Optical spectroscopy of interstellar and circumstellar molecules
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Introduction
1.1 Introduction

Modern astronomy is still mainly based on the observations of the material that is surrounding the Earth. Most conclusions and theories about the main building blocks, the species, and even the formation and ongoing development of the Universe are based on the observations of light that reaches the Earth’s atmosphere in each moment. Light in this respect is a universal carrier of vast information about our past as well as our present. To understand the information that is encoded in form of electromagnetic wave packages is the task of spectroscopists and is the task I was facing when starting my thesis.

Detecting light of different energies that reaches us from places far away from the Earth can give information about the ongoing chemistry, molecule formation, reaction channels and even about the physical conditions that occur in environments far away from Earth. Last but not least the information that we obtain from the spectroscopic investigation of light gives also hint about formation and creation of life. The origin of life provides a strong motivation to investigate the chemistry that is going on thousands of lightyears away and that took place millions of years ago.

The challenge that modern astrochemistry is facing is the limited number of building blocks that we know about, it is the harsh conditions in circumstellar shells, in proto-planetary disks, in photon-dominated regions (PDRs) or in general in the interstellar medium (ISM). These harsh conditions put constraints on possible reaction pathways. The restrictions and different conditions push researchers to a re-think of the rules of chemistry and physics prejudiced by the experiences we make on Earth.

The field of observational astrophysics combined with experimental astrophysics or astrochemistry is a complex field and will be limited here mainly to reflect the ongoing search of the molecules in the ISM. The search for the “Molecular Universe”, its main building blocks and its understanding and the challenges that it provides will be described in the following chapters.

1.2 This Thesis

In this thesis the importance of the correlation between laboratory spectroscopy and observational astronomy is discussed. It will be shown how the two different approaches correlate to each other and that mainly due to the combination of both techniques, the laboratory ~ and the observational study, conclusions can be drawn on the molecular inventory of the interstellar and circumstellar medium. The outcome of the study on the molecular inventory can in turn put constraints on the chemistry and also on the physical conditions in specific environments.

1.3 Observational Spectroscopy of Molecules in the ISM

Information of the species that are abundant in space is important. The information assist our understanding of the mechanisms that drive the evolution of the universe. Atoms or
molecules are not only abundant around stars, but they are also an important component in the medium in between the stars. As stars evolve, stellar winds can blow-off material from the stars that subsequently enriches the ISM. That way atoms like H, He, but also C, O and N become part of the ISM. Supernovae can also form heavier elements that also enrich the ISM. The molecular constituents of the ISM are known to be important for the heating and cooling mechanisms. At low densities for example, CO is an important coolant and dominates the process because of the high abundance of CO compared to other species. At higher densities, other species take over and dominate the cooling in molecular clouds, for example H2O and O2. In neutral regions, HI regions, heating can be traced mainly by observations of other ionized trace species, mainly larger molecules, but also dust grains. Dust grains can also be important in regions with a strong UV field. Here they absorb the photons and become excited. De-excitation can be through emission of photons in the IR, which lead to the so-called PAH (polycyclic aromatic hydrocarbons) emission bands at specific frequencies. The emitted photons can in turn excite other molecular species ro-vibrationally. In this way molecules have a strong influence of the mechanisms that drive the ISM, they influence the thermal balance and provide coupling between key processes that also drive star and planet formation. The spectra of molecules also provide a sensitive tool to study the excitation and/or de-excitation mechanisms, which eventually reflect the radiation field, temperatures and densities of their environment (see Tielens (2005) for an overview on this topic). Eventually they are the key ingredients for the formation of life.

1.3.1 The Molecular Inventory

Table 1.1 gives an overview of the molecules that have been identified in the ISM and in circumstellar shells up to now. About 170 molecules proof that the molecular inventory is rich and provides a basis for a large chemical reaction network (see also (Herbst & van Dishoeck 2009, Tielens 2005)).

1.3.2 The Radio Regime of the ISM

A major fraction of the molecules displayed in table 1.1 is organic in nature, i.e. they contain carbon. Especially the larger species are dominated by carbon atoms forming often chain-like structures, as can be seen by the largest species identified so far: HC11N (Bell et al. 1997). Only recently the C60 and C70 molecules were detected (Cami et al. 2010). The molecules can be divided in saturated and unsaturated species, depending on their radical nature. Radical species contain double or triple bonds, that become saturated if sufficient hydrogen is available. The majority of these molecules have been identified mainly through the comparison of their rotational transitions with laboratory data. In order to be observable by rotational transitions the molecules require a dipole moment, which is the case for polar species. A spectrum showing the manifold of species that can be detected in the submillimeter regime is depicted in Fig. 1.1. The formation process of these unsaturated carbon chain species involves a simple chemistry which enhances formation in harsh environments and thus detection of the species.
Table 1.1 – Molecules in the ISM or in circumstellar shells (December 2010, data taken from CDMS (Cologne Database for Molecular Spectroscopy)).

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(?) Some detections that have been reported as secure ones are indicated by (?), because (partial) overlap of lines cannot be ruled out at the moment or because the line list is somewhat small.

The year most relevant to the detection (including isotopic species or vibrationally excited states) is given for recent results – the past two to three years.
Formation of molecules inside dense clouds involves photodissociation of CO to form C and O by the cosmic-ray induced photons following excitation of H\textsubscript{2} into the Lyman and Werner bands. Starting with carbon, reactions with H\textsuperscript{+} can take place to form smaller species, i.e. CH\textsuperscript{+}. Upon reaction with another H\textsubscript{2} hydrocarbon ions can be formed, for example: CH\textsuperscript{3+} or CH\textsuperscript{5+}. Upon proton transfer or dissociative electron recombination neutral species like CH\textsubscript{3} and CH\textsubscript{4} can form.

\[
\begin{align*}
C + H\textsuperscript{+} & \rightarrow CH\textsuperscript{+} + H \\
CH\textsuperscript{+} + H\textsubscript{2} & \rightarrow CH\textsuperscript{2+} + H \\
CH\textsuperscript{2+} + H\textsubscript{2} & \rightarrow CH\textsuperscript{3+} + H \\
CH\textsuperscript{3+} + H\textsubscript{2} & \rightarrow CH\textsuperscript{5+} \\
CH\textsuperscript{5+} + electron & \rightarrow CH\textsubscript{4} + H
\end{align*}
\]

Insertion reactions of C\textsuperscript{+} followed by dissociative electron attachment lead to longer carbon chains or hydrocarbon-chains, for example C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} and C\textsubscript{2}H\textsubscript{2} (acetylene) (Tielens 2005).

\[
\begin{align*}
C\textsuperscript{+} + CH\textsubscript{4} & \rightarrow C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} + H \\
C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} + electron & \rightarrow C\textsubscript{2}H\textsubscript{2} + H
\end{align*}
\]

An important reaction to start interstellar chemistry is the formation of CH\textsubscript{2}\textsuperscript{+} from C\textsuperscript{+} and H\textsubscript{2} that proceeds rapidly under interstellar conditions:

\[
C\textsuperscript{+} + H\textsubscript{2} \rightarrow CH\textsubscript{2}\textsuperscript{+} + h\nu
\]
That way cationic and neutral species, saturated ~ and unsaturated ones, can be formed in the gas phase. The formation of saturated molecules mainly happens on surfaces of dust grains. These reactions can also be simulated in the laboratory and it seems that especially pathways for the formation of H$_2$O and larger species such as methanol or formic acid, i.e. CH$_3$OH or HCOOH, are enhanced on grain surfaces or icy mantles (Ioppolo et al. 2008, Fuchs et al. 2009, Öberg et al. 2009, Ioppolo et al. 2010).

1.3.3 The Infrared Spectrum of the ISM

Shifting the wavelengths of observations from the radio regime to the mid-IR regime another plethora of spectral features is revealed. This wavelength regime mainly only opened up with space based or airborne observatories (Haas et al. 1995). In this regime molecules cannot only be traced due to their rotational transitions but also due to their vibrational transitions. In this regime many observations have been carried out and a complex inventory was revealed by the spectra that could be taken from the Infrared Astronomical Satellite (IRAS), Infrared Space Observatory (ISO) or the Spitzer Space Telescope. IRAS discovered wide-spread emission in the ISM (the IR cirrus) around 12 $\mu$m. Many more of these bands were discovered subsequently and are located around: 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 $\mu$m. Nowadays, it is widely accepted that these emission bands originate from photon-pumping of larger molecules, mainly C$_{20}$ - C$_{100}$ (Allamandola et al. 1989, Puget & Leger 1989, van Dishoeck 2004, Tielens 2008). The emission features are plotted in Fig. 1.2 and can be detected in HII regions, reflection nebulae, young stellar objects and in the outflows of post-AGB stars (for example HD 441799 associated with the Red Rectangle proto-planetary nebula).

These large molecules, so called PAHs (polycyclic aromatic hydrocarbons), show fluorescent emission between 5 and 20 $\mu$m, illustrate the richness and dominance of molecular species in a wide variety of environments. It was shown that these species possess large UV cross-sections and that way they can absorb light in the UV. Due to large ro-vibrational overlap of the manifold of states, internal conversion and energetic dissipation of the absorbed photon energy is possible and the energy can efficiently be transferred to lower energy levels. Re-emission of the energy causes the emission bands in the IR. That way the species can survive harsh conditions of strong UV radiation fields in the ISM. Emission of radiation then occurs at very specific frequencies, corresponding to certain vibrational modes, i.e. bending and stretching modes of hydrocarbons (Duley & Williams 1979) as could be verified in laboratory studies. The molecules that may contribute to the PAH emission features are schematically depicted in Fig. 1.3.

The chemistry of such molecules seems to be more complex than the ion-molecule chemistry. Most likely these species are reformed in a sooting process in ejecta of carbon-rich AGB stars (Latter 1991, Cherchneff et al. 1992) and very similar to soot formation on Earth (Frenklach & Feigelson 1989, Allamandola et al. 1989). CO as well as C$_2$H$_2$ (acetylene) molecules have been found to be very abundant in AGB objects. Mainly all carbon in these objects is locked up in form of these two molecules. The formation of larger PAHs mainly follows from the reaction of acetylene with hydrogen.
1.3 Observational Spectroscopy of Molecules in the ISM

Figure 1.2 – The spectrum shows the richness and dominance of the so-called PAH IR emission bands. These bands can be detected over a wide variety of objects in space. Figure adopted from Tielens (2008).

\[
3 \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_5 + \text{H}
\]

In short, two acetylene molecules react under hydrogen abstraction with a third acetylene molecule. The resulting C₆H₅ radical forms upon ring closure the first aromatic ring species (Frenklach & Feigelson 1989). If for once these ring-bearing species could be formed, they enrich the ISM by winds from the central star (Speck & Barlow 1997, Boersma et al. 2006). Once the ring-bearing species have been formed, they can condense to form larger molecules of poly-condensed rings: polycyclic aromatic hydrocarbons. Some of the species that are formed that way are plotted in Fig. 1.3.
Figure 1.3 – Some examples of condensed ring-bearing species are shown - polycyclic aromatic hydrocarbons (PAHs). Figure adopted from Salama et al. (1996).

1.3.4 The Optical Spectrum of the ISM

As we have seen the mid-IR regime, but also the radio regime of the ISM, shows a variety of species and is remarkably rich in its spectral features. But the longest standing history of observations of the interstellar material is the one of optical spectroscopy. Hartmann (1904) reported for the first time cases of a stationary ionized calcium line towards a spectroscopic binary. Two decades later the identification of both the interstellar calcium H & K lines, as well as the Na D₁ and D₂ lines were well accepted (Struve 1927, 1930).

Mary Lea Heger in 1922 was the first person to report two new possible stationary diffuse absorption lines in the optical spectra of several B-type stars (Heger 1922).

Systematic studies started with Merrill (1934), who studied binary systems and soon discovered four more interstellar absorption bands centred around ~ 5780.4, 5796.9, 6283.9 and 6613.9 Å. In 1937 Merrill et al. (1937) discovered 5 more lines. The idea that interstellar molecules could cause some of the absorption bands came up by Swings & Rosenfeld (1937) and subsequently molecules like CH and CN could be identified (McKellar 1940) at ~ 3874.6 Å and ~ 4300.2 Å. After comparison with laboratory
Figure 1.4 – A simulated spectrum of the DIBs catalogue as available online by Hobbs et al. (2009).

data Douglas & Herzberg (1941) identified the CH$^+$ cation in the spectra at $\sim$ 4232.6 Å, 3957.7 Å and 3745.3 Å. Especially the advances in laboratory spectroscopy lead to the identification of most molecular species in the ISM (see table 1.1).

Up to now more than 400 absorption bands have been detected in the ISM in diffuse clouds that are seen towards reddened stars. These so-called diffuse interstellar bands (DIBs) are still elusive, even now, nearly 100 years after their discovery and despite of all the advances in radio and IR astronomy and technical developments in the laboratory.

The DIBs seem to be easily reproduced by the different environments occurring in the interstellar medium, since the bands have been detected in different lines of sight. In 1975 Herbig (1975) published a first systematic survey of the DIBs as detected on photographic plates. Some 39 DIBs were recorded at this time. Jenniskens & Desert (1994) started a systematic search for the DIBs in the spectra of four reddened stars and his research group detected another 64 new bands and in addition another 69 “possible” DIBs, that still needed to be confirmed at this time. Only 6 years later, in 2000, Tuairisg et al. (2000) published a new survey of the DIBs and raised the number of DIBs to 226, along with $\sim$ 25 “possible” detections awaiting confirmation. Finally, Hobbs et al. (2009) published the most recent study up to now, using Echelle spectra of HD 183143 with a resolving power of $R = 38,000$. This most recent catalogue has a total number of 414 bands and an additional list with 71 “possible” DIB detections is presented.
Fig. 1.4 shows the observed DIB spectrum, simulated here from the data as available online from Hobbs et al. (2009). Nowadays, nearly 100 years later, unambiguous identification of the DIBs is still lacking. Solid state particles, such as silicates, were excluded due to lack of polarization (Adamson & Whittet 1992). The idea that the DIB carriers are in the form of gas-phase species more than in or on grains, is implied by the fact that some DIBs reveal substructures in their absorption bands. This substructure seems to indicate not fully resolved rotational substructure, as can be the case for molecular gas-phase species. Recent studies seem to indicate that the similar behaviour of the DIBs in different environments—and thus under different environmental conditions—reflect structurally related carriers. The behaviour may reflect an interplay of ionization, electronic excitations, formation and destruction mechanisms of carbonaceous species (Herbig 1993, Cami et al. 1997, Sonnentrucker et al. 1997). Examination of the DIBs has revealed correlations that suggest that the DIBs or the family of DIBs respond differently due to ionizing radiation, shielding by interstellar grains and possibly a different behaviour because of different ongoing chemistry. With this idea the characterization of DIBs into certain families of bands has been pushed forward. Krelowski & Walker (1987) have proposed three families of bands, based on the variations in strengths they found in different lines of sight. Among the most likely carriers – as it is thought nowadays – are pure carbon chains and hydrocarbons, cationic PAHs and fullerenes (Ehrenfreund & Foing 1995, Salama et al. 1996, Tulej et al. 1998, Foing & Ehrenfreund 1994, 1997, Zhou et al. 2006, Linnartz et al. 2010, Maier et al. 2010).

1.3.4.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Since neutral PAHs have been found to absorb in the UV and re-emit in the IR, it was supposed that the DIBs may be caused by cationic species of PAH molecules. The absorption bands that way shift to smaller energies. PAHs seem to be among the abundant carbon species in the ISM and the fingerprints of emission bands in the IR can be seen in various environments (Puget & Leger 1989). About 1-10% of the galactic carbon could that way be locked up in form of PAHs.

1.3.4.2 Fullerenes

Fullerenes are a special form of pure carbon, like graphene or diamonds. Kroto et al. (1985) discovered the polyhedral structure and Krätschmer et al. (1990) synthesized the first fullerene C\textsubscript{60} from condensed soot. The stability is remarkable and this suggests that fullerenes may be around in interstellar space (Ehrenfreund & Foing 1995). Indeed the first C\textsubscript{60} and C\textsubscript{70} molecules were just identified in the ISM and may strengthen the hypothesis further (Cami et al. 2010).

1.3.4.3 Pure Carbon and Hydrocarbon Chains

In the laboratory carbon chains as well as hydrocarbons have been found to absorb and emit light strongly in the optical spectrum. Identification of many pure carbon chains and
hydrocarbons in different interstellar environments are often used to make the connection to carbon chains as possible DIB carriers (Bell et al. 1997, Gottlieb et al. 2000, McCarthy et al. 2006, Brünken et al. 2007, Linnartz et al. 2010, Maier et al. 2010). In 2003 the identification of $C_3$ in the ISM was achieved by (Maier et al. 2001). In 2010 a broad absorption band of a hydrocarbon plasma showed overlap with the $\lambda5450$ DIB, one of the broad DIBs in HD 183143 (Linnartz et al. 2010) (see Chapter 3). This band has very recently been in the focus of another study that identifies the band as the linear propadienylidene molecule, $1$-$H_2C_3$.

1.4 Post-Asymptotic Giant Branch (AGB) Objects

The research of the molecular inventory goes to more and more complex species, as a recent review by Herbst & van Dishoeck (2009) shows. The five main types of sources in that especially the larger and more complex molecules have been detected (see Table 1.1) are: circumstellar envelopes around evolved stars, cold interstellar cores, hot cores and corinos, lukewarm corinos, outflows of post AGB stars. The latter object is interesting since especially during its late AGB evolution stellar pulsations and a strong external dusty mass loss is developed. Within timescales of $10^4 – 10^5$ years this mass loss will remove essentially the whole envelope. Molecules like methanol (CH$_3$OH), methyl formate (HCOOCH$_3$), acetonitril (CH$_3$CN) and ethanol (C$_2$H$_5$OH) have been detected in the outflows of post-AGB stars. Chemical reactions that further take place in the outflows enhance the formation of larger molecules or dust grains (Cami et al. 2010, van Winckel 2003). More than 60 different molecular species have been identified in the outflows of such objects as well as dusty minerals, silicates and carbonaceous grains (Waters et al. 1996, Molster et al. 2002b,a,c, Cernicharo et al. 2001, Pardo et al. 2007, Kwok 2009). Just recently the largest molecules so far, C$_{60}$ and C$_{70}$, were identified in TC-1, a planetary nebula, formed from a post-AGB object. Also molecules like larger aromatic species, PAHs, are likely to be abundant in these environments. This argument is strengthened by the fact that benzene, polynyes and cyanopolyynes could already be identified in these environments (Cernicharo et al. 2001, Pardo et al. 2007).

1.4.1 The Red Rectangle Proto-Planetary Nebula

A special post-AGB object in this respect is the Red Rectangle proto-planetary nebula. The post-AGB object HD 44179 that is associated with the Red Rectangle nebula has caught special attention since its identification in 1975 (Cohen et al. 1975). The figure on the cover shows a Hubble Space Telescope (HST) image of the Red Rectangle nebula. Most likely the central object is a binary (Waelkens et al. 1996), that cannot be seen directly, but is obscured by an optically and geometrically thick disc (Roddier et al. 1995, Osterbart et al. 1997, Bond 1997). The Red Rectangle itself is often cited as the prototype of a carbon-rich post AGB star (Cohen et al. 2004). The nebula itself is carbon-rich and shows pronounced PAH emission features (Russell et al. 1978) in the infrared. In the optical the spectrum shows a broad and extended red emission (ERE) seen only in
carbon-rich environments (Furton & Witt 1992), for example in reflection nebulae (Witt & Boroson 1990), in spectra of HII regions (Perrin & Sivan 1992, Darbon et al. 1999, 2000), in the galactic cirrus cloud (Guhathakurta & Tyson 1989, Szomoru & Guhathakurta 1998), the diffuse interstellar medium (DISM) (Gordon et al. 1998) and in other galaxies (Perrin et al. 1995). This broad emission band, spanning about 250 nm in the optical, was attributed to photo-luminescent processes of silicate particles or carbonaceous grains (Witt et al. 1998, Ledoux et al. 1998, Wada et al. 2009). On top of the ERE, narrow emission features, were detected (Schmidt et al. 1980). While the ERE is widespread, the narrow emission bands superimposed on the ERE are unique. A spectrum of the Red Rectangle nebula is shown in Fig. 1.5. The emission bands show a lack of polarization (Schmidt et al. 1980) and exhibit molecular characteristics of gas-phase species. In several studies it was shown that these unique emission bands shift in wavelength to the blue and also become more narrow with distance to the central star (Sarre et al. 1995, Van Winckel et al. 2002) (see also Chapter 7 of this thesis). Some of these bands have caught special attention since with distance they shift very close to the band positions of some of the diffuse interstellar absorption bands. The narrow emission bands superimposed on the ERE will be described in more detail in Chapters 6 and 7.

The nebula itself has been found to be carbon rich, including the blue luminescence (Vijh et al. 2004), the ERE and the PAH emission bands. Some smaller species have been identified in the UV and in the IR (Hall et al. 1992, Bakker et al. 1996, Hobbs et al. 2004) and only C₂ could be identified in the optical (Sarre 2006, Glinski et al. 2009, Wehres et al. 2010a) (see also Chapter 6). The disk surrounding the central star instead is oxygen rich, with molecules like OH, ¹²CO, ¹³CO, as well as CO₂ in the gas phase and maybe also in the solid state (Leger & Puget 1984, Reese & Sitko 1996, Waters et al. 1998). The very weak microwave emission of CO (Jura et al. 1995) in the Red Rectangle, but the otherwise strong emission features of PAHs, as well as the ERE, seem to imply that further processing of the dusty outflows took place in a circumbinary rotating disk.

Oxygen rich silicates were later found in the ISO spectrum of the Red Rectangle (Waters et al. 1998). This seems to indicate a spatially separated chemistry that is going on in this object and that the dusty disk and the nebula were formed at different evolutionary phases of the post-AGB phase. Most likely the oxygen-rich material in this carbon-rich environment has been formed earlier than the carbon-rich material.

1.5 Thesis Outline

The results described in this thesis address some of the key questions modern astrophysics is facing nowadays. The questions discussed here aim mainly in the direction towards the chemical compounds in the Universe. In this thesis we restrict ourselves to the molecules found in the ISM and moreover we will focus on the identification of molecules detected in the visible regime. The approach we are following is to compare the observational spectra of astronomical environments or specific objects in the ISM to laboratory spectra of specific molecules. The questions that arise from this approach are:

- Is it possible to simulate astronomical environments in the laboratory in such a
way, that we can create molecular species that can be detected in the ISM, more specifically, molecules which can be detected in diffuse interstellar clouds or in the Red Rectangle environment? The experimental approach will be described in Chapter 2 and the laboratory spectra will be discussed in Chapters 3 – 6.

• Is it possible to identify these species in the laboratory and subsequently in the ISM? Is it possible to put constraints on species that cause the DIBs or molecules that cause the emission bands that we detect in the Red Rectangle proto-planetary nebula? This question will be discussed in detail in Chapters 3 and 6.

• If we know about the molecules that are observed in the ISM, can we conclude on physical conditions that are necessary in order to form these species in a certain environment? In Chapter 6 we discuss the identification of a molecular species (C\textsubscript{2}) in the environment of the Red Rectangle nebula. The implication of the identification is discussed and physical conditions are determined. Chemical implications will be discussed subsequently.

• If we know the physics in a specific environment, i.e. temperatures, radiation fields, densities of molecules, is it possible to determine on reaction pathways and estimate abundances of molecules in this environment?

• If we know the physics and chemistry, is it possible to determine on formation and destruction pathways and timescales in specific environments? These two questions will be explained in detail in Chapter 6, where likely reaction mechanisms of C\textsubscript{2} in the Red Rectangle are studied that at the end also lead to an estimate of the abundance of C\textsubscript{2}.

• If we know about specific molecules, their chemistry, their network of reactions and the physics going on in certain environments in the ISM, is it possible to modify reaction schemes for other environments?
Finally, if we understand the mechanisms that drive the formation and destruction schemes of molecules, if we know about the physical conditions and ongoing chemistry, is it possible to also put constraints on the formation of life?

The last two bullet points are beyond the scope of this thesis but provide a strong motivation for studying the reactions of molecular species in the ISM.

In Chapter 2 an introduction to the laboratory experiments are given. The techniques are described that are used to form molecules of astrophysical interest and how their spectrum is obtained. This addresses the first bullet point mentioned above and shows the techniques that are used in order to form molecular species that then are identified in the ISM. For the creation of molecular species two specific plasma sources are used. The spectrum of molecules are recorded using two different techniques: cavity ring-down spectroscopy and laser induced fluorescence spectroscopy. Both techniques will be explained and spectra will be shown and described. The spectra will be compared to observational spectra of diffuse interstellar clouds and to the Red Rectangle proto-planetary nebula. For this purpose it will briefly be summarized how it is possible to simulate the laboratory spectra under different conditions as we may face them in different regimes in the ISM. Observational methods for obtaining optical long-slit spectra of the Red Rectangle nebula and an optical echelle spectrum of the diffuse cloud seen in the line of sight towards HD 183143 will be explained.

In Chapter 3 a laboratory study of a hydrocarbon plasma absorption spectrum as recorded in the laboratory is discussed and compared to spectra of the diffuse interstellar cloud towards HD 183143. The study shows a clear overlap of the laboratory and the observational study, but a clear assignment of the carrier could not be obtained. The experiment did, however, put constraints on the carrier of this specific absorption band in the ISM.

In Chapter 4 a specific molecule, HC$_7$H, formed from a hydrocarbon plasma, as explained in Chapter 2, is discussed. The laboratory absorption spectrum is compared to the diffuse interstellar cloud towards HD 183143, as online available (Hobbs et al. 2009). Several rotational transitions could be assigned in the laboratory study and information of the intrinsic molecular constants is obtained. That way simulations were run to model the spectrum for different temperatures and resolutions that allow for detailed comparison to observational spectra. No match between the simulations and the absorption spectrum of HD 183143 is obtained.

Chapter 5 discusses the C$_9$H$_3$ molecule recorded through an expanding hydrocarbon plasma. We describe the laboratory approach to determine intrinsic molecular parameters that allow for identification of the geometry of the carrier of the laboratory absorption band. Two transitions of the same carrier are identified in the laboratory study. Simulations were run to compare the bands to the diffuse interstellar absorption bands of diffuse interstellar cloud towards the star HD 183143. No overlap between the simulation and
the astronomical absorption spectrum could be obtained, although this species is said to be the seed of ring-bearing species in the ISM (Schmidt et al. 2003b).

In Chapter 6 the laboratory excitation spectra of the C_2 Swan bands are recorded and compared to the observational study the Red Rectangle nebula, HD 44179. Identification of two narrow emission bands is discussed and conclusions on the ongoing chemistry and the physical conditions in this environment are drawn. The reaction pathways for the formation and destruction of C_2 are described and the abundance with distance to the central star is derived.

In Chapter 7 we finally show an overview of all long-slit spectra of the Red Rectangle that were recorded with the New Technology Telescope in La Silla, Chile. An inventory of all optical emission bands superimposed on the extended red emission is presented. The emission bands are summarized in band position, band widths and intensities with respect to the position in the outflows of the post AGB object. A comparison of the narrow emission bands to the DIBs will be discussed and constraints on the carriers will be summarized.