated by the potential difference between the \( A1 \) and \( A2 \) plates. Prompt ions that are generated travel during the time between \( t_1 \) and \( t_2 \) in the direction of plate \( A2 \). As a result, they gain a lower kinetic energy when the extraction pulse is applied on plate \( A2 \) than ions that are generated by pulsed-field ionization of the high-\( n \) Rydberg states. Prompt ions are thus reflected by the reflectron plates before reaching the MCP detector. In Figure 2.11b an experimental scheme is presented that enables pulsed-field ionization without the need for significant electrostatic fields during excitation to discriminate prompt and delayed ions. To this purpose, two voltage pulses are generated. The first, a weak pulse, is used to attract the ions created close to plate \( A1 \). The second pulse, the extraction pulse, results in field-ionization of molecules excited to high-\( n \) Rydberg states and accelerates prompt and delayed ions towards the reflectron. Here, the difference in kinetic energy is used to selectively reflect
the delayed ions to the MCP detector. Tables 2.2 and 2.3 give typical values of the used voltages and time delays for the MATI experiments.

Table 2.2. Typical voltages and time delays used for MATI experiments with a single voltage pulse.

<table>
<thead>
<tr>
<th>$V_{A1}$ offset</th>
<th>$V_{A1}$ pulse amp.</th>
<th>$V_{A1}$ pulse delay</th>
<th>$V_{A2}$</th>
<th>$V_{XY2}$</th>
<th>$V_{R1}$</th>
<th>$V_{R2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2807 V</td>
<td>220 V</td>
<td>3 $\mu$s</td>
<td>2799 V</td>
<td>125 V</td>
<td>2915 V</td>
<td>gnd</td>
</tr>
<tr>
<td>3808 V</td>
<td>400 V</td>
<td>5.5 $\mu$s</td>
<td>3800 V</td>
<td>120 V</td>
<td>3830 V</td>
<td>gnd</td>
</tr>
</tbody>
</table>

Table 2.3. Typical voltages and time delays for MATI experiments with two voltage pulses. For both $V_{A1}$ and $V_{A2}$ the offset voltage is 0 V.

<table>
<thead>
<tr>
<th>$V_{A1}$ pulse amp.</th>
<th>$V_{A1}$ pulse delay</th>
<th>$V_{A2}$ pulse amp.</th>
<th>$V_{A2}$ pulse delay</th>
<th>$V_{XY2}$</th>
<th>$V_{R1}$</th>
<th>$V_{R2}$</th>
<th>$V_{FOC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 V</td>
<td>6 $\mu$s</td>
<td>0.45 V</td>
<td>100 ns</td>
<td>5 V</td>
<td>179 V</td>
<td>284 V</td>
<td>110 V</td>
</tr>
<tr>
<td>400 V</td>
<td>7 $\mu$s</td>
<td>0.9 V</td>
<td>100 ns</td>
<td>5 V</td>
<td>180 V</td>
<td>288 V</td>
<td>110 V</td>
</tr>
</tbody>
</table>

Standard - if not indicated otherwise - the ion lens and directing plates $FOC$ and $XY1$ are grounded. The voltage on plate $XY2$ ranges from 0 V to 125 V for optimal signal intensity without any noticeable correlation with other potentials.

When the setup is used to detect electrons, voltages need to be applied to the $EFT$, $P1$, $P2$, $A1$, and $A2$ plates. Because of the larger charge-to-mass ratio of electrons compared to ions, the required strength of accelerating and flight-controlling electrostatic fields is considerably lower than for the ion detection scheme. Typically used voltage values are given in Table 2.4. For the ZEKE measurements (see Chapter 2.6), a pulsed voltage needs to be applied on plate $A2$ to separate electrons originating from pulsed field ionization from the electrons generated by direct ionization. Therefore, typically 100 - 300 ns after high-$n$ Rydberg state excitation, the $V_{A2}$ potential is set from a background value to the extraction level. In this way, the prompt electrons can drift away with the help of a small background potential from the extraction field region before the extraction voltage is switched.

Table 2.4. Typical voltage values for plates used for electron detection experiments.

<table>
<thead>
<tr>
<th>$V_{A1}$</th>
<th>$V_{A2}$</th>
<th>$V_{P1}$</th>
<th>$V_{P2}$</th>
<th>$V_{EFT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (grounded)</td>
<td>-3 V - -10 V – extracting voltage for ZEKE: 0 V - -0.3 V – background voltage</td>
<td>7 V - 9 V</td>
<td>7 V - 9 V</td>
<td>40 V - 90 V</td>
</tr>
</tbody>
</table>
2.6 Overview and description of performed multiphoton ionization experiments

The three previously described independent nanosecond laser sources generating UV, visible, and IR light allow us to use various spectroscopic techniques to obtain detailed information on the electronic and vibrational structure, as well as the photodynamics of molecular systems. In this thesis the following approaches have been employed.

2.6.1 One- and two-color Resonance Enhanced MultiPhoton Ionization (REMPI) spectroscopy

REMPI spectroscopy is a powerful approach to map out the molecular electronic manifold, the vibrational structure in electronically excited states, and the photodynamics of excited states. Many variations differing in the number and sequence of photons required for ionization of the sample molecule have been proposed. Here we will explain the concept of Resonance 2-Photon Ionization (R2PI) (Figure 2.12).

In R2PI two photons originating from one or two lasers are used to ionize a molecule. In the most simple, one-color version (Figure 2.12a) a single laser pulse provides two photons. If the photon energy \( h\nu_1 \) matches the energy gap \( \Delta E \) between ground and excited state, the first photon can excite the molecule into an excited state. Subsequent absorption of second photon then leads to ionization. Since simultaneous absorption of two photons without an intermediate energy level is much less probable than the sequential resonance-enhanced process, scanning of the laser frequency and observation of the ion yield provides the excitation spectrum of the accessible energy levels. Under the assumption that the probability for absorption of the second photon is approximately
equal for all excited states, the intensities of the observed spectral lines are directly proportional to the transition probabilities between ground and excited state levels.

The two-color R2PI technique (Figure 2.12b) requires two independent laser sources providing excitation and ionization photons of different energy. This approach has a number of advantages over the one-color approach. Since the second photon can have more energy than the first one, one can study without problems molecular systems in which excited state levels are below half of the ionization potential. Moreover, the possibility to control independently the intensity of the laser pulses responsible for excitation and ionization provides a much larger flexibility when studying molecules in which the transition probabilities of these two processes are significantly different. Finally, the possibility to introduce a delay between excitation and ionization pulses enables time-resolved studies. Since the decay of the initially excited state normally leads to a lowering of the ionization probability with the second photon, such time-resolved studies allow one to determine the lifetime of the excited state, [34] and give insight into its photodynamic processes [35].

In the present thesis we have used the R2PI technique as well for high-accuracy measurements of the ionization potential (IP). To this purpose the ionization laser is scanned while monitoring the ion yield. At the moment the total energy exceeds the adiabatic ionization potential, the ionization process changes from a three-photon into a two-photon ionization process, leading to a sharp increase in ion yield. In the case of a one-color measurement non-resonant multiphoton ionization process is used. In a two-color approach, the first laser is fixed at a known transition to an excited state and the second laser is scanned over the ionization potential.

2.6.2 UV-UV depletion and UV-UV hole-burning spectroscopy

Molecules of interest often can adopt more than one stable conformation. In such cases the excitation spectra of the different conformations will overlap and impede analysis of the spectrum. UV-UV depletion [35-37] and hole-burning [38] techniques allow for the investigation of conformational heterogeneity, and can provide conformation-selective excitation spectra. The concept on which the two techniques are based is depicted in Figure 2.13.
Figure 2.13. Scheme of UV-UV depletion and UV-UV hole-burning experiments.

Two laser beams, labeled as pump and probe, are introduced to the sample with a constant time delay. In the case of UV-UV depletion, the first beam (the pump beam) is scanned over a particular excitation region while the second beam (the probe beam) is fixed at one particular transition. If pump and probe are at transitions that belong to the same conformation - and thus have a common ground state -, the ground-state population of this conformation is efficiently depleted by the pump laser, and the ion yield due to the probe laser reduced. On the other hand, the signal from the probe laser is not affected by the pump laser if the pump laser ionizes a different conformation. Repeating this procedure and fixing the probe laser at different bands in the excitation spectrum allows for the assignment of bands to particular conformations. As a result, conformation-specific excitation spectra are obtained.

In UV-UV hole-burning the role of pump and probe beams is reversed. Now the pump laser is fixed on a particular transition while the probe laser is scanned. The signals generated by the probe laser in the presence and absence of the pump laser are then subtracted, and allow one to determine whether bands originate from the same conformation. The advantage of hole-burning spectroscopy over depletion spectroscopy is that with the former significantly better signal-to-noise ratios can be obtained since it is in principle a zero-background technique. On the other hand, UV-UV depletion allows for the detection of transitions that do not appear in the REMPI spectrum due to lack of ionization efficiency [39]. In both cases an intense pump beam is desirable to obtain efficient ground state depopulation. The delay time between both laser pulses requires some attention since it should be chosen in such a way that ionization of excited states by the probe beam is minimized.
2.6.3 IR-UV depletion and IR-UV hole-burning spectroscopy

IR-UV [17, 35-37, 40] depletion and hole-burning [40, 41] spectroscopies follow the same principles as their UV-UV counterparts methods. The required laser pulse sequence is depicted in Figure 2.14.

*Figure 2.14. Scheme of IR-UV depletion and IR-UV hole-burning experiments.*

The IR laser is used now as the pump beam, and is either scanned or fixed in the spectral region of vibrational transitions of $S_0$. Depopulation of the ground state by the IR pulse leads to a reduction of the ion signal generated by the probe beam. In case of hole-burning (IR laser fixed at a chosen transition while the UV laser is scanned over the electronic excitation region) low-noise electronic excitation spectra are obtained of conformations for which the chosen IR frequency is resonant, while the depletion technique (probe laser fixed and pump laser scanned) allows one to record conformation-selective $S_0$ vibrational spectra. The choice of the time delay between pump and probe laser is less crucial than for the UV-UV methods, since no electronically excited states are generated by the IR pump laser.
2.6.4 Zero Kinetic Energy (ZEKE) Photoelectron and Mass Analyzed Threshold Ionization (MATI) spectroscopy

ZEKE [22-26] photoelectron and MATI [27-30] spectrosopies provide insight into the vibrational structure of molecules in ionic states. The laser pulse sequence employed is very similar to the one described for the REMPI technique, and is shown in Figure 2.15.

![Figure 2.15. Scheme of ZEKE and MATI experiments.](image)

The basis of the technique is two-color resonant (Figure 2.15a) or one-color non-resonant (Figure 2.15b) excitation of long-lived high-$n$ Rydberg states converging upon the various rovibronic levels of, normally, the $D_0$ ionic ground state. After an appropriate delay, these Rydberg states are ionized by a pulsed electric field. ZEKE and MATI methods rely on the selective detection of the resulting time-delayed electrons and ions, respectively, using the techniques described in Chapter 2.5. The advantage of MATI spectroscopy lies in the capability to perform mass-resolved measurements, whereas with ZEKE spectroscopy electrons arising from ionization of sample impurities can easily interfere with the measurements. A conceptually important difference between one-color non-resonant and two-color resonant ZEKE/MATI techniques is that with the former technique one projects the properties of $S_0$ onto the ionic manifold, while with the latter method an electronically excited state is projected. ZEKE/MATI spectra can thus be very different for the two cases even though the same $D_0$ vibrational manifold is probed (see, for example, Chapter 3).
2.7. Liquid helium nanodroplet setup

A significant part of the results presented in this work has been obtained using helium nanodroplet spectroscopy. These measurements have been performed on the setup developed and run by dr. Marcel Drabbels in the Laboratoire de Chimie Physique Moléculaire at the Ecole Polytechnique Fédérale de Lausanne (EPFL) in Lausanne, Switzerland. A detailed description of this setup has been reported elsewhere [42-44], here only a brief description will be given.

Liquid helium nanodroplet spectroscopy differs from the previously described supersonic beam methods in the way that cold, isolated sample molecules are prepared. Instead of a jet expansion of a carrier gas, a matrix of liquid helium at 0.38 K is used which serves to embed each sample molecule into its own cryogenic nanodroplet. The scheme of used setup is presented in Figure 2.16.

![Figure 2.16. Scheme of the helium nanodroplet setup at the Ecole Polytechnique Fédérale de Lausanne.](image)

The setup consists of four separately pumped vacuum chambers: a source chamber, a doping chamber, a differentially pumped chamber, and a detection chamber. The first one is equipped with two large turbomolecular pumps (Pfeiffer TMU 1601P) with a pumping speed of 1600 l/s each and backed by a compact dry scroll pump (Edwards XDS10).
Liquid helium nanodroplets are formed by expanding high purity (99.9999%) helium gas at a pressure of 30 bars into the vacuum through a 5 µm orifice (Frey A0200P). This part of the system is cooled by a closed-cycle refrigerator system (Sumitomo Heavy Industries RDK-205D). During the experiments the temperature can be changed in the range of 11-20 K with an accuracy of 100mK using an assembly of a 25 W heater and a Lake Shore Cryotronics Model 331 temperature controller. In this way conditions of droplets creation can be altered as to change their mean size and the flux density. In the experiments described in this thesis droplets have been made that consist on the average of 2000-20000 helium atoms, corresponding to mean radii of 28-60 Å. The whole assembly can be aligned in three dimensions with micrometer manipulators for accurate positioning of the droplet beam source with respect to the orifice leading to the second vacuum chamber.

The helium nanodroplet beam enters the doping chamber via a skimmer (Beam Dynamics Model 2) with a diameter of 0.3 mm and positioned at 9 mm from the droplets source. This part of the setup is pumped by a Pfeiffer TMU521 turbomolecular pump with a pumping speed of 500 l/s. The liquid helium nanodroplets are doped with sample molecules via collisions. The proper pressure of the sample vapors in the range of $10^6 - 10^5$ mbar, depending on the droplets size and other experimental conditions, can be obtained with an adjustable leak valve (Balzers UDV235), or, in case of samples requiring higher sublimation temperatures, an internal oven through which the droplet beam passes. Normally, the mean droplet size and pressure of the sample vapor is chosen such that on the average less than one sample molecule is picked up per helium droplet. If dimers or higher-order clusters are the subject of interest, the pressure and/or mean droplet radii can be increased to enlarge the collision cross section. After embedding in the droplet the internal energy of the molecules is reduced by surface evaporation of helium atoms (~5 cm$^{-1}$ per atom) and the molecules are cooled down to a temperature of 0.38 K.

The doped droplets enter the detection chamber via a differential pumping stage equipped with a Pfeiffer TMU 250 turbomolecular pump. In this chamber vacuum is sustained by a single Pfeiffer TMU1601P turbomolecular pump with a high pumping speed of 1600 l/s. Back-up vacuum is provided by a smaller turbomolecular pump (Pfeiffer TMH071P) in order to attain ultrahigh vacuum conditions. To further lower the pressure in the detection chamber, internal high-yield heating and cooling systems are utilized. After each opening of the setup to atmospheric conditions, the interior of the detection chamber is baked out with a set of quartz lamps for speeding up the process of desorption of impurities from internal surfaces. During the experiment heating is turned off and cryoshields can be filled up with liquid nitrogen to minimize further release of adsorbed species. As a result, a base pressure of $3 \cdot 10^{-11}$ mbar is obtained and a pressure
as low as $1 \cdot 10^{-9}$ mbar can be sustained in the detection chamber in the presence of the liquid helium beam.

Production and doping of the helium droplets is monitored by a quadrupole mass spectrometer (Balzers QMG422) positioned at the far end of the chamber. During the experiments the helium-embedded sample molecules are ionized with laser pulses in an ion imaging setup. Created charges are steered into a short (395 mm) TOF tube where they can be separated according to their masses. Finally, they reach the detector consisting of a 75 mm diameter chevron MCP assembly and a P-20 phosphor screen (Galileo S-3075-25-I-PS). A fast high-voltage switch (Behlke HTS 31-GSM) with a nominal minimum pulse width of 80 ns allows the temporal gating of the gain of the front MCP and by this the recording of the presence of the ions in a mass-selective way. The image created on the phosphor screen is captured with a 1024x1024 pixel CCD camera (Basler AG A200) equipped with a f=50 mm objective, and transferred to a personal computer for further analysis. Due to this arrangement of detection system, and the usage of an asymmetric immersion lens and an Einzel lens for charge imaging, accurate velocity-imaging of the ionization spot is achieved. A three-dimensional velocity distribution of the ions or electrons is reconstructed from the two-dimensional image using the iterative Abel inversion method. In this way information about the ionization event, the mass of the created ion, and the velocity vector and kinetic energy of the resulting charges can be obtained.

Two sets of dye lasers pumped by Nd:YAG nanosecond lasers (Quanta-Ray models 250 PRO and GCR-170) and operating at a 20 Hz repetition rate provide UV/Vis radiation in the spectral range of 215-900 nm. The same laser system is used to generate IR radiation for wavelengths from 1.5 to 5.0 µm in a similar way as has been described in Chapter 2.1. Additionally, IR radiation in the 1.0-1.5 µm region can be generated by a hydrogen-filled Raman cell. For non-resonant ionization a femtosecond laser system is available. This system consists of a mode-locked oscillator (Clark-MXR NJA-5) and a chirped pulse amplifier system (Clark-MXR CPA-1000). The $\lambda=780$ nm output has a pulse duration of 150-200 fs and a pulse energy of 1.0-1.5 mJ.
References