Development of a molecular beam mass spectrometer and a supersonic jet expansion pyrolyzer for the characterization of reactive organic intermediates

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To my parents and Oana,

may it be beneficial.


Siddharta Gautama

Die Wissenschaft fängt eigentlich erst da an interessant zu werden, wo sie aufhört.

Justus von Liebig
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1. Summary

In the fundamental research of organic chemistry, the analysis of highly reactive intermediates (e.g. radicals, carbenes, nitrenes) improves our understanding of the chemical bond, as well as the interactions between molecules. For the characterization of such reactive intermediates it is important to have suitable methods for their creation and stabilization during the spectroscopic analysis. In the frame of this task three distinct areas have been the core of this work:

1. A molecular beam setup for an quadrupol mass spectrometer (MBMS) has been developed. This allows the use of the "supersonic jet expansion pyrolysis" SJEP (detailed explanation in Chapter 2.4 and 2.5) for the thermal decomposition, and mass spectroscopic analysis, of suitable precursors towards highly reactive open shell molecules.\[1-5\]

2. For the supersonic jet expansion technique, a pulsed pyrolyzer has been developed from scratch. This device can be implemented in mass spectroscopic and cryogenic matrix isolation setups. It gives the possibility of combining SJEP with various spectroscopic techniques (MS, UV/VIS, FTIR, EPR), for the fast and reliable characterization of reactive intermediates.

3. In the application of the SJEP in matrix experiments, several generations of pulsed pyrolyzers were optimized, due to challenges which had to be solved step by step. The latest version of the pyrolyzer has been applied in a pyrolysis study of 1,2,3,4,5-pentafluoro-6-iodobenzene. The thermal decomposition mechanism for this system is not fully understood, and leads to the complete breakdown of the molecule into smaller fragments of CF$_2$, CF$_3$ and CF$_4$.\[6\] In MBMS experiments, mainly the expected C$_6$F$_5$ radical was observed, while matrix isolation IR spectroscopy resulted in several new species, of which the strongest absorption bands could be assigned to the C$_6$F$_5$ radical as well as the C$_6$F$_4$ ortho-diradical. To compare the developed SJEP pyrolyzer to other pyrolysis systems (e.g. "flash vacuum pyrolysis", FVP) two additional pyrolyzer systems were applied in this study (see Chapter 5.2).
1.1 Development of the Molecular Beam Mass Spectrometer

Based on a quadrupol mass spectrometer (qMS), which was optimized for the use of flash vacuum pyrolysis, a setup for molecular beam techniques has been developed. This allows the use of a SJEP pyrolyzer. The original setup (Scheme 1) included a sample injection system, the FVP unit, and the chamber for the quadrupol MS as well as a vacuum pumping setup with rotary vane pumps and a high vacuum turbo-pump for the establishment of sufficient vacuum quality around $10^{-8}$ mbar.

![Scheme 1](image)

**Scheme 1.** Setup of the "FVP-MS", effusive sample injection followed by a quartz flash vacuum pyrolytic reactor (see Scheme 38, Chapter 5.2.2) heated over a tantalum wire up to 800°C. The ultra high vacuum (UHV) pumping system allows for pressures down to $10^{-9}$ mbar and the mass analysis is done through a quadrupole ion separator.

To implement a molecular beam setup, a chamber for directing a supersonic gas expansion towards an internal molecular beam skimmer was added, which had to be closely connected to the MS chamber. The position of the expansion orifice towards the skimmer is of vital importance in this system. To ensure an optimal positioning, adjustments are often necessary. A mechanism for moving the expansion orifice in all three dimensions of space, relative to the internal skimmer, had to be implemented.

Finally the qMS has been enhanced by a second chamber, which is used to remove the residual gas of the molecular beam after it passed the MS, in order to improve the spectroscopic background.

Not to limit the sample injection possibilities of the mass spectrometer, the setup for FVP has been kept in, orthogonal to the MB system. In the following Scheme 2 the final setup of the MBMS is shown:
Scheme 2. Final setup of the MBMS / FVP-MS: the FVP section was maintained while extensions through a supersonic jet expansion chamber, as well as a molecular beam "catching tube", have been added. The expansion chamber comes with a positioning device for the pulsed pyrolyzer to assure correct alignment towards the internal molecular beam skimmer.

To use the available material in the best possible way, the setup has been build from already available chambers. This came along with many necessary compromises, e.g. in terms of space and distance parameters (see Chapter 3.3.2).

1.2 Development of the "Pulsed Pyrolyzer"

Based on the works of P. Chen et al.,[3] a "pulsed pyrolyzer" (PP) has been developed, which can be used for the SJEP in the MBMS, as well as in matrix isolation setups. Throughout the development process, several generations of pyrolyzers where optimized in order to fully understand the key details and to combine them in a final version. To fit the latest version of the pyrolyzer (Scheme 3) into the MBMS expansion chamber, limitations in terms of space had to be dealt with. The main consequence of these limitations was a minimal amount of electric feedthroughs (oven heating, valve control, temperature detectors).
Scheme 3. Latest version of the developed pulsed pyrolyzer for SJEP applications. After several years of development and optimization this final setup for the pulsed pyrolyzer has lead to satisfactory and reproducible results of the thermal decomposition of 1,2,3,4,5-pentafluoro-6-iodobenzene in matrix applications as well as mass spectroscopic studies (see Chapter 5.2.3).

The pyrolyzer consists of a Parker General Valve Series 9 pulsed valve, closely connected to a water cooled mounting plate which is also the socket of the MACOR thermo shield that contains the siliziumcarbide pyrolyzer tube between two graphite electrodes. The tube can be heated resistively up to 1800K. Temperature detection is established through a type C thermocouple (W/Re 5% vs. W/Re 26%), which is directly attached to the outer surface of the SiC tube. Since the pulsed valve can be damaged at temperatures above 150°C, the mounting plate is closely attached to a water cooling housing for the pyrolyzer. The cooling is effective enough to allow experiments at highest temperatures, without limitations in time. Since this setup requires a high pressure of a carrier (noble) gas, for the supersonic jet expansion towards the skimmer, it limits the possible precursors in terms of their volatility. An attempt to overcome these limitations was the development of a post mixing chamber, based on the works of Vladimir Miscic of the workgroup of T. Bally in Fribourg (Scheme 4).[7]

Scheme 4. Post mixing chamber for low-volatility samples. Samples can be put into a quartz container that is held by a hollow screw. Upon heating to ~ 80°C, the sample can enter the gas phase and be "picked up" by the incoming gas pulses, while the pressure between pulses is kept at ~10⁻⁴ mbar.
This chamber is placed between the pulsed valve and the mounting plate of the pyrolyzer, thereby a vacuum can be established inside it, through to the pumping system of the expansion chamber (~$10^{-4}$ mbar). It can be kept at variable temperatures (RT-80°C) through a heating wire, wrapped around it, to allow low volatile precursors to enter the gas phase, which then can be picked up by the incoming noble gas pulses to be carried into the pyrolyzer tube.

### 1.3 Reference Experiments

To test the developed MBMS and the pulsed pyrolyzer, reference spectra have been measured. As a first step, the creations of several radicals in mass experiments were tested, e.g. the Allyl-radical 2 with the Allyl-iodide precursor 1, as already shown by Zhang et al.\cite{5}

![Scheme 5. Pyrolysis of allyl-iodide 1 towards the allyl-radical 2. Mass spectroscopic experiments, as well as matrix isolation IR experiments have shown promising results with the used pulsed pyrolyzer.](image)

The results of this pyrolysis study displayed the desired radical 2, which encouraged further studies with the developed PP towards new systems.

### 1.4 Pyrolysis towards N-Centered Radicals

The first attempts to investigate new systems included nitrogen-centered radicals. A broad variety of precursors has been tested in mass experiments, prior to matrix-IR experiments. Here, two different precursors have shown promising results: acetone-azine 3 and methyl hydrazine 4 (Scheme 6).
During this study, new challenges in the optimization of the pyrolyzer appeared, for instance the gas flow through the heated siliziumcarbide tube could not be kept stable upon tempering the pyrolyzer. These challenges could be solved by redesigning the "carrier plate" of the tube as will be shown in Chapter 4.2.

1.5 Thermal Decomposition of 1,2,3,4,5-pentafluoro-6-iodobenzene

In previous investigations, by Butler and Snelson in 1980, the pyrolysis of C₆F₅I 5 did not result in the expected formation of the C₆F₅ radical 6 (Scheme 7), but instead lead to an unexpected breakdown of the molecule into smaller fragments of CF₄, CF₃ and CF₂.⁶ Due to the massive shift in fluorine, the mechanisms which attempt to explain this breakdown usually included fluorine atoms in the gas phase, but so far no conclusive evidences could be found. Butler and Snelson worked with a low pressure platinum pyrolysis reactor. To further study this phenomenon, the well established FVP and two versions of the pulsed pyrolyzers have been used. While the FVP resulted, among others, in the formation of the expected C₆F₅ radical and its hydrogen-absorption product, the pulsed pyrolysis with a short heating zone has shown results similar to the results of Butler and Snelson. No formation of the C₆F₅ radical was observed, instead smaller fragments formed in considerable amounts. Pulsed pyrolysis with a long heating zone, on the other hand, showed complex temperature dependent spectra.
Mainly the formation of both the C₆F₅ radical, as well as smaller fragments around 900°C, and the formation of the ortho-C₆F₄ at higher temperatures, around 1100°C. In the following Scheme 7 the identified products are displayed.

Scheme 7. The pyrolysis study of 1,2,3,4,5-Pentafluoro-6-iodobenzene 5 through several pyrolysis approaches (PP & FVP). In mass spectroscopic and matrix isolation IR experiments, complex spectra were observed. The shown molecules could be identified through comparison with literature spectra.

2. Introduction and Theory

2.1 Matrix Isolation

The matrix isolation technique was introduced 1954 by Pimetel et al. and it has been established as an important method for the characterization of instable organic molecules. The idea is to create a reactive molecule out of a precursor, through pyrolysis or photolysis, which then is being frozen in a noble gas on a spectroscopic window (CsI) to inhibit further reactions. In such an cryogenic inert matrix, the molecules can be inhibited from translational and most rotational movements, which also greatly simplifies the accessible spectra. The information gained through spectroscopy at such a matrix-stabilized molecule are easier to interpret then most room-temperature spectra.
To make this possible the matrix material has to be fitting towards the technique of spectroscopy being used to characterize the enclosed molecules (IR, UV-VIS, EPR, fluorescence & phosphorescence). This means the matrix material has to be "invisible" in the spectral region of relevance for the different methods. In most cases noble gases or nitrogen matrices are being used. The matrix material is being directed simultaneously with the reactive molecules in a ratio of 100:1 - 10000:1 towards a spectroscopic window (CsI) being kept at low temperatures (3-10K) through a closed helium cryostat (Scheme 8).\textsuperscript{10}

\begin{center}
\textbf{Scheme 8.} A matrix "head" with an pulsed pyrolysis deposition unit.\textsuperscript{15} The water cooled valve pulses high pressure noble gas doped with precursor molecules on the CsI window, which is kept by a He cryostat at temperatures down to 3K. From reference [10] by I. Dunkin.
\end{center}

The housing around the helium-cryostat can be cycled around it, so that deposition can be exchanged with spectroscopic tools (IR, UV-VIS, EPR,...). Even in such a setup, it is not common that the desired radicals are captured in the matrix. Details like distances, deposition parameters and sources for the reactive intermediates create challenges for the experimenter. To realize the matrix-deposition of a desired highly reactive species, various techniques can be applied.

The deposition of a precursor, followed by photolysis, is a commonly used way to create matrix isolated high-energy molecules. The rigidity of the matrix prevents translational movement of molecules inside it and thus inhibits bimolecular reactions, the disadvantage of this factor in photolysis experiments is the close proximity of two newly created reactive molecules.
This leads in many cases to recombination reactions inside the matrix cage. To avoid this recombination reactions the creation of reactive species has to be done before they are isolated inside the matrix.

Here flash vacuum pyrolysis (FVP) is a viable technique that has also proven a useful tool. The disadvantage here is the occurrence of surface reactions and collision reactions in the gas phase that lower the intensity of reactive species formed. To avoid these, the supersonic jet expansion pyrolysis (aka. "Pulspyrolysis") has been introduced.

### 2.2 Supersonic Jet Expansion

To stabilize reactive intermediates, by cooling them down, the supersonic jet expansion can be used. Through this kind of expansion the temperature of molecules in the gas phase can be lowered drastically.[11]

If a reactive intermediate is created in situ inside of a noble gas of relatively high pressure (~1-2bar), and afterwards expanded through a nozzle of small inner diameter into a high vacuum area, the gas undergoes such an adiabatic/supersonic jet expansion and the molecules are cooled down.

In this method, the noble gas acts somewhat like an inert matrix, since it also gives the reactive intermediates chemically inert collision partners. Kantrowitz and Grey were the first to use this method,[1] while Miller et al. made a summary of the physical properties involved (Figure 2).[12]
Figure 2. Schematic diagram of a free jet expansion. Shown below the expansion is a scale measuring distance (X/D) downstream in units of the nozzle diameter (D). Given at various positions downstream are the Mach number, the temperature, the density in torr at standard temperature and pressure (S.T.P.); 1 S.T.P. torr = 3.54 x 10^{16} molecules per cubic centimeter], the pressure (in millitorr), and the number of collisions between X/D = 5 and the indicated point. It is assumed that the stagnation pressure behind the nozzle is 10 atmospheres of Helium at 300 K; for the collision calculation, D = 0.15 mm, and a collision cross section of 50 square angstroms is assumed. From reference [12] by T. A. Miller.

To apply this method practically it is necessary to either establish a very good vacuum pumping system, or to make use of a pulsed valve between the two pressure zones. Gentry et al. have done the pioneer work in combining supersonic jet expansion with a pulsed valve system.[13]

The orifice diameter in such a system is usually between 0.1 mm and 1 mm.[12] By opening the valve, the high pressure gas expands into the vacuum, hereby unifying the translational direction and speed of the molecules inside the expansion. With further distance to the orifice, the expansion cools down while increasing its speed. The Mach number given in Figure 2 is proportional to the square root of the temperature, thus it increases drastically with the distance to the orifice. But the speed of the expansion relatively to the hull of the expansion chamber is not that high, it maxes out around the common speed of sound.[12] Along the expansion, the collision between molecules diminishes, and this leads to a speed-cap. For Helium in such expansions, extreme speeds of up to mach 200 have been measured.[14]

Miller et al., interpreted the absolute velocity not as the most important property of this expansion, but the width of the velocity distribution, which constitutes a direct measure of the gas’s translational temperature.[12]
This width corresponds to a temperature of less than 10K at X/D = 10 (Figure 2) and subsequently drops to less than 1K; under more extreme conditions the translation temperature can approach 0.01 K. The collisions during this expansion leads towards equalizing the energy levels of the molecules, thereby reducing the internal degrees of freedom of the molecules (vibrational, rotational energy levels) to the same low temperatures as the translational's. The density of the gas decreases alongside the expansion, subsequently leading to lower collision numbers. Thus, the ultimate distribution of internal excitation in a molecule may not reach precise equilibrium with the translational temperature of the molecule. The rotational-translational equilibrium is usually established quickly, while rotational temperatures are rarely greatly different from translational ones in a simple expansion. Vibrational-translational equilibrium is usually not as efficient, and is often dependent on the details of the vibrational structure. Nevertheless, substantial vibrational cooling is also typically observed. The density of the gas drops by a factor of more than 500 in the first ten nozzle diameters (X/D), and afterwards drops by a comparably small factor of less than 40 in the next 50 nozzle diameters. It is reasonable to assume that most of the n-body (n ≥ 3) collisions occur at X/D ≤ 5 for these expansion conditions. Because the initial step in molecular condensation requires n-body (n ≥ 3) collisions, condensation must initiate mostly for X/D ≤ 5.

The degree of condensation can be reduced by using a mixed gas expansion, for example a noble gas dilutedly seeded with the organic molecule. The region very close to the nozzle is difficult to model theoretically and may vary considerably from expansion to expansion because of details in the nozzle design. However, the region beyond X/D ≥ 5, where 2-body collisions predominate, can be rather accurately modeled. Lubman et al. reported useful results describing the collision frequency in this region. The flow velocity was used to convert this collision frequency into the number of 2-body collisions suffered by a typical molecule downstream from the point X/D = 5. Most of the collisions have occurred by X/D = 20 to 40, but inside this region they are quite frequent. Miller et al. interpret, this region of 2-body collisions as the most interesting, because "hot" radicals can be injected into the jet and thermalized to low temperatures, characteristic of the expansion.
2.3 Pulsed Supersonic Jet Expansion Pyrolysis

The concept of supersonic jet expansion can be combined with pyrolysis.\cite{2} By using a pulsed valve which directly connects to the pyrolyzer, Chen et al. has shown this useful application in 1983 at the methyl-radical.\cite{3} The setup and application of such a pulsed pyrolyzer for the characterization of reactive organic molecules has been reported repeatedly, especially Peter Chen and Barney Ellision et al. have done much of the pioneer work in this area.\cite{2-5}

The schematics of such a pulsed pyrolyzer was given in Scheme 8. The pulsed valve is usually a Parker General Valve, series 9 (or 99) valve (Scheme 9), while the pyrolyzer itself consists of a siliziumcarbide tube, with an inner diameter of 1 mm and a length of ~30 mm.

![Scheme 9. A Parker General Valve Series 9 pulsed valve. The main valve for the application in pulsed pyrolyzers.](image)

It is resistively heated through two carbon-electrodes, up to temperatures of 1800°C, and often shielded by either aluminum or MACOR to prevent a loss of heat.\cite{4}

To apply this method, the precursor is seeded into a noble gas, at a relatively high pressure > 1 bar (e.g. 0.01% precursor in argon), and pulsed into the evacuated pyrolyzer tube (~10^-6 mbar). These conditions limit the precursors to those who can be seeded into noble gases at the given pressure region. The benefit of this method, compared to other pyrolysis methods, is that surface reactions are substantially diminished due to the low percentage of precursor in the noble gas.
The gas mixture is being heated up mostly by noble gas atoms colliding with the heated walls of the pyrolyzer and, in turn, the heated noble gas atoms act as the energy transference medium towards the organic precursor molecules. The noble gas also acts as a collision partner for the in situ created radicals, thus recombination reactions are diminished as well. By leaving the pyrolyzer tube into the high vacuum expansion chamber, the seeded gas undergoes the supersonic jet expansion and thereby, the reactive intermediates are stabilized. This method poses an ideal thermal source for matrix isolation experiments, due to the noble gas, that also becomes the "matrix-material" in which the reactive species are frozen on the cryogenic window (Scheme 10).\textsuperscript{[2, 5]}

![Scheme 10. Combination of pulsed pyrolysis followed by a supersonic jet expansion into a laser ionization unit of the TOF MS, in combination with matrix-isolation IR spectroscopy. From reference [5] by X. Zhang et al.](image)

The combination of pulsed pyrolysis in mass- and matrix-IR experiments is a useful tool for characterizing reactive intermediates.

### 2.4 Molecular Beam Technique

The free jet expansion of a gas, inside a high vacuum, consists of several regions where local pressure, density and flow velocity differ. Scheme 11 summarizes the shockwave structure of a free expansion under continuum (steady state) conditions.\textsuperscript{[17]}
Introduction and Theory

Scheme 11. Shockwave structure of a free jet expansion, the central "zone of silence" is surrounded by compression waves and leads to the formation of a Mach disk. From reference [17] by D. R. Miller.

The source is a short conical nozzle. As mentioned in Chapter 2.4., the pressure difference between \( p_0 \) and \( p_b \) leads to an acceleration of the gas, which in turn leads to several important characteristics: In the zone of silence, the beam parameters are independent of boundary conditions (walls, \( p_b \)), which is caused by the fact that information propagates at the speed of sound, whereas the gas moves faster. To create a molecular beam, a specially formed skimmer has to be placed in this zone of silence. In order to extract a stable flow of molecules with the desired properties, from the remaining expansion cone (Scheme 12).

Scheme 12. An example for the use of a molecular beam in a mass spectrometer, after "cutting" into the zone of silence of the supersonic expansion, another skimmer removes the spreading parts of the beam, in order to increase molecular beam quality. From reference [18] by M. Sablier.
If the background pressure is small enough, a smooth transition to molecular flow occurs and no further shock structures emerge. In this case, the beam is only affected by residual gas scattering. Thus, the best conditions for molecular beam experiments are determined by the quality of the vacuum pumping system.

Such a molecular beam can be analyzed by different spectroscopic methods. In mass experiments it is used to stabilize the reactive intermediates after their creation, till they reach the ionization unit of the mass spectrometer.\textsuperscript{[19, 20]}

### 2.5 Quantum Chemical Calculations

The matrix isolation technique is applied to highly reactive molecules, which cannot be observed under ambient conditions. To characterize these species via IR spectroscopy, it is necessary to compare the bands with the known bands of functional groups. This in itself is insufficient, since a convincing identification of a certain molecule includes not only known functional groups, here the often very complex bands of the fingerprint area have to be analyzed. Comparisons with experimental reference-spectra can be done whenever possible, to characterize these bands, here the wave numbers and intensities have to fit.

Often it is not possible to find reference-spectra, since only known substances are being found in the various databases. Unknown substances have to be compared with calculated IR reference spectra. Since the position and intensity of bands can be very sensitive to structural changes in a molecule, theoretical IR-spectra from quantum-chemical calculated geometries can give detailed information. Furthermore information about energies and spin states of the molecule can be achieved. Theoretical chemistry gave us a broad variety of quantum chemical methods for these calculations, e.g. \textit{ab initio} methods, which work with the wave function, for which the eigenvalues and eigenfunctions are calculated. For the calculation of small to medium sized molecules, methods are applied which are usually not so extensive. The density functional theory (DFT) makes use of the electron density, for which there are databases of density functions for various molecules. The most common DFT-method is the B3LYP-method,\textsuperscript{[21, 22]} which also has been used in this work. Experience shows, that DFT gives good results for reactive intermediates, only much more extensive methods like \textit{coupled-cluster} give similarly good results. For the calculations of perfluorinated molecules, B3LYP with the basis set aug-cc-pvtz has been used in this work.
Due to the high electro negativity of the fluorine the ionic character of bonds is increased, the calculations have shown good results by using a basis set that includes this parameter.

3. Development of the MBMS Machine

3.1 Introduction

The first molecular beam mass spectrometer (MBMS) using a quadrupole mass analyzer has been reported by Oleander and Waddel in 1968 (Scheme 13).\cite{23} The success of this technology has lead to a broad variety of applications, making it a common tool in instrumental analytics nowadays.


Quadrupole mass spectrometry often makes use of an electronical ionization (EI) unit, which uses a standard energy of 70eV to increase signal intensity. The first applications of MBMS in combination with supersonic jet expansion pyrolysis have commonly relied on time of flight (TOF) mass analyzers instead of quadrupole mass analyzers.\cite{3}
TOFMS is based on the principle that different masses with the same initial kinetic energy will have different velocities and, therefore, arrive at the detector at different times.\textsuperscript{[24]} An important feature of this system is the use of a laser ionization (LI), instead of an electron impact (EI) unit, in order to ionize the samples. This provides a low energy (10.5 eV) source of ionizing radiation with a narrow energy spread ($1.2 \times 10^{-4}$ eV).\textsuperscript{[24]} The lower ionization energy of the LI reduces fragmentation of ionized species and generally simplifies the resulting mass spectra. The pulsed ionization of a TOF LI system can be aligned to the pulsed sample injection of the supersonic jet pyrolysis unit, and results in a harmonic system for the mass analysis of thermal decomposition products. For these reasons, TOF has often been preferred to quadrupole MBMS systems for the analysis of pulsed pyrolysis products.

In this work we attempted to create a similarly successful buildup, on the basis of a quadrupole mass spectrometer, which has been designed specifically for pulsed experiments (by HIDEN). In Chapter 3.3.1. the planning of this machine is discussed in detail.

### 3.2 Mass Spectroscopy

#### 3.2.1 Introduction

Mass spectroscopy has been one of the most important methods of analysis in organic chemistry. Since 1960 it developed to a powerful analysis tool in various areas.\textsuperscript{[25]} The range of mass spectroscopy nowadays includes high resolution mass spectroscopy (distinguishing masses at $10^{-6}$amu - atomic mass unit), as well as analysis of macromolecules (up to 100,000amu).\textsuperscript{[25]} The analysis of bio-macromolecules, for example to characterize the length of a DNA-sequence, is a modern application of this technique.\textsuperscript{[26]} The HAL7 RC(7U)-series quadrupol mass-spectrometer from HIDEN is used in this work. It is equipped with an electronical ionization unit that allows analysis of masses in the area of up to 3500amu. Since most organic reactive intermediates are relatively small in mass, it is fully sufficient. Furthermore, this specific quadrupol spectrometer allows the analysis of pulsed signals. Here, the physical detector is split in two virtual detectors, which take data at different points during the measurement.
In this way, one can measure difference-spectra, which are calculated from the peaks of consecutive gas-pulses, without any "background" signals that lay between them. This is the very basis of the molecular-beam mass spectrometer in this work, since supersonic gas expansion pyrolysis is dependent on a pulsed gas-flow. Without a suitable pulse-valve, the continuing supersonic jet expansion would overburden the high-vacuum pumps up to an area of pressure higher than $10^{-7}$ mbar. This would damage the spectrometers electron multiplier.

In the following, the general buildup of a mass spectrometer is shown, and compared to the individual spectrometer for the molecular beam machine developed in this work. Generally, a mass spectrometer can be divided into four compartments: sample feeding, ion-generation, mass-separation and ion detection (Scheme 14).[^27]

[Scheme 14. The basic conceptual buildup of a mass spectrometer, after the sample injection into the ion source - cations are created. These are accelerated and focused into the magnetic field of a mass separator followed by an ion detection unit. From reference [27].]
3.2.2 Sample Feeding

The sample feeding can be done in various ways. In many cases, it is standard to ionize the samples in the gas phase under high vacuum conditions. To get the sample into the gas phase, simple sublimation or evaporation is the easiest way of sample feeding. In this case the pressure can be controlled by suitable valves. Another method is the Matrix Assisted Laser Deposition (MALDI). Here the sample is enclosed into a solid matrix, which then can be evaporated into the gas phase, by shooting in with a suitable laser. In this way very controlled short pulses of sample molecules are created. Furthermore, there are various spray-techniques, which will not be explained further here: Electro Spray Ionization (ESI), Atmospheric Pressure Chemical Ionization (APCI) und Atmospheric Pressure Photo Ionization (APPI). These techniques all include an ionization of the molecules and are often used for samples with low volatility that cannot be evaporated or sublimated otherwise.

3.2.3 The Ion Source

The Ion source of the quadrupole MS is a high energy electron beam, which is created between a filament and an electron trap. Its energy can be controlled by varying the electric potential. The sample enters the beam, and electrons collide with the molecules, thereby abstracting another electron out of the orbital's of the sample molecule. In this way positively charged radical-cations are created:

\[ M + e^- \rightarrow M^{++} + 2e^- \]

In the given qMS the energy can be varied from 0 eV - 300 eV. The common value is 70eV, which creates a high amount of radical cations, and can also lead to substantial fragmentation of the molecule. Through these fragments, structural information about the sample can be collected. In the case of trying to optimize the pyrolysis conditions of a given precursor the mass spectra have to be measured during changing pyrolysis temperatures.
Here it is ideal to have a high intensity molecular ion signal, which is strongly determined by diminished fragmentation through the electronic ionization of the spectrometer. To do so, we lower the energy of the ionization beam to values between 10 eV and 15 eV. To counteract the resulting lower amount of radical-cations created, we increase the emission of electrons. In this way fewer fragments are created while still (ideally) being ionized, thereby we achieved satisfactory results for several tested precursors. The molecules which are not being ionized are pumped out of the spectrometer by ultra-high vacuum pumps.

The created ions are accelerated and focused through electric fields, into a homogenous ion-beam which is directed into the quadrupole electro-magnetic field of the mass separation unit.

The relative velocity of the ions is given by the following equation:

\[ z \cdot U = \frac{m \cdot v^2}{2} \]

*Equation 1.* Ion velocity in the mass spectrometer, mass m, velocity v, charge z and acceleration potential U

### 3.2.4 The Mass Analyzer

The mass separation unit makes use of the mass depended trajectories of cations inside the magnetic field (Scheme 14). The ions with lower mass to charge (m/z) ratio are influenced stronger due to their lower inertia. Thereby, it is possible to steer the trajectory of the ions of a determined mass into the detector, by precisely controlling the magnetic field. The deflection radius inside a simple magnetic field (as shown in Scheme 6) can be calculated as followed:

\[ r_m = \frac{m \cdot v}{z \cdot B} \]

*Equation 2.* Calculating the deflection radius of ions in the magnetic field, strength of the magnetic field: B

Equation 1 and 2 combined give the basic equation of mass-spectroscopy:

\[ \frac{m}{z} = \frac{r_m^2 \cdot B^2}{2 \cdot U} \]

*Equation 3.* Basic equation of mass spectroscopy for the mass to charge ratio
The detected mass to charge ratio is determined by the strength of the magnetic field, the deflection radius and the acceleration potential. By controlling these values in a given spectrometer, the mass analysis can be achieved. The mass spectrometer used in this work is based on a quadrupole mass analyzer, which forces the ions on a sinus trajectory inside a quadrupole electromagnetic field. Only certain ions (m/z) can pass this field and are detected, while others leave the field before they can be detected.

The mathematical description of this analyzer is more complex than shown by the simple equations 1-3. The potential here is created by four parallel electrodes (Scheme 15).

![Scheme 15. A quadrupole mass analyzer: the opposing electrodes are connected together electrically, and a radio frequency (RF) voltage is applied between one pair of rods and the other. A direct current voltage is then superimposed on the RF voltage. From reference [28].](image)

Further techniques will just be mentioned, but not explained in detail. The "time of flight" (TOF), the various "ion trap's (IT), as well as the "ion cyclotron resonance" (ICR), make it possible to analyze a broad variety of samples in extremely high resolution and mass ranges (e. g. bio macro-molecules).[26]

### 3.2.5 The Ion Detection

In Equation 3 the acceleration potential and the deflection radius can be set as a constant, thereby follows equation 4:

$$\frac{m}{z} = konst. B^2$$

**Equation 4.** Relation of the m/z ratio to the strength of the magnetic field
By doing so, the mass to charge ratio only depends on $B$ - the strength of the magnetic field. By controlled variation of $B$, every detected ion has to have a specific mass, and thus the mass spectra is gained. The ion-detection compartment is based on a secondary electron multiplier (SEM), which greatly increases the signal strength of an incoming ion (Scheme 16).

Scheme 16. Principal of a secondary electron multiplier: the incoming ion collides with the surface of an electrode, which leads to an emanation of up to several additional electrons. These are accelerated by the next electrode, collide with it, and again more electrons are ejected. This happens many times, till even the smallest signals reach detectable dimensions.

3.3 Building the MBMS

3.3.1 Planning

The mass spectrometer buildup of this work has been developed on the basis of a HIDEN HAL7 RC(7U)-series quadrupole mass spectrometer, which has been designed to allow continuous, as well as pulsed experiments. The components of this research-oriented spectrometer can be controlled by the available HIDEN software. The electronical ionization unit is of particular importance, since the energy of the electron beam can be lowered down. This flexibility allows for lesser fragmentation of the samples, similar to the LI in TOF systems. The lower amount of ions created (signal intensity) can be counteracted by using a higher emission current between the filaments. In this case, one has to adjust the conditions for each individual sample. Since the ionization potential of a precursor, as well as its thermal decomposition products, can vary drastically; the energy of the EI has to be optimized for every new system.
Starting from a FVP-MS (Scheme 17) we attempted to add a pulsed pyrolysis source combination with a molecular beam skimmer.

Scheme 17. Setup of the "FVP-MS", effusive sample injection followed by a quartz flash vacuum pyrolytic reactor heated over a tantalum wire up to 800°C. UHV pumping up to $10^{-8}$ mbar and mass analysis through a quadrupole ion separator.

For learning this technique in detail, we worked closely together with the workgroup of Prof. Bally in Fribourg University (ch). The general design of our MBMS machine has been developed using the concepts learned there, a very similar machine is displayed in Scheme 18.

Scheme 18. Time of flight molecular beam mass spectrometer, makes use of a three stage system: first the creation of the molecular beam through a skimmer in a supersonic jet expansion chamber, second the ionization and mass analysis, and third the residual gas removal to increase background vacuum quality. From reference [29] by A. L. Brown et al.

The "Stage #1" chamber was designed for the expansion of the gas after exiting the orifice of the supersonic jet nozzle.
Here a system had to be developed that allows the alignment of the pyrolyzer and its water cooled housing, relative to the internal molecular beam skimmer.

In the "Stage #2" chamber the quadrupole mass spectrometer, with its electronical ionization unit, is placed. An internal positioning system has been implemented, to make it possible to correct its position relative to the molecular beam, and thereby to increase signal quality.

The "Stage #3" chamber has been designed to "catch" the molecular beam in order to improve the spectral background (signal to noise), by removing residual gas during measurements.

The complete system has been planned with a suitable vacuum pumping system of (diffusion) pre-pumps, and ultra high vacuum (turbo) pumps, to achieve vacuum pressures in the range of $10^{-9}$ mbar. During pulse experiments, the vacuum pressure in the expansion chamber varies, of course, in much higher regions, around $10^{-5}$ mbar, while the mass spectrometer and "catching tube" ("Stage 2, 3") is being kept under vacuum pressures of $10^{-8}$ - $10^{-7}$ mbar. The chambers are being separated by gate-valves to be able to steer the vacuum individually.

The sample injection chamber of the FVP and the expansion chamber for the MB are often repressurized, while the MS chamber has to be kept at a steady vacuum pressure. Several vacuum sensors at the different stages of the spectrometer have been implemented, to be able to control the pressures accordingly. The following Chapters will give a detailed description of the work.

### 3.3.2 The Expansion Chamber

In the early stages of this work, a basic chamber for the supersonic jet expansion has been tested. The first chamber, which was used in the attempt to establish a molecular beam, was a simple design as shown in Scheme 19:
As expected, the distance between the jet orifice and the molecular beam skimmer was too long in this chamber (~ 10-15 cm). To "capture" a beam out of the zone of silence (Scheme 9, Chapter 2.6), it was necessary to move the jet orifice close to the skimmer inside the chamber.

For several reasons, the skimmer and the pulsed valve have been placed in the center of the chamber. First it is possible to make visual adjustments, since the chamber has been planned with two observation windows in the two main axes (from the top and from the side, Scheme 20).

Scheme 19. First expansion chamber, taken over from previous works related to the pulsed sample deposition of the mass spectrometer.

Scheme 20. Central placement of the skimmer and the pyrolyzer. The windows for visual adjustment (mainly of the distance between the skimmer and the pyrolyzer.)
Another reason for this placement is the length of the pyrolyzer. The chamber had to be extended with the 3D placement device (shown on the right side in Scheme 21), which resulted in an increased distance between the mount of the pyrolyzer (green plate) and the skimmer. To still hold the pyrolyzer in balance, inside this relatively short plate, it was important not to build it too long. Moving the skimmer closer was a step to deal with this factor.

This alignment poses some technical difficulties, since the valve has to be kept in stable vacuum, and still has to have sufficient mobility (up to 10mm in all directions). As shown in Scheme 21, by the red, green and blue colored parts, it is necessary to make use of a positioning device. This enables the alignment of the pyrolyzer inside the chamber, which is held by a water cooling system (red) inside the vacuum chamber. By aligning the jet expansion cone and its "zone of silence" towards the skimmer, a beam can be extracted from the rest of the expansion. Steering the quality of the molecular beam is possible by varying the distance and position of the pyrolyzer orifice towards the skimmer.

Scheme 21. 3D alignment system of the expansion chamber, the different plates are shown in blue, green and red. The distance between the skimmer and the pyrolyzer is controlled by the red housing while the remaining two dimensions can be adjusted by positioning the plate, shown in green.
The blue plate is mounted on the outer casing of the chamber, while the green plate can be moved on the surface between the blue one and the mounting plate. This is been done by adjusting screws from the outside. This allows the orthogonal alignment of the pyrolyzer orifice relative to the skimmer. The green plate is kept under pressure, in a way that an o-ring is sealing the chamber from the ambient pressure. The red part is the housing of the pyrolyzer, and simultaneously a water cooling system (Scheme 22).

![Scheme 22. Water cooled housing of the pyrolyzer, with a matrix head mounting plate](image)

The housing is held by two o-rings in the alignment system (green plate, Scheme 21), and can be positioned on the main axis of the device. Thereby, the distance between pyrolyzer and skimmer can be adjusted. Shown in Scheme 21 is the closest possible distance, the distance to the skimmer can be increased by using positioning screws from the outside. Further details are given in Chapter 4.3.

### 3.3.3 The "Beam Catching" Chamber

To improve the vacuum quality inside the spectrometer it is necessary to remove the residual gas of the dispersed molecular beam. The "Stage 3" chamber (Scheme 23) is placed in the trajectory of the molecular beam, thereby "catching" and removing the gas after it passed the mass spectrometer. The simple design used, mainly consists of a tube and a high vacuum pumping system, connected via a gate valve to the mass spectrometer chamber.
Scheme 23. The molecular beam "catching" chamber, provided with a high vacuum pumping system for establishing pressures of $10^{-9}$ mbar. The window on the backside of the chamber makes it possible to align the pyrolyzer and the mass spectrometer, using a laser (Chapter 3.3.5).

3.3.4 The Final Buildup

In the final stages of combining the different chambers, several details like electronics, valves, sensors, sample feeding (mixing chamber) and pumping systems have been implemented as well. From the basic concept shown in Scheme 24, a relatively complex machine has been built.

Scheme 24. The final setup of the MBMS / FVP-MS. The flash vacuum pyrolysis section was maintained, while extensions through a supersonic jet expansion chamber, as well as a molecular beam "catching tube" have been added. The expansion chamber comes with a positioning device for the pulsed pyrolyzer, to assure correct alignment towards the internal molecular beam skimmer.
The Expansion Chamber

The pre-vacuum ($1 \times 10^{-3}$ mbar) in this chamber is established via an Oerlikon TRIVAC NT5 rotary vane vacuum pump, which gives the initial vacuum pressure needed for the start of a Oerlikon TURBOVAC TMP 361 C water cooled high vacuum pump. The vacuum quality is reduced ($1 \times 10^{-6}$ mbar) due to the O-ring sealing system of the positioning device. This pumping system has been chosen for its high tolerance towards pressure variations, which are caused by the pulsed high pressure gas injections during experimental conditions. The pre-vacuum quality of this chamber is controlled via a Varian Type 0531 Vacuum gauge connected to a Varian 845 vacuum ionization gauge (labeled "VP2"), and the high-vacuum quality respectively via a Leybold Penningvac high voltage vacuum sensor (measurement range $1 \times 10^{-9}$ mbar to $1 \times 10^{-2}$ mbar, labeled "UHV2"). This sensor is connected to a Leybold COMBIVAC CM 31 (PM measurement channel).

The sample feeding system of this chamber consists of a 2L stainless steel mixing bottle, which can withstand pressures up to 2000mbar. For the evacuation of this section, as well as the degassing of precursor samples, a vacuum of $1 \times 10^{-3}$ mbar can be established via a Oerlikon TRIVAC NT5 rotary vane vacuum pump. It is controlled via a Varian Type 0531 Vacuum gauge (labeled "RP4"), connected to a Varian 804-A Thermocouple vacuum gauge.

The Mass Spectrometer Chamber

The pre-vacuum ($1 \times 10^{-3}$ mbar) in this chamber is established via an Oerlikon TRIVAC NT10 rotary vane vacuum pump, which gives the initial vacuum pressure for the start of a Oerlikon TURBOVAC TMP 361 air cooled high vacuum pump ($1 \times 10^{-9}$ mbar). This pumping system has been chosen for its high vacuum quality. The pre-vacuum quality of this chamber is controlled via a Varian Type 0531 Vacuum gauge, connected to a Varian 845 vacuum ionization gauge (labeled "VP1"). The high-vacuum quality is controlled via a Leybold Ionivac ultra high vacuum gauge sensor (measurement range $2 \times 10^{-11}$ mbar to $1 \times 10^{-2}$ mbar, labeled "UHV1"), also connected to the Varian 845 vacuum ionization gauge. Under experimental conditions pressures in the region of $10^{-8}$ mbar to $10^{-7}$ mbar are used. If high pressure peaks occur ($>1 \times 10^{-6}$ mbar), a failsafe system switches off the mass spectrometer interface unit, in order to protect the spectrometer from damage.
The "catching Chamber"

The pre-vacuum (1x10⁻³ mbar) in this chamber is established via an Oerlikon TRIVAC NT10 rotary vane vacuum pump, which gives the initial vacuum pressure for the start of a Oerlikon TURBOVAC MAG air cooled high vacuum pump (1x10⁻⁹ mbar). This pumping system has been chosen for its high vacuum quality.

The pre-vacuum quality of this chamber is controlled via a Varian Type 0531 Vacuum gauge (labeled "VP3") connected to a Varian 804-A thermocouple vacuum gauge. The high-vacuum quality via a Leybold Ionivac ultra high vacuum gauge sensor (measurement range 2x10⁻¹¹ mbar to 1x10⁻² mbar, labeled "UHV3"), connected to a IONIVAC IM 540 vacuum gauge.

The FVP Chamber

The effusive sample feeding system of this chamber is supported by a pre-vacuum pump, for the evacuation of this section, as well as for the degassing of the precursor samples. Here a Oerlikon TRIVAC NT5 rotary vane vacuum pump is used.

The vacuum quality is controlled via a Varian Type 0531 Vacuum gauge (labeled "sample 5"), connected to a Varian 804-A Thermocouple vacuum gauge. To establish high vacuum (1x10⁻⁹ mbar), the FVP chamber is opened to the MS chamber, which allows the high vacuum pumping system to evacuate both departments (vacuum sensor "UHV2" applies here as well).

The four described chambers are connected, and can be sealed from each other through three gate valves (labeled "A, C & F" at the spectrometer), which are manually opened and closed whenever necessary.

3.3.5 Molecular Beam Alignment and Optimization

To test the alignment system, a laser can be used. The device shown in Picture 1 on the left side can be kept in the same position as the pyrolyzer orifice inside the chamber. It was built in a way that upon rotation the laser beam does not change its position. It is kept stable on the central axis for several meters, thereby it can be used to make pre-positioning optimizations for the PP (positioning device, Scheme 21.).
The laser alignment system (l), keeps the beam stable on the central axis upon rotation. The active device inside the chamber(r), directed towards the tip of the molecular beam skimmer.

The optimal alignment position for a supersonic expansion consists theoretically of the highest intensity of the laser-beam, after it passed through the skimmer, and the mass spectrometer (Picture 2). This has been used to align the position of both: the pyrolyzer and the mass spectrometer, prior to the first molecular-beam mass-experiments.

The cylindrical mass-spectrometer can be moved inside its chamber by adjusting the position of three screws around a corrugated bellow, which serves as its casing. In this case the position of the MS can be observed through a window, as shown in Picture 2 on the left side.

After the laser-alignment, the pulsed valve has been implemented in the system in order to make the final adjustments through a continuous mass experiment.
Theoretically, the highest peak intensity of molecules entering the mass analyzer should define the ideal (central) position of the pulsed pyrolyzer valve. To adjust the system directly on the build-in pyrolyzer, a noble gas has been pulsed in, while the position-dependent signal intensity of the ions has been measured. In this way, the final position optimization for the pyrolyzer could be achieved. However the positioning process of the MS posed some problems.

Upon variation of the MS position, the intensity of detected ions did not vary in a noticeable dimension. We assume that the passing of the molecular beam through the narrow ionization unit (1 mm) leads to turbulences and the collapse of the beam into diffusive movement. Further experimental optimizations with pulsed sample detection will be presented in Chapter 3.3.6.2.

### 3.3.6 The Software

#### 3.3.7 Basic Measurements

To define an experiment in HIDEN's MASsoft control program of the MS, the "scan tree" is used (Figure 2). All details of the spectrometer can be controlled through several areas. These are: the "Global: RGA" (global environment editor), "Scan 1: mass" (scan editor), "SEM" (input selection), "Repeated" (scan cycles structure) and "Shutdown" (shutdown environment editor). The header "events" can be used for more complex measurements. Here the “events” can be defined in order to change certain parameters of the hardware during an ongoing measurement, at a given point in time. In the following Chapter, a brief explanation for the different areas is given.
Figure 1. Scan tree defines any possible experiment of the mass spectrometer: the general control of the hardware, the type of experiment, the data acquisition and the “scan cycle structure”.

The global Environment Editor

In this editor, the hardware can be controlled: the ionization source, the ion detector etc. (Figure 3). For the optimization of parameters for pyrolysis experiments, the most important features are concerning the ionization unit. The electron energy has to be lowered to minimize fragmentation (~15eV), while the emission current can be increased (~400µA) in order to achieve higher signal intensities. In a pulsed pyrolysis experiment there are some more values to be controlled. This will be explained in detail in Chapter 3.3.6.2.

Figure 2. Global environment editor controls the hardware in its minimal and maximal limits.
The analysis is commonly done in "RGA" mode (residual gas analysis, cations), which was the standard for all experiments done in this work. However there are some more possibilities - for example the analysis of anions (-ion RGA), or the two SIMS.

The Scan Editor

In the scan editor, the type of measurement is defined. Here there are three basic possibilities: bar-mode, profile-mode and MID-mode (Figure 4).

What is called "bar-mode" gives the detected counts per second, in the form of a bar diagram, as a function of the "mass to charge" ratio (m/z) in a defined area of atomic mass units. Figure 5 shows the spectrum of \textit{m-}xylol as an example.
Figure 4. "Bar-Mode" spectrum of \( m \)-xylol, with a mass resolution of 1 amu. The molecular ion is detected at \( m/z = 106 \), and the main ion at \( m/z = 91 \) through the abstraction of a \( CH_3 \) group.

In the "profile-mode" it is possible to measure at higher increment values (to increase resolution). This gives a more detailed spectrum, with bands instead of bars. In the following Figures 6 and 7, the profile-mode spectra of \( m \)-xylol with increment values of \( x = 0.05 \) and \( x = 0.8 \) are given (measurements are taken every \( x \) value).

Figure 5. "Profile-Mode" spectrum of \( m \)-xylol with an increment value \( x = 0.5 \), which is the minimal increment value of this mode.
In "mid-mode" (multiple ion detection) it is possible to monitor the intensities of defined ions in function of the time (Figure 8). This makes it particularly easy to observe the intensity variations of e. g. the molecular ion and the fractionated ions during a pyrolysis experiment. In the optimizations of pyrolysis experimental conditions, this method has been used to observe the time dependent increase of a desired radical formation, in function of the current temperature in the pyrolyzer.

**Figure 6.** "Profile-Mode" spectrum of $m$-xylol with an increment value $x = 0.08$, which is the maximal increment value of this mode.
Figure 7. "MID-spectrum" of m-xylol: during pyrolysis the temperature has been increased up to 800°C till 00:17:00, and afterwards cooled down again.

The Input Selection Editor

This editor is controlling the details of data acquisition (Figure 9). First the detector is defined under the header "Available inputs", this becomes more important for pulsed measurements and will be presented in Chapter 3.3.7.1. Second, the "Acquisition range" defines the signal intensity which will be considered for date collection. Finally the rates by which the ion detection unit works are defined: how long the spectrometer takes to measure one data point ("dwell time"), and how much time there is between two measurements of data points ("settle time").
Development of the MBMS Machine

Figure 8. Input selection editor defines the data acquisition of the detection unit (can be divided into background and foreground gates), the range of acquisition and the dwell and settle times.

The standard dwell- and settle- times are 100 ms (or 100%). This leads to a certain length of a mass experiment, depending on the mass range and the mode of the data collection (standard or pulsed). To increase quality it is necessary to also increase the measurement time. For a pyrolysis experiment this means that the conditions in the pyrolyzer have to be kept stable over a long period of time.

Scan Structure Cycles and Shutdown Environment Editor

After the spectrometer went through a measurement cycle, defined through "environment", "scan" and "detection", the "repeated" header is triggered (Figure 2). Here the scan structure cycles editor (Figure 10) is defining the amount of repetitions for this experiment, which can also be switched to continuous scanning. In this case the experimenter manually switches off the measurement when it is finished.
Development of the MBMS Machine

Figure 9. Scan structure cycles editor is used for experiments over an extended period of time. In pyrolytic optimization experiments often several hundred cycles are measured.

After the measurement reached the defined amount of cycles, or it is being switched off manually, the "shutdown environment" (Figure 11) is triggered. In the corresponding editor, the various parts of the spectrometer are controlled, just as in the global environment editor. Here it is possible to switch off only defined areas of the spectrometer, while others stay active. In a complex scan tree, with several levels of measurements, this can be useful.

Figure 10. The shutdown editor resembles the global environment editor in a reverse "manner" by deactivating the different parts of the hardware.
### 3.3.7.1 Pulsed Measurements

During molecular-beam experiments, the physical detector is being divided into two virtual detectors ("gates"): foreground and background. In this way pulsed sample injections can be analyzed by defining the foreground inside an incoming sample pulse and the background between two pulses. Observing a MID spectrum, of a pulsed sample injection, the difference between gating measurement and classical measurement is most obvious.

![Figure 11. Pulsed sample injection in continuous- (l) and "gating"- (r) ion detection](image)

To use pulsed sample injection, an IOTA one pulsgenerator has been implemented. This generator gives parallel signals to the mass spectrometer interface unit (MSIU) in order to give input signals for the gating system. In the following the wiring and the pulse control will be explained.

**Connecting the Pulsgenerator to the MSIU**

During a pulsed sample injection, the valve opens in a controlled way through signals of the IOTA ONE pulsgenerator. To allow the gating system to measure precisely inside an incoming pulse, the MSIU has to rely on external signals from the generator. The following Scheme 25 displays the wiring between the MSIU, the pulsgenerator and the oscilloscope, which is used to measure pulsed sample injections and to optimize the gating system.
The MSIU comes with four cables, necessary for gating measurements: FG (foreground) input and output, and BG (background) input and output. The input channels transmit the external signals of the pulsgenerator to the software, to give the basis for an on-time measurement of an incoming pulse. The output channels are used to optimize the “gating” via an oscilloscope, and this will be explained later in detail. To open the pulsed valve, the generator sends a +5 V square wave through the output, which is also connected to the FG and BG channels. The details of how long the wave is transmitted (opening time), and in which frequency, can be controlled at the pulsgenerator. To measure the sample correctly, on the basis of an incoming signal from the pulsgenerator, the software settings have to be optimized.

Setup of the Software for gating Measurements

The incoming signals through the FG and BG channels have to trigger the “gating” system of the software to do a pulsed measurement. The FG measurement has to be aligned with the incoming sample pulse, while the BG measurement has to take place between two sample pulses. The first step to set up a pulsed measurement, after setting up the hardware, is to define a measurement, as shown earlier, in any of the possible modes. As an example, the pulsed measurement in MID mode will be explained. First, the detector has to be defined, which can be done in the input selection editor (Figure 9). There are several available inputs which can be chosen, the standard is the secondary electron multiplier (SEM), which is the physical detector.
It can be defined as:

\[ SEM = foreground + background. \]

If the gating is being used, it is possible to choose either one of the two gates as an input device. If the background gate is defined as input, measurements only occur during background gating, while the foreground input is defined as:

\[ foreground = SEM - background \]

Here a clear distinction between the two gates is made, which is needed for pulsed sample acquisition.

Second, after defining foreground as the input gate, the dwell time is very important for pulsed measurements. The gate_width (measurement time of a gate) will be defined in the global environment editor (Figure 13), and it has to be aligned to the dwell time (Figure 9). As mentioned before, the dwell time defines the amount of time the software takes to measure a single data point. This means e.g. that a dwell time of 100 ms has to fit to the opening time (ON time) of the pulsed valve, and the corresponding gate_width. For example, if the gate_width is defined as 100 μs, which is a reasonable length to measure inside a gas pulse, it would be necessary to measure 1000 openings of the pulsed valve for the collection of one single data point.

Even with pulse-frequencies of up to 50 Hz, the standard dwell time of the spectrometer leads to very long measurements, during which the conditions inside the pyrolyzer have to be kept stable. This has proven to be a challenge, that can be minimized by applying shorter dwell times down to a minimum of 1 ms. The possible frequencies of the pulsed valve are conditioned by the strength of the vacuum pumping system, since a vacuum of at least $10^{-7}$ mbar, in the mass spectrometer chamber, has to be kept stable. To control the gating system in the global environment editor (Figure 13), several options have to be considered.
Figure 12. Gating options ("other") in the global environment editor, they define the details of pulsed data acquisition.

- **gating**
  Here the gating is switched on (gating = 1) or off (gating = 0).
  In case it is active, the following parameters will be used by the software during the measurement:

- **gate_width**
  This parameter defines the opening time of the two gates *foreground* and *background*.
  It is important to consider the opening time of the pulsed valve as a basis for this value.
  If the gate_width is defined as zero, the two delay parameters are not used. Instead, the defined gate (input selection) will measure without any delay.

- **background_delay**
  This delay timer is triggered by the external signals of the pulsgenerator. After the defined delay time has passed, the *background* gate will start collecting data.
  The standard delay time here is 0.1 \( \mu \text{s} \), which means that the measurement starts practically instantly. The maximal delay of this gate is 6553.5 \( \mu \text{s} \).
  It has to be set in a way that the background measurement takes place as "far away" from the incoming gas pulse as possible. To achieve this, the measurement should take place before the incoming sample pulse, with a minimal delay time of 0.1 \( \mu \text{s} \).
**background_invert**

This is the condition under which the background_delay is triggered. There are two options: 0 and 1. In this case "0" corresponds to an external incoming voltage of +5V (transition 0V to 5V) and "1" corresponds to the respective drop in voltage from +5 V to 0 V. Since the IOTA ONE pulsgenerator is transmitting a +5V square wave at the moment of the opening of the valve, this parameter has to be defined as 0. Due to the translational time of the sample, from the orifice of the valve, to the ionization unit of the spectrometer, the background gate is triggered before the sample arrives.

**foreground_delay**

This is the pendant to the background_delay. Here the optimizations done with an oscilloscope can be used to find out optimal delay times. This will be explained in detail, in the optimization section.

**foreground_invert**

The pendant to the background_invert, the trigger should be defined as 0 as well, so the opening of the valve happens in the same time with the delay trigger of the measurement.

**Optimization of a pulsed measurement**

After the measurement is defined in the software, there are still some optimizations to be done. To optimize the remaining conditions, a "dry" pulsed experiment can be used. First, the pulsgenerator has to give input signals to the MSIU and, second, the hardware has to be activated, without doing an actual measurement. This can be controlled in the software over the "lightning symbol" (Figure 14). In this way the reactions of the two gates towards the external signals can be monitored by an oscilloscope (wiring, Scheme 25).

![Figure 13. "Lightning" symbol for the activation of the hardware, without having a measurement started.](image-url)
In the following Figures, the graphs display the voltage as a function of time. The graph on top corresponds to the incoming signal of the puls generator, the middle graph displays the reaction of the foreground gate and the lower graph the background gate (Figure 15).

**Figure 14.** Optimization of the gating system via oscilloscope; a TDS 2024 oscilloscope of Tektronix has been used.

If the puls generator is started, in continuous mode, the square wave will be displayed accordingly. Now, the hardware of the mass spectrometer can be activated as explained, and the two gates show their reactions to the incoming square wave, as defined by the software. The gate width can be observed (and controlled) by the broadness of their signals, while the relative position of the two gates to the incoming signal corresponds to their delay timers (Figure 16).

**Figure 15.** Monitoring the software during experimental conditions, the oscilloscope displays the reaction of the MSIU to external signals of the puls generator.

During such a monitoring experiment, the conditions can be changed in the software. It is also possible to do an MID experiment (e.g. with Argon) to monitor the resulting peak intensities of the gating experiment.
If the two gates are placed correctly, a relatively constant and high signal intensity for the sample should be observed in the MID spectrum. This experiment can also be done to roughly check the length of the incoming gas pulse (the quality of the molecular beam). Placing the background gate at the beginning of an incoming pulse resulted in high intensities, due to the travel time of the sample inside the spectrometer.

3.3.8 Conclusion

One of the main purposes of this machine is the optimization of the conditions for pyrolysis experiments, in effusive (FVP) and pulsed (SJEP) sample injection. The two sample injection systems have been implemented and tested. While effusive experiments pose no problems, the establishment and the detection of a pulsed molecular beam did. The alignment system of the pulsed pyrolyzer works in satisfactory dimensions, and allows a correct positioning of the supersonic expansion towards the internal molecular beam skimmer. Upon laser alignment, and experimental "mass intensity"-alignment, it was possible to optimize the position of the pyrolyzer. Nevertheless, a "sharp" molecular beam could not be observed in the mass spectrometer, presumably due to gas turbulences at the ionization unit of the spectrometer itself.

The hardware of the spectrometer has a minimal measurement ("dwell") time of 1 ms, while the minimal ("settle") time between two measurements is again 1 ms. Standard experiments are done with measurement- and pause times of 100 ms, to increase the quality of the spectra. While the opening time of the pulsed valve can be controlled to a minimum value of 0.15 ms, the resulting pulse shows a broadness of approximately 1.3 ms (Zhang et al.[5]). By going to the limits of the spectrometer, we attempted to observe the molecular beam signal. It was possible to observe signals which peaked after 4 ms of measurements and then kept on at that peak intensity for several more ms. This is too slow, and too broad for confirming an undisturbed molecular beam. Theoretically, the mass spectrometer should be able to measure inside a molecular beam, but experimentally this is not completely sure. However, it is safe to assume that the stabilizing effects of the molecular beam, for the reactive intermediates "travelling" with it, are taking place. This should last at least until the ionization unit of the MS is reached, since there are no other obstacles in its path.
In the moment of turbulences’ occurring, the molecules are also ionized and analyzed, thereby giving information for the optimization of the pyrolysis experiments. This has lead to useful results for different systems, and will be discussed in the following chapters. Thereby, the developed setup fulfills the task of optimizing the experimental conditions, even though it still could be developed further in future projects.

To avoid turbulences, inside the narrow ionization unit, the molecular beam has to be very thin and precise (stable diameter below 1 mm). Since a "one-skimmer system" does not seem to provide the necessary diameter, as it does for TOF systems with broad and barrier free laser ionization units, it would be an improvement to install a second skimmer - inside an additional chamber, connected to a high vacuum pump. This could not be done in this work due to time limitations.

4. Development of the Pulsed SJEP Pyrolyzer

4.1 Introduction

Two of the most common techniques for the generation of reactive organic species (e. g. radicals) are photo dissociation\cite{30, 31} and thermal dissociation\cite{2, 32} of suitable precursors in various experimental setups.

It has been known for almost 60 years that radicals can be isolated by freezing in cryogenic matrices. Matrix isolation remains an important tool for studying organic radicals, since high number densities of these reactive species can be accumulated in these matrices and held virtually unperturbed for days.

However, this technique poses some challenges concerning the two mentioned sources for reactive species. The \textit{in situ} photo dissociation of matrix isolated radical precursors can lead to secondary bimolecular reactions inside the matrix cage (e.g., radical - radical recombination, disproportionation), and thereby reduces the formation of reactive species. Flash vacuum pyrolysis is a viable method to prevent these reactions, due to the formation of reactive species in the gas phase prior to cryogenic trapping on the matrix window. However, the disadvantage of this technique is the occurrence of surface reactions, as well as n-body collisions in the gas phase, which again can lead to diminished formation of reactive species.
Peter Chen et al. were the first to present a flash pyrolysis nozzle for the generation of radicals in a supersonic jet expansion in 1992\textsuperscript{[2]}.

As mentioned before, this technique theoretically reduces surface reactions, as well as reactions in the gas phase, due to the noble gas carrier. Thereby it is avoiding the disadvantages of both: FVP and photo dissociation techniques. Chen et al. reported several successful applications of this technique.\textsuperscript{[33-36]} Based on the pioneering work in this area, a pulsed pyrolyzer has been developed in this work, for applications in the molecular beam mass spectrometer and matrix isolation setups.

4.2 The Pyrolyzer

In the process of optimizing parameters, several generations of pulsed pyrolyzers have been developed. To distinguish them, they are labeled in a chronological order (g\textsubscript{1} to g\textsubscript{4}). Based on previous works in our workgroup of Prof. Dr. W. Sander at the Ruhr-Universität Bochum (OC II), a first generation (g\textsubscript{1}) pulsed pyrolyzer has been developed.
It consisted of a 3 cm silicon carbide tube held between two molybdenum electrodes inside a MACOR shielding. This has been mounted on the faceplate of a *Parker General Valve, Series 9* pulsed valve. Due to the vibrations of the valve, during pulsed experiments, the pyrolyzer is shaken in its position between the electrodes. This has lead to instabilities in the electric current, thereby making it difficult to keep the temperature stable over longer periods of time. Also, the temperature migration inside the system has lead to an overheating of the pulsed valve, making it impossible to maintain experiments over extended periods of time.

To improve these parameters, the electrode material has been changed to graphite and a different holding system of the MACOR shielding was designed, in order to improve stability. The head plate of the pulsed valve was rebuild in a way that it could be implemented in a water cooling housing, to ensure a stable temperature of the pulsed valve. The SiC tube was held in three different places: two are the graphite electrodes and the third one is the socket inside the mounting plate. Here the precision mechanics build the socket as a close fit to the SiC tube, to maximize its sealing properties. The incoming gas pulses travel from the orifice of the pulsed valve, through two connected tubes (of the plate and of the pyrolyzer), with a constant inner diameter of 1 mm. In the following Scheme 27, the second generation pyrolyzer (g2) is displayed.
The pulsed pyrolysis experiments with this pyrolyzer design displayed stable temperatures of the pyrolyzer and the pulsed valve. The spectra collected with the different pyrolyzer generations will be discussed in the following Chapters. They will be mentioned here briefly, to explain the decisions made during the optimization process of the hardware.

In mass spectroscopy, dozens of known and unknown precursors have been analyzed in pyrolysis experiments, among them the well studied Allyl-radical \(2\).\[^5\] Pyrolytic conditions have been optimized for these systems. During this phase of measuring reference spectra, the MACOR shielding broke, presumably due to its thin walls and the strong temperature variations during the experiments. A third generation pyrolyzer (g3) with a thicker MACOR shielding and an adapted water-cooled mounting plate was build to counteract this instability (Scheme 28).
Upon application attempts to investigate new systems towards N-centered radicals, the pulsed pyrolysis mass spectra of, again, dozens of precursors have been analyzed. The most promising results were found for Acetone-azine 3 and Methyl-hydrazine 4.

Upon matrix isolation experiments new challenges came up, which were not observed to this extend before. The gas flow through the pyrolyzer itself seemed to diminish drastically during the tempering of the pyrolyzer tube. The investigation towards N-centered radicals could not be continued with this pyrolyzer, since experiments in matrix-setups showed only minimal amounts of sample being isolated in the cryogenic matrices during the heating phases. Apparently, the socket of the SiC tube inside the mounting plate was not sufficient to ensure a stable gas flow through the tube itself, upon the tempering of the system.

Here several challenges came up: first the SiC tubes are not perfectly round, but show an inconsistent surface. This leads to diminished sealing properties, inside the socket of the tube, which is drilled perfectly circular by the micromechanics building the different hardware pieces.
To ensure the sealing quality of the tubes, their outer surface has been mechanically smoothened, into a rounder shape. However, this could only been done for up to a length of 2 mm at one end of the tube. Trying to increase this length would break the tube under the pressure of the manufacturing process. This factor diminished the possible depth of the socket which is holding the tube inside the mounting plate. To counteract the difficulties discovered, a fourth generation \((g4)\) pyrolyzer has been developed (Scheme 29).

Scheme 29. The fourth generation \((g4)\) pulsed pyrolyzer. The \(g3\) mounting plate has been split into three different functional plates: first, the pulsed valve head-plate used to reduce "poppet consumption"; second, the MACOR socket plate for the SiC tube to improve sealing properties and ensure gas-flow through the pyrolyzer during tempering; and third, the redesigned mounting plate holding the MACOR heat shield with the graphite electrodes. An additional positioning device has been added to make it possible to implement a post mixing chamber, for low volatile samples, in a flexible way (further information in Chapter 4.4).

The water-cooled mounting plate for the MACOR shield, the SiC tube and the pulsed valve have been redesigned, and split into three different parts.

- First, the head plate for the pulsed valve has been split from the other plates, to make it possible to remove the pyrolyzer from the valve without making it necessary to dismantle the valve completely. Opening the valve makes it necessary to exchange the poppet inside it (Scheme 9, Chapter 2.5), since its sealing properties cannot be guaranteed after usage.
Second, the socket of the SiC tube has been placed in a MACOR socket plate which fulfills several tasks:

- The plate has comparably low temperature conducting properties, therefore it further protects the pulsed valve from overheating.

- It enabled us to build an improved mounting socket, in terms of depth and stability, than in the case of the metallic \( g_3 \) mounting plate.

These changes improved the sealing properties and ensured a stable gas flow during the tempering phase of the pyrolyzer.

- The third plate is a redesigned version of the \( g_3 \) mounting plate. Its main functions are to ensure the water cooling of the pulsed valve and to provide a stable mounting of the MACOR heat shield, and its implemented graphite electrodes.

The latest pyrolyzer design (\( g_4 \)) has been applied in a thermal decomposition study of 1,2,3,4,5-Pentafluoro-6-iodobenzene \( 5 \). The spectra measured in matrix isolation IR experiments displayed several new species, which had not been observed before. The sealing properties of the SiC tube were improved successfully, and this lead to results that will be discussed in Chapter 5.3.

4.3 The Cooling Housing

During the construction phase of the second generation pyrolyzer (\( g_2 \)), a water cooling housing has been developed in order to inhibit temperature migration from the pyrolyzer to the pulsed valve (Scheme 30).
Scheme 30. Water cooling housing of the pulsed pyrolyzer: it has been build to allow extended experimental times. The mounting plate for the "matrix heads" has been added to allow additional applications in cryogenic matrix isolation setups. A stable vacuum can be maintained inside the cooling device due to O-ring sealing at the pyrolyzer.

To maximize the cooling effect of the housing, the mounting plate between the pyrolyzer and the pulsed valve has been build with an "expansion slit". The slit can be bend open by an expansion screw (Scheme 31), to increase the diameter of the plate and maximize the contact surface to the housing.

Scheme 31. Mounting plate between (g3) the pyrolyzer and the pulsed valve. An expansion slit has been added to allow the variation of the diameter, thereby making it possible to maximize the contact surface to the water cooling housing. A similar system has been implemented in the g4 mounting plate, as well as the post mixing chamber.
This system simultaneously fixes the position of the pyrolyzer inside the housing. This is especially important for the **g4** pyrolyzer.

An additional positioning device, which allows the movement and the repositioning of the pyrolyzer inside its housing, has been also implemented. This allows the flexible implementation of a “post mixing chamber”, which is used for samples with low volatility. The repositioning device has the disadvantage that it can lead to instabilities inside the pyrolyzer positioning. This factor is counteracted by expanding the mounting plate. In the next Chapter this will be explained in detail.

### 4.4 The Post Mixing Chamber

A positioning device has been added, to make it possible to vary the length of the pyrolyzer without having to rebuilding it. This is important for the flexible implementation of a "post mixing chamber" (Scheme 32), which allows the use of precursors with low volatility.

**Scheme 32.** The post mixing chamber: it can be implemented and removed according to the volatility of the sample. A given sample is deposited in a quartz tube and held by a hollow screw next to the "pick up tube" of the chamber. The sample can be heated by a proper wiring wrapped around the chamber, while vacuum pressures of $10^{-4}$ mbar are established between two incoming gas pulses from the pulsed valve. After the gas "picked up" the sample molecules in the gas phase, it is transmitted into the pyrolyzer and can be decomposed. The resulting fragments can then be analyzed.

The post mixing chamber has been build following the designs presented by Vladimír Miscic from the workgroup of T. Bally, Fribourg University.\(^7\)
Due to time limitations, the heating wiring has not jet been implemented, and the presented chamber design could not be tested.

4.5 Reference Spectra

4.5.1 Pyrolysis Condition Optimizations of Organic Systems in the MBMS

The second generation pyrolyzer g2 has been used to reproduce the first reference spectra in mass spectroscopic setups. A broad variety of precursors has been tested to understand the SJEP technique in our setup, and how it is applied accordingly. The precursors had to fulfill certain conditions to be analyzed by the pulsed technique. First, they had to have a sufficient volatility under ambient temperature conditions. Second, as a target for the decomposition, they had to have a "weak" bond (relatively low bond dissociation energy, in comparison to the rest of the molecule), at a predefined position in the molecule. This makes it easier to dissociate the molecule in a controlled way, under pyrolysis conditions.

The goal was to measure a high intensity signal for a given reactive intermediate, and to maximize this intensity, through the conditions used during the experiment. To do so, the multiple ion detection (MID) mode of the mass spectrometer has proven most useful. In this mode, the intensity of the molecular ion and the main fragments (radicals) can be monitored over time.

During the course of a pyrolysis optimization experiment the temperature in the pyrolyzer is raised while observing the MID spectrum of the relevant ions. A given point of time in the spectrum relates to specific conditions in the pyrolyzer (electric current, voltage, temperature), as well as to conditions of the pulsed valve (frequency, opening time). As an example the g2 pyrolysis optimization MID spectrum of (Iodomethyl)trimethylsilane is given in Figure 17.
Figure 16. MID mass analysis of the pulsed pyrolysis of (Iodomethyl)trimethylsilane. In this example, the pulsed
pyrolyzer is being heated for 4:44 minutes, and then allowed to cool down again. The drop of intensity of the molecular
ion (m/z = 214) and the simultaneous increase of intensity of the main radical (m/z = 87) defines the beginning of the
pyrolysis. The maximum intensity of the radical at minute 00:04:02 corresponds to the optimum conditions for the
pyrolyzer.

Similar experiments have been done for different precursors, to further investigate the
viability of this method. In Scheme 33 the precursors tested with the g2 pulsed pyrolyzer
are summarized. In the course of these studies, the pyrolyzer overheated the pulsed valve
and broke the MACOR heat shield. It was thereby redesigned into the g3 pyrolyzer, as
described in Chapter 4.2.
Development of the Pulsed SJEP Pyrolyzer

Scheme 33. Precursors investigated with the g2 pulsed pyrolyzer in MID pyrolysis optimization experiments. The formation of the Allyl radical 2 was achieved in high yield. Methyl radical 9 could be detected, but the intensities were relatively low. For 10 the pyrolysis did not result in significant formation of the radical or the carbene. The pyrolysis of 13 resulted in a high yield of the ketene 15, while the radical 14 has been observed in low intensity. 16 could not be observed, due to its full fragmentation during electron impact ionization. The pyrolysis of 19 resulted in a high yield of 20, as shown in Figure 17. The pyrolysis of 21 has lead to the formation of benzene, while the Phenyl radical 22 was observed only in low yields.

Since a set of pyrolysis conditions is dependent on the individual pyrolyzer system (g2 → g3), the pyrolysis optimizations for some reference systems had to be done again. Allyl iodide 1 was chosen as the main reference system for the g3 pyrolyzer. Here optimizations in MBMS and measurements in matrix isolation FTIR experiments have been done. In the following Chapter this will be discussed in detail.
4.5.2 The Allyl Radical Reference Analysis

The allyl radical is one of the simplest conjugated hydrocarbon radicals. It can be generated by homolytic breaking of the C-I bond of allyl iodide (Scheme 34). This can be done by photo dissociation, as well as thermal dissociation.

\[
\begin{array}{c}
\text{H}_2\text{C} = \text{C} - \text{CH}_2 \\
\text{1} \quad \text{1} \quad \text{1} \quad \text{1} \quad \text{1}
\end{array}
\]

\[
\text{H}_2\text{C} = \text{CHCH}_2
\]

\[
\text{2} \quad \text{2} \quad \text{2} \quad \text{2}
\]

*Scheme 34.* Formation of the allyl radical 2: done by homolytic dissociation of the C-I bond in the precursor allyl iodide 1.

The resonance stabilization of the allyl radical 2 is generally reckoned to be roughly 40 kJ mol\(^{-1}\),\(^{[37]}\) As a consequence of the importance of this resonance stabilization, the thermochemistry of the allyl radical 2 has been carefully studied. Among others\(^{[38-43]}\), the infrared absorption spectrum of the allyl radical 2 has been investigated thoroughly. Nandi et al. reported an FTIR study of CH\(_2\)CHCH\(_2\) (\(\bar{X}\)) \(^2\)A\(_2\), which relied on a pulsed SJEP source for the formation of the radical 2 from precursor 1.\(^{[44]}\) This work has been used as a reference for the pyrolysis of allyl iodide 1 with the g3 pyrolyzer.

First, the mass spectrum of commercially available allyl iodide 1 has been measured (Figure 18), with an ionization energy of 15 eV and an electron beam emission of 40 µA in the mass spectrometers ionization unit. The sample was injected via the pulsed valve (10 Hz frequency, 300 µs opening time), as a mixture of 1% precursor in Helium at 1000 mbar. This was done to investigate the purity of the precursor, as well as to test for the optimal ionization energy, being used in the mass spectrometer. Increasing the ionization energy leads to increased fragmentation of the molecule. This in turn decreases signal intensity of the molecular ion. To optimize pyrolysis conditions, it is useful to observe the molecular ion with sufficient intensities. Therefore, it was necessary to perform the measurements at the lower limit of the available ionization energy spectrum (0-300 eV). For the allyl iodide 1, an electron energy of 15 eV has proven to be ideal for pyrolysis conditions: lower energy leads to a loss of overall signal intensity, and higher energy, to a loss of molecular ion signal intensity.
Figure 17. Bar mode mass spectrum of allyl iodide with an ionization energy of 15 eV. The two main ions are observed in sufficient intensities, while the atomic iodine is not being observed - presumably due to the low ionization energy being used to increase signal intensity of the molecular ion.

The two main ions have been monitored in an MID pyrolysis experiment (Figure 19) to investigate optimal conditions for the matrix isolation experiments.

Figure 18. MID mode mass spectrum of the pyrolysis of allyl iodide 1. The highest radical intensity was measured under the following conditions of the pyrolyzer: a current of 1.27 A with a voltage of 18 V (~800K), a pulse frequency of 20 Hz with an opening time of 700 µs.
This has been done, as previously explained in the example of (iodomethyl)trimethylsilane (Figure 16).

The fragmentation pattern of this precursor leads to differences in the intensity development, compared to the previously shown example. As displayed in Figure 17, the electronical ionization already leads to a high fragmentation of the molecule and an intense signal of the allyl radical (m/z = 41).

The pyrolysis conditions are optimized by monitoring the behavior of both the allyl radical and its precursor ion. Upon pyrolysis the initial intensity pattern changes: first the overall intensity drops due to the thermal decomposition of the precursor. Then the formation of the radical gradually increases up to a maximum, which leads to an opposing trend between the two monitored ions. Upon further increasing the temperature, the radical ion is also being pyrolyzed, thereby its intensity drops again. During the cool-down phase, the reverse behavior is observed. In pyrolysis, this kind of pattern behavior is observed in general, for precursors which undergo high initial fragmentation upon electronic ionization in the MS.

The condition optimizations for this pyrolysis system have been repeated several times. Optimal intensity was achieved under a current of 1.27 A and a voltage of 18 V at the pyrolyzer (temperature ~800 K), while pulsed injection had to be limited somewhat due to increasing pressure in the MS chamber.

In the MBMS experiments of this thesis, the optimal pulse conditions for this system are a pulse frequency of 20 Hz and an opening time of 700 µs. Nandi et al. used pulse frequencies of 30 to 10 Hz with opening times of 150 - 300 µs.\textsuperscript{44} While these conditions were tested in our MBMS, the resulting signal intensities were overall very low. For low settings of the opening time, the pulsed valve displayed difficulties opening at all. This observation was also reported by Zhang et al., who mentioned that longer opening times of the pulsed valve lead to lesser conversion of the precursor - presumably due to a higher gas flux through the SiC tube, which results in a poorer heat transfer and lower average temperature of the gas.\textsuperscript{5} In the presented paper by Nandi et al.\textsuperscript{44} it hasn't been mentioned which kind of poppet material has been used in the pulsed valve (Scheme 35).
Scheme 35. Parker General Valve Series 9 pulsed valve. Several poppet materials are commercially available, while the standard material (silicone) can lead to lowered performance concerning the precision of the opening times. Newly developed PEEK poppets increase the performance of the valve.

The function of the poppet is to seal the valve in its relaxed state. There are various kinds of materials available which might substantially influence the performance of the valve. In this work the high performance polymer "PEEK" (Polyether ether ketone) has been used as poppet material. Nevertheless with the presented setup the pyrolysis optimizations for this system have resulted in longer opening times then presented by Nandi et al. In the following matrix isolation FTIR experiments the found pyrolyzer conditions were used (1.27A, 18V, ~ 800K). For the pulsed valve several settings have been used, to include the settings found in the MBMS experiments, as well as the values presented by Nandi et al. in the reference. During longer opening times, in FTIR setups, low conversion of the precursor has been observed, as has been predicted by Zhang. Lowering the opening time to 150 - 250 µs resulted in a permanently closed valve, while opening times of 300 µs have lead to a satisfactory conversion of the precursor.

Table 1 gives the experimental vibrational frequencies reported by Nandi et al. for the allyl radical 2.
Table 1. Experimental vibrational frequencies ($\nu$/cm$^{-1}$) and relative infrared intensities (A/km mol$^{-1}$ as a percent of the base peak) for the matrix-isolated allyl radical 2.$^{[44]}$

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>local mode description</th>
<th>$\nu$/cm$^{-1}$</th>
<th>A/$%$</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>$a_1$ CH$_2$CHCH$_2$ asymmetric CH$_2$ stretch</td>
<td>3109</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>CH$_2$CHCH$_2$ symmetric CH$_2$ stretch</td>
<td>3052</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>CH$_2$(C-H)CH$_2$ stretch</td>
<td>3027</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>symmetric CH$_2$ scissors</td>
<td>1478</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>CH$_2$-CH-CH$_2$ stretch + CH$_2$ scissors</td>
<td>1242</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>CH$_2$-CH-CH$_2$ stretch + CH$_2$ rock</td>
<td>na</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>CH$_2$-CH-CH$_2$ bend</td>
<td>na</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>$a_2$ CH$_2$CHCH$_2$ out-of-phase umbrella</td>
<td>775?</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>CH$_2$-CH-CH$_2$ out-of-phase twist</td>
<td>na</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>$b_1$ CH$_2$(C-H)CH$_2$ out-of-plane bend</td>
<td>983</td>
<td>22</td>
</tr>
<tr>
<td>11</td>
<td>CH$_2$CHCH$_2$ in-phase umbrella</td>
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<td>100</td>
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<td>15</td>
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<td>asymmetric CH$_2$-CH-CH$_2$ stretch + CH/CH$_2$ scissors</td>
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<tr>
<td>17</td>
<td>asymmetric CH$_2$-CH-CH$_2$ stretch + CH bend</td>
<td>1182</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>asymmetric CH/CH$_2$ rock</td>
<td>na</td>
<td>-</td>
</tr>
</tbody>
</table>

The reference spectrum for the matrix isolated allyl radical 2 has been plotted from Table 1 to identify it in the measured pyrolysis deposition IR spectra. In the following Figure 20 the fingerprint region is displayed, synthesis of the allyl radical 2 via pulsed pyrolysis of allyl iodide 1 can be observed under the described conditions.
Figure 19. IR spectrum of the "fingerprint" region of the matrix isolated (Ar, 3K) pyrolysis deposition products of allyl iodide 1. (a) IR Spectrum of allyl iodide 1 after 1h of deposition of a mixture of 1% sample in argon, with a puls frequency of 10Hz and an opening time of 400 µs. (b) IR spectrum of the matrix isolated pyrolysis products after 1.5h of deposition at 2A and 18V (~800K) g3 pyrolyzer settings, with 50Hz puls frequency and 300 µs opening time of the pulsed valve, in argon at 3K. (c) Reference IR spectrum which has been plotted from Table 1, for the identification of the allyl radical 2.

After 1.5h of pyrolysis deposition in a matrix isolation setup, the most intense bands of the allyl radical 2 could be assigned. The conversion of the precursor is satisfactory under the given conditions. The remaining bands of higher wavenumbers are analyzed in Figure 21. Higher band intensities can be achieved by longer deposition times; however, this has not been done due to time limitations.
In the following Table 2, the measured bands are compared to the reference in terms of vibrational frequencies and infrared intensities. The vibrational frequencies are in agreement with the reference, while IR intensities in the region of higher wavenumbers differ - presumably due to the short deposition times.
Table 2. IR spectroscopic data of the matrix-isolated allyl radical 2.

<table>
<thead>
<tr>
<th>ν</th>
<th>Symm.</th>
<th>$\tilde{\nu}_{\text{exp.}}$ [cm$^{-1}$][a]</th>
<th>$I_{\text{rel.}}$[a, b]</th>
<th>$\tilde{\nu}_{\text{ref.}}$ [cm$^{-1}$][c]</th>
<th>$I_{\text{rel.}}$[c, b]</th>
</tr>
</thead>
<tbody>
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<td>3109</td>
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<td>3052</td>
<td>0.05</td>
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<td>3027</td>
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<td>4</td>
<td></td>
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<td>-</td>
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</tr>
<tr>
<td>8</td>
<td>$a_2$</td>
<td>-</td>
<td>-</td>
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[a] Ar, 3K. [b] Band intensity relative to the strongest absorption. [c] Ar, 10K

Based on the experience gathered by the matrix isolation of the allyl radical, it has been decided to approach new systems with the g3 pyrolyzer.

4.5.3 Hydrogen Abstraction Reactions of the Phenyl Radical in the Gas Phase

The phenyl radical (C$_6$H$_5$) is a highly reactive aromatic hydrocarbon ring intermediate, formed from homolytic cleavage of a CH bond in benzene.$^{[45-47]}$ Due to its reactivity, this radical plays a key role in combustion, especially for fossil fuels which are rich in aromatics.$^{[48, 49]}$ It is one of the simplest prototypes for open-shell aromatic species. The radical is partially stabilized due to the resonance structures arising from electron delocalization in the aromatic system.
Given the importance of the phenyl radical, there has been considerable effort extended toward its detailed spectroscopic characterization. In spectroscopic setups pyrolysis of suitable precursors has been an important method of synthesizing the phenyl radical. Due to its high reactivity, hydrogen abstraction reactions are often observed for this species, leading to the re-formation of benzene.\textsuperscript{[45]} It is not completely clear whether these reactions occur intermolecular in the gas phase, or due to surface reactions.

One of the first applications of the \textit{g3} pyrolyzer was the investigation of this matter in MBMS experiments, which will be presented in the following.

In a given pyrolysis experiment (Scheme 36) an in situ created, perdeuterated phenyl radical can either abstract an hydrogen atom somewhere from the environment (walls), or it can abstract an deuterium atom intermolecular through two body collisions with another deuterated species in the gas phase. Therefore the mass spectroscopic analysis of the pyrolysis of iodobenzene-d5 should provide useful information about the secondary reaction behavior of this model species.

\begin{center}
\begin{tikzpicture}
  \node (iodobenzene) [anchor=west] at (0,0) {\includegraphics[width=0.2\textwidth]{iodobenzene.png}};
  \node [above=0.5cm of iodobenzene] {Pyrolysis};
  \node (phenyl) [anchor=west] at (2,0) {\includegraphics[width=0.2\textwidth]{phenyl.png}};
  \node (benzene) [anchor=west] at (4,0) {\includegraphics[width=0.2\textwidth]{benzene.png}};
  \draw [->, thick] (iodobenzene) -- (phenyl) node [midway, above] {Wall collisions};
  \draw [->, thick] (iodobenzene) -- (benzene) node [midway, below] {Gas phase collisions};
\end{tikzpicture}
\end{center}

\textbf{Scheme 36.} Pyrolysis of iodobenzene-d5 results in the formation of the perdeuterated phenyl radical, and as a secondary step to benzene-d5 and benzene-d6.

Three different precursor gas-mixtures have been created for the MBMS analysis of this system: a mixture of 1 % precursor in argon, 0.3 % precursor in argon and 0.035 % precursor in argon. Secondary reactions in the gas phase are more probable for mixtures with higher concentration of the deuterated species, thereby we expected to see a higher degree of $C_6D_6$ for the mixtures of higher concentrations.
In the following figures the experimental spectra are displayed.

**Figure 21.** Pyrolysis of iodobenzene-d5 as a mixture of 1% in argon at 2000 mbar. Colored graphs: blue $\text{C}_6\text{D}_5\text{I}$, red $\text{C}_6\text{D}_5$, green $\text{C}_6\text{D}_6$, light blue $\text{C}_6\text{D}_5\text{H}$. Upon heating up, the formation of $\text{C}_6\text{D}_5\text{H}$ predominates, while at higher temperatures the formation of $\text{C}_6\text{D}_6$ gets more intense.

**Figure 22.** Pyrolysis of iodobenzene-d5 as a mixture of 1% in argon at 2000 mbar. Colored graphs: blue $\text{C}_6\text{D}_5\text{I}$, red $\text{C}_6\text{D}_5$, green $\text{C}_6\text{D}_6$, light blue $\text{C}_6\text{D}_5\text{H}$. Upon heating up, the formation of $\text{C}_6\text{D}_5\text{H}$ predominates.
Figure 23. Pyrolysis of iodobenzene-d5 as a mixture of 1% in argon at 2000 mbar. Colored graphs: blue C₆D₅I, red C₆D₅, green C₆D₆, light blue C₆D₅H. Upon heating up, the formation of C₆D₅H predominates.

Based on these results a mixture of deuterium- and hydrogen-abstraction reactions are indicated, whereas the hydrogen-abstractions predominate in all cases. However with higher concentrations of precursor, going to higher temperatures also increases the signal intensity for C₆D₆. This indicates the suspected result, that at higher concentrations of precursor also higher amounts of secondary reactions in the gas phase take place. In alternative setups like e. g. FVP this factor might be much stronger since there is no noble gas carrier "shielding" the radicals from each other.

In a further experiment the formation of the C₆D₄ diradical was monitored too. Here a parallel behavior to the formation of C₆D₆ was found for pyrolysis temperatures around 350°C. This indicates that deuterium-abstraction reactions between two radicals take place.

Further studies should include a quantitative analysis of the products, this has not been done in this work due to time limitations.
5. Studies on Organic Systems

5.1 MBMS & FTIR Studies towards N-Centered Radicals

5.1.1 Introduction

Nitrogen-centered radicals have been studied extensively in the context of radicals derived from amino acids and peptides.\cite{50, 51} The substituent effects for amino radicals have shown that nitrogen-centered radicals are more electron-deficient species, as compared to the corresponding carbon analogs. The electron donating ability of alkyl groups is stabilizing in both cases. However, the effect is significantly larger in the methylamino radical (radical stabilization energy: \( \text{RSE} = -29.4 \text{ kJ mol}^{-1} \)), as compared to the ethyl radical (\( \text{RSE} = -13.8 \text{ kJ mol}^{-1} \)). Adding a second alkyl group is also leading to more significant stabilization, as e. g. in the N,N-dimethylamino radical (\( \text{RSE} = -52.1 \text{ kJ mol}^{-1} \)), compared to the isopropyl radical (\( \text{RSE} = -23.3 \text{ kJ mol}^{-1} \)). The attachment of large \( \pi \) systems, as for example the phenylamino and the diphenylamino radicals (\( \text{RSE} = -49.2 \) and -82.2 \( \text{kJ mol}^{-1} \)), results in a stabilization of the radical center in much the same way as for carbon-centered radicals. Nevertheless, in clear contrast to alkyl radicals, the attachment of carbonyl groups to the nitrogen-centered radicals is destabilizing in general. This is a result of resonant delocalization of the unpaired spin into the \( \pi \) system of the carbonyl group, which comes along with the loss of resonant interaction between the carbonyl group and the nitrogen lone pair.\cite{50-52} To investigate the properties of such radicals, matrix isolation should pose a suitable method.

In this work the attempt to synthesize such nitrogen-centered radicals, via the pyrolysis deposition of suitable precursors in matrix isolation experiments. Preliminary mass spectroscopic pyrolysis optimizations of several dozens of precursors have been done. Based on these experiments the pyrolysis of acetone-azine 3 and methyl-hydrazine 4 was investigated in further IR experiments.
5.1.2 Pyrolysis of Acetone-Aazine

Prior to the investigation of the pyrolysis of acetone-azine 3 and methyl-hydrazine 4 in matrix isolation setups, a mass spectrometric pyrolysis study was done. A broad approach was used, comparing SJEP results of the MBMS with the established FVP approach.

![Figure 24. Pyrolysis (FVP) behavior of acetone-azine 3 (m/z = 112) and its radical (m/z = 56) through homolytic splitting of the N-N single bond. The ion intensity is plotted against the temperature in °C. The ionization was done with an electron energy of 20eV and an electron emission of 400µA.](image)

A high intensity signal of the ion at m/z = 56 was observed at temperatures between 400 °C and 650 °C. However, it is expected to have a simultaneous drop of intensity for the precursor, in case of its pyrolysis at a suitable temperature. This could not be observed here. Instead, both observed ion signal intensities began to drop around 700°C, indicating a pyrolysis process.

The interpretation of Figure 22 does not encourage relying on the ion intensities of m/z = 56, which is indicating the presence of the desired radical. However, the pyrolysis behavior of the precursor could still be observed. According to the observations, pyrolyzer temperatures between 700 °C and 800 °C should result in the decomposition of this precursor.
As a next step, the pulsed pyrolysis using the g3 pyrolyzer was monitored in the MBMS. A plot of the two signal intensities of the main ions with respect to the pyrolysis temperature is given in the following Figure 25.

![Figure 25. SJEP behavior of acetone-azine 3 (m/z = 112) and its resulting radical (m/z = 56), through homolytic splitting of the N-N single bond. Intensity of the ions plotted against the temperature in °C, ionization energy of the kathodic beam 16 eV with an electron emission of 400 µA. Pulsed nozzle parameters were 30 Hz puls frequency with an opening time of 600 µs.]

The electronic ionization has lead to an initial fragmentation of the precursor, thereby giving a high intensity signal of the signal at m/z = 56 from the start. As mentioned before, an opposing trend in the intensity development of the two graphs (after a brief drop of the overall intensity) should indicate the beginning of the pyrolysis. This could not be observed for precursor 3. To interpret Figure 25 in a way that leads to optimized pyrolysis conditions is difficult. Since the precursor seems to be pyrolyzed to a high degree, at temperatures over 900 °C, it was decided to investigate the pyrolysis products under these conditions also in matrix isolation. The best results have been achieved with a pyrolysis temperature of 1000 °C, and Figure 26 summarizes the IR spectra.
Figure 26. IR spectrum of the matrix isolated (Ar, 3K) SJEP deposition products of acetone-azine 3. (a) Calculated IR spectrum of acetone-azine at the B3LYP/cc-pvtz level of theory. (b) IR spectrum of the matrix isolated precursor 1h of deposition with 30 Hz puls frequency and 600 µs opening time of the pulsed valve, in argon at 3K. (c) IR spectrum of the matrix isolated pyrolysis products after 2h of deposition at 1000°C pyrolyzer settings, with 30Hz puls frequency and 600 µs opening time of the pulsed valve, in argon at 3K. (d) Calculated IR spectrum of the (CH$_3$)$_2$CN· radical at the B3LYP/cc-pvtz level of theory.

Besides strong absorption bands of CO$_2$, water and some more species that could not be assigned, some absorption bands of the (CH$_3$)$_2$CN· radical could be found as a result of the pulsed pyrolysis of precursor 3. However, an overall low intensity of bands at higher temperatures was observed in all experiments. This has lead to the suspicion that a leak at the base of the SiC tube developed during higher temperatures. Thereby, inhibiting the precursor to pass through the pyrolyzer and instead to be pumped out, during diffusive movement, inside the high vacuum chamber.

The effusive deposition of acetone-azine 3, and its corresponding flash vacuum pyrolysis, did not result in a good precursor conversion (Figure 27), presumably due to impurities in the pyrolyzer.
5.1.3 Pyrolysis of Methyl-Hydrazine

Prior to the investigation of the methyl-hydrazine 4 pyrolysis in matrix isolation setups, a mass spectrometric pyrolysis study was done. A similar approach was used as in Chapter 5.1.2, comparing supersonic jet expansion pyrolysis results of the MBMS with the FVP approach.
Figure 28. Pyrolysis (FVP) behavior of methyl-hydrazine 4 (m/z = 46) and the desired radical (m/z = 30) through homolytic splitting of the N-N single bond. Intensity of the ions plotted against the temperature in °C, ionization energy of the cathodic beam 20eV with an electron emission of 400µA.

In this optimization experiment the highest radical intensity was observed for temperatures around 800°C. This temperature was therefore used for the pyrolysis investigation in matrix isolation setups.

The pulsed deposition of the precursor 4 displayed a different pattern. Around 800°C the conversion of the precursor started to increase, up to a temperature of 1000°C. Afterwards the pattern changed more slowly up to 1400°C.
Figure 29. SJEP behavior of methyl-hydrazine 4 (m/z = 46) and the desired radical (m/z = 30) gained through homolytic splitting of the N-N single bond in the precursor. The intensity of the ions plotted with respect to the temperature in °C. The ionization energy of the kathodic beam was set at 20eV, with an electron emission of 400µA. The pulsed nozzle parameters were 30 Hz pulse frequency, and an opening time of 600 µs.

In matrix isolation experiments, the FVP did not result in any more useful spectra. Neither the precursor nor the radical could be observed. In the pulsed deposition spectra of 4 it was possible to assign absorption bands to the precursor, however the pyrolysis did not display any new species (Figure 29). In fact, the overall intensity seemed to drop drastically upon tempering the pyrolyzer.
5.1.4 Conclusion

The pulsed pyrolysis of acetone-azine $3$ has lead to a weak formation of the desired nitrogen centered radical in matrix isolation experiments. Nevertheless, the overall low intensity of the absorption bands indicated an insufficient gas flow through the pyrolyzer. FVP has not shown any useful information in the matrix isolation experiments, even though the mass spectra were promising.

The pyrolysis of methyl-hydrazine $4$ in matrix isolation did not result in the isolation of the desired radical. As a consequence of the results presented in this chapter, the $g_3$ pulse pyrolyzer has been redesigned.
5.2 Thermal Decomposition of 1,2,3,4,5-pentafluoro-6-iodobenzene

5.2.1 Introduction

The phenyl radical 22 (Scheme 37), being one of the most basic and important organic radicals, was studied extensively both through theory and experiment.\textsuperscript{[45, 47]} To generate this radical different techniques were used: e.g. photo dissociation, FVP with an effusive source and SJEP with a hypothermal nozzle.\textsuperscript{[45]} For further characterization, the radicals have often been trapped in cryogenic noble gas matrices.\textsuperscript{[45]}

![Scheme 37. Generation of the phenyl-radical 22 in previous matrix isolation studies by A. V. Friederichsen et al.\textsuperscript{[45]}](image)

The perfluorination of the iodo-precursor changed the mechanism of the thermal decomposition drastically. The expected C\textsubscript{6}F\textsubscript{5} radical has not been observed in the matrix isolation studies of its iodo-precursor, using pyrolysis in a low pressure platinum reactor.\textsuperscript{[6]} Fluorine substitution often leads to kinetic stabilization of reactive species, that are otherwise too reactive to be isolated.\textsuperscript{[53, 54]} This stabilization cannot be observed for this system. Instead, the thermal decomposition of perfluorated iodobenzene 5 (Scheme 38) has lead to a complete breakdown into smaller fragments (CF\textsubscript{2}, CF\textsubscript{3} and CF\textsubscript{4}).\textsuperscript{[6]}
Mechanisms have been proposed which include free fluorine atoms in the gas phase, this is likely due to the shift in fluorine. However, upon pyrolysis experiments in matrix isolation setups, with oxygen doped matrices, no FO₂ was formed, indicating the absence of free fluorine atoms.⁶ Dotation of the argon matrix at 10K with 5% O₂ resulted in the formation of CF₃O₂, as well as CO₂ and CO, as products of the pyrolysis of 5.⁶ Since photo dissociation experiments with perfluorated precursors (e.g. o,m,p-C₆F₄I₂; 1,3,5-C₆F₃I₃) have resulted in their desired radicals,⁴⁰,⁴¹,⁵⁵ it can be assumed that surface reactions inside the pyrolyzer played a key role in the observed fragmentation during the pyrolysis of precursor 5 in a low pressure platinum reactor. To avoid such reactions the residence time and number of wall-collisions of the radicals inside the source has to be diminished. A successful attempt in doing so is the pulsed pyrolysis technique. Also common flash vacuum pyrolysis (FVP) has shown good results in attempts to create organic radicals in high yields,⁶⁶ even though further reactions, both due to wall-collisions and secondary reactions in the gas phase, are still a noticeable issue for this technique.

### 5.2.2 Photodissociation Study

To identify the pentafluorophenyl radical 6, calculations at the B3LYP/aug-cc-pvtz level of theory have been done. In an experiment with pulsed precursor deposition, the photo dissociation of precursor 5 in argon at 3K was attempted (Figure 31). Due to the clear formation of the radical 6, the resulting IR spectrum has been used as a reference for identifying species 6 in every IR experimental pyrolysis study presented in this work.
Figure 31. IR Spectrum of the matrix isolated (Ar, 3K) C₆F₅ radical 6. (a) IR spectrum of the precursor 5 after 1h of pulsed deposition of a gaseous mixture of 0.5% sample in Ar at 3K. (b) Difference IR spectrum after irradiation of the precursor 5 with 254nm light for 105 min in Ar at 3K, new unidentified bands marked with a *. (c) Calculated IR spectrum of the pentafluorophenyl radical 6 at the B3LYP/aug-cc-pvtz level of theory.

The following table gives a detailed assignment of the measured bands for species 6.

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<th>$\tilde{v}_{\text{calc.}}$ [cm$^{-1}$][c]</th>
<th>$I_{\text{rel., calc.}}$[c]</th>
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</table>

[a] Ar, 3K. [b] Band intensity relative to the strongest absorption. [c] B3LYP/aug-cc-pvtz

The experiment resulting in the spectra presented in figure 31 has been done after a pulsed pyrolysis attempt with almost no precursor conversion.
However some thermal reactions took place, thereby creating an mixture of precursor 5 with minor impurities. Since the formation of radical 6 has been the only photolysis product, the resulting bands could be used to identify this species in further experiments.

### 5.2.3 Flash Vacuum Pyrolysis Study

The FVP study has been done with a quartz pyrolysis reactor, heated via a tantalum coil filament closely attached to it (Scheme 39). The temperature detection was established via a “type M” thermocouple.

![Scheme 39](image-url)  
*Scheme 39.* Flash vacuum pyrolyzer (range up to 800°C): consists of a quartz tube of 10 cm length - heated through a closely attached tantalum wiring that is set under electric current through copper electrodes. The whole system is held inside a water cooling housing, temperature detection is done “via type M” thermocouple.

First, the mass spectrum of the precursor 1,2,3,4,5-pentafluoro-6-iodobenzene 5 has been measured (Figure 32) at 15 eV and 400 µA.
Figure 32. Mass spectrum of 1,2,3,4,5-pentafluoro-6-iodobenzene 5, at 100°C FVP temperature, 15 eV ionization energy and an emission of 400 µA. The pyrolyzer was heated out before, at 800°C, in order to increase spectral background quality. However, there were still some low intensity impurities observed at m/z = 18, 56 and 99, that appear independent from the presence of the precursor.

Secondly, the FVP of precursor 5 has been monitored through MS measurements, to determine the optimal conditions for matrix isolation experiments (Figure 33).
The impurities inside the pyrolyzer became prominent at higher temperatures. By comparing the spectra (h) and (i), the pyrolysis products can be identified - here the main product of the flash vacuum pyrolysis is the C₆F₅ radical cation. Smaller intensities display the formation of the radical cations C₆F₆, C₆F₅I, CF₂, CF₃, and an unidentified signal at m/z = 253. Due to the high precursor conversion into the radical 6 (C₆F₅), at 800°C, this temperature has been chosen as the pyrolysis temperature for the following matrix isolation IR experiments.
First, after 1h of deposition of the precursor 5 in argon at 3K the IR spectrum has been measured. The gas phase IR spectrum of 5 was chosen as a reference (Figure 34).\textsuperscript{[57]}

![Figure 34. IR spectrum of 1,2,3,4,5-pentafluoro-6-iodobenzene 5. (a) IR spectrum after 1h of deposition with precursor 5. (b) IR reference spectrum of 5 in the gas phase at ambient conditions.\textsuperscript{[57]}](image)

The FVP of precursor 5 was investigated next. A broad variety of new bands appeared after 1h pyrolysis at 800°C (Figure 35 I) and II). Good conversion of the precursor, as indicated through the MS spectra at 800°C, could not be achieved in matrix isolation experiments. Several attempts to increase the precursor conversion, by decreasing the sample flow through the pyrolyzer, resulted in similar spectra, just with lower band intensity. Further increasing of the pyrolysis temperature beyond 800°C was not possible, due to the thermal instability of the quartz reactor tube. The high temperatures of the oven have presumably lead to matrix-heating, thereby increasing the broadness of the observed bands.

However, the most intense band of the radical 6 can be observed as a new band at 1501 cm\textsuperscript{-1} in the pyrolysis product spectrum (b), compared to the precursor spectrum (a).
Figure 35 I) and II). IR spectrum of the FVP deposition of precursor 5, in argon at 3K. (a) IR spectrum after 1h precursor 5 deposition in argon at 3K. (b) IR spectrum of the FVP products from precursor 5 after 1h of deposition at 800°C, matrix isolated in argon at 3K. (c) Difference IR spectrum after irradiation of precursor 5 with 254nm light for 105 min, IR absorption of the radical 6 pointing down, in argon at 3K.
The presence of smaller fragments like CF₄, CF₃ and CF₂ was indicated by some bands as pyrolysis products, these were also reported by Butler and Snelson.⁶ Similar to experiments with the FVP depositions towards the phenyl radical (from its iodo-precursor), the hydrogen abstraction product (C₆F₅H) of the radical 6 was observed. In the region of lower wavenumbers, several intense bands of the radical 6 could be identified. The formation of the hydrogen abstraction product is again suggested by several bands.

After a detailed analysis of all new bands in the Spectrum (b) of Figure 35 I) and II), the radical 6 and its hydrogen absorption product were identified. Through the literature research, no further species could be assigned. By using a theoretical approach, a clear assignment of additional species was not possible, due to the amount and broad overlap of the bands in question. The FVP for precursor 5 has lead to similar results as the pyrolysis of the non-fluorated C₆H₅I. Which resulted in the formation of the phenyl radical, as well as benzene as a secondary product, due to hydrogen abstractions.⁵⁸
5.2.4 Pulsed Pyrolysis Study

In the pulsed pyrolysis study two different pyrolyzers have been used: the \textit{g4} pyrolyzer and a more “basic” model (named here \textit{g0}) for matrix applications (Scheme 40). In the phase of redesigning the \textit{g3} pyrolyzer to the \textit{g4} pyrolyzer, this model has been used for the investigations of pulsed pyrolysis of precursor 5 in matrix isolation setups.

\textbf{Scheme 40.} The “basic pulsed pyrolyzer” \textit{g0} for matrix isolation setups. \textit{Parker General Valve Series 9} pulsed valve connected to a vacuum sealed housing. The silicium carbide tube pyrolyzer is heated resistively, and being held by, two molybdenum electrodes with a distance of 15 mm.

In the two following Figures 36 I) and II), the deposition of pulsed pyrolysis products is displayed. Since this \textit{g0} pyrolyzer cannot be implemented in the expansion chamber of the MS, preliminary MS optimization experiments were not possible.
Figure 36 I) and II). IR spectrum of the matrix isolated pulsed pyrolysis products of precursor 5, with the \( g0 \) pyrolyzer. 
(a) IR spectrum of the pulsed precursor 5 deposition after 15 min as a mixture of 0.02\% (through dilution) in argon isolated at 3K. (b) IR spectrum of the pyrolysis deposition products at 70W pyrolyzer power, for 20 min as a mixture of 0.02\% in argon, isolated at 3K. (c) Difference IR spectrum after irradiation of precursor 5 with 254nm light for 105 min, IR absorption of the radical 6 pointing down. In argon at 3K.
With the $g_0$ pyrolyzer it was not possible to monitor the pyrolysis temperature. In order to optimize pyrolysis conditions the electric power has been used as a reference. Below 40W no new bands appeared in the IR spectra, while at higher watt numbers (up to 70W) new bands appeared at [cm$^{-1}$]: 1273, 1251, 1221, 1101, 1023, 853, 843 and 707. These could be assigned mainly to the smaller fragments CF$_4$, CF$_3$ and CF$_2$, while the bands at 1023, 853 and 854 cm$^{-1}$ could not be assigned. A good conversion of precursor could not be achieved with the $g_0$ pyrolyzer. The result of this pyrolysis experiment resembles the reported results found by Butler and Snelson,[6] which was the breakdown of the precursor 5 into smaller fragments during its pyrolysis. In this report it was proposed that mechanisms including surface reactions in the pyrolyzer lead to the observed breakdown of radical 6. If the pulsed pyrolysis technique for the $g_0$ pyrolyzer worked as predicted by theory, surface reactions should have been avoided almost completely.

Ensuring an ideal behavior of a pulsed pyrolyzer poses a challenge, due to several factors: For example, its high demands towards stability, in spite of the high frequency vibrations (caused by the pulsed valve) which can lead to leaks. Here a weak point is the connection between the SiC tube and the orifice of the pulsed valve. Ensuring the quality of the gas sealing of this point is difficult, and it needs to be stable for longer experimentation times. The pyrolyzer described in Scheme 40 keeps the SiC tube under pressure in its socket, in order to improve the gas sealing quality. Nevertheless, during longer experiments, the screws causing this pressure are being loosened due to the vibrations of the pulsed valve. This in turn leads to gas leaks and lower conversion of precursor, over longer periods of time. As described before, similar difficulties were observed for the $g_3$ pyrolyzer developed in this work.

The approach to improve this point has lead to the development of the $g_4$ pyrolyzer. After finishing the construction phase, the $g_4$ pyrolyzer has been used in the MBMS to investigate the pyrolysis properties of precursor 5 (Figure 37).
In this optimization experiment the best conversion of precursor was observed at temperatures between 900°C and 1100°C (spectra e - g). Several new signals appeared at 1100°C in the region of m/z = 133 - 143, which could not be observed upon the repetition of this experiment. They have been discharged as temporal impurities. The displayed species in Figure 39 are the main products of the pulsed pyrolysis of precursor 5 in the MS setup. Upon the cooling down of the pyrolyzer from 1100°C to 600°C the mass spectra have been measured (Figure 38), to check the “symmetry” of the “pyrolysis behavior”. The reversed behavior was observed, while the highest intensity of radical 6 was a result of the pyrolysis at 1100°C.
Figure 38. Mass spectra measured during the "reversed pulsed pyrolysis" of 1,2,3,4,5-pentafluoro-6-iodobenzene 5 with pyrolyzer g4. (a) The MS spectrum measured at 1100°C while injecting a mixture of 0.025% (through dilution) precursor 5 in helium at a puls frequency of 10 Hz and an opening time of 400 µs. The MS electronic ionization worked at 16eV energy with an emission current of 400µA. The following spectra were measured using the same settings, while subsequently decreasing the pyrolyzer temperature: (b) 1000°C, (c) 900°C, (d) 800°C, (e) 700°C, (f) 600°C.

Based on this experiments, the optimized values of the g4 pyrolyzer have been applied in a matrix isolation study of precursor 5. The settings for the pyrolyzer temperature between 900°C and 1100°C showed promising results, therefore they were used in this study as well. Argon was chosen as a carrier gas for the precursor 5, while the same composition of the injected gas mixture was used (0.025% precursor, established through stepwise dilution). The pulsed valve was set to a pulse frequency of 10 Hz and an opening time of 400µs for the entire study.

A variety of new bands appeared upon pyrolysis deposition for temperatures > 900°C, the following figures present a detailed analysis of the matrix isolated pyrolysis products. To simplify the analysis, the spectra are divided in two regions: 400 to 1200 cm\(^{-1}\), and 1200 to 1550 cm\(^{-1}\).
Unidentified bands are marked with a *. (a) IR spectrum of the pulsed precursor 5 deposition after 15 min as a mixture of 0.02% (through dilution) in argon isolated at 3K. (b) Difference IR spectrum after the irradiation of precursor 5 with 254nm light for 105 min, IR absorption of the radical 6 pointing up, in argon at 3K. (c) IR spectrum of pulsed pyrolysis products of precursor 5 as a mixture of 0.025% in argon with a pulse frequency of 10 Hz and an opening time of 400 µs, heating with 50 W to a temperature of 900°C. Deposition time 30 min, products isolated at 3K. (d) IR spectrum of pulsed pyrolysis products of precursor 5 as a mixture of 0.025% in argon with a pulse frequency of 10 Hz and an opening time of 400 µs, heating with 70 W to a temperature of 1100°C. Deposition time 30 min, products isolated at 3K. (e) Plot of the experimental IR spectrum of 1,2-didehydro-3,4,5,6-tetrafluorobenzene (o-C\textsubscript{6}F\textsubscript{4}) 7 as a reference, matrix isolated in argon at 9K after a photo dissociation experiment with matrix isolated tetrafluorophthalic anhydride.\textsuperscript{59} (f) IR spectrum of o-C\textsubscript{6}F\textsubscript{4} 7 calculated at the B3LYP/aug-cc-pvtz level of theory.
Upon pyrolysis several new bands appeared. Depending on the pyrolysis temperature distinct species can be identified. First, the pyrolysis at 900°C resulted in a spectrum which indicated the formation of radical 6 under this conditions, its most intense bands at 1501 cm\(^{-1}\) and 1058 cm\(^{-1}\) could be identified (Figure 39). By increasing the pyrolysis temperature to 1100°C, several bands undergo an intensity shift compared to the 900°C spectrum, indicating the formation of a secondary species. The bands indicating the presence of radical 6 decrease, while the ones at 1484.1(s), 1457.3(m), 1074.0(m), 1070.4(w) and 970.9(s) cm\(^{-1}\) increase significantly, giving the most intense bands of the spectrum. These bands could be assigned to 1,2-didehydro-3,4,5,6-tetrafluorobenzene (\(o\)-C\(_6\)F\(_4\)) 7, by comparison with the literature references\(^{55}\) and the calculations at the B3LYP/aug-cc-pvtz level of theory.

Wenk \textit{et al.} did a photo dissociation study towards perfluorated C6 aromatic \(o,m\)-diradicals and reported a successful formation of diradical 7 by photolysis of tetrafluorophthalic anhydride in an Argon matrix at 9K.\(^{55}\) Due to the close proximity of radical 7 and CO, CO\(_2\) in the matrix cage (after photolysis), the most intense absorption at 1488.6 cm\(^{-1}\) was split into several components (Spectrum (e) in Figure 39). Radziszewski \textit{et al.} reported a similar splitting of matrix IR absorptions for the parent benzyne (\(o\)-C\(_6\)H\(_4\)), generated by photolysis of phthalic anhydride.\(^{59}\)

Calculations done in this work (Graph (f), Figure 39), in accordance with Wenk \textit{et al.}\(^{55}\), predicted no such splitting since CO\(_2\) and CO in close proximity to 7 have not been included. Through the experimental approach of SJEP this could now be confirmed. The formation of 7 in the gas phase prior to the matrix isolation with the use of a different precursor leads to no pressure induced van der Waals complexes with CO or CO\(_2\) in the matrix cage. Thereby, the splitting of the most intense mode \#22 was not observed in this approach. The C≡C stretching vibration was predicted (B3LYP/aug-cc-pvtz) to be at 2018.7 cm\(^{-1}\) with a very low intensity of 0.6 km mol\(^{-1}\) compared to 616.0 km mol\(^{-1}\) of the most intense absorption at 1502.1 cm\(^{-1}\). In the presented study, a weak absorption band at 2025.1 cm\(^{-1}\) was observed. This might indicate the C≡C stretching vibration of 7. Table 4 shows the spectroscopic data for this species.
Table 4. IR spectroscopic data for the matrix-isolated 1,2-didehydro-3,4,5,6-tetrafluorobenzene (o-C$_6$F$_4$) 7

<table>
<thead>
<tr>
<th>Mode</th>
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<th>$I_{\text{rel., exp.}}$ [a,b]</th>
<th>$\tilde{\nu}_{\text{ref.}}$ [cm$^{-1}$][c]</th>
<th>$I_{\text{rel., ref.}}$ [c,b]</th>
<th>$\tilde{\nu}_{\text{calc.}}$ [cm$^{-1}$][d]</th>
<th>$I_{\text{abs., calc.}}$ [d]</th>
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<td>-</td>
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<td>2018.7</td>
<td>0.6</td>
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Besides the formation of the **ortho**-diradical 7, an increased absorption intensity was observed, for bands that can be assigned to C$_6$F$_5$ (1534.6 cm$^{-1}$ and 1001.0 cm$^{-1}$). Increasing the pyrolysis temperature from 900 °C to 1100 °C also resulted in the increased formation of smaller fragments of CF$_4$, CF$_2$ and CF$_3$, indicating a shift of fluorine. To understand the mechanism leading to these fragments, intermediate species have to be assigned. A step in that direction is the observation of o-C$_6$F$_4$ 7, after the obvious first step of breaking the C-I bond in 5, a secondary step of severing the C-F bond in **ortho** position to the radical occurs.

Several absorption bands still need to be assigned: [cm$^{-1}$] 926.5(w), 947.8(w), 985.9(m), 1115.6(w), 1164.4(w), 1172.2(w), 1259.5(m), 1262.5(m), 1304.5(w), 1402.0(w), 1411.3(w), 1416.1(w), 1427.2(w), 1520.6(s), 1532.0(s), 1556.6(m). The identification of the **ortho**-diradical 7 proved a fluorine abstraction from the main radical 6. This might also indicate the presence of other multi radicals (**meta**, **para**-diradical), or even triradicals - see Scheme 41.
Wenk et al. reported the IR spectra for 1,3-didehydro-2,4,5,6-tetrafluorobenzene 23, isolated in Ne at 3K after a photo dissociation experiment with 1,3-diiodo-2,4,5,6-tetrafluorobenzene. Here the most intense bands are at [cm$^{-1}$] 952.3, 981.3, 992.7, 1534.2, 1605.4 and 1823.8. Upon comparison with the unidentified absorption bands measured after pulsed pyrolysis deposition, this *meta*-diradical could not be identified.

Wenk also reported IR spectra for 1,4-didehydro-2,3,5,9-tetrafluorobenzene 24, which was synthesized via photo dissociation of 1,4-diiodo-2,3,5,6-tetrafluorobenzene in neon at 3K. It was observed that 24 easily undergoes a ring opening reaction to 1,3,4,6-tetrafluoro-hex-3-ene-1,5-diyne 26 upon radiation with 260 - 320 nm light (Scheme 42).

Some of the bands appearing in pulsed pyrolysis experiments might indicate the presence of both 24 and 26. Due to the overlap and the low intensities of the absorption bands, it is not completely clear whether or not these species are present here. In the following Tables 5 and 6 a rough assignment is done:
Table 5. IR spectroscopic data for the matrix-isolated 1,4-didehydro-2,3,5,9-tetrafluorobenzene (p-C_6F_4) 24.

<table>
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<th>Symm.</th>
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<th>l_{exp}^{[a,b]}</th>
<th>v_{ref} [cm^{-1}]^{[c]}</th>
<th>l_{rel., ref.}^{[c,d]}</th>
<th>v_{calc} [cm^{-1}]^{[e]}</th>
<th>l_{rel., calc.}^{[e,d]}</th>
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</table>


Under pyrolysis conditions the para diradical 24 should easily undergo a ring opening reaction towards species 26. In Table 6 the strongest absorption band is at 2340.4 cm^{-1}, which might indicate the presence of 26.

Table 6. IR spectroscopic data for the matrix-isolated 1,3,4,6-tetrafluoro-hex-3-ene-1,5-diyne 26.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Symm.</th>
<th>v_{exp} [cm^{-1}]^{[a]}</th>
<th>l_{rel., exp.}^{[a,b]}</th>
<th>v_{ref} [cm^{-1}]^{[c]}</th>
<th>l_{rel., ref.}^{[c,d]}</th>
<th>v_{ref} [cm^{-1}]^{[e]}</th>
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<td>-</td>
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</table>

[a] Ar, 3K. [b] Band intensity as w (weak) and m (medium). [c] Ne, 3K. [d] Band intensity relative to the strongest absorption. [e] B3LYP/aug-cc-pvtz, unscaled. [f] Strong overlap with other bands.
Venkataramani et al. reported IR spectra of the matrix isolated trifluoro-1,3,5-tridehydrobenzene 25 synthesized in a FVP study from 1,3,5-trifluoro-2,4,6-triiodobenzene. The most intense absorption bands at 1738 cm$^{-1}$ and 1560 cm$^{-1}$ could not be found in the pulsed pyrolysis spectra of precursor 5.

In an attempt to further identify potential species of the decomposition process, a theoretical study was done, assuming a gradual breakdown of the ring structure into increasingly smaller fragments. Here no free fluorine atoms have been included yet, which limited the breakdown process to the C2 level (difluoroacetylene). Further decomposition into CF$_2$, CF$_3$ or CF$_4$ should include a fluorine source. However, this attempt did not result in any clear identifications due to a strong overlap of the bands in question.

Brahms and Dailey reported the IR spectrum of matrix isolated difluoroacetylene in 1989. The strongest absorption band of the CF stretching vibration at 1340.7 cm$^{-1}$ could not be observed in the spectra of SJEP experiments presented in this work.

Calculations based on Scheme 42 did not result in clear assignments of any of the given species, in fact most of them could be excluded.

Also it is not clear what happens to the "missing" carbon during the decomposition process, after the first step of forming radical 6, the carbon - fluorine ratio is 6 : 5, while at the end of the breakdown process the ratio is greatly inversed into at least 1 : 2. The observed formation of CO$_2$ and CO might explain this result. This should lead to the necessary presence of oxygen in the decomposition process. Butler and Snelson reported a significant formation of CO$_2$ and CO in their experiments, as well as the complete breakdown of the C6 ring structure. To investigate this, the measured spectra of pyrolysis experiments have been analyzed with a focus on species containing carbon, fluorine and oxygen. Scheme 44 summarizes the molecules, used as literature references.

![Scheme 43](image)

Scheme 43. Reference molecules for the analysis of IR spectra from pulsed pyrolysis precursor 5 deposition.

Molecules 27 to 31 could be excluded, since their most intense bands were not present in the measured IR spectra.
However, absorption bands of 32 and 33 could be assigned to some of the pulsed pyrolysis product bands. Kotting et al. reported the IR spectrum of matrix isolated difluoroketene 32 synthesized during a photo dissociation study in argon at 7K. The strongest absorption bands at 1426.8 cm\(^{-1}\) found for the CCO s-stretching vibration and the CF\(_2\) a-stretching vibration at 1274.4 cm\(^{-1}\) (shoulder in a broader band) can also be found in the spectra of precursor 5 SJEP deposition presented in this work (Figure 42).

The IR spectrum of matrix isolated (Ar, 12K) trifluoromethyl-peroxyradical 33 was reported by Butler and Snelson in 1979. A rough assignment of the strongest absorption bands of 33 was done in the presented SJEP IR spectra of 5, as shown in Table 7.

Table 7. IR spectroscopic data for the matrix-isolated trifluoromethyl-peroxyradical 33.

<table>
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<td>vs</td>
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\(^{[a]}\) Ar, 3K. \(^{[b]}\) Relative band intensity as w (weak), m (medium), s (strong) and vs (very strong). \(^{[c]}\) Ar, 10K

The presence of oxygen might play a role in the decomposition process. To further clarify this, additional experiments are necessary. Due to time limitations this could not be completed in this work.
5.2.5 Conclusion and Outlook

A general problem of the pyrolytic synthesis of radicals and other species of similar reactivity is the occurrence of surface related side-reactions, like hydrogen abstractions and radical recombination. To diminish this effect, the pulsed supersonic jet expansion pyrolysis approach makes use of a highly diluted precursor, carried in a noble gas. This leads to an energy transfer mainly through noble gas atoms, instead of precursor molecules colliding with the heated wall of the pyrolyzer. Therefore, side-reactions should be diminished substantially. However, this technique comes with its own challenges due to its complexity. In flash vacuum pyrolysis the energy transfer inside the pyrolyzer is not mediated by a carrier gas. Nevertheless, this technique proved its validity for many precursor systems.

Both approaches have been used for the synthesis of 1-dehydro-2,3,4,5,6-pentafluorobenzene \(6\) in matrix isolation experiments. A good conversion of precursor could not be achieved with FVP, however the shift in intensity in the region of 1501.8 cm\(^{-1}\) suggests the presence of a new species. Radical \(6\) could be assigned due to its strongest absorptions in the FVP IR spectra. Besides the radical, a significant formation of the hydrogen abstraction product (\(C_6F_5H\)) was observed, alongside ring degradation fragments like \(CF_4\), \(CF_3\) and \(CF_2\). These smaller fragments indicate the breakdown of the ring structure of radical \(6\), but it was not possible to assign any intermediate species of this process in the FVP experiments.

The supersonic jet expansion approach of a pulsed pyrolysis resulted in a fairly good conversion of the precursor and the strong formation of radical \(6\) at 900°C, followed by a significant secondary formation of the ortho-diradical \(7\) at 1100°C alongside \(C_6F_6\) and ring degradation fragments (mostly \(CF_2\)).

Due to the absence of \(CO_2\) and \(CO\) in the matrix cage, no splitting of the strongest absorption band at 1484.1 cm\(^{-1}\) for \(6\) was observed, as has been reported in the photolysis approach of Wenk et al. who used tetrafluorophthalic-anhydride as a precursor. Due to the large amount of bands in the fingerprint region of the pyrolysis deposition IR spectra it was difficult to clearly assign further species.

The presence of para-diradical \(24\) and its ring-opening product \(26\) might be indicated by some of the strongest bands of these species at 1501 cm\(^{-1}\) for \(24\) and 1072 cm\(^{-1}\), as well as 2340.4 cm\(^{-1}\) for \(26\).
Oxygen containing species might indicate the necessity of O$_2$ in the complete
decomposition of the ring structure of 6, however the only species that are suggested by
the measured spectra were at the C2 level. Absorption bands of difluoroketene 32 and
trifluoromethyl-peroxyradical 33 are suggested due to pyrolysis product bands (at 1100°C
pyrolysis temperature).

Further species could not be assigned by use of literature references and theoretical
methods. Future experiments on the basis of pulsed pyrolysis might result in a better
understanding of the decomposition mechanism leading towards the C1 fragments of
perfluorated radical C6 species. A possible approach would be studying matrix isolation
annealing experiments with oxygen doped matrices. Also the EPR analysis of SJEP
depositions of 5 might give additional information in this matter. These could lead to
further assignments of intermediate species for the thermal decomposition process of 5.
6. Experimental

6.1 Matrix Isolation

**Apparatus**

The fundamental set-up of matrix isolation spectroscopy and all standard techniques are given in the book of Dunkin. A Sumitomo Heavy Industries RDK-408 D three-staged closed-cycle helium cryostat was used for temperatures around 4 K. To obtain high vacuum a preliminary oil diffusion pump in combination with the main rotary vacuum pump was used. A second rotary vacuum pump was used for the evacuation of gas tanks and gas lines. A Penning vacuum gauge was used for high vacuum measurement. IR measurements are made with a CsI window (MIR) connected to a copper framework of the cryostat and a thermal contact is made using an indium wire.

**Deposition Conditions**

The matrices were generated according to the used technique of deposition. In the effusive approach co-deposition of the compound with a large excess of inert gases, based on slow-spray on techniques, was used. All precursors were sublimed separately from a second arm using a furnace (Büchi GKR-51) and heating bands when needed. For the pulsed techniques the precursors were pre-mixed in a large excess of inert gas and then deposited together through the pulsed nozzle. The standard composition of such a mixture would be between 0.01 % and 0.025 % of precursor in the noble gas at pressures around 2000 mbar, several steps of diluting initial high percentage of precursor ensured the targeted percentage values of the composition. For the pulsed deposition the conditions of puls-frequency and the opening-time of the nozzle may vary according to the system investigated. The spectroscopic window was retained at 20 K for depositions with argon, in order to obtain optical clear matrices. Normal deposition times were between 20 minutes and two hours. In case of the effusive deposition, the flow of the inert gases was controlled using a MKS mass-flow controller with a MKS type 247 four channel readout apparatus. The flow rate was kept constant between 0.7 sccm and 2 sccm per minute. All inert gases were purchased from Messer Griesheim with purity of 99.9999 %.
Flash Vacuum Pyrolysis

For FVP a pyrolysis oven was used, which consisted of a quartz tube with an inner diameter of 8 mm, coiled over a length of 8 cm with tantalum wire. The coil could be heated by electrical resistance using an external power supply. The outward heat radiation was minimized using a sheet of tantalum metal taped around the heating zone; the sheet was slightly bigger in diameter than the quartz tube. The external part of the apparatus was cooled using water circulation (10 °C). The sample is sublimed into the pyrolysis zone at high vacuum and trapped, with an excess of codeposited inert gas, on top of the spectroscopic window. The temperature of the pyrolysis was measured using a PT100-sensor, which is placed at the exit of the oven in a way that contact to the quartz surface is avoided. The pyrolysis deposition was performed with spectroscopic window temperatures around 20 K. Impurities in the oven are removed through pre-heating of the oven to temperatures between 700 °C and 800 °C. The usual FVP deposition time was between one and two hours.

6.2 Mass Spectrometer

For mass spectra, a Hiden HAL7 RC(7U)-series quadrupol mass spectrometer was used. The spectrometer consists of four chambers: two for the sample injections (using either effusive- or pulsed methods), the main chamber of the mass detection unit and a chamber for removing residual gas.

The Pulsed Sample Injection Chamber

The pre-vacuum (1x10⁻³ mbar) in this sample injection chamber is established via an Oerlikon TRIVAC NT5 rotary vane vacuum pump, which gives the initial vacuum pressure for the start of a Oerlikon TURBOVAC TMP 361 C water cooled high vacuum pump. Vacuum pressures of 1x10⁻⁶ mbar are achieved, the vacuum quality is reduced due to O-ring sealing system of the positioning device. This pumping system has been chosen for its high tolerance towards pressure variations, which is caused by the pulsed high pressure gas injections during experimental conditions.
The pre-vacuum quality of this chamber is controlled via a Varian Type 0531 Vacuum gauge connected to a Varian 845 vacuum ionization gauge (labeled "VP2"), and the high-vacuum quality via a Leybold Penningvac high voltage vacuum sensor (measurement range $1 \times 10^{-9}$ mbar to $1 \times 10^{-2}$ mbar, labeled "UHV2") connected to a Leybold COMBIVAC CM 31 (PM measurement channel). The sample feeding system of this chamber is a 2 L stainless steel mixing bottle, for pressures up to 2000 mbar. For the evacuation of this section, as well as the degassing of precursor samples, a vacuum of $1 \times 10^{-3}$ mbar can be established via a Oerlikon TRIVAC NT5 rotary vane vacuum pump. It is controlled via a Varian Type 0531 Vacuum gauge (labeled "RP4") connected to a Varian 804-A Thermocouple vacuum gauge.

**The Ion Detection Chamber**

The pre-vacuum ($1 \times 10^{-3}$ mbar) in this chamber is established via an Oerlikon TRIVAC NT10 rotary vane vacuum pump, which gives the initial vacuum pressure for the start of a Oerlikon TURBOVAC TMP 361 air cooled high vacuum pump ($1 \times 10^{-9}$ mbar). This pumping system has been chosen for its high vacuum quality. The pre-vacuum quality of this chamber is controlled via a Varian Type 0531 Vacuum gauge, connected to a Varian 845 vacuum ionization gauge (labeled "VP1"), and the high-vacuum quality via a Leybold Ionivac ultra high vacuum gauge sensor (measurement range $2 \times 10^{-11}$ mbar to $1 \times 10^{-2}$ mbar, labeled "UHV1"), also connected to the Varian 845 vacuum ionization gauge. Under experimental conditions, pressures in the region of $10^{-8}$ mbar to $10^{-7}$ mbar are used. Upon high pressure peaks ($>1 \times 10^{-6}$ mbar), a failsafe system switches off the mass spectrometer interface unit, in order to protect the spectrometer from damage.

**The Chamber for Residual Gas Removal**

The pre-vacuum ($1 \times 10^{-3}$ mbar) in this chamber is established via an Oerlikon TRIVAC NT10 rotary vane vacuum pump, which gives the initial vacuum pressure for the start of a Oerlikon TURBOVAC MAG air cooled high vacuum pump ($1 \times 10^{-9}$ mbar). This pumping system has been chosen for its high vacuum quality.
The pre-vacuum quality of this chamber is controlled via a Varian Type 0531 Vacuum gauge (labeled "VP3"), connected to a Varian 804-A thermocouple vacuum gauge, and the high-vacuum quality via a Leybold Ionivac ultra high vacuum gauge sensor (measurement range $2 \times 10^{-11}$ mbar to $1 \times 10^{-2}$ mbar, labeled "UHV3") connected to a IONIVAC IM 540 vacuum gauge.

**The Effusive Sample Injection Chamber**

The effusive sample feeding system of this chamber is based on a pre-vacuum pump, for the evacuation of this section, as well as the degassing of precursor sample. Here a Oerlikon TRIVAC NT5 rotary vane vacuum pump is used. The vacuum quality is controlled via a Varian Type 0531 Vacuum gauge (labeled "sample 5") connected to a Varian 804-A Thermocouple vacuum gauge. To establish high vacuum ($1 \times 10^{-9}$ mbar), the FVP chamber is opened towards the MS chamber, this allowing the high vacuum pumping system to evacuate both departments (vacuum sensor "UHV2" applies here as well).

The four described chambers are connected, and separated, through three gate valves (labeled "A, C & F" at the spectrometer), which are manually opened and closed whenever necessary.

**Mass Experiments**

Unless otherwise mentioned, all mass experiments have been performed with the values shown in table 8. Samples have been prepared according to their injection mechanism. In the case of the FVP the samples were degassed several times before being fed into the spectrometer by use of a needle valve to ensure precise flow. The pulsed sample injection for the molecular beam machine has to rely on a high pressure gas mixture of a very low percentage of precursor in an excess of noble gas (mostly helium was used). In a standard experiment stepwise dilution of the gas mixture ensured precise values of 0.01% - 0.025% precursor mixed in 2000 mbar helium. The flow is regulated through the settings of the pulsed valve, which had to vary according to the different precursors in use, as has been previously described.
Table 8. Settings of the mass spectrometer for the performance of a standard mass experiment.

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6.3 IR Spectrometer

Matrix infrared spectra were recorded with Bruker IFS66 and IFS66s FTIR spectrometers with a standard resolution of 0.5 cm\(^{-1}\), using a detector range of 400 - 4000 cm\(^{-1}\). For each spectrum 500 - 2000 scans were accumulated. The spectrometer and outer windows were purged with dry air in order to get rid of CO\(_2\) and water from the atmosphere.

6.4 Source of the Precursors

All precursors have been purchased from Sigma Aldrich in the following degrees of purity: Allyl iodide 98%, Acetone azine 98%, Methyl hydrazine 98%, Iodopentafluorobenzene 99%. The purity has been analyzed by use of mass spectroscopy for each precursor. If necessary, additional purifications have been done, prior to further investigations.

6.5 Quantum Chemical Calculations

Quantum chemical calculations were carried out using Gaussian 03 and Molpro 2001 on Linux PCs as well as on SGI power challenge and SGI Origin work stations. Geometry optimizations and frequency calculations were done with the Gaussian 03 and 09 program packages. The visualization of the optimized structure, molecular orbitals, and normal modes was done with Gauss View and Molden. The geometry optimizations of all molecules were fully done using a DFT functional (B3LYP) and analytic second derivatives were calculated to characterize the stationary points as minima of transition states. Tight convergence criteria for gradients with maximum residual forces on nuclei below 0.000015 au were used throughout in order to obtain accurate geometries. For open-shell systems a spin-unrestricted formalism was used. All π electron orbitals were chosen as active spaces in multi-reference calculations. For molecules containing a σ radical, this orbital has also been taken in the active space. For most computations a basis set of cc-PVTZ or aug-cc-PVTZ has been chosen.
6.6 Calculations

![Structure of 1,2-Diisopropylidenehydrazine](image)

1,2-Diisopropylidenehydrazine 3, b3lyp/cc-pvtz

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Absorption bands of 2-Propanimine, 3lyp/cc-pvtz

2-Propanimine, 3lyp/cc-pvtz

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\text{H}_3C
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2-Iminopropyl, b3lyp/cc-pvtz

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Experimental

Methylhydrazine, b3lyp/cc-pvtz

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Methanamine, b3lyp/cc-pvtz

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Absorption bands of Methanamine, b3lyp/cc-pvtz

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Absorption bands of 1,2-didehydro-3,4,5,6-tetrafluorobenzene, b3lyp/aug-cc-pvtz

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![Diagram](image.png)

1,3-didehydro-2,4,5,6-tetrafluorobenzene, b3lyp/aug-cc-pvtz

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Absorption bands of 1,3-didehydro-2,4,5,6-tetrafluorobenzene, b3lyp/aug-cc-pvtz

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1,2,3,4,5-Pentafluorobenzene, b3lyp/aug-cc-pvtz

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Absorption bands of 1,2,3,4,5-Pentafluorobenzene, b3lyp/aug-cc-pvtz

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Absorption bands of Hexafluorobenzene, b3lyp/aug-cc-pvtz

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Scheme 44. The expansion chamber (1), the positioning device (2/3), the cooling housing (4) and the SJEP pyrolyzer in its latest version (5) and the molecular beam skimmer (7). On the top left the "catching" chamber for the molecular beam is shown.
7.1 Developed Parts For The Expansion Chamber

Scheme 45. The molecular beam skimmer (2), held by ring (1), on its mounting plate (3). Prolonging through tube (4) in order to move the skimmer in a central position inside the expansion chamber.
Drawing 1. Technical data for the parts (1) - (3), shown in Scheme 46.
Drawing 2. Overview of the positioning device. (1) connects the device to the expansion chamber, (2) holds the cooling housing, and with it the pyrolyzer, in position. (3) is used to press (1) and (2) together in order to vacuum seal the chamber through an o-ring.
Drawing 3. Technical data for part (1), shown in Drawing 2.
**Drawing 4.** Technical data for part (2), shown in Drawing 2.
**Drawing 5.** Technical data for part (3), shown in Drawing 2.
7.2 The Cooling Housing

**Drawing 6.** Overview of the cooling housing. (1) is held inside the positioning device for molecular beam alignment, (2) are the two o-rings for vacuum sealing of the chamber, (9/11/13) are the different tubes building the water cooling chamber. (14/15) are the "connecting plate" for matrix isolation experiments.
**Drawing 8.** Technical data for part (9/11), shown in Drawing 6.
**Drawing 9.** Technical data for part (13), shown in Drawing 6.
Drawing 10. Technical data for part (14), shown in Drawing 6.
**Drawing 11.** Technical data for part (15), shown in Drawing 6. This is the "faceplate" for irradiative heat sealing towards the matrix window.
7.3 The Beam "Catching" Chamber

Drawing 12. Technical data of the beam "catching" chamber
7.4 The g3 and g4 SJEP Pyrolyzer

The technical drawings of the g3 and g4 pyrolyzer as well as the post mixing chamber will be presented here. Common for both are the electrical feedthroughs and the carbon electrodes (Drawing 13 and 14).

**Drawing 13.** Technical data for the electrical feedthroughs of the different SJEP pyrolyzers.
**Drawing 14.** Technical data of the carbon electrodes for the g3 and g4 SJEP pyrolyzer.
Scheme 46. Overview of the g3 pyrolyzer. (2) is the main plate with electrical feedthroughs, (3) the pulsed valve, (4/5) the gas sample feeding tube, (6) the electrical feedthrough for the temperature detection, (7) the feedthroughs for oven heating and the pulsed valve and 8 the water cooled mounting plate for the MACOR tube and the SiC pyrolyzer tube.
Drawing 15. Technical data of the main plate (2) shown in Scheme 47.
Scheme 47. The g3 pyrolyzer: (1) is the water cooled mounting plate, (2) the MACOR heat shield, (3) the SiC tube and (4) the carbon electrodes.
**Drawing 16.** Technical data of the MACOR heat shield (g3 and g4), shown in Scheme 48 and 49.
**Drawing 17.** Technical data of the SiC pyrolyzer tube (g3 and g4), shown in Scheme 48 and 49.
Scheme 48. The g4 SJEP pyrolyzer: (2) is the main plate with electrical feedthroughs, (3) the pulsed valve, (6) the electrical feedthrough for the temperature detection, (7) the feedthroughs for oven heating and the pulsed valve, (8) the water cooled mounting plate for the MACOR tube, (11) the head-plate of the pulsed valve, (16) the mounting plate for the SiC tube and (17) the flexible inlet for tube (18).
Drawing 18. Technical data of the main plate (2) shown in Scheme 49.
**Drawing 19.** Technical data of the water cooled mounting plate (8) shown in Scheme 49.
**Drawing 20.** Technical data of the pulsed valve head plate (11) shown in Scheme 49.
Drawing 21. Technical data of SiC mounting plate (16) shown in Scheme 49.
**Drawing 22.** Technical data of tube (17) shown in Scheme 49.
**Drawing 23.** Technical data of tube (18) shown in Scheme 49.
Scheme 49. The g4 SJEP pyrolyzer with an additional post mixing chamber (10). A sample screw (15) and a expansion screw (14).
Drawing 24. Technical data of the post mixing chamber (10), shown in Scheme 50.
**Drawing 25.** Technical data of the expansion screw (14), shown in Scheme 50.
Drawing 26. Technical data of the sample screw (15), shown in Scheme 50.
8. References


9. Acknowledgement

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01/2011 – 03/2011: Philosophie I, Institute of Delhi

04/2008 – 03/2010: Master of Science, Abschlussnote: 1,0, Studiengang Chemie, Ruhr-Universität Bochum, Spezialisierung Organische Chemie, Thema der Abschlussarbeit: Aufbau einer Anlage für die Pulspyrolyse am Massenspektrometer zur Spektroskopie reaktiver Intermediate


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08/1993 – 06/1999: Realschulabschluss
Berufspraxis

06/2010 – 12/2014: Wissenschaftlicher Mitarbeiter

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• Analytik und Beratung (Massenspektroskopie) bei verschiedenen Promotionsprojekten
• Betreuung von Studenten (z.B. Praktika in grundlegender und fortgeschrittener organischer Synthesechemie)

04/2009 – 05/2010: Wissenschaftliche Hilfskraft

• Durchführung von massenspektroskopischen Experimenten zur Charakterisierung organischer Radikale


• Einarbeitung in HIDEN HAL7 RC(7U) Quadrupol Massenspektrometer zur Analytik der Gasphase von "Flashvakuum-Pyrolyse" Experimenten (FVP)

04/2008 – 05/2008: Wissenschaftliche Hilfskraft

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• Synthese und Charakterisierung

EDV-Kenntnisse

• Office-Paket: sehr gute Kenntnisse
• Analytik Software: sehr gute Kenntnisse
  (OPUS, MasSoft)
• Bildbearbeitung: gute Kenntnisse
  (Corel Draw, Inkscape)
• Chem.-Office sehr gute Kenntnisse
  (Marvin, Chemdraw)

Sprach-Kenntnisse

Deutsch: Muttersprache
Englisch: Sehr gute Kenntnisse, verhandlungssicher
Französisch: Grundkenntnisse

Ort / Datum:

Unterschrift: