Astrochemistry
Programme

April 12, 2010
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1. General Introduction

The origin and evolution of the molecular universe starts with the injection of material – much of it in molecular form – by stars in the later stages of their life, the subsequent processing of this material in the interstellar medium by the prevalent ultraviolet radiation fields, energetic particles, and strong shocks, and ends with the incorporation of this material into newly formed stars and their budding planetary systems (Fig. 1.1). During this evolution, simple molecules and atoms combine to form larger species while complex molecules and dust are broken down to smaller species. This “chemical dance” of the elements leads to a rich and varied chemical inventory in the interstellar medium of galaxies. In the end, the chemical processes taking place in the interstellar medium will be inherited by newly forming planetary systems.

Figure 1.1. A schematic of the lifecycle of molecules in the interstellar medium. The chemical processes taking place at every stage in this process – from the birth of molecules in circumstellar shells, their passing through the physical gauntlet of the interstellar medium ultimately fueling star and planet formation – make up the heritage of planetary systems.

During this evolution, molecules exert a direct influence on their environment. Molecules dominate the cooling of gas inside dense molecular clouds. Molecules also control the ionization balance in such environments and thereby the coupling of magnetic fields to the gas. Through this influence on the forces supporting clouds against gravity, molecules will affect the process of star formation. Large molecules are also thought to be a major contributor to the heating of diffuse atomic gas in the interstellar medium. Thereby they affect the physical conditions in such environments and the phase structure of the interstellar medium, which set the stage for the star formation process. Likewise, the presence of small molecules may have controlled cooling in the early Universe and in that way the formation of the first stars.

Besides through their influence on the processes involved in star formation, molecules provide also key probes of the Universe. Molecules possess a myriad of electronic, vibrational, and rotational levels whose excitation is sensitive to the local physical conditions over a wide range of astrophysically relevant densities and temperatures. Molecular abundances are also sensitive to the local physical conditions. Hence, molecules provide a sensitive probe of the dynamics and the physical and chemical conditions in a wide range of objects at scales ranging from budding planetary systems to galactic and extragalactic sizes.
Molecules are directly interwoven into the fabric of the universe. They are an important component of the Universe and play a central role in many key processes that dominate the structure and evolution of galaxies. Understanding the origin and evolution of interstellar and circumstellar molecules is therefore a fundamental goal of modern astrophysics. Likewise, developing molecules as an astronomical tool to study the physical conditions and dynamics of a wide variety of objects in the Universe will be of key importance for astronomy in the coming decade.
2. Network Goals and Objectives

Over the next five years, European ground-based and space-based missions will open up the Universe to high spatial and spectral resolution studies at infrared and submillimeter wavelengths and astronomical groups in the Netherlands are deeply involved in these efforts. In May 2009, the European Space Agency has launched the Herschel Space Observatory with the heterodyne instrument, HIFI, – developed by an international consortium under PI-ship of the Dutch space agency, SRON – that will open up the THz frequency regime for systematic studies of the chemical inventory and the role of water in space, in particular in regions of star and planet formation. The European Southern Observatory, ESO, is a major partner in the construction of the sub-millimeter interferometer, ALMA, in Chile. When it starts scientific operations in 2011, this interferometer, with its unprecedented spatial resolution and sensitivity at sub-millimeter wavelengths, will be the forefront instrument for studying the cold molecular gas and dust that constitute the very building blocks of stars, planetary systems, and galaxies. The Netherlands Research School For Astronomy (Nederlandse Onderzoeksschool voor Astronomie, NOVA) is responsible for the design and construction of the band 9 receivers for ALMA. NOVA, is also responsible for the design and building of the Spectrometer Main Optics Module (SMO) of the Mid Infrared Instrument, MIRI, that will fly on board of the James Webb Space Telescope – a joint NASA-ESA-CSA project to be launched in 2014. Among many other things, MIRI will be instrumental to study the distribution of simple molecules such as H$_2$O, HCN, C$_2$H$_2$, and CH$_4$ as well as more complex species such as polycyclic aromatic hydrocarbons in the habitable zone of regions of star and planet formation. Hence, these missions provide us with the tools to study key astrophysical and astrochemical processes involved in the formation and evolution of planets, stars, and galaxies.

Over the last few years, new physical chemistry methods have been developed that carry the promise of opening up new avenues of research in astrochemistry and chemistry and molecular physics groups in the Netherlands are very active in this arena. These include, for example, a double-resonance hole-burning spectroscopy scheme developed at the FOM institute in Rijnhuizen for the study of bioactive molecules that can be adapted for infrared absorption spectroscopy of large molecular species of astrophysical relevance. At the Sackler Laboratory in Leiden, UHV surface science set ups have been built to study the key chemical processes that control surface chemistry in the formation of interstellar ices under cryogenic conditions. At the Laser Center of the Vrije Universiteit, an optical cavity ring-down plasma experiment has been put together that mimics interstellar clouds for optical spectroscopy of hydrocarbon radicals in relation to the Diffuse Interstellar Band problem. In Groningen, protocols for handling phyllosilicates in surface science experiments have been developed which opens the way to study dust surface chemistry in the inner Solar Nebula. In addition, new self-consistent two-dimensional chemo-physical models of protoplanetary disks enable the study of gas phase, gas-grain and surface chemistry under a wider range of astrophysical conditions. On the theoretical side, Moore’s law enables ever-larger systems to be accurately treated. In particular, Density Functional Theory techniques have steadily improved and allow now accurate calculations on the IR vibrational spectra of large (100+ C-atom) molecules. It is also now possible to model solid state processes using molecular dynamics techniques on systems containing some 500 molecules. These developments in chemical physics and molecular physics allow us to address now questions and systems that were not possible even only 10 years ago. Analysis and interpretation of the data that these new missions will return in terms of the physical and chemical characteristics of the astronomical sources will require detailed astronomical modeling tools supported by laboratory measurements and theoretical studies of chemical reactions and collisional excitation rates on species of astrophysical relevance.

Progress in this area will require close collaboration of scientists active in molecular physics, surface science, astronomy, and chemistry. The Netherlands has been an active player in the field of astrochemistry for many years. However, the many Dutch astronomy, molecular physics, surface science and chemistry groups active in this area, largely contribute from their own perspective. Here, we propose a highly interdisciplinary network combining the astronomical and chemical expertise in the Netherlands with the goal of
understanding the origin and evolution of molecules in space and their role in the Universe. This goal will be reached through a highly integrated and coherent program of astrochemical and astrophysical experiments, quantum chemical calculations, and laboratory spectroscopy of astronomically relevant species in combination with an active program on modeling and observations of astronomical sources.

The field of molecular astrophysics is a highly interdisciplinary field where molecular physics, laboratory spectroscopy, surface science, theoretical chemistry, astrochemistry, astronomical observations, and astronomical modeling intersect. Within this broad field we have defined four major astrochemical themes where Dutch astronomy and chemistry have particular strong expertise and experience as well as access to unique observational or experimental facilities. The four selected themes are 1) Gas phase astrochemistry where formation and destruction as well as the excitation of simple molecules are studied; 2) The solid universe where the relationship between dust and molecules is addressed; 3) From PAHs to chains, rings, and cages, which studies the chemical evolution of polycyclic aromatic hydrocarbon molecules in space; 4) The prebiotic Universe which studies possible links between interstellar precursor molecules and key biomolecules. Within each theme a number of specific and highly interwoven science projects have been defined that together address the joint astrochemical objectives of that theme and that draw upon the strength of the scientific disciplines in the Netherlands. For each theme, these projects comprise laboratory studies and/or quantum chemical studies that are then combined with astronomical modeling studies and supplemented by observations of molecules in space. In this way, the network proposes a coherent and integrated end-to-end scientific program that transcends in many ways the goals and objectives of individual research proposals.

Some of the most pressing questions in astrochemistry cut across the four themes in the network. These include: “What is the stability of molecules in space?” and the network addresses questions such as “How does that depend on the size of the molecule?”, “What is the role of molecular structure?”, and “How does this differ between gas phase and solid state?”. Another red thread through the four themes concerns the question: “What is the origin of molecular complexity in space?” where the network focuses among other things on “What is the role of gas phase processes versus those in or on dust and ice therein?”, “How is the chemistry of large hydrocarbons related to that of small ones?”, and “What does this imply for the origin of molecular complexity in the habitable zone of regions of star and planet formation?”. A final common denominator to be highlighted is: “What are the observational characteristics of molecules under astrophysically relevant conditions?” and the themes address such key issues as “What are the spectral characteristics of relevant photo products?” and “How do the excitation and observational characteristics of species relate to the local physical conditions?”. In addition, the cross-fertilization in the use of complementary experimental, theoretical, and observational techniques will provide much synergy and added value to the research proposed in this network setting. Finally, the network will provide a unique learning experience for the students appointed by the projects. They will be provided with a well-rounded education where they will experience, first hand, the multi-disciplinary approach associated with joint research objectives, as well as the educational efforts provided at the network level such as summer schools in the field of astrochemistry. In addition, through the embedding in the astronomical community, the appointed students will be able to fully profit from the educational and research facilities offered by NOVA. In this way, the network will create the putative future scientific leaders of this field. In all, the themes in the network address key astrochemical questions from very different angles, using complementary techniques while training the next generation of astrochemists, and it is these commonalities that carry the promise of providing a much deeper insight in the origin and evolution of the molecular Universe than isolated projects could provide.
3. Gas phase astrochemistry

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3.1 Background

Interstellar gas is a harsh environment for molecules, differing in many respects from traditional terrestrial and laboratory settings. The extreme conditions of space – specifically the low density and temperatures, the strong UV field, and the energetic particles – give rise to a unique chemistry resulting in a highly unusual organic inventory with – beside simple hydrides and oxides – a diversity of unsaturated species, radicals and ions. Interstellar chemistry has traditionally focused on gas-phase processes, invoked to explain the abundances of the first molecules discovered in space (CH, CH$^+$ and CN). Although it is now clear that –by themselves– gas-phase models fail to explain the abundances of most complex molecules in dense star-forming regions, they still control the chemistry of many small molecules, ions, and radicals. This is even more true for the more general molecular interstellar medium of our own and other galaxies: gas-phase chemistry dominates the abundances of many of the observed small molecules.

Soon after their detection in 1937–1941, Dutch physicists, stimulated through discussions with astronomers Oort and van de Hulst, were the first to put forward kinetic models in which molecular bonds are formed through radiative association and destroyed through processes like photodissociation (Kramer and Ter Haar 1946 [1]). Another destruction process, dissociative recombination, was added a few years later following developments in atmospheric chemistry (Bates and Spitzer 1951 [2]). With the subsequent realization of the importance of ion-molecule reactions at low temperature (Herbst and Klemperer 1973 [3]), these models have formed the basis of much of modern gas-phase astrochemistry. As this short history illustrates, gas-phase chemistry has benefited greatly from the close interactions with physicists and chemists who have provided reliable rate coefficients under interstellar conditions for a large variety of processes through a combination of theory and experiments [Millar and Williams 1988 [4]; Herbst and Millar 2008 [5], plus references cited]. As a result, many of the thousands of reactions in gas-phase chemical networks are quite well known. Sensitivity analyses such as carried out by Wakelam et al. [6] are able to pinpoint those reactions for which accurate rates are most urgently needed. In many cases, these combined chemical physics/astronomy studies have also led to new insight into basic molecular processes. For example, radiative association does not occur under Earth-like conditions and had never been considered in detail before, and neutral-neutral reactions are now known to be orders of magnitude faster at low temperatures than thought previously.

Gas-phase processes do not always lead to reaction: a collision between two species can also lead to exchange of energy. Such inelastic collisions dominate the excitation of most interstellar molecules and accurate information on their rate coefficients is essential to extract temperatures, densities and abundances from the observed line intensities. Most of the collisional rate coefficients used in astronomy have come from quantum chemical calculations of the potential surfaces and subsequent dynamics (see Schöier et al. [7] for a recent summary). The group at the Radboud University has been very active in the experimental studies of collisional excitation rate coefficients of astrophysically relevant species over the past 25 yr and this effort has proven to be crucial in order to benchmark the theoretical results.
3.2 Objectives

Within this theme, we have chosen to focus on two areas in which the Netherlands has particularly strong expertise and in which we can expect significant steps forward in the next 5 years: photodissociation and inelastic vibration-rotation collisions. Both topics are important for astronomy and for both there are new fundamental chemical physics challenges to be addressed. The proposed program is a true end-to-end fully integrated mix of projects in which the theoretical and experimental molecular data are incorporated into state-of-the-art astrochemistry, molecular excitation and radiative transfer models, summarized in publically available databases, and applied to interpretations of observations of molecules in star-forming regions, protoplanetary disks, and extragalactic regions.

Specific questions addressed in the photodissociation studies are:

- What are the photodissociation rates and mechanisms of key small molecules in astrochemistry, in particular for N$_2$ and CO? How does this vary among the isotopologues and what is the importance of self-and mutual shielding?
- What are the branching ratios of the photodissociation products, especially for molecules consisting of more than 3 atoms? For example, does CH$_3$OH dissociate primarily to CH$_3$ + OH, CH$_2$OH + H, or CH$_2$ +H$_2$O, etc.? How does this depend on photon energy?
- Do the branching ratios change between molecules in the gas-phase and in ices? (This is a link with the "Solid-state astrochemistry" theme).
- How stable are complex (i.e., molecules containing at least 6 atoms) organic molecules [non-polycyclic aromatic hydrocarbons (PAHs)] against UV radiation because of internal conversion? Where does the cross-over occur from very efficient dissociation as found for small molecules to high stability as found for large molecules? How does this depend on the structure of the molecule?

Specific questions addressed in the inelastic collision studies are:

- How large are the collisional rate coefficients for vibration-rotation transitions and under which astronomical circumstances are they important? Are those for collisions with atomic H indeed more than an order of magnitude larger than those with H$_2$, as suggested for CO-H vs. CO-H$_2$?
- How do the collisional rate coefficients for pure rotational transitions of deuterated species differ from those of normal ones?
- What are the collisional rate coefficients for the recently discovered ions such as OH$^+$ with H and H$_2$?

The following leading Dutch scientists are involved in the described projects:

**Photodissociation**
- Prof. Ewine F. van Dishoeck, Leiden Observatory, UL, Theory, astrochemical models
- Dr. Gerrit Groenenboom, Radboud University Nijmegen, RU, Quantum chemistry, theory
- Prof. Marc C. van Hemert, Theoretical Chemistry, UL, Quantum chemistry, theory
- Prof. Dave Parker, Radboud University Nijmegen, RU, Experiments predissociation
- Prof. Wim Ubachs, Laser Center, VU, FUV spectroscopy experiments
- Prof. Harold Linnartz, Leiden Observatory, UL & LCVU, Laboratory studies

Some collaboration with the experimental groups of M. Janssen (VU; femtosecond photodissociation dynamics) and W. van der Zande (RU) is expected, building on existing relations. There is also a direct interaction with the ice photochemistry experiments carried out in the Leiden Sackler laboratory, led by H. Linnartz.
The resulting rates and product branching ratios are expected to be used by other NL groups, such as I. Kamp (RUG; protoplanetary disk models) and M. Spaans (RUG; PDR/XDR models). These modelers in turn will provide important insight into those processes for which better data are needed, thus closing the loop between experiments, theoretical calculations, observations, and astrochemical modeling.

**Inelastic collisions**

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<thead>
<tr>
<th>Name</th>
<th>Institution</th>
<th>Field</th>
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<tbody>
<tr>
<td>Dr. Gerrit Groenenboom</td>
<td>Radboud University Nijmegen, RU</td>
<td>Quantum chemistry and dynamics</td>
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<tr>
<td>Prof. Ad vd Avoird</td>
<td>Radboud University Nijmegen, RU</td>
<td>Quantum chemistry and dynamics</td>
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<tr>
<td>Prof. Dave Parker</td>
<td>Radboud University Nijmegen, RU</td>
<td>state-selected experiments</td>
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<tr>
<td>Prof. Marc C. van Hemert</td>
<td>Theoretical Chemistry, UL</td>
<td>OH-H$_2$</td>
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<tr>
<td>Dr. Floris vd Tak</td>
<td>Astronomical Institute RUG</td>
<td>Support dynamics calculations, LAMDA database, analysis Herschel, ALMA data</td>
</tr>
<tr>
<td>Prof. Ewine F. van Dishoeck</td>
<td>Leiden Observatory, UL</td>
<td>Analysis mid-IR observations disks</td>
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The resulting collisional rates will also be used by other NL groups, such as for CO infrared observations of disks by R. Waters (UvA) and I. Kamp (RUG) and for analysis of sub-mm observations by M. Spaans (RUG), S. Muehle (JIVE), F. P. Israel (UL), P. van der Werf (UL), and others.
3.3 Projects

3.3.1 Photodissociation

In any region in which UV photons can penetrate, photodissociation is the major destruction mechanism of (neutral) gas-phase molecules. This includes diffuse and translucent clouds, dense clouds exposed to either intense UV from nearby young stars (so-called Photodissociation or Photon-Dominated Regions, PDRs) or to X-rays (XDRs) in our own and other galaxies, the envelopes around evolved stars, and the surface layers of protoplanetary disks. Even deep inside dense clouds and disks, the UV photons produced by the interaction of cosmic rays with H₂ provide a weak field which can dissociate both gas-phase and solid-state molecules (ices). Photodissociation processes may well be responsible for the isotopic anomalies observed in meteorites in our own solar system. While data on a number of molecules are available from the older literature (e.g., Okabe [8]; see van Dishoeck, van Hemert & Jonkheid [9] for an overview and www.strw.leidenuniv.nl/~ewine/photo for tabulations), information on several key rates and processes is lacking.

The NL community has a rich record of photodissociation studies over the past 25 years. Both Nijmegen and Leiden have top-of-the-world expertise in theoretical quantum chemistry calculations of excited potential surfaces and transition dipole moments using state-of-the-art ab initio multi-reference programs. They have also developed fully quantal and semiclassical wavepacket propagation dynamics programs to study the photodissociation dynamics on the potential surfaces. These have resulted in absolute cross sections and product state distributions as functions of wavelength for a variety of diatomic and triatomic molecules of astrophysical interest. Where necessary, spin-orbit and/or non-adiabatic couplings have been computed and used to computed (pre)dissociation rates, including the first complete treatment of coupled state dissociation [10]. Systems studied involve the diatomics OH [11, 12], CH [13], HCl [14], SH [15, 16], O₂ [17–19] and S₂ [20], and the triatomics CH₂ [21, 22], NH₂ [23], HCO⁺ [24], H₂O [25, 26], N₂O [27], SO₂ [28], O₃ [29], and NO₂ [30]. Most recently, van Hemert & van Dishoeck [31] have pushed existing programs to the limit to provide (upper limits on) the rates of a number of larger carbonaceous molecules found in PDRs.

Experimentally, the pioneering far-ultraviolet (FUV) laser facility of the VU has provided key data on the basic electronic spectroscopy of CO and its isotopologues, including line width data from which lifetimes and predissociation rates can be extracted [e.g., 32–37], which have been used in astrochemical models developed in Leiden [38,39]. The Amsterdam group has also been heavily involved in studies of the iso-electronic N₂ system [40–47].

The velocity map imaging technique invented by the Nijmegen group has been applied to building up a complete understanding of diatomic molecule photodissociation with projects including photodissociation of OH [12, 48, 49] (and SH [15]), CO, NO, H₂, and especially O₂ [30, 51] (and S₂ [20]), and also on the photodissociation of van der Waals clusters involving these molecules. The Nijmegen methods include femtosecond pump-probe studies and time resolved photoelectron imaging, but the main work has been on final product detection stressing product branching ratios and correlation diagrams. The methodology built up for diatomics is now being applied to increasingly larger molecules, such as triatomics including NO₂ [30], OClO [52], OCS [53], and most recently direct photodissociation of CO₂ and predissociation of water and its isotopomers [54]. Another recent focus has been on the photodissociation of methanol, CH₃OH [55] and the isovalent molecule methylmercaptan, CH₃SH [56].

Finally, the Leiden Sackler laboratory for astrophysics has a long tradition of photodissociation and photochemistry studies of ices including simple ones such as pure H₂O, CH₄ and NH₃ [e.g., 57]. The most recent ultra-high vacuum experiments on thin ices allow the individual reaction steps and branching ratios to be unraveled, providing information that can in principle be directly compared with that obtained from the gas phase [58, 59].
Project 3.1: Photodissociation experiments on small molecules
W. Ubachs and H. Linnartz, Laser Centre VU Amsterdam

Carbon monoxide is the second most abundant molecule in interstellar space, after molecular hydrogen. Its presence is crucial for the cooling in star-forming regions, as well as for the chemical reactivity, which is driven by atoms formed upon absorption of short-wavelength interstellar radiation. Thus, CO can be viewed as a key transformer of stellar radiative energy into chemical energy. In contrast with many other small molecules, the photodissociation of CO at vacuum ultraviolet wavelengths proceeds via pre-dissociation. The absorption occurs via bound states of singlet symmetry, which are heavily perturbed via Rydberg-valence interactions and by spin-orbit interactions with states of triplet symmetry; the bound states couple to repulsive states of both singlet and triplet character giving rise to predissociation. The resulting spectrum consists of resonances, which are narrow or broadened to widely varying degrees; moreover the spectra are heavily perturbed and in many cases difficult to assign. All these coupling phenomena exhibit a resonant behavior and are therefore strongly dependent on isotope. This peculiar behavior is demonstrated in the $E^1\pi, v=1$ state of CO, which was investigated for six different isotopomers ($^{12}C^{16}O$, $^{12}C^{17}O$, $^{12}C^{18}O$, $^{13}C^{16}O$, $^{13}C^{17}O$, $^{13}C^{18}O$) [34,110]. From a photo-chemical perspective the understanding of the photodissociation structure of CO poses a complex puzzle. From the astrophysical perspective not only mutual shielding processes (overlap with the hydrogen spectrum), and self-shielding processes give rise to isotopic fractionation; also the photo-dissociation rates themselves are now known to be strongly isotope dependent, thereby adding to the complexity of isotopic fractionation.

In the past decade we have used the unique extreme ultraviolet laser facility at the Laser Centre VU (tunable in the range 90 – 115 nm, at a bandwidth of 0.01 cm$^{-1}$ or 300 MHz, corresponding to $\lambda/\Delta\lambda \sim 10^7$) for the investigation of a large number of the resonances occurring in CO and in a few cases for its isotopologues. Accurate data have been extracted for the lifetimes and predissociation rates [e.g., 32–37]. These data have recently been incorporated by Visser et al. [38] in Leiden to build a new model of the photodissociation and self-shielding of interstellar CO, following the widely used [39] model. A wealth of information has been gathered on the ro-vibronic structure and predissociation of the CO isotopologues, but still the information is far from complete. More generally, there is still significant controversy even on the basic mechanisms involved [65] (see recent debate in Science in June 2009) as well as a lack of fundamental understanding how oscillator strengths and predissociation rates for the same state can differ by such large factors (order of magnitude) from one isotopologue to the next. From the photo-chemical perspective many of the couplings yielding perturbation and predissociation are not understood, and from the astrophysical perspective accurate $J$-dependent predissociation rates are lacking. In our studies we target both scientific issues. Phenomenologically, there is a direct interest in determining the relevant lifetimes for all the observable features. But, extracting a complete database is difficult, a viable strategy is also to aim at an understanding of the absorption and predissociation spectrum, such that it can be cast into a molecular physics model, where all relevant processes are modeled and parametrized. For this purpose insight in the Rydberg-valence and singlet-triplet coupling mechanisms is indispensable, and such information is aimed for in our studies. This project is the opportunity to finally ‘nail down’ the photodissociation parameters and rates of CO and its isotopologues for UV radiation <13.6 eV.

Furthermore, the Amsterdam group has investigated, also with the narrowband and tunable XUV-laser system, the iso-electronic $N_2$ system, yielding accurate information on predissociation rates as well as insight into the perturbation mechanisms [40–47]. Also here information is still lacking, see link with project 3.2.

We will make the unique XUV-laser facility at LCVU Amsterdam (see Fig. 3.1) available for the here proposed investigation, and we will also use its extensions that were recently added. The detection technique applied thusfar limited the observation of states with lifetimes not too short (i.e. predissociation rates not too large). Rapidly predissociated states, even for large absorption cross sections remained invisible for the 1 XUV + 1 UV photo-ionization detection scheme. The velocity-map imaging detection setup that was recently added (and applied in detecting photodissociation in hydrogen [106]) will be used for detecting the dissociation fragments. This
technique will open up the window for revealing information on the very-short lived resonances in N₂ and CO (linewidths exceeding 1.5 cm⁻¹).

Figure 3.1: On the left a photograph of the pulsed-dye-amplifier laser system, which is at the basis of the narrowband and tunable XUV-laser system in Amsterdam, with a Fourier-transform limited bandwidth, previously used for measuring pre-dissociation phenomena in N₂ and CO. On the right a photograph of the plasma-jet expansion in which the production and detection of N₂⁺ ions and metastable N₂ molecules was demonstrated; at the sides the cavity-ring down mirrors are visible.

In addition we will use a second setup for the present study: a plasma-gas jet expansion equipped with cavity-ring-down detection (See Fig. 3.1). In this setup we will produce intermediate metastable states, which are known to exist in the CO and N₂ molecules; the detection of N₂ metastables has already been demonstrated [107]. In CO we will populate the long-lived a³π state and from thereon measure in direct absorption the widths of some relevant highly excited resonances. An interesting possibility, which will be pursued, is the use of the long-lived 1Σ intermediate state in CO [108]. In N₂ there is the highly-excited a"1Σ⁺ metastable state, forming a target for the CRD studies. These direct absorption measurements will yield information on predissociative states complementary to XUV photo-ionization.

As a third experimental technique we propose to use the novel Fourier-transform spectrometer of the DESIRS beamline at the SOLEIL synchrotron. This is a unique high-resolution (although less than the XUV-laser) spectroscopic facility from which information on the absorption cross sections can be extracted (this is not possible from the laser experiments). We have experience in using the setup while performing three observation runs in the period 2008-2009 investigating the spectrum of H₂ [109]. In particular we plan to record a broad overview spectrum for ¹⁴N¹⁵N at a resolution of 0.3 cm⁻¹.

Workplan and synergy within the consortium: The first year would focus on the most urgent N₂ experiments on which a first paper will be written. In year 2 and 3, there will be a balance between N₂ and CO experiments, as well as direct interaction with the modelers. If time permits, any other small molecules can be studied as well. In year 4, all experimental data will be analyzed and published.

The connection with other researchers in the proposed Astrochemistry network are twofold. On the one hand the Nijmegen (Groenenboom) and Leiden (van Hemert) theory groups will develop accurate models for the interaction of the relevant excited electronic states of N₂ and CO to study the J-dependent oscillator strengths and predissociation rates of the various isotopologues. Here the aim is to come to understanding of the molecular physics ultimately aiming at a model description of the entire photo-absorption and photodissociation spectrum of CO and N₂, including their isotopologues.

On the other hand the Leiden group of van Dishoeck will implement the relevant (J-dependent) line positions, oscillator strengths and predissociation rates for N₂ and CO into their astrophysical models of the interstellar clouds and protoplanetary disks. This will reveal the lack of specific molecular data (or need for higher accuracy) and will prioritize the various bands in importance. This information will be fed back to us experimentalists at Amsterdam.
Project 3.2: Photodissociation and excitation of molecules in protoplanetary disks
E.F. van Dishoeck, UL

Although the photodissociation rates of many small molecules are well known [9], N₂ is a prominent exception. N₂ is the dominant nitrogen-bearing molecule in dense clouds, but can only be observed indirectly through tracers like N₂H⁺. Recent observations and models have suggested that not all nitrogen is converted to molecular form even inside a dense cloud but that a significant fraction is still atomic [e.g., 60]. Similarly, models of the surface layers of protoplanetary disks suggest that the nitrogen chemistry is strongly affected by whether or not a star has sufficiently high energetic UV radiation to photodissociate N₂ [61]. Finally, large ¹⁵N/¹⁴N ratios have been observed in some meteoritic material [e.g., 62], interplanetary dust particles [e.g., 63] and comets [64], which are thought to originate in the interstellar cloud from which our solar system formed. One possible explanation is isotopic selective photodissociation, along the same lines as invoked and demonstrated for CO to explain ¹²C/¹³C and ¹⁶O/¹⁸O/¹⁷O anomalies in clouds and meteorites [38].

Like CO, the N₂ photodissociation occurs primarily through line absorptions but in contrast with CO, the N₂ photodissociation in interstellar clouds has never been treated properly. This is mostly because of lack of accurate molecular data for the very highly excited (Rydberg) electronic states through which the photodissociation occurs. Thanks to recent detailed experimental and theoretical work of Brenton Lewis and Glenn Stark in collaboration with the Amsterdam group (see above refs and project 3.2), some of these data are now available. Providing the first comprehensive treatment of N₂ photodissociation is a major goal of both projects 3.1 and 3.2.

A second project is a detailed treatment of the photodissociation products. For diatomic and triatomic molecules, the specific electronic states involved and their correlation with dissociation products are often known well enough to determine the product states. A case in point is the dissociation of OH, which was predicted by van Dishoeck & Dalgarno [67] to produce ~50% O(1D), a fact which was subsequently used by [68, 69] to explain the [O I] ¹D → ³P 630 nm red line emission from proplyds and protoplanetary disks. A second example is direct OH formation in high rotational states following photodissociation of H₂O through the B electronic state, a process studied extensively by van Harrevelt & van Hemert [104] and observed in interstellar shocks by [105]. This process is initiated by Ly α radiation and disk models with and without Ly α will be studied. It will be also be interesting to investigate how collisional excitation of OH competes with direct formation from H₂O photodissociation in producing the observed OH emission from disks (link with projects 3.4-3.6).

A third avenue of research will be to investigate to what extent (modified) RRKM theory (see, e.g., Chowdary & Gruebele [71]) (as commonly used for PAHs) could provide insight into the dissociation efficiency and possible branching ratios (link with project 3.3).

Workplan and synergy within the consortium: For N₂, the first step would be for the PhD student to collect all the relevant (J-dependent) line positions, oscillator strengths and predissociation rates for ¹⁴N₂ and ¹⁴N¹⁵N from the literature (see above references), use standard scaling models for data not (yet) available, compute the photodissociation rates with depth into a simple cloud model and check where self-shielding and mutual shielding by H₂, H and CO could occur. This study will reveal where there is a lack of molecular data (or need for higher accuracy) and will prioritize the various bands in importance. This information should be ready within yr 1 and will immediately be fed back to the experimentalists at Amsterdam. For CO, such a list of experimental needs is already available based on the study by Visser et al. (2009) [38]. The new experimental and theoretical N₂ and CO results will subsequently be built back into the Leiden astrochemical model. At the end of year 1, the PhD student is expected to initiate a second line of study on the photodissociation products, focusing on the OH excitation. At the end of year 2, the photodissociation efficiency of larger molecules will be tackled. This will involve a) a search through the literature on experimental data on photodissociation of large organic molecules of astrophysical interest; b) use of (modified) RRKM theory to compute their stability and compare – where possible – with experiments such as those carried out in Nijmegen; and c) make estimates of photodissociation rates for molecules for which such
information is not available from experiments. Finally, in year 4 all the new information on the photodissociation rates will be incorporated into astrochemical models (especially of disks) to investigate their effects on abundances and compare with observations. At the same time, the Leiden photo website will be updated so that the astrochemical community has easy access to the results. A quantitative comparison will be made with the [66] photodissociation tabulations. He/she will also naturally interact with the Nijmegen and Groningen groups on vibration-rotation and pure-rotational collisional rate coefficients which are needed for the models, and will thus serve as a “beta tester” of those data.
Project 3.3: Photodissociation branching ratios of large molecules

D. Parker, RU Nijmegen

For stable large molecules such as CH$_3$OH, the overall FUV absorption cross section with wavelength is often well known from experimental data dating back to the 1950’s. There is an almost complete lack of information, however, on the most likely products of the dissociation process and how these vary with dissociation energy. Some easy-to-detect products are sometimes identified by experimentalists (e.g., through fluorescence), but hardly ever quantified or compared with other possible products. Okabe [8] and Huebner et al. [66] have provided extensive tables with energy thresholds for various products, but there is no a priori reason why the energetically most stable products should be favored in the dissociation process. Most astrochemical models use simple assumptions for branching ratios, either by just picking one or two sets of low-lying products or by providing equal weight to each of the possible products. This can significantly affect the abundances of molecules further down the chemistry chain and is particularly relevant for solid-state chemistry where the radical products can recombine to lead to more complex organic molecules. For example, CH$_3$OH is often assumed to photodissociate primarily into CH$_3$ + OH, yet CH$_2$OH + H may well be the dominant channel (Öberg et al. 2009 [58]).

A related question is what fraction of the absorptions actually lead to dissociation. For large gas-phase molecules, usually only an UV absorption cross section is known. As the molecule becomes bigger and bigger, not all absorptions necessarily lead to dissociation anymore. Internal conversion is a well-known process by which most of the electronic excitation energy can be converted back to ground-state vibration-rotation energy which can subsequently slowly decay down to the lowest bound levels through radiative and collisional relaxation. PAHs are an example of a class of large molecules that are much more stable against photodissociation than small molecules, at least once the number of carbon atoms is larger than about 20.

So far, little or no work has been done to investigate to what extent large organic molecules other than PAHs are stable against photodissociation. This question is important for the chemistry in the inner regions of protoplanetary disks, where UV radiation fields are high, at least in the surface layers.

Workplan and synergy within the consortium: The main experimental work would be carried out at Nijmegen and the initial target molecule would be CH$_3$OH for which experiments using the 157 nm F$_2$ laser have already been carried out (PhD thesis Z. Chen). The photoproducts H, O($^3$P), O($^1$D), CH$_3$, and CH$_3$O have been detected, and direct detection of OH, CH$_2$OH and H$_2$ as nascent products is possible. The power of imaging in state-selective detection of, for example, CH$_3$ ($v = 0$) is that the velocity mapped image gives internal energy information of the pair-correlated OH channel that cannot be obtained by separate measurements of CH$_3$ and OH. Other channels can be studied as well. After CH$_3$OH is completed, other related stable molecules would be targeted, including CH$_3$CH$_2$OH, CH$_3$OCH$_3$ and HCOOCH$_3$, all of which are molecules commonly observed in star-forming regions. The next step would be to determine how the product branching ratios change with energy. This would require construction of an intense source at 118 nm using tripling of 355 nm in Xe and repeating the measurements for the various species. Some of this work may best be done at a synchrotron facility such as those in Hamburg, Orsay, Berkeley, or Taiwan. Parker et al. have good connections with all four facilities, and also with Xueming Yang in Dalian, who has made the most relevant measurements on methanol in the past.

The PhD student would focus in the first year on getting familiar with the experiment and studying CH$_3$OH photodissociation products as a function of wavelength. Also, proposals for beam time at various facilities will be written and a comparison with the solid state photodissociation of CH$_3$OH will be made. Theoretical models will be stimulated where needed. In year 2 and 3, the other complex molecules will be studied in depth at the various facilities. In year 4, all experimental data will be analyzed and published.

The same set of molecules will be studied in the solid state in the Sackler laboratory in Leiden by Linnartz and co-workers, where information on the branching ratios will be extracted from the observed reaction products with time. The incident UV radiation in the Sackler lab is provided by a broad-band hydrogen lamp covering the 7 – 10.5 eV range, including a strong peak at Lyman $\alpha$ 10.2 eV. This spectrum should be representative of the UV field inside a dark
cloud. Wavelength dependence is studied by including a filter which cuts out the higher energy photons, including Ly α.

For the simpler molecules, a partnership with theory (Groenenboom, van Hemert) is highly desirable in predicting and explaining absorption spectra, product correlations, direct and predissociation channels, and product polarization. From a pure molecular physics point of view, it would also be interesting to compare the product branching ratios obtained from photodissociation with those obtained from dissociative recombination (see Geppert & Larsson 2008 [70] for a recent overview). In both cases, the molecule is put on an excited dissociative potential, but the states and dissociation processes involved may be quite different.
3.3.2. Inelastic collisions

Because of their rich energy level structure, molecules are excellent probes of the physical conditions in which they reside. In order to extract any information about temperatures, densities and abundances, the state-to-state collisional rate coefficients need to be known over a range of temperatures (typically 10 K – few thousand K). Over the last decades, there have been significant efforts in computing and measuring collisional rate coefficients for astrophysically relevant molecules with the main collision partners H₂ and H (Flower 1990). The Molecular Universe EU network (2004-2008, led by Tielens) has been particularly active in providing new data on a number of species, most importantly H₂O, crucial for interpretation of Herschel Space Observatory data. The relevant collisional data are summarized in a format that is easy to couple with radiative transfer programs in the LAMDA database at www.strw.leidenuniv.nl/~moldata [7], currently maintained by F. van der Tak (SRON).

Almost all of the data summarized in LAMDA concern pure rotational rate coefficients. Most recently, observations using the Spitzer Space Telescope combined with ground-based 8-m class telescopes have detected a wealth of mid-infrared (3-30 µm) lines of small molecules like CO, HCN, C₂H₂, CO₂, H₂O, and OH. These are mostly the vibration-rotation lines (but in the case of H₂O and OH also very highly excited pure rotational lines). Very little is known about collisional rate coefficients for vibration-rotation transitions; even for “simple” systems like CO-H or CO-H₂ uncertainties are still an order of magnitude. Another issue with LAMDA is that the data for higher temperatures (say, 500 – 2000 K), are often obtained by scaling the results of low energy calculations, introducing increased uncertainties at higher energies.

Nijmegen has a particularly strong record in inelastic scattering through studies of a wide range of atom-diatom and molecule-molecule systems, both theoretically and experimentally. Theoretically, high-level methods are used to compute potential energy surfaces and/or performing coupled channel calculations to obtain elastic and inelastic cross sections. Most of the work to date was motivated by interest in the spectroscopy and dynamics of van der Waals molecules (van der Avoird and collaborators) and ultra-cold (< 1 K) collisions (Groenenboom and collaborators). A prime example of the latter work is Xe-OH collisions, which is the first system in which a Stark decelerator was used to control the velocity of the molecular beam in an inelastic scattering experiment [72]. Examples of systems studied involving a single ground state potential energy surface are He-CO [73], He-O₂ [74], He-CaH [75–77], and He-NH [78]. The He-O₂ and He-CaH studies included the vibrational coordinate.

Collisions involving a Π state diatomic molecule require at least two potential energy surfaces. For an atom-diatom system like He-OH(Π³) this is relatively straightforward, since the two potentials have different symmetries [79, 80], but for a diatom-diatom system like HCl-OH(Π³) this requires the inspection of the electronic wave functions to construct diabatic states [81, 82].

The astrochemically relevant system of this type, OH-H₂, has been studied extensively theoretically in Leiden by van Hemert and collaborators and experimentally in Nijmegen by ter Meulen and his group [83, 84] and their rate coefficients are widely used in astronomical studies. The Nijmegen group has also made key experimental studies on the NH₃-H₂ system [85]. Finally, Groningen (van der Tak) and Leiden (van Dishoeck) have been active over the past decade in collecting all available inelastic rate coefficients in data files that are easy to use by astronomers and can readily be coupled with radiative transfer packages [7, 86]. The widely cited website and papers (161 and 54 citations dd. January 1, 2010) are a testimony to the worldwide need for such comprehensive summaries and packages, especially in the ALMA and Herschel eras.
The CO $\Delta v=1$ vibration-rotation transitions near 4.7 $\mu$m are commonly observed from low-and high-mass star-forming regions, protoplanetary disks and external galaxies using modern mid-infrared spectrometers on ground-based telescopes [e.g., the $\lambda/\Delta\lambda = 10^5$ 1-5 $\mu$m spectrometer CRIRES on the ESO Very Large Telescope (VLT) [e.g., 87, 88]]. Indeed, these CO bands are rapidly becoming one of the best probes of the presence of warm (several hundred K) and hot (a few thousand K) molecular gas arising from, for example, the inner few astronomical units of disks. An added advantage compared with sub-mm data is that the infrared lines can be observed with very high spatial resolution of 0.2'' thanks to the Adaptive Optics (AO) system at the VLT. Most analyses of these data so far use Local Thermodynamic Equilibrium (LTE) excitation. However, the critical densities are high enough (of order $10^8$ – $10^{10}$ cm$^{-3}$) that this is unlikely to be a good assumption in all regions from which CO infrared emission is observed. Both infrared and UV fluorescent excitation and radiative de-excitation can compete. The main obstacle to non-LTE calculations is the lack of accurate collisional rate coefficients. Summaries of our current understanding can be found in Sec. 4.1.2 of Ref. [89] and Appendix B of Ref. [90]. The currently adopted rate coefficients are largely based on empirical fits of old experimental data dating back to Millikan & White (1963) based on Landau-Teller theory. In this theory, the CO-H excitation rate coefficients are a factor of 50 higher than those for CO-H$_2$. Individual ro-vibrational rate coefficients are then obtained with the infinite order sudden approximation. Some limited higher-level theoretical studies by Reid et al. (1987) suggest reasonable agreement with these simple formulae for CO $(v=1)$ relaxation by ortho- and para-H$_2$ below 300 K, but even this study is 20 year old and uses potentials of much lower quality (and dimensions) than possible today. One important outcome of this work would be to determine whether atomic hydrogen is indeed much more effective than H$_2$ (or He) in ro-vibrational excitation, and to what extent more accurate rate coefficients can be captured in such simple formulae.

The second most urgent system to compute is the H$_2$O-H$_2$ system for which both the $\nu_3$ 3 $\mu$m [e.g., 91] and $\nu_2$ 6 $\mu$m lines [e.g., 92] have been observed, in addition to a wealth of pure rotational lines seen in the mid-infrared by Spitzer and in the far-infrared by the Herschel Space Observatory. As illustrated in Ref. [93], the full non-LTE treatment of the H$_2$O excitation has a significant effect on the predicted spectrum. If the remaining years, either HCN-H$_2$ or CO$_2$-H$_2$ could be studied as well. For CO$_2$-H$_2$, the current status of our understanding is described in the appendix of [94]. As for the case of CO, the rate coefficients for CO$_2$-H$_2$ are predicted to be at least a factor of 50 larger than those with He but lower than for CO$_2$-H.

Although the fundamental approach to inelastic scattering calculations is well known, many opportunities exist for theory and method development. For example, the fitting of potential energy surfaces is still labor-intensive, in particular if one wants to go beyond interpolation methods and construct potentials with accurate long range parts as, e.g., required for low energy scattering. A number of fitting and interpolation techniques, including contributions to new methods, are described in [74, 97]. Another complication is the $n^3$ scaling of the cpu-time with the number of channels ($n$) for a coupled channel calculation. At the higher energies associated with vibrational transitions, the fully coupled calculation may become prohibitive and other avenues need to be explored and bench-marked. Finally, transitions involving large changes in rotational states (large $\Delta J$ transitions) have relatively small cross sections, but they may be important. The uncertainty in the cross sections of such processes is typically large. In previous work on vibrational predissociation of the (HF)$_2$ and (HCl)$_2$ dimers it was found that model potentials may fail completely for processes that were not considered when constructing the potential [98].

Workplan and synergy within the consortium: The first systems to study are the CO-H and H$_2$O–H$_2$ ($\nu_2$, $\nu_3$) systems. We will follow the well established steps of starting from calculations of an accurate potential energy surface and subsequently computing the dynamics using close-coupling theory. For these two systems accurate potential energy surfaces including the vibrational coordinate are already available from the work of Refs. [95, 96]. This will allow a “flying start” of the program and should allow to finish the calculations on these systems in the first two years of the program. For the case of H$_2$O–H$_2$, for which a 9D potential surface exists,
a close collaboration with Wiesenfeld (Grenoble), who has planned a sabbatical in Nijmegen in September 2010, is expected. The CO-H\textsubscript{2} system is also being studied by that group, so that overlap can be avoided. We will also collaborate with the group of Parker (Nijmegen), who will carry out collision experiments of CO with H and H\textsubscript{2} at specific energies and for specific ro-vibrational transitions and thereby allow a probe of the accuracy of the relevant parts of the potential energy surface and (ratios) of individual rate coefficients. These calculations are expected to take at least the first 2 yr of the PhD student. The last 1-2 yr will be used to study HCN-H\textsubscript{2} or CO\textsubscript{2}-H\textsubscript{2}. Some fraction of the Nijmegen theory effort will also be spent on investigating the $J$-dependent oscillator and predissociation rates in highly-excited states of CO and N\textsubscript{2}, in a link with projects 3.1 and 3.2.
Project 3.5: Experimental studies of vibration-rotation inelastic collisions
D. Parker, RU Nijmegen

The theoretical projects discussed in project 3.4 will be closely linked with experiments carried out in Nijmegen. On the experimental side, there are two crossed-beam scattering apparatus for studies of inelastic scattering in the group of Parker, one of which is to be used for pure rotational studies (see below), the second is available for the study of vibrationally excited inelastic scattering, in particular CO scattering with H and H₂. The addition of velocity map imaging now delivers the ultimate information in the form of state-to-state differential cross sections, which provide the most stringent test of the quality of a potential energy surface. From an ongoing study of CO₂ photodissociation there is experience in nascent CO \((\nu = 1)\) detection, in producing an intense source of H atoms using pulsed discharges, in producing state-selected para-H₂, and with F. Harren in Parker’s group there are powerful IR lasers (overtone CO lasers) that may be useful for vibrational pumping. Also, the recent collaboration with K. Liu in Taiwan using pulsed IR lasers for pumping CH₄ should be useful for CO. Another option is to purchase a pulsed tunable IR OPO laser, which is now commercially available. The Linnartz group in Leiden is willing to share such a laser source. These experiments would be carried out at specific collision energies and for specific ro-vibrational transitions and thereby allow a probe of the accuracy of the relevant parts of the potential energy surface and (ratios) of individual rate coefficients. The bulk of the rate coefficients to be used in astrochemical models come from theory such as that described under project 3.4, but these need to be tested against experiments.

In recent work on H₂O-H₂ pure rotational collision cross sections, the potential and the molecule-molecule scattering algorithms are evaluated in collaboration with Wiesenfeld of the Grenoble group. This work is being extended to revisit the OH-H₂ case (see also project 3.6).

Workplan and synergy within the consortium: The PhD student on project 3.3 will be shared for 30% of his/her time with this project to carry out the CO-H and CO-H₂ experiments. The Nijmegen-Parker group has recently received support for imaging studies of inelastic and reactive scattering of OH from CW-ECHO. A new PhD student Mr. Ashim Saha has started November 1, 2009. With permission from CW, Ashim will be able to also take part in the Astrochemistry program. There will be a close connection with the theorists in Nijmegen (project 3.4) as well as with van Hemert (Leiden) on OH. Groningen (van der Tak) and Leiden (van Dishoeck) would make the rate coefficients available for the LAMDA database and explore the importance of various approximations on models of various types of astronomical objects.
Project 3.6: Pure rotational inelastic collisions
F.F.S. van der Tak, SRON/RuG, G.C. Groenenboom, RU Nijmegen

Although collisional data for pure rotational transitions are now available for about 30 of the 150 detected interstellar molecules thanks to the concerted effort of many people, such data are still lacking for several key species. One class of molecules without collision data are radicals and ions such as OH⁺, H₂O⁺, and CCH. Indeed, one of the early surprises of data from the Herschel Space Observatory is the widespread detection OH⁺ and H₂O⁺. These molecules are used as tracers of energetic radiation (UV, X-rays), not only in galactic clouds but now also in extragalactic systems out to high redshifts. Collisional data would allow astronomers to develop these molecules as diagnostics of physical conditions in regions where molecular gas is exposed to shocks and/or energetic (dissociative) radiation. There are a number of other recent examples where collaboration between theoretical chemists and astrophysicists has turned seemingly exotic interstellar molecules such as NO and HNC into valuable diagnostic tools [106,107].

Another radical which continues to be of great importance is OH, which is now being observed in much greater detail with Herschel than before, in particular as part of the “Water in Star-forming Regions with Herschel” (WISH) key program involving van der Tak and van Dishoeck. Initial observations [111] already show line ratios that do not agree with theory (e.g., the two 3Π₁/₂ 163 µm doublets show non-equal intensities). Thus, continued studies on the OH-H₂ system such as already underway in Nijmegen and in collaboration with van Hemert in Leiden also fit very well within this program.

A second class of molecules for which collisional data are lacking are deuterium-bearing species. These molecules are key probes of dense, cold regions where most CO is frozen onto grain surfaces, leading to molecular D/H ratios which are spectacularly enhanced over the elemental ratio by factors up to 10₁² [99, 100]. The accuracy of these studies is limited by the assumption that the collisional cross sections are unchanged upon isotopic substitution (e.g., DCO⁺, DCN, DNC). For species where the substitution breaks the symmetry, only old calculations are available (HDO: [101]) or none at all (H₂CO, CH₃OH). These are commonly observed molecules where collision calculations would have a major impact. Accurate collisional data would allow astronomers to develop these molecules as diagnostics of physical conditions in regions where traditional tracers do not work because of strong molecular depletion on grain surfaces.

Workplan and synergy within the consortium: The postdoc would be stationed in Groningen but with frequent visits to Nijmegen (and/or Grenoble, where similar efforts are ongoing) for interaction on the calculation of the potential energy surfaces and subsequent dynamics, especially in the first year. In year 2, the research would shift more toward astrophysical applications. Observations at sub-mm telescopes will be initiated in year 1 and carried out in year 2, to develop the astrophysical application of the collision data through the analysis of observational data.

As for the vibration-rotation transitions, the theoretical studies start with ab initio calculation of the potential energy surface and subsequent determination of the dynamics using close-coupling theory. For N- and D-bearing molecules, hyperfine structure resolved data is relevant for the lower J transitions [102]. Including the hyperfine states increases the number of channels, but the small energy separation between hyperfine levels offers opportunities for accurate approximate treatments. Generally, the rate coefficients will be computed over the 5–300 K range; extrapolation to higher temperatures may be performed using fitting functions but artificial neural networks such as proposed by Neufeld et al. (2010) [103] may also be tested. Candidate systems for study are OH⁺, H₂O⁺, CCH, OH, DCO⁺, DCN, DNC, HDO and HDCO. The final selection will be made together with Laurent Wiesenfeld, who will spend a sabbatical in Nijmegen from September 2010 and who will coordinate activities with the group in Grenoble.

The Groningen group of van der Tak will incorporate the newly computed data into LAMDA and apply them to astrophysical systems, including high-mass protostellar objects studied within WISH. Similarly, other NL astronomical groups will use the new results to analyze their data. In turn, the astronomers will feed back information to the chemists, for example on line ratios that cannot be fit with current molecular data and they will involve the chemical PhD students in such analyses to expose them to these reality checks.
3.4 Overview of the projects

The Table below summarizes the projects including requested positions.

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<tr>
<th>Nr.</th>
<th>Short name</th>
<th>PI(s)</th>
<th>Requested</th>
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<tr>
<td>3.1</td>
<td>Photodissociation experiments on small molecules</td>
<td>Ubachs (VU)</td>
<td>1.0 PhD student</td>
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<tr>
<td>3.2</td>
<td>Photodissociation and excitation in protoplanetary disks</td>
<td>van Dishoeck (UL)</td>
<td>1.0 PhD student</td>
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<tr>
<td>3.3</td>
<td>Photodissociation experiments on large molecules</td>
<td>Parker (RU)</td>
<td>0.7 PhD student</td>
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<tr>
<td>3.4</td>
<td>Theory of vibration-rotation inelastic collisions</td>
<td>Groenenboom (RU)</td>
<td>1.0 PhD student</td>
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<td>3.5</td>
<td>Experiments of vibration-rotation inelastic collisions</td>
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<td>3.6</td>
<td>Theory of pure rotation inelastic collisions</td>
<td>van der Tak (RuG)</td>
<td>2 yr PD</td>
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References


4. The solid Universe  
- Dust and Ice -

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4.1 Background

The conditions in space are extreme and not in favour of an efficient chemistry: temperatures are low, radiation fields are intense and particle densities are exceedingly small. Nevertheless, more than 150 different molecular species have been identified in star-forming regions. These comprise both small and complex species as well as stable and transient molecules and are the result of an exotic chemical evolution. Today, astrochemists explain the chemical complexity in space as the cumulative outcome of gas, grain and gas-grain interactions. Gas phase models explain the observed abundances of the smaller and many of the larger radical species. These models, however, fail to explain the presence of stable and complex, partially organic species in space, such as acetonitrile, a precursor molecule for the simplest amino acid glycine. It is generally accepted now that such species form on icy dust grains, small solid particles that are an important ingredient of the material that is found between the stars. These dust particles play an essential role, because they provide opacity (blocking regions of the galaxy from UV radiation), they are the basic material from which icy planetisimals and ultimately planets are formed, and they act as reservoirs and catalytic sites for molecule formation. Thermal and ultraviolet processing as well as atom bombardment of icy dust grains trigger a fascinating and largely unexplored solid state astrochemistry. Understanding the cycle of matter in galaxies, the origin of stars and planetary systems and the complex (organic) chemistry that is found in molecular clouds and proto-planetary disks is intimately linked to the study of the role solids have in space. The research projects discussed in this section address this goal and focus on the chemical and astronomical properties of dust and ice by combining the Dutch expertise in surface and solid state laboratory astrophysics, theoretical chemistry and astronomical observations and modelling.

4.2 Objectives

Large areas of space are filled by molecular clouds that consist of gas (mainly hydrogen) and (sub)micron sized silicate and carbonaceous dust grains. This so called interstellar matter forms a crucial link in the birth and death of stars and planetary systems. Stars and planetary systems are born from contracting molecular clouds. During the gravitational collapse the cloud becomes optically opaque and as light penetration is hindered, the cloud cools down and gas starts accreting onto the dust grain surfaces that act as highly effective cryopumps. This results in layered geometries of partially mixed ices on top of the grains. The gravitational collapse goes on until densities get so high that a new star forms and the gas and dust become part of an envelope that feeds the central protostar. Part of the gas and dust ends up in a rotating disc surrounding the young star, the so called protoplanetary disk, and provides the basic material from which icy planetesimals and planets are formed. Once the star starts burning these icy dust grains are irradiated by additional UV light and are bombarded by a continuous flux of atoms triggering an exotic solid state chemistry. In a later stage, the grains warm up and thermally induced processes become important. Molecules and reaction products start desorbing from the dust surfaces and start participating in gas phase reactions in which new species are formed that paint additional pathways toward molecular complexity. At the end of their life stars return a significant fraction of their mass to the interstellar medium through stellar winds and supernovae. This ejected material, which is enriched with the products of nuclear fusion in their cores and envelopes, mixes with that already present, thus also increasing the "metal" content of interstellar matter, and providing a new starting point for a next generation of planets and
stars. Dust therefore provides an excellent snapshot tool to study different stages in the chemical evolution of the universe.

This section of the Dutch Astronomy Network proposal describes seven complementary research projects that focus on key questions in modern solid state astronomy:

- What are the physical and chemical pathways towards dust grain formation in space?
- What is the chemical composition and structure of interstellar dust grains?
- How does the nature of a surface affect grain surface induced chemistry?
- Which chemical processes govern solid state ice chemistry under astronomical conditions?
- How complex can molecular chemistry become in inter- and circumstellar ices?
- Are the building blocks of life formed in the solid state?

These questions are closely connected to the other three topics within this network proposal; volatile PAHs freeze onto dusty ice grains, dust particles likely also comprise PAHs, and gas phase observations of molecules around young stellar objects and solid state reaction pathways are directly connected, and ultimately, UV irradiation of ice provides a pathway towards the formation of prebiotic molecules.

It is a challenging task to quantitatively characterize the physical and chemical processes that are involved. Within the Netherlands much expertise exists to tackle these questions using principally different approaches. Dust grains and inter- and circumstellar ices are spectroscopically accessible and observational data provide information that is needed to conclude on the local chemical conditions. The properties of dust grains and ices as well as the chemistry on icy dust grains upon thermal processing, photon irradiation or particle bombardment can be studied under fully laboratory controlled conditions and provide information to interpret and guide astronomical observations as well as the fundamental parameters needed to run astrochemical models. Both laboratory and astronomical studies benefit from detailed theoretical work that interprets macroscopic processes at the level of molecular motions of individual particles and that allows extending conclusions beyond the accessible boundary conditions in regular laboratory experiments. The projects that are described here comprise observational, modelling, laboratory and theoretical studies in which the following leading Dutch scientists (in alphabetical order) are involved:

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<tr>
<th>Name</th>
<th>Department</th>
<th>Institution</th>
<th>Specialization</th>
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<tr>
<td>Prof. F. Matthias Bickelhaupt</td>
<td>Theoretical Chemistry</td>
<td>VU Theory</td>
<td>Laboratory studies</td>
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<tr>
<td>Prof. Wybren Jan Buma</td>
<td>Physical Chemistry</td>
<td>UvA Laboratory studies</td>
<td>Observations</td>
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<tr>
<td>Dr. Elisa Costantini</td>
<td>SRON, Utrecht</td>
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<td>Dr. Herma Cuppen</td>
<td>Leiden Observatory, UL</td>
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<tr>
<td>Prof. Ewine F. van Dishoeck</td>
<td>Leiden Observatory, UL</td>
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<td>Observations, modelling</td>
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<tr>
<td>Prof. Carsten Dominik</td>
<td>Astronomical Institute, UvA</td>
<td>Radboud University Nijmegen, RU</td>
<td>Observations, modelling</td>
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<tr>
<td>Dr. Fedor Goumans</td>
<td>Theoretical Chemistry, UL</td>
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<td>Laboratory studies</td>
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<tr>
<td>Dr. Frank Helmich</td>
<td>SRON Groningen</td>
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<tr>
<td>Prof. Marc C. van Hemert</td>
<td>Theoretical Chemistry, UL</td>
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<td>Dr. Ludo Juurlink</td>
<td>Chemistry, UL</td>
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<tr>
<td>Dr. Inga Kamp</td>
<td>Astronomical Institute RUG</td>
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<td>Observations, modelling</td>
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<td>Prof. Willem Kegel</td>
<td>Van 't Hoff Laboratory, UU</td>
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<td>Prof. Geert-Jan Kroes</td>
<td>Theoretical Chemistry, UL</td>
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<td>Prof. Harold Linnartz</td>
<td>Leiden Observatory, UL &amp; LCVU</td>
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<td>Observations, modelling</td>
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<tr>
<td>Dr. Michiel Min</td>
<td>Astronomical Institute, UU</td>
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<td>Prof. Jos Oomens</td>
<td>FOM Rijnhuizen</td>
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<td>Prof. Petra Rudolf</td>
<td>Zernike Institute, RUG</td>
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<td>Dr. Floris vd Tak</td>
<td>Astronomical Institute RUG</td>
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<td>Prof. Alexander Tielens</td>
<td>Leiden Observatory, UL</td>
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<tr>
<td>Dr. Cor de Vries</td>
<td>SRON, Utrecht</td>
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<td>Observations</td>
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<tr>
<td>Prof. Rens Waters</td>
<td>Astronomical Institute, UvA</td>
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4.3 Projects

4.3.1. Dust

Characterizing grain surfaces and grain composition is a key in understanding grain chemistry and processing in different environments such as the outflows of evolved stars, the diffuse interstellar medium, molecular clouds and proto-planetary disks. Interplanetary and meteoritic dust — the picture shows a GEMS particle, Glass with Embedded Metals and Sulfides — attest to the complexity of dust chemistry in space and at the same time provide only a single tiny piece in the whole lifecycle of dust. Moving beyond the simple picture of bare silicates and graphite grains and identifying the complexity of dust chemistry requires a multidisciplinary approach.

In stellar outflows, "stardust" condenses and provides an important source of opacity for driving the wind that injects dust into the interstellar medium (ISM). There is strong evidence for non-equilibrium chemistry, freeze-out of chemical reactions at low densities, and inhomogeneous condensation of metals in the grains. Here, the condensation of oxygen-rich dust (70% of dust in space is oxygen-rich) and the role of Fe in this process are not well understood. However, Fe is crucial for the opacity at the near-infrared wavelength, where most of the stellar photons are emitted.

Once in the ISM and exposed to strong shocks, cosmic rays and energetic photons, the stoichiometry, chemical composition and lattice structure of the stardust grains are altered. Observations indicate that the grain lifetime is significantly shorter than the stardust production rate, implying an as yet unknown formation process that could take place in denser but cold molecular clouds. Using infrared and X-ray absorption studies we found that interstellar silicate dust is Mg-rich and Fe-poor; it still remains to be understood how Fe can be locked into these interstellar dust grains. Here, further X-ray studies enabled by new laboratory data of cosmic dust analogues can provide important clues.

The chemical evolution of gas in molecular clouds and proto-planetary disks is intimately linked to the chemical and physical properties of grain surfaces. The morphology (fluffy or compact) and grain chemical composition determine the type of reactions that can occur on the grain and in the ice that covers it. These effects have so far not been studied in detail. The grain chemical composition may also play a role in the short-range forces that govern grain growth in proto-planetary disks. Since the microphysics of dust affects the evolution of the global structure of proto-planetary disks, knowing the forces that act between dust grains is crucial for our understanding of the early phases of planet formation.

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Metallic Fe in astrophysical environments: Iron is an important element in the formation of solids in space. Gas-phase spectroscopy of interstellar Fe shows that it is strongly depleted with respect to hydrogen: the vast majority of Fe (~99%) is in the solid phase. The question arises how Fe becomes incorporated in solid material, and what the role of metallic Fe is in interstellar and circum-stellar chemistry. There is growing evidence from astronomical observations that metallic Fe nano-particles form and become incorporated into chemically inhomogeneous dust grains. These observations are (i) infrared spectroscopy of dust surrounding evolved stars, (ii) X-ray absorption and scattering measurements of interstellar dust in the galaxy, (iii) laboratory studies of Interstellar Dust Particles that contain the most primitive material in the solar system, the so-called GEMS (Glass with Embedded Metals and Sulphides). These independent observations show that metallic Fe nano-particles play an important role in the formation and evolution of solids in space. However their role has so far not been studied in depth, so that many questions remain unanswered: 1) What are the optical and infrared properties of Fe nano-clusters and how do these compare to bulk material? This is important to know because the opacity of dust is strongly influenced by even small amounts of Fe. 2) What are the physio-chemical properties of metallic Fe nano-clusters, i.e. what role do they play in the condensation of solids, and what chemical reactions are relevant for the formation and destruction of metallic Fe clusters? 3) How stable are metallic Fe clusters in interstellar space? This is important because in interstellar space there is evidence that iron remains in the solid phase while Mg and Si are already in the gas phase, suggesting that the Fe inclusions in silicate dust survive the harsh conditions of interstellar space. So metallic Fe nano-particles could be abundant in interstellar space.

The origin of FeS in the solar system: The formation of solid FeS is a long-standing problem in the physics and chemistry of interstellar matter. FeS is particularly important because the dominant source of sulphur in our solar system is solid FeS. This implies an extremely efficient chemical pathway to FeS that is capable of converting all gas-phase S to FeS. The question is where and how this happens. FeS is also believed to be an important catalyst in primitive reproductive reactions on the young earth. Astronomical observations of gas-phase S show that virtually all S is in the gas-phase in the diffuse interstellar medium. In molecular clouds, however, most S is not found in the gas phase any more, but where it is locked is not known. It is possible that S is converted to FeS by gas phase solid reactions involving metallic Fe and e.g. H$_2$S, but this reaction requires temperatures of several 100 K and so seems kinetically inhibited at the conditions that prevail in cold dense molecular clouds. Chemical equilibrium models for the proto-solar cloud predict the formation of FeS in the inner regions where temperatures are high enough for reactions to occur, but it seems unlikely that such a local process can be responsible for large-scale conversion of S to solid FeS. Whether or not Fe nano-particles play a role in the formation of FeS at lower temperatures is not known. Solid FeS has been tentatively detected in the mid-infrared spectra of two proto-planetary disks 8, but this detection is questionable and requires much more analysis using a better understanding of the infrared properties of small FeS clusters. So, what is the nature of sulphur chemistry in molecular clouds and in proto-planetary disks, and can gas phase S be converted to FeS in an efficient way under molecular cloud conditions? What role do metallic Fe nano-clusters play?

Approach: In order to address these questions gas phase spectroscopy of Fe-containing nano-clusters will be conducted. The FELIX group at FOM Rijnhuizen has ample experience in the IR spectroscopy of small gas-phase metal clusters. These clusters are generated in a supersonic molecular beam expansion with a Smalley-type laser ablation source. Typically, mass spectra recorded with a reflectron time-of-flight mass spectrometer display a distribution of clusters ranging in size from 5 to 100 atoms, depending on experimental settings. The clusters are entrained in the carrier gas of the supersonic expansion and are then spectroscopically interrogated with the radiation produced by the free electron laser FELIX. Stable neutral clusters

are in many cases observed to undergo ionization (via thermionic emission), which can be used directly in action spectroscopy schemes to obtain IR spectra of these neutral clusters\textsuperscript{9}. Ionic clusters have also been studied via several IR photo-dissociation schemes. Apart from pure metal clusters, various studies of metal carbides and metal oxides have been carried out. These species are generated by co-expanding C- and O-atom containing gaseous molecules, such as CH\textsubscript{4} and O\textsubscript{2}, in the carrier gas. Such clusters have mainly been studied because of their relevance to heterogeneous catalysis, but they are also of interest in astrophysics because of their possible occurrence in the Interstellar Medium. For instance, titanium carbide nano-clusters have been investigated and their spectrum, averaged over a substantial size distribution, has been compared to the interstellar 21 \( \mu \)m band found in the spectra of post-AGB stars\textsuperscript{10}. Other species investigated with astrophysical relevance include titanium oxide and aluminium oxide clusters\textsuperscript{11}.

The IR spectra are of interest as they can be directly compared with astronomical spectra to search for bands which can identify interstellar species. However, the IR spectra also contain important information on the (geometric and electronic) structure of the clusters. Such information can be recovered from the IR spectra by comparison with theoretical IR spectra calculated for different geometric structures and spin states, using electronic structure calculations. Knowledge of the cluster structures can be used to estimate optical properties of the species. In the framework of the Dutch Astrochemistry Network, we propose to apply the methods described above to study the spectroscopy of Fe nano-clusters, which have been studied in their anionic state by photo-electron spectroscopy\textsuperscript{12}, but not in their neutral and cationic states and moreover, not by IR spectroscopy. Iron oxide clusters have been studied successfully (Kirilyuk, A. et al., unpublished) and here we intend to produce and study iron sulphide clusters, which are of specific astrophysical interest. We also propose to investigate the possibilities to directly obtain experimental information on the optical properties of these clusters by application of UV/VIS spectroscopy, to be performed in the group of Buma at the UvA.

The current molecular beam time-of-flight setup will be equipped with a laser ablation cluster source. Optical characterization of Fe and FeS clusters will then be carried out by application of various optical action spectroscopy methods. REMPI spectroscopy will be used to study the properties of neutral clusters, while ZEKE and MATI techniques may be applied to obtain information on the ground state of the cations. Photo-electron spectroscopy can be applied to study anionic clusters.

Project 4.2: Mapping the silicate content in the interstellar dust in the X-rays
E. Costantini, C. de Vries, L.B.F.M. Waters, M. Min

Introduction: A long standing problem in the interstellar dust physics is the balance between life and death of dust in space. Dust is efficiently produced by cool evolved stars and supernovae. However, the exposure of such dust particles to the radiation field and cosmic rays, makes their life-time very short (~ 5×10^8 years). This is at odds with the observed abundance of heavy elements in the Galaxy. There must be a source of dust other than evolved stars in the interstellar medium. Since dust is formed in high density environments, molecular clouds have been proposed as sites of dust formation. Clearly, the processes that destroy and re-form silicates in interstellar space may have strong impact on their nature and chemical composition. For instance, while about 10 percent of the silicates produced by evolved stars is crystalline, interstellar grains are found to be amorphous with an upper limit to the abundance of crystalline silicates of about 2 percent. It is clearly important to investigate the dust chemical composition along different line of sights in order to understand the (uneven) distribution of metals in the Galactic plane. X-rays studies have proved to be a powerful tool in this respect.

![Figure 4.1. Left panel: Scattering extinction curve at a given scattering angle for CygX-2. The vertical dashed lines indicate the energy of the scattering features: O, Mg and Si. The best fit model privileges Mg:Fe of 5:2 (Costantini et al. 2005). Center panel: Evidence of EXAFS in the absorbed spectrum of ScoX-1. The macroscopic deviations around the O K edge are also due to absorption by dust (details in de Vries & Costantini, 2009). Right panel: synchrotron measurements of iron crystals (adapted from Lee & Ravel 2005).]

X-ray absorption and scattering by interstellar dust: In the X-ray band the dust properties can be simultaneously studied from two different points of view: scattering and absorption. The method is to observe an X-ray emitter located behind a layer of interstellar dust. The X-ray radiation will be absorbed by dust (and analyzed trough a spectrograph, e.g. XMM-Newton-RGS, Chandra-HETGS) and at the same time scattered at a very small, forward directed, scattering angle. The effect of scattering is to produce a diffuse halo around the source. This is analyzed using CCDs (e.g. XMM-Newton-EPIC). One of the crucial issues in dust studies is the amount and the nature of iron compound. X-rays are advantageous in this respect as the soft X-ray band (E<2 keV) hosts the absorption edges of the main constituents of silicates: O, Mg, Si K and Fe L shells. A pioneering study using X-ray spectroscopy of the scattered radiation, a predominance of Mg-rich silicates with a ratio Mg:Fe of 5:2 on a specific line of sight13 (See figure, left panel). This composition can explain the depletion of Mg and at the same time shows that iron could be combined with other species or locked in silicates in such a way not to be straightforwardly detected. Therefore, in agreement with infrared analysis, X-ray absorption spectra of interstellar dust suggests that interstellar silicates could be Fe-poor and Mg-rich. This connects to the material in the early solar system, which consisted of Mg glass with metals (e.g. iron) and sulphide inclusions (GEMS). Another recent study unveiled for the first time the presence of extended-X-ray-absorption fine structures (EXAFS) in the vicinity of the oxygen edge14 (de Vries & Costantini 2009) (See figure, center panel). A preliminary analysis shows the possible contribution of icy materials. The edge structure itself in this, and other similar sources,

appears very complex and significantly different by absorption of pure atomic gas (centre panel). The modelling points to calcium-rich silicates as well as ices. The role of dust in causing absorption is evident. However, in the X-ray band, we suffer from a severe lack of laboratory measurement to confront our data with. Small-scale absorption structures are extensively studied in solid state physics, but never with a specific interest in astronomically relevant compounds. The identification of ices is hampered by a lack of laboratory measurements of X-ray absorption spectra of astrophysical relevant materials.

**Characterization of dust compounds:** At SRON-Utrecht we are taking action to collect the crucial laboratory measurements at X-ray energies, especially focusing on samples of amorphous silicates that may be considered representative for silicates in interstellar space. Absorption with different amount of Mg:Fe ratios produce different spectral features that we can compare using the edge environments of all important constituents of silicates. As the X-ray band covers almost two decades in energy (0.3–10 keV), we have the unique possibility to characterize silicates both at low energy (< 2 keV) with O, Fe, Mg, Si and S and high (E ~ 6–7 keV) energy, measuring the Fe K shell absorption. In particular, we will measure a series of Mg(1-x)Fe(x)SiO₃ compounds with (x=0–0.6). Also silicates with two metals per silicon atom will be measured (FeMgSiO₄, Mg₂FeSiO₄, Mg₁.₈Fe₀.₂SiO₄, Mg₁.₆Fe₀.₄SiO₄, Mg₃SiO₄ and Fe₂SiO₄). These compounds can be made in both crystal and amorphous form.

The first measurements are foreseen in the summer 2010, when Mg₀.₆Fe₀.₄SiO₃ and MgFeSiO₄ will be characterized with the DUBBLE beamline in Grenoble. This beamline will provide us with the details of the Fe K edge. An example is provided in Fig. 4.1 (right panel), where two compounds, in crystal form, are compared with pure iron. The resolution in the figure is similar (~ 2–3 eV) with the one provided by the calorimeter on board of the future X-ray observatory IXO. The next step is to measure, with other facilities, the transmission of these compounds at lower energies, for a complete characterization in the X-ray spectrum. A strong point of X-ray analysis is also that EXAFS/NEXAFS look at the average neighbourhood (about 10-15 atom distances in width) of atoms. X-ray analysis can see if Fe atoms have lots of other Fe atoms around them (Fe nano-particles) or if they are evenly distributed among other atoms. X-ray absorption studies in synchrotron can look at laboratory-made materials, or at real meteoritic samples which have small (10 µm sized) real interstellar particles inside them, using small (10 µm) beam sizes. We will probe laboratory made samples of compounds representative for the various scenarios for interstellar dust. Using small synchrotron beam sizes however, we can also look at real samples of interstellar dust particles as e.g. thought to exist as micron-sized inclusions in some meteorites. This kind of investigation is important in understanding the way iron is released in stellar outflows and its subsequent inclusion in silicates. This large experimental project is done in collaboration with Jena University and the Debye Institute of Utrecht University. New laboratory measurements and improving the observational techniques, will be fundamental in the interpretation of data from both current and future instruments (namely Astro-H and IXO). New technology will provide indeed unprecedented energy resolution in the high (6–8 keV) energy band (ΔE ~ 2–5 eV). At the same time, the energy resolution will go down to ~ 2-3 eV over all the low-energy band (0.3–2 keV).

**The project:** The candidate will deal with the implementation of post-processed laboratory data to models for astronomical data. After ten years of operation, the public archives of the X-ray observatories XMM-Newton and Chandra contain a wealth of data to be exploited. We estimated that at least 40 sources are suitable for this study. Indeed dust lies mostly on the plane of our Galaxy, where also bright X-ray binaries, which are used as background light, are. Thanks to the versatility of X-ray instruments, we will be able to study the combined information from absorption and scattering along a same line of sight (e.g. Costantini *et al.* 2005, 2010). Observations will be tested against existing models. This work will provide both a solid theoretical background and an important observational legacy for the upcoming X-ray missions (the closest in time will be Astro-H in 2014).

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Project 4.3: Dust surface chemistry in the inner Solar Nebula: The formation of organic molecules through catalytic reactions on silicate surfaces
P. Rudolf, I. Kamp

**Introduction and Goal:** Silicate grain surfaces in the inner regions of young protoplanetary disks can function as catalyst for the formation of more complex organic molecules through Haber-Bosch and Fischer-Tropsch type reactions. Through large scale mixing processes, such organic matter can eventually reach colder outer regions of the disk and experience additional processing (e.g. deuteration, ice formation). This catalyzed organic component could form a substantial fraction of the organic matter detected in meteorites and comets in our Solar System. This project aims at the study of chemical reactions on silicate dust surfaces using X-ray photoelectron and infrared spectroscopy as well as temperature programmed desorption.

**Description of research project:** Observations begin to reveal a rich organic chemistry (e.g. H$_2$O, CO$_2$, C$_2$H$_2$, HCN) in the disks around young T Tauri stars. To which extent can complex organic molecules be formed in situ in the inner warm regions of the disks? Recent experiments indicate that gas-grain catalytic reactions may present a viable route to the formation of organic molecules and also macromolecular carbonaceous coatings. Meteoritic samples in our Solar System show the presence of phyllosilicates which were generated before the material was incorporated into meteorites and the system was closed off. Such silicate grain surfaces can be catalysts for the formation of more complex organic molecules through Haber-Bosch and Fischer-Tropsch type reactions. Recent experiments have shown that the macromolecular coating building up during surface reactions of CO and H$_2$ constitutes a more efficient catalyst for these reactions than the bare grain surface itself. If this holds true, then surface reactions do not shut down as the possible surface sites are saturated, but actually proceed as long as the grain is sitting in a warm (few 100 K) molecular gas phase environment. To include such processes in chemo-physical models of the early Solar Nebula, we need to understand these surface reactions and the formation and composition of the macromolecular coatings in detail: The binding mechanisms and sites, which molecules are formed, the temperature dependence of the reactions and the stability of the mantle to thermal fluctuations and UV and X-ray irradiation.

Observations of protoplanetary disks and our Solar System indicate still a large uncertainty on the mass distribution and hence pressures and temperatures in the inner regions of young planetary systems. Astrochemical models enable us to probe a large range of possible physical and chemical regimes. The modelling forms thus an extension of lab experiments for understanding the chemical processes that occur in the early stages of planetary systems.

**Experiments:** We shall study how a single layer of phyllosilicate platelets or clay dust grains consisting of multiple layers, deposited on a conducting substrate, interact with gas mixtures. The samples will be exposed to different gas mixtures (H$_2$-H$_2$O/O$_2$-CO/CH$_4$-N$_2$/NH$_3$) at pressures and temperatures in accordance with the modelling and the reaction products will be successively identified by X-ray photoelectron spectroscopy (XPS) and reflection absorption infrared spectroscopy (RAIRS). Information on the binding energy of the molecules will be deduced by temperature programmed desorption (TPD), a method of observing desorbed molecules when the surface temperature is increased. The influence of UV irradiation during the reaction as well as the stability of the reaction products under X-ray irradiation typical for the inner regions of the Solar Nebula will also be investigated. We shall study also in particular whether the catalytic activity of the hydrocarbon layer formed in the initial reaction is higher than that of the bare phyllosilicate surface as claimed by Nuth et al (2008), and assess whether the reaction products formed on the molecular coating are different from those formed on the bare grain surface. Additionally, for the multilayered samples, we shall study the influence of

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the inclusion of water into the mineral structure, by exposing the silicate material to warm water vapour before reaction with the gas mixture as well as during interaction with the other gases. Differences in reaction products as a function of reaction time will be evidenced. The results can be used in chemical models of the early Solar Nebula to address the adsorption process, surface alteration and the respective timescales in a larger context.

**Astrochemical modelling:** We use the two-dimensional thermo-chemical code ProDiMo\(^{20}\), that calculates the pressure structure of the nebula self-consistently with a gas phase chemical network (stationary and time-dependant). It already comprises a detailed model of adsorption and desorption processes on dust surfaces and we plan to add surface chemistry to track the layered structure of the reactive dust mantles and the processing of the solid surfaces with time (thesis work of G. Chaparro in Groningen). As input, we use the measured experimental data such as reaction rates and diffusion coefficients. With these models, we can explore the identified chemistry in a wider context and identify the regions in which prebiotic molecules efficiently form through "warm dust grain surfaces". The results will be compared to the "cold formation route" in ice mantles (see “ice” part of the solid universe).

![H2O abundance in the Minimum Mass Solar Nebula. Iso-pressure and isotherms relevant for the experiments are overplotted.](image1)

![UHV system for high resolution X-ray photoelectron spectroscopy and temperature programmed desorption to which a little high pressure chamber will be connected for the experiments described here.](image2)

**Work Plan:**

**Year 1:** Experimental training of the PhD student (various techniques of RAIRS, XPS, TPD) - first setup of experiment with bare silicates and simple gas mixtures (H\(_2\)-CO), - publish which molecules form on grains and in the gas phase. **Year 2:** Expand experiments with bare silicates to different gas mixtures - training with ProDiMo (collaboration with G. Chaparro) and first modelling using the laboratory results as input - publish the impact of catalytic surface reactions in the Solar Nebula. **Year 3:** Expand experiments to water intercalated phyllosilicates - study differences in molecular products due to H\(_2\)O - publish molecular compositions and comparison with near- and mid-IR observations of young protoplanetary disks (Spitzer, ground-based VLT/Keck). **Year 4:** Irradiation experiments (UV and X-rays) - assess the role of irradiation on organic coatings - explore wider implications of laboratory results within the network.

**Network Collaborations:** These experiments tie into the ice surface experiments carried out at the Sackler Laboratory in Leiden (Linnartz), but focus on the high temperature reactions that occur on warm bare grains. The modelling developed here can also be applied to much colder low pressure environments such as the ones studied by van Dishoeck, and Cuppen. We rely on the expertise of S. Cazaux (VENI postdoc Groningen) for MC simulations of the molecule formation on dust grains. The results of these experiments can also prove relevant for the in situ formation of large carbonaceous molecules (PAHs, Tielens) and carbonaceous dust.

Project 4.4: A colloidal model system for dust grains in space
W.K. Kegel

Introduction and goal: Dust particles on the order of micrometers in size are believed to play a key role in the initial step toward planet formation. We propose to determine the forces between dust grains in space under static conditions. If these forces are known, aggregation behaviour and the occurrence of growth instabilities can subsequently be studied experimentally by developing appropriate model systems. We propose to develop and study colloidal model systems in apolar solvents, i.e., solvents with low dielectric constants, as in outer space. A great advantage of using solvents is that buoyant forces effectively compensate the earth gravitational field. We propose to study the systems by confocal microscopy, available in the Van't Hoff laboratory. The experiments will be backed up and extended by using statistical mechanics techniques and/or computer simulation.

Description of research project: The goal of this project is to establish the dominating interactions between dust grains in space and develop colloidal model systems to study their aggregation behaviour. Dust particles on the order of micrometers in size are believed to play a key role in the initial step toward planet formation. Several studies have appeared on aggregation processes using model grains\(^{21}\), but there are still important open questions\(^{22}\). These questions are related to the (origin of) the dust grains themselves, and to their aggregation behaviour:

1. What is the origin of dust grains in space? In other words, by what process have they been formed?
2. What quantities determine the clustering behaviour of dust grains?

The clustering process is a complex interplay between statics and dynamics. Static quantities are essentially surface properties: these quantities determine the strength of the interactions between the grains, i.e., van der Waals forces, hydrogen bonds, density of electrical charges. Dynamic effects are, e.g., collision velocities that determine whether a dust grain will stick to a growing cluster, or whether it will bounce off or fragment the cluster. Charge effects are thought to be governed by friction. However, other charging mechanisms, e.g., by UV radiation, should also be considered. Colloids or granular systems with long-range (electrostatic) repulsion, and short-range attraction may in principle provide important model systems to study grain clustering in space.

Considering the expertise in the network, at this stage we propose to concentrate on static properties, i.e., the properties that determine the forces between the grains under static conditions. If these forces are known, aggregation behaviour and the occurrence of growth instabilities can subsequently be studied experimentally by developing appropriate model systems. We propose to develop and study model systems in apolar solvents, i.e., solvents with low dielectric constants, as in outer space. A great advantage of using solvents is that buoyant forces effectively compensate the earth gravitational field. We propose to study the systems by confocal microscopy, available in the Van't Hoff lab. Image techniques in principle reveal quantitative information on the structure and dynamics at the grain level\(^{23}\). The experiments will be backed up and extended by using statistical mechanics techniques and/or computer simulation; we have considerable experience and reputation in that field. We propose to address the following concrete (sub) questions:

I. What is the potential of mean force between dust grains?

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This depends on the surface composition of the grains. In principle, the net force is composed of attractive and repulsive contributions. Attractive contributions are van der Waals forces (almost certainly the dominant source of attractions). The magnitude of this force is mainly determined by the refractive index of the grains, being comparable for most inorganic materials\textsuperscript{24}. However, the detailed surface composition and structure of the grains is expected to be important. For example, hydrogen-bond forming molecules at the surface may lead to significant short-range attractive forces.

Repulsive contributions to the potential of mean force are expected to be dominated by electrostatics. Once electrical charges are present on the grain surfaces, excluded volume and steric interactions will be relatively weak. The main source of charge generation under static conditions is by (UV) radiation. We propose to find out, given the surface composition, how wavelength (distribution) and radiation pressure influence the level of charge carried by a dust grain. In fact in the limit of high radiation pressure we expect the grains have constant electrical potential. In this part the surface composition is (also) essential: the level of charge will depend on the density of chargeable molecules at the surface. The charge / potential can be measured in vacuum on ‘real’ grains, and in solvents using a Malvern zetasizer (available in our lab).

II. What is the real-space behaviour of model dust grains in apolar solvents? For this confocal microscopy can be used. Charges will be generated by (UV) radiation. The situation is complicated and entirely nontrivial by the fact that radiation induces inhomogeneous charge distributions, determined by the orientations of the grains relative to the UV source, and ‘shadowing’ by other grains.

We expect that there will be significant added value in answering question I. The second experiment is very well possible technically in the van ‘t Hoff laboratory, but only makes sense with input from the first project and in a collaborative context as possible within this network.

Network collaborations: In the van ‘t Hoff laboratory the network gains access to surface / synchrotron X-ray techniques, directly and via the inorganic chemistry department at the UU. It is natural to collaborate with the group of Petra Rudolf (RUG) on this issue, and with Cor de Vries / Elisa Costantini (SRON), who are interested in X-ray diffraction from dust particles. Moreover, Inga Kamp (also RUG) has significant expertise on interstellar dust and her expertise will be valuable to extend the laboratory results to astronomical environments.

Working plan

- Determination of the relation between grain surface composition and interaction potential between grains: surface techniques (with RUG), microscopy (1\textsuperscript{st} year).
- Determination of the level of charge on grains under several (interstellar) conditions (experiments, theory, simulation) (2\textsuperscript{nd} year).
- Set-up colloidal model system for interstellar dust and the study of aggregation behaviour in real space by time-resolved confocal microscopy (3\textsuperscript{rd}/4\textsuperscript{th} year).

\textsuperscript{24} Israelachvili, J., Intermolecular and surface forces, AP, (1992).
**4.3.2 Ice**

Powerful new telescopes have established that dust grains are covered by thick (50 – 100 monolayers) icy mantles in cold (<100 K) and ‘dense’ clouds. In particular, observations with the Infrared Space Observatory and Spitzer Space Telescope toward bright infrared sources reveal deep and broad absorption bands which can be compared with laboratory ice data and that show that interstellar ices comprise primarily of water, but also ices containing CO, CO₂, NH₃, and other species (see figure and table). The comparison also learns that ices in space are amorphous and consist of both rather pure and partially mixed constituents, depending on segregation, accretion and desorption history.

*Ice abundances in high- (W33A) and low-mass (Elias 29) star forming regions, normalized to water (100).*

<table>
<thead>
<tr>
<th>Molecule</th>
<th>H₂O</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>CH₃OH</th>
<th>H₂CO</th>
<th>OCS</th>
<th>NH₃</th>
<th>HCOOH</th>
<th>HCN</th>
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<tr>
<td>W33A</td>
<td>100</td>
<td>9</td>
<td>14</td>
<td>2</td>
<td>22</td>
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<td>0.3</td>
<td>15</td>
<td>0.4-2</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Elias29</td>
<td>100</td>
<td>5.6</td>
<td>22</td>
<td>&lt;1.6</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>-</td>
<td>&lt;0.1</td>
<td>&lt;9.2</td>
<td>-</td>
</tr>
</tbody>
</table>

In the coldest regions where new stars and planets are forming, these ices can be the major reservoir of elements heavier than H and He: except for H₂, most molecules are in solid rather than gaseous form. Most of them must be formed in situ on the grain by surface chemistry rather than through simple freeze-out from the gas. However, the grain surface mechanisms leading to molecular complexity are not at all understood and even the basic reactions for forming small molecules like CO₂ and CH₄ are not yet known.

In astronomical literature several solid state reaction pathways are discussed that provide effective reaction pathways to molecular complexity in space. These can be roughly separated in ‘light processing of ices’ and ‘particle (atom, ion, electron) bombardment of ices’.

Energetic processing of simpler ices (such as CH₃OH, NH₃ and CH₄) by cosmic rays and UV photons photodissociate existing ices into smaller fragments which subsequently diffuse and recombine into more complex species. Cosmic rays can penetrate deep into cloud cores or protostellar envelopes and induce an internal UV field through interactions with molecular hydrogen. Thus energetic processing of ices through both direct cosmic ray irradiation and the secondary UV field are possible during the cold, protected stages of star formation. Later on in the star formation sequence, additional UV light becomes available from the star itself. Formation of complex molecules in the ice takes place during the slow warm up of ices in the infalling protostellar envelope. The increasing temperature towards the protostar (20-100 K) allows for the diffusion of heavier radicals, such as CH₃ and CH₂OH, which continue to recombine forming larger and larger molecules. A consistent modelling of these processes is not possible, as for most reactions quantitative data on photodissociation branching ratios, diffusion barriers of the resulting radicals and binding energies of complex molecules are missing.

The other, competing scenario is the formation of complex molecules through exothermic H-, N-, O-, C- or S-atom additions that originate from the central star. It has been suggested that hydrogenation of molecules and radicals, such as CO and HCCO, or through a combination of hydrogenation and oxidation starting with acetylene (C₂H₂) explains the observation of complex gas species around young stellar objects. Laboratory data are largely missing. So far only the laboratory production of formaldehyde (H₂CO) and methanol (CH₃OH), water, and ethanol (CH₃CH₂OH) from hydrogenation reactions of CO, O₂ and acetaldehyde ice, respectively, have been reported. It is likely that the two scenarios are effective and that the resulting chemistry is based on both.
Goal: The overall objective of this project is to study the photoprocessing of interstellar ices both from an experimental and theoretical point of view. Dedicated UHV experiments will be performed irradiating ices that have been grown with monolayer precision with broadband UV light. Kinetic Monte Carlo simulations will be performed to simulate the photoprocessing of the ices. The focus will be on the long term effects and formation of new molecular species through reactions of photo-fragments.

Description of research project:

Experiment. A new setup - MATRI²CES (Mass Analytical Tool of Reactions in Interstellar ICES) - will be used to study the photochemical impact of UV light on inter- and circumstellar ice analogues under UHV conditions. This setup has the unique feature that it is able to study in situ and in real time (with ms time response) ice reaction products by combining soft laser ablation and proton-transfer time-of-flight mass spectrometry. The ice is irradiated by the output a broadband hydrogen-microwave discharge lamp that simulates the interstellar radiation field, peaking around 121 nm (Ly α) and covering 115-170 nm (~ 7.5-10.5 eV) with a variable photon flux covering roughly 1-10x10¹³ photons cm⁻²s⁻¹ at the substrate surface.

The setup has been constructed within the NOVA 3 instrumentation program, and is currently tested with the expectation to exceed the sensitivity of regular UHV surface techniques – RAIRS and TPD - by several orders of magnitude. The latter methods already shown to be capable to study photodesorption, photodissociation and photochemistry in simple ices. This sensitivity is an absolute prerequisite to detect reactive intermediates as well as large complex molecules that will be produced in much smaller amounts. This will also hold for the formation of prebiotic compounds. Indeed previous studies showed a rich variety of amino acids and other compounds upon UV exposure of astronomically relevant ice mixtures (comprising water and several other constituents – see table), but only after the organic refractory was extracted by a gas chromatogram following heat up to room temperatures.

Theory. Before it is possible to make accurate predictions on the molecules that could form on these interstellar ices, it is necessary to understand the processes that bring reactants together in icy layers. Most of the current astrochemical models to simulate grain chemistry do not consider the structure of the ice and completely ignore any layering or structural effect. Recent combined computational and experimental studies of the formation of H₂O and CH₃OH indisputably showed that the structure of the ice is central to the reactivity and lifetimes of molecules in the ice. Attempts are underway to increase the amount of detail in the current models; however, as long as we lack an understanding of the processes that control the formation of icy mantles, the introduction of more complex expressions will not necessarily lead to a more accurate description. As soon as one leaves the submonolayer regime, i.e., once ice layers start to build, the chemistry becomes much more complex and less intuitive. Advances can be made through a multidisciplinary approach in which physico-chemical expertise is applied to astrophysical problems.

The theoretical work will focus on the chemical alteration of ices by photoprocessing. Molecules embedded in interstellar ices can photodissociate leading to radicals. In astrochemical models, these radicals are often used to produce complex molecules. However, it is not clear whether

these radicals will be mobile enough to meet and react. This will be studied theoretically, with emphasis on reaction products formed upon photoprocessing of water ice. Detailed Molecular Dynamics simulations will follow the photo-products, OH and H, the first couple of pico-seconds after the initial single photodissociation event\(^\text{31}\). In laboratory experiments ices are followed over a longer period of time during UV irradiation\(^\text{32}\). Here radicals can build up to react together and form new species. The Molecular Dynamics simulations show that photo-fragments can travel over a large distance before they equilibrate with their environment. The consequences of this diffusion mechanism for the chemistry have not been studied and could be severe. Moreover, similar processes are most likely important for different chemical systems as well. The Molecular Dynamics simulations further showed that hydrogen atoms are more likely to leave the ice than OH radicals. In this way the ice layer will be slowly depleted from hydrogen atoms as was shown in earlier Monte Carlo simulations. This will lead to layering in the ice with more oxygen-rich species like ozone in the lower layers and water in the top layers.

**Work plan:** The requested PhD student will get a combined and parallel experimental and theoretical training and the research project comprises both a laboratory and a modelling component.

**UV-photoprocessing:** The UV photochemistry will be studied for CH\(_3\)OH ice and for NH\(_3\)-containing H\(_2\)O/CO\(_2\)/CH\(_4\)-ices. Methanol ice has proven to be an ideal starting point for the formation of complex organics upon UV irradiation and the formation of for example dimethylether and ethylene glycol could be proven. The ammonia containing mixtures provide a formation route to amino acids. A kick-off study\(^\text{33}\) has shown the feasibility of this work that will be extended for different ice mixtures and ice temperatures. Also, in comparison with CH\(_3\)OH, a UV photochemical study on the astronomically relevant CH\(_3\)CN is planned, with the aim to observe nitrogen containing complex molecules. Both CH\(_3\)OH and CH\(_3\)CN ices mixed with other astronomically relevant ice constituents – particularly water - will be photoprocessed. It will be studied, for example, under which conditions CH\(_3\)CH\(_2\)OCHO and C\(_3\)H\(_7\)CN are formed, both species that were recently discovered towards the astronomical source Sagittarius B2(N). The link with the theoretical part of this project is among others through the role water and water fragments play in this scheme.

**Monte Carlo simulations:** The PhD student will start working with the Monte Carlo code and implementing the probabilities obtained from the MD simulations. Subsequently experimental conditions will be simulated for different temperatures and be compared to experimental data. Upon a reasonable agreement the simulations will be extended to interstellar conditions for different scenarios. Simultaneously a start will be made for a similar model to describe methanol photoprocessing with the goal to simulate this under interstellar conditions. The final touch is that the full collection of results will be used to extract prescriptions to simulate photoprocessing of ices in astrochemical models with reasonable accuracy. These prescriptions need to be general, easy to implement in rate equation based models, and computationally cheap.

**Network collaborations:** There are clear cross-links with projects 4.3 (Rudolf, Kamp), 4.6 (Bickelhaupt) and 4.7 (Kroes, van Dishoeck) within the solid state proposal. Particularly the outcome of project 4.3 on ice structure data will add to the work described here. The outcome of the present work is important for the work proposed by van der Tak in the gas phase part and by Ehrenfreund in the prebiotic part. Within Leiden collaborations are pursued with Juurlink and Goumans.

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Project 4.6: Molecular complexity in the solid state: theory meets experiment
F. M. Bickelhaupt, H. Linnartz

Introduction and Goal: It is generally expected that more complex molecules, such as polycyclic aromatic hydrocarbons (PAHs) are also present in space. Infrared fluorescence of PAHs is regarded as the most likely origin of the UIRs (the unidentified infrared emission bands) that are observed along many lines of sight. These species must be abundant, ubiquitous and an important component of the interstellar medium, but despite many efforts no specific PAH or even classes of PAHs have been unambiguously identified in space. Hence, the intrinsic physical and chemical properties of these species are largely unknown and a quantification of their role in astrochemical networks is lacking. The majority of the laboratory studies has been focussing on gas phase work of PAHs and PAH-cations (see also PAH section of this network). The project described here, describes an alternative route, through the solid state, as non-volatile species as PAHs should freeze out and accumulate in time on cold grains offering a reservoir in this way.

New spectral fingerprints and UV induced chemistry of PAHs in water ice are studied using a recently constructed and fully operational setup. In parallel, the molecular properties of PAHs in a water ice environment will be simulated using state-of-the-art density functional techniques that focus on three aspects: (1) predicting trends in structure, stability and vibrational spectroscopy as PAH systems are embedded in a water ice environment as compared to the gas phase; (2) an understanding of the structure and stability of these PAHs both, in the gas phase and in ice, obtained with sophisticated electronic structures analyses; (3) an exploration of possible reactive pathways of such species in an water ice environment.

Support is requested for the theoretical part of this project. The experimental part will be financed externally within the framework of a NWO VICI grant.

Description of research project

Experiment: A new setup in Leiden allows the spectroscopic and photo-dynamical study of PAH containing ices upon UV irradiation\textsuperscript{34}. The setup consists of a high vacuum chamber in which ice is grown, a microwave hydrogen discharge source generating UV light for the photoprocessing, and a special Xe-arc light source emitting broad-band light (200-1000 nm) that is transmitted through the ice onto a fast and fully computer controlled monochromator equipped with a sensitive CCD camera. The solid or fluid precursor species is brought into the gas phase through resistive heating and a HeNe laser is used to determine the ice thickness growth of the highly diluted mixtures. The innovative aspect of this setup is that it combines sensitive broadband spectroscopy with a resolution that is more than sufficient to monitor solid state features - i.e. it is possible to cover large spectral ranges without loss of spectral details - and that the time resolution allows monitoring ice chemistry in real time. Several studies have been performed meanwhile on water ices comprising highly diluted (1/10000) amounts of pyrene, anthracene, and benzo[ghi]perylene. The Figure shows the 310-500 nm spectrum of the Py:H\textsubscript{2}O ice at 10 K after 1200 s of \textit{in situ} photolysis in absorbance mode. The spectrum is baseline subtracted and given in optical depth units. Since the spectrum recorded before UV irradiation is taken as

reference, bands with positive OD values arise from species produced by photolysis while the carriers of negative OD bands reflect a density decrease. The shown spectrum is only one snapshot (an averaged spectrum of a few hundred recordings of ~5 ms length). The integrated band intensity can be recorded as a function of time, i.e. as function of fluence, correlating precursor and reaction products and consequently providing insight into possible reaction pathways. And this can be done for different temperatures. It turns out that ion-mediated processes play a very important role. Py is efficiently converted into Py+ and the charge remains largely located in the ice, also when the UV photolysis source is switched off. Other products are observed as well.

Up to now solid state PAH chemistry has been barely studied and the outcome of this pilot study shows that the potential role and reactivity of PAHs in inter- and circumstellar ices may have been underestimated.

Theory: As pointed out above, PAHs and PAH cations are intriguing species because of their likely occurrence in space in combination with the fact that they have not been unambiguously identified in astronomical observations. This alone asks for a careful theoretical exploration of the structure, stability and spectroscopic properties of these species in order to arrive at a better understanding of their behaviour and of ways to "catch" them through experimental observation.

(1) To this end, extensive series of state-of-the-art density functional theory (DFT) calculations, as implemented in the Amsterdam Density Functional (ADF) program,35 will be conducted. Here, it is important to treat both, small models and large, realistic PAH molecules and cations. Modern DFT is able to treat even larger poly-aromatic systems and still achieve a satisfactory and consistent accuracy through which trends can be computed in structure and stability in the gas phase (intrinsic properties) as well as the changes that are associated with absorbing the systems of interest into a water ice environment. Whereas the intrinsic (i.e., gas phase) properties can be well described with traditional GGA functionals, the situation in the condensed phase in which interactions with water-molecules and, depending on concentration, also aromatic stacking occur, asks for more sophisticated approaches, such as the newest meta-GGAs, hybrid functionals and dispersion-corrected DFT.36 It is useful to obtain, for the smallest model system, ultra-high accuracy benchmarks for sensitive properties on the basis of conventional ab initio calculations.

(2) A problem, closely related to the above explorations, is obtaining and understanding of the behaviour and properties that will be found there. Achieving this objective expands the scope of this project enormously because it enables one to construct a physical model through which the knowledge obtained becomes applicable outside the range of computationally studied systems. Thus, advanced electronic structure analyses will be carried out to reveal the basic patterns in the bonding mechanisms that are behind the "computationally observed" behaviour.37 The analyses are carried out in the framework of the quantitative molecular orbital (MO) model contained in the Kohn-Sham approach to DFT.38 These consist of MO electronic structure analyses, quantitative bond energy decomposition analyses (EDA) as well as analyses of the electron density distribution and effects of intra-molecular (intrinsic properties of PAH systems) and inter-molecular interactions (stacking, solvation in water ice).39

(3) Finally, reaction pathways in water ice and, for comparison, in the gas phase, will be explored with the above DFT methods (meta-GGA, hybrid-GGA and dispersion-corrected DFT)
and stationary points are characterised through vibrational and IRC analyses. An understanding of the trends will be achieved through activation strain analyses.\textsuperscript{40}

**Network collaborations:** The direct link of this work is with the projects presented in the aromatic universe section of this proposal. The experimental (Jos Oomens) and modelling (Xander Tielens) studies described in that section focus on gas phase experiments, and the work proposed here offers additional information to study gas-grain interactions. Furthermore, useful synergy can be obtained through collaboration with Dr. Gerrit Groenenboom regarding ultra-high accuracy benchmarks for small model systems.

**Work plan:** This research project will be shared by two postdocs, one located at Leiden and the other at Amsterdam. The idea is that measurement and calculation will go hand-in-hand, supporting and guiding each other. Regular meetings are guaranteed, as Linnartz has a special chair at the LCVU. This project is challenging, particularly from the theoretical side, therefore we request an experienced researcher to perform the calculations.

Project 4.7: MD/MC simulations of photo-induced reactions of H₂O photofragments with CO ice
G.J. Kroes, E.F. van Dishoeck

Goal: Molecular dynamics (MD) and Monte-Carlo (MC) simulations will be performed on photo-induced reactions of photo-fragments of H₂O with CO molecules adsorbed on or in water ice, with relevance to astrochemistry. The goal is to address the key question whether such reactions are more important for producing molecules like CO₂ and complex organic molecules in astrochemical environments than thermal molecule-surface reactions. The MD calculations will use pair potentials modelling the interaction of the dissociating water molecule and its photofragments with the adsorbed molecule.

Description of research project: In interstellar space, water ice, present on dust particles in dense clouds, is exposed to ultraviolet photons which can dissociate molecules through absorption into excited electronic states and lead to energetic fragments which can subsequently promote reactions with other species. Excited electronic states following absorption of UV radiation have long been postulated to play a key role in the formation of interstellar ices. A key question is how relevant such photo induced reactions are compared to thermal molecule-surface reactions. A prime example of a molecule for which this question is important is CO₂, one of the most abundant species after the dominant H₂O. Since the reaction of O(³P) with CO is spin-forbidden, the alternative route of OH + CO → CO₂ + H has been proposed, where OH is produced by photodissociation of H₂O ice. This process is in competition with the reaction of hot H (resulting from the same H₂O photodissociation process) with CO to form HCO, and ultimately H₂CO and CH₃OH. Both reactions may also occur with thermal OH and H accreted from the gas.

Goals of the project on the reaction of OH and H with CO on ice are to find answers to questions like: What are the probabilities for reaction of energetic OH and H with CO to produce CO₂ and HCO, following H₂O ice photodissociation through excited electronic states? What is the relative importance of these processes compared with reactions of CO with thermal H and OH? In the case that the reaction is initiated by photodissociation, do the product molecules leave the surface in excited rovibrational states?

To study the photo induced reactions, first an amorphous ice surface with an adsorbed CO molecule will be constructed using a molecular dynamics (MD) code with intermolecular pair potentials. Second, a random H₂O molecule will be picked in the ice and excited into the first excited state with UV radiation in the 7-10 eV range, representative of the interstellar radiation. The initial coordinates and momenta of the atoms in the H₂O molecule needed in the MD calculations are obtained from a Wigner distribution fitted to the ground-state H₂O vibrational wavefunction. This dynamical approach has been shown to yield accurate results for gas phase photodissociation of water. The chosen H₂O will dissociate and form OH and H with ~3 eV kinetic energy. These energetic fragments are then followed using classical trajectories until they leave the surface, become accommodated at separate locations, recombine to H₂O, or react with a CO molecule. The PES of the first excited repulsive electronic state of H₂O ice (i.e., of a water molecule in the first excited electronic state interacting with electronic ground state molecules) will be taken from our previous fits of ab initio potentials, as will the H-H₂O and OH-H₂O potentials. The interaction of H with the adsorbed CO will be described by the H-CO potential, whereas that of OH with CO will be based on the state-of-the-art HOCO potential.

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developed by the Leiden group. All of these potentials are based on high-level ab initio electronic structure calculations. The calculations will result in reaction probabilities for the formation of HCO or CO$_2$ as functions of various parameters such as temperature, initial layer of dissociating H$_2$O molecule (top or bulk), and CO coverage.

Our previous H$_2$O photodissociation calculations indicated that a significant fraction (~30%) of the dissociation events result in H and OH being trapped in the ice when the initial H$_2$O molecule is in the bulk, i.e., below the first two monolayers. Reaction of these trapped species with CO can still proceed through a diffusive Langmuir-Hinshelwood mechanism because of the long timescales available in space. The rate for this process can be quantified using Transition State Theory (TST), in which the reaction probability depends on the minimum energy path connecting reactants and products. Initial results on diffusion coefficients of H on amorphous H$_2$O ice have recently been obtained and this work will be continued in the research here proposed.

The calculation of the reaction of thermal H or OH accreted from the gas with adsorbed CO is more straightforward. The first step in constructing the potentials is the same as above. Subsequently, classical trajectory calculations of H or OH colliding with the surface will be run and followed until they either leave the surface, accommodate on the surface, or react with CO to form HCO or CO$_2$, through a hot atom or an Eley-Rideal mechanism. If the H or OH become accommodated, reaction can still occur through the diffusive mechanism, which can be quantified with the TST methods mentioned above.

**Work plan and Network collaborations:** Laboratory experiments on all proposed systems will be carried out in the Sackler Laboratory for Astrophysics in Leiden, so that direct comparisons and tests of the models are possible. The project will be carried out by a postdoc over 3 years.

- The first step will be the calculation of the thermal H and OH with adsorbed CO reactions, because they are more straightforward than the photo-induced reactions. Including start-up time to become familiar with the topic and computer programs, this part is expected to take 15 months up to publication.
- The bulk of the time will be spent on studying the photo induced reactions of OH and H with CO, months 15-36, and is expected to result in several publications. This includes investigation of the astrochemical implications of the reaction probabilities using Monte Carlo simulations in collaboration with H. Cuppen in Leiden.

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4.4 Overview of the projects

Seven projects will tackle in detail and on a quantitative basis different aspects of solid state astrochemistry. Four projects have their principal focus in dust studies, and three projects focus on the experimental and theoretical description of chemical processes in inter- and circumstellar ices. In total the equivalent of four 4 yrs PhD research positions and two 2 yrs of postdocs is requested, complemented by two 2 yrs PhD support through FOM and SRON, and 2 yr postdoc through a VICI-NWO grant.

<table>
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<tr>
<th>Nr.</th>
<th>Short name</th>
<th>PI(s)</th>
<th>Requested</th>
<th>Background</th>
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<td>Costantini (SRON), de Vries (SRON)</td>
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<td>Laboratory, observational, modelling</td>
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<td>Kroes (UL), van Dishoeck (UL)</td>
<td>2 yrs PD</td>
<td>Theory</td>
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5. From PAHs to chains, rings and cages

Jos Oomens
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5.1 Background

The well-known IR emission features dominate the mid IR spectra of almost all objects, including HII regions, reflection nebulae, young stellar objects, planetary nebulae, post-asymptotic giant branch objects, nuclei of galaxies, and ultraluminous infrared galaxies (Verstraete et al. 1996, 2001, Flagey et al. 2006, Genzel et al. 1998, Moutou et al. 1999, Hony et al. 2001, Peeters et al. 2002, Brandl et al. 2006, Geers et al. 2006, Armus et al. 2007). Moreover, the IR cirrus, the surfaces of dark clouds, and the general interstellar medium (ISM) of galaxies are set aglow in these IR emission features (Mattila et al. 1996, Abergel et al. 2002, Regan et al. 2004, Smith et al. 2007). These features are generally attributed to IR fluorescence of far-ultraviolet-pumped polycyclic aromatic hydrocarbon (PAH) molecules, containing 50–100 C atoms (Sellgren 1984; Allamandola, Tielens & Barker 1989; Puget & Leger 1989). PAHs are thus an important component of the ISM, and their presence has major ramifications. These species dominate the heating of neutral gas through the photo-electric effect (Verstraete et al. 1990; Bakes and Tielens 1994) and thereby dominate the temperature structure of PhotoDissociation Regions (PDRs) – the atomic zones that separate the molecular gas from the ionized gas in regions of massive star formation – and influence the phase structure of the ISM (Wolfire et al. 1995). Inside dense clouds, PAHs will be the dominant negative charge carriers and hence control the ionization balance through neutralization reactions with atomic and molecular cations (Tielens 2005). In that way, PAHs affect ion-molecule chemistry that builds up simple gas-phase species (Wakelam & Herbst 2008) and the ambipolar diffusion process of magnetic fields that support molecular clouds against gravitational collapse and star formation (Ciolek & Mouschovias 1994). The IR signatures of PAHs are also omnipresent in the spectra of regions of star and planet formation. Observed spectral variations indicate the importance of extensive chemical processing in the disk environment (Sloan et al. 2007; Boersma et al. 2008; Keller et al. 2008; Pino et al. 2009). The organic inventory of the Solar system may have evolved along similar lines. Determining the inventory and the origin and evolution of interstellar molecules is important to understand possible prebiotic roots of life in the universe as well as recognize and distinguish life’s signatures on Solar system planets (eg., Mars and Martian meteorites; McKay et al., 1996) as well as exoplanets. For a recent review see Tielens (2008).

PAHs are, thus, an abundant and important component of the interstellar medium of galaxies and directly influence key processes related to the energy and ionization balance and hence the evolution of interstellar gas and thus galaxies. Hence, understanding the origin and evolution as well as the role of PAHs in the interstellar medium of galaxies is a key question in astrophysics.

Interstellar PAHs are generally thought to be injected into the interstellar medium by cool C-rich stellar outflows as a key intermediary or byproduct of the soot formation process in such environments (Frenklach and Feigelson 1989). The PAH family injected into the ISM is likely to be wide and varied but subsequent processing by the omnipresent UV photons will rapidly weed out the less stable species (Fig. 5.1). Indeed, the IR spectral characteristics of post-AGB objects – the stellar sources of PAHs – are typically very different from the spectra observed from PAHs in the interstellar medium (Sloan et al. 2007) and this has been attributed to the effects of this chemical weeding process (Pino et al. 2008). Processing by energetic ions in strong shock waves driven by supernova explosions may also contribute greatly to funneling the injected PAH distribution into its ‘strongest’ members (Micelotta et al., 2010). Either process (UV photo absorption or ion bombardment) will leave the PAH in a highly vibrational excited state where it is prone to fragmentation. However, ion bombardment generally transfers more energy into
internal energy of the species than available through UV photons in the ISM (with energies < 13.6 eV) and hence may well open up different fragmentation channels. Several channels for fragmentation can be open depending on excitation energy; e.g., H-loss and C\textsubscript{2}H\textsubscript{2} loss (Ekern et al. 1998). Under interstellar conditions, fragmentation will preferentially occur through the “weakest link” and this is expected to lead to (almost) complete H-loss (Fig. 5.1). Isomerization and further processing of these dehydrogenated PAHs will then favor the formation of fullerenes, cages, and/or rings, and chains depending on the internal energy. Some of these intermediary products may be very stable and become prominent members of the interstellar molecular inventory.

In this ‘trickle down’ chemistry, interstellar PAHs may ‘father’ a wide variety of related species but under the most extreme conditions, only the most stable species would dominate. This may be of particular relevance in regions of high UV field intensity – e.g., near the surfaces of photodissociation regions (PDRs) – or near supernova remnants. Observationally, the brightest PDR surfaces are characterized by very similar and unique infrared emission spectra (Werner et al. 2009), possibly reflecting this weeding down of the interstellar PAH family to the most stable members and/or reaction products. In addition to these stable products, fragmentation of PAHs could be the source of the unexpectedly high abundance of small hydrocarbon radicals in these environments (Pety et al., 2005). Likewise, dehydrogenated PAHs have often been considered as key to understanding the spectral pattern in the infrared emission features in particular for the CH out-of-plane bending modes (Leger and Puget 1984; Pauzat et al., 1997) and the Diffuse Interstellar Bands (DIBs) (Duley 2006). However, except for C\textsubscript{60} itself (Sellgren et al. 2007), the contributions of fullerenes and carbon cages to the interstellar emission spectra have not been considered. In a large measure, this reflects the fact that their spectra have not been studied systematically.

Figure 5.1. The chemical evolution of PAHs in the interstellar medium under the influence of UV photons and energetic ion bombardment combines the effects of dehydrogenation and fragmentation with those of isomerization. Fully hydrogenated PAHs – injected by stars into the ISM – are at the top right side. UV photolysis and ion bombardment will lead to complete H-loss and the formation of graphitic sheets. These sheets may isomerize to various types of cages or even fullerenes depending on internal energies. Further fragmentation may also lead to the formation of flats, rings, and chains.
The chemistry outlined in figure 5.1 is likely very relevant for the carriers of the Diffuse Interstellar Bands (DIBs) as well. The DIBs compose a set of visible absorption bands discovered almost 100 years ago in stellar spectra. The DIB spectrum is rich, with some 200 DIBs known with varying strength and width. The (stronger) DIBS correlate reasonably but not perfectly with each other. Generally, these absorptions are now attributed to electronic transitions in an extended family of molecular species present in the interstellar medium (cf., Tielens & Snow, 1995; Herbig 1995). Despite vigorous efforts by the world’s leading spectroscopy groups, the identification of these bands with specific carriers has remained enigmatic. Among the carriers considered are PAH cations and dehydrogenated PAHs, which have unpaired electrons and, therefore, electronic absorptions in the visible (Brechignac & Pino 1999, Salama et al. 1999, Ruiterkamp et al. 2002; Duley 2006). Despite tantalizing claims, no unambiguous identification has been made with a specific PAH species. Possibly, reflecting essential molecular physics characteristics of these types of molecules, electronic transitions are intrinsically either too weak or too broad to be responsible for the strongest DIBs (Tielens 2008). Alternative identifications for the DIBs include a variety of carbon chains. Here too tantalizing claims have not held up against detailed scrutiny (Tulej et al. 1998; Galazutdinov et al. 1999; Motylewski et al. 1999). Nevertheless, large odd-numbered carbon chains and/or carbon rings are still the leading candidates for the carriers of the DIBs (Maier et al. 2006), if an efficient formation route for these types of species in the ISM can be identified (Tielens 2008).

5.2 Objectives

Here we propose a coherent program, combining laboratory experiments, astrophysical modeling, astronomical observations and theoretical chemical studies, to investigate the chemical evolution of interstellar PAHs under the influence of UV photons and energetic ions in the interstellar medium. This program will focus on

1) Identifying key chemical routes and stable intermediaries and quantifying their dependence on the molecular characteristics of the original PAH.

2) Measuring the spectral characteristics of the resulting species in the infrared and UV/visible.

3) Determining the abundance of these species by comparison to observed IR emission spectra and visible absorption spectra.

4) Quantifying the evolution of PAHs in space.

This coherent and integrated approach will lead to a deep understanding of the evolution of interstellar PAHs and the characteristics of the emitting and absorbing species in the infrared and UV/visible.

The Netherlands has a long-standing interest in the physics and chemistry of interstellar PAHs. There is a strong astrochemistry group at Leiden Observatory focused on the IR emission characteristics of PAHs in space based upon IR spectra obtained by the Short Wavelength Spectrometer on Board of ESA’s Infrared Space Observatory and the InfraRed Spectrograph on board of NASA’s Spitzer Space Telescope as well as VISIR observations on the Very Large Telescope. At the Pannekoek institute, astronomers are very active in developing cutting edge instrumentation for ESO’s Very Large Telescope and this provides Dutch astronomers with direct access to these state-of-the-art instruments. With the IR laser facility, FELIX, Fom/Rijnhuizen provides a unique facility for the study of the IR characteristics of PAHs and other astrophysically relevant species and the Molecular Dynamics group has a proven record of success in this area. Construction has started on the Far-IR/TeraHertz Free Electron Laser in Nijmegen that will extend these types of studies into the long wavelength regime now being probed by ESA’s Herschel Space Observatory. Likewise, the atomic and molecular physics group at the KVI has much experience with studies on the interaction of energetic ions with molecules of astrophysical interest. The Laser Center of the Free University and the Molecular Photonics group at the University of Amsterdam have extensive expertise in the area of molecular
spectroscopy in the UV and visible region of the spectrum. Finally, the aromatic network group links well to the astrochemistry groups at NASA Ames Research Center. In particular, the quantum chemistry group at NASA Ames has developed much expertise in the calculation of the vibrational frequencies of large (100-150 C-atom) containing PAHs which will be of great help in guiding the interpretation and analysis of the fragmentation and isomerization studies. There are a number of groups in the world focusing on aspects of the proposed science: These include the PIRENEA experiment at the CESR in Toulouse (Bacchitta and Joblin 2008), which addresses the photochemistry of PAHs. However, because this set up has no spectroscopy component, identification of reaction products is very challenging and direct comparison of reaction products to astronomical data is not possible. The spectroscopy group of John Maier in Basel is very active in the study of carbon chains and rings in connection to the DIBs (Maier et al. 2006). Here, we focus on that same aspect but connect this to the larger question of reactivity and stability of molecular intermediates in space and use that question to select putative candidate species from among the many possible isomers.

The following leading Dutch scientists (in alphabetical order) are involved in the described projects:

Prof. Wybren Jan Buma  Physical Chemistry, UvA  Laboratory studies
Prof. Lex Kaper  Pannekoek Institute, UvA  Astronomical observations
Prof. Harold Linnartz  Leiden Observatory, UL & LCVU  Laboratory studies
Prof. Jos Oomens  FOM Rijnhuizen, Nieuwegein  Laboratory studies
Dr. Thomas Schlathölter  KVI, RUG  Laboratory studies
Prof. Alexander Tielens  Leiden observatory, UL  Astronomical observations, modelling
Prof. Wim Ubachs  Laser Center, VU  Laboratory studies
Prof. Wim van der Zande  Radboud University Nijmegen, RU  Laboratory studies
5.3 Projects

**Project 5.1: The photochemical evolution of PAHs**

We propose to study the UV photolysis of PAH species that are astrophysically relevant, using an existing experimental set up at the FELIX facility at FOM/Rijnhuizen. Under the harsh conditions of space, PAHs are expected to undergo UV photoprocessing forming dehydrogenated and fragmented species (Ekern *et al.* 1998; Le Page *et al.* 2003; Mulas *et al.* 2008; Bacchitta and Joblin 2008). While the spectroscopy of neutral as well as cationic PAHs has now been studied to some extent, virtually no spectroscopic information is available on the PAH photoproducts. These photofragments may hold important clues to understanding IR emission as well as visible absorption spectra observed toward many interstellar sources. The focus of this study will be on determining the dominant fragmentation and isomerization reaction routes and products (cf., fig. 5.1) as well as the IR characteristics of the reaction products. The results of this study will be compared to those from the ion-processing study (project 5.2) to assess the differences and similarities of these two processes and will serve as input for the astronomical study on the evolution of the interstellar PAH family and the observational consequences thereof (project 5.4). The electronic absorption features of these species will be characterized using UV photo-dissociation spectroscopy (project 5.3). **We request one PhD student position for this part of the project to be stationed primarily at FOM/Rijnhuizen.**

![FTICR-MS](image)

**Figure 5.2.** Ionized PAHs are produced via electrospray ionization (ESI) and mass-selectively stored in the FTICR tandem mass spectrometer. A UV source is then used to induce dehydrogenation, fragmentation and/or isomerization. The photoproduct of interest is then mass selected and its structure is probed by IR spectroscopy using the free electron laser FELIX.

IR spectra of PAH photofragments will be recorded via IR multiple photon dissociation (IRMPD) spectroscopy using the free electron laser FELIX. Ionized gas-phase PAHs can be produced by electrospray ionization (ESI) of a solution containing the PAH molecule (Knorke *et al.* 2009). The ions are subsequently mass selected in a Fourier Transform Mass Spectrometer (FTMS) available at the FELIX facility. Dehydrogenation, fragmentation and/or isomerization will be induced by UV irradiation using a broadband source in the mass spectrometer (Ekern *et al.* 1998). Individual fragments will then be mass-isolated and investigated with IRMPD spectroscopy.

This study is designed to probe the molecular structure of the photo-fragments, which is anticipated to directly reveal the photochemistry of PAH ions. This method has been very successful in the structural characterization of ionic fragments of protonated peptides (Polfer *et al.* 2005), which has aided in understanding the chemistry underlying peptide sequencing methods in proteomics. Here we will apply it to UV-photoproducts of PAH ions. An important and to date unanswered question is whether the aromatic carbon framework of the PAH will be retained upon (complete or partial) dehydrogenation. Possibly, the fragments rearrange to more stable carbon species, such as linear chains or large rings (Fig. 5.1; Gotts *et al.* 1995), although such processes are not only governed by thermodynamic stability, but also by reaction kinetics.
Comparison of the experimental IR spectra of the PAH fragments with those calculated by DFT methods for different candidate structures will be applied to assign fragment structures. This information will be crucial to (theoretical) analyses of PAH fragmentation chemistry under astrophysically relevant conditions.

In addition to this main goal, the IR spectra will also provide new insights in the characteristics of interstellar PAHs through comparison with details of the interstellar IR emission spectra. Dehydrogenation of PAHs may cause sensitive shifts in the aromatic CC stretching modes, which is of importance because they are believed to give rise to the interstellar 6.2 μm emission band; however, attempts to match the interstellar emission and laboratory PAH spectra reveal a small but systematic mismatch for this band (Peeters et al. 2002). Likewise, systematic shifts appear in the peak position of the CC modes that are possibly driven by photochemical evolution in extreme environments (Peeters et al. 2002; Sloan et al. 2007). The IRMPD technique is ideally suited to characterize trends in the vibrational spectrum in an extended sample of species and has already been used this way to address aspects of the interstellar PAH emission spectra (Oomens et al. 2003).

These experiments will also set the stage for future spectroscopic investigations of PAH fragment ions using IR-UV hole-burning methods in a cryogenically cooled ion trap (Stearns et al. 2007), which is currently under development in collaboration with Prof. S. Schlemmer (Cologne). These experiments are not based on multiple photon excitation and are performed at low temperature, so that higher spectral resolution is attainable. Comparison of IRMPD and linear IR spectra can give information on the vibrational anharmonicities (Oomens et al. 2003), which play an important role in the appearance of interstellar IR emission spectra (Cook & Saykally, 1998). Moreover, different fragment isomers may be selectively addressed in the UV excitation step, whereas an IRMPD experiment would give a mixture of spectra in the case of multiple isomers. Application of this technique to the IR spectroscopy of astrophysically relevant PAHs is funded separately under an advanced ERC grant. Finally, experiments in such a cold trap may hold the key to a possible identification of certain PAH fragments as DIB carriers (project 5.3).

In summary, we propose to study the IRMPD spectroscopy of UV photoproducts of PAHs, building up from small PAHs to larger ones over the first two years of the project. We expect to study around 5 to 8 PAHs and their most important fragment ions in those two years with an emphasis on characterizing the photochemistry of PAHs and the structure of the key photofragments. The second half of the project will be devoted to analyses of the spectra and the implications for interstellar PAHs. A few promising photofragments may be investigated using the more-involved hole-burning technique for detailed comparison to interstellar IR spectra. Moreover, we will expand our studies to the far-infrared (λ > 20 μm), where the very characteristic PAH drumhead modes are expected. These data may become particularly relevant in the near future when Herschel has probed this spectral regime systematically for PAH dominated sources such as PDRs. These modes are expected to be relatively weak and powerful far-IR laser sources will be required to probe these modes. We plan to use the free electron laser for intra-cavity experiments (FELICE, Bakker et al. 2010) for studies in the 20-100 μm range. The Nijmegen far-IR FEL that is currently under construction (FLARE) may be used in the future to probe the spectrum beyond 100 μm.
Project 5.2: The chemical evolution of PAHs driven by energetic ion interaction

We propose to study the interaction of energetic ions with PAH species that are astrophysically relevant, using an existing experimental set up at the KVI in Groningen (see below). The focus will be on determining the dominant reaction routes and products. In addition, the set up will be hooked up to the FELIX laser facility at FOM/Nieuwegein to determine the IR characteristics of the reaction products. The results of this study will be compared to those from the photolysis study (project 5.1) to assess the differences and similarities of these two processes and will serve as input for the astronomical study (project 5.4) on the evolution of the interstellar PAH family and the observational consequences thereof. The electronic absorption spectra of species that are identified as stable intermediaries (project 5.3) will be determined in the UV through near-infrared for comparison to the DIB spectrum. We request one PhD position for this part of the project to be stationed primarily at the KVI/Groningen.

Ion processing of interstellar PAHs is dominated by the effects of ~100 km/s shocks, which typically occur on a timescale of 100 Myr in the ISM (Micelotta et al. 2010). Typical ion-PAH interaction energies are then 50 (200) eV for protons (alpha particles). Young supernova remnants are characterized by slightly more energetic ion-PAH collisions (T~10^7 K, 0.5keV). There is little experimental data on the interaction of ions with astrophysically relevant PAHs, particularly at these low energies. At the KVI, a research line focusing on molecular ionization of energetic collisions was established starting in the mid 90s, when collisions of multiply charged keV ions with CO and C_60, van-der-Waals and covalent clusters were investigated (Folkerts et al. 1996; Schlathölter et al. 1999; Hadjar et al. 2000; Tappe et al. 2002; Arion et al. 2008).

Currently, a main research focus are ion and photon interactions with molecules of biological relevance, such as DNA building blocks and their clusters, amino acids and water (de Vries et al. 2003; Schlathölter et al. 2005; Schlathölter et al. 2006; Bari et al. 2008; Alvarado et al. 2005). Recently, a pilot study on keV ion-anthracene collisions has been performed (Postma et al. 2010).

![Experimental set up for ion-PAH fragmentation](image)

Small molecules can be evaporated without decomposition and an effusive gas target can be produced from an oven. This target is crossed by e.g. a pulsed beam of singly or multiply charged ions. Charged collision products are then extracted by a static electric field into a reflectron-type high resolution time-of-flight mass spectrometer (Fig. 5.3). Fragments can be detected in coincidence to obtain an even deeper insight into the dissociation dynamics. Besides
relative fragmentation cross section and fragment correlations, also fragment kinetic energies can be obtained. In addition to the effusive molecular target, a supersonic jet is currently being installed to study either seeded isolated molecules or molecular clusters. Furthermore, the reflectron will be replaced by a reaction microscope, i.e. a linear time-of-flight system with position sensitive detector, allowing for determination of the 3-D momenta of the charged dissociation products in coincidence. For smaller molecules this technique in principle allows kinematically complete experiments.

More complex molecules will thermally decompose upon heating. These species will be injected by an electrospray ion source, in which the molecule of interest is dissolved in a solvent such as methanol. Electrospray ionization leads to formation of protonated or deprotonated molecular ions that subsequently pass a radiofrequency mass filter for selection of the desired mass and charge state. The ions are trapped in a radiofrequency ion trap (Paul trap) and cooled by collisions with pulsed He buffer gas to obtain a sufficiently dense target. The cooled and trapped complex molecular ions can than be bombarded with ions. The trap content is then extracted into a time-of-flight mass spectrometer. This setup will be upgraded in the near future to a system in which the molecular ions are not trapped. Instead, an intense pulse of molecular ions will be generated that can then be crossed e.g. with an ion beam. With this crossed beam technique, it will be for instance possible to use a reaction microscope as well to investigate the dissociation dynamics in great detail.

Recently, a sub keV ion gun was installed on the effusive-beam setup that allows to study collisions at ion energies of a few 100 eV. For the 10-100 eV range, a dedicated source will be installed. The systems described above can easily be transported, e.g. to the FELIX facility to probe the IR characteristics of the reaction products. The electrospray setup will be upgraded with an additional RF-ion guide and RF-mass filter. At FELIX, this would allow to produce a mass selected beam of PAH ions, irradiate them with a low energy ion beam, mass select a product ion and trap it as a target for FELIX.

In summary, we propose to study the ion fragmentation of PAHs, building up from small PAHs to larger ones over the first two years of the project. We expect to study around 4 PAHs and their most important fragment ions per year. The goal is to characterize the fragmentation process of PAHs and the structure of the key fragments. The second half of the project will be devoted to probing the IR characteristics of the particularly promising fragments using the FELIX facility to further elucidate their structure as well as for comparison for interstellar spectra.
Project 5.3: The visible and UV absorption characteristics of stable intermediates

We propose to measure the electronic absorption characteristics of the stable intermediaries and other relevant species identified in the UV photochemistry (project 5.1) and ion-interaction studies (project 5.2) from the UV all the way to the near-infrared. These species will be produced and mass-isolated in an ion trap reflectron time-of-flight mass spectrometer that is currently being constructed at Leiden (see below). It is anticipated that the resolution of these spectra taken at room temperature will be too low (see e.g. Boyarkin et al. 2006; Mitric et al. 2007; Rajput et al. 2010) for a direct comparison to the Diffuse Interstellar Band (DIB) spectrum. However, the results of this study will be used to select out the species that may be considered as viable candidates for DIB carriers (project 5.4). Initially, the focus will be large PAHs and fullerenes that we have in our possession. Specifically, the spectrum of C\textsubscript{60}\textsuperscript{+} and its relationship to the 960 nm DIBs will be investigated.

We request one PhD position for this part of the project to be stationed primarily at the Laser Center of the Free University but with involvement of the Sackler Laboratory at Leiden University and the Molecular Photonics Group at the University of Amsterdam.

Figure 5.4. Experimental set up for the photochemistry of gaseous ions. After gentle evaporation and ionization, the ions are stored in an ion-trap. A tunable UV light source is used to excite the ions, leading to dissociation. After release, a time-of-flight mass spectrometer (TOF) measures the abundance of the parent species and the photolysis products. After mass spectrometry identification, the same experiment can store ions in the ion trap for further spectroscopic investigation using UV/Vis lasers.

At the Sackler laboratory (Leiden) an experimental set up will be developed to measure the kinetic parameters governing the photochemistry of PAHs, supported by an ERC advanced grant (Fig. 5.4). In this set up, after gentle evaporation and ionization, cations are stored in an ion-trap where they can be probed by (tunable) light sources. Here, this setup will be adapted to study the visible and UV absorption characteristics – using tunable and monochromatic radiation sources – of stable intermediaries and other relevant species formed by fragmentation and isomerization of PAHs. These studies will be performed in Leiden and at the Laser Center of the Vrije Universiteit (LCVU), which is well equipped for these types of experiments. Experiments are also scheduled at the Paris synchrotron facility. The experimental set up is designed to be mobile and will be coupled to existing laser-based experiments at the LCVU.

In the group of Prof. Ubachs (director LCVU) and Linnartz (special chair Molecular Laboratory Astrophysics at the VU) a number of pulsed and cw laser systems are available that cover the deep UV to the NIR with high spectral resolution. A special focus is on the generation of deep-UV (< 300 nm) radiation. Radiation with wavelengths between 198-220 nm are realized, for example, using frequency tripling of the red output of a SIRAH dye laser, operated on standard dyes, such as Rhodamine (B or 101) and DCM, pumped by a 532 nm unseeded Nd:YAG laser. Frequency tripling is then realized by doubling red light in a KDP crystal, to rotate it and to collinearly mix it with the visible carrier in a second non-linear BBO crystal. Spectral coverage of 215-270 nm, in addition, is achieved via frequency doubling of the output of the blue and green output of a dye laser pumped at 355 nm by an injection-seeded Nd:YAG laser using Coumarine laser dyes. More regular wavelengths (300-750 nm) are accessible using a series of available pulsed and cw dye lasers, providing spectral coverage with high spectral resolution of the order of a few hundred MHz. Here overlap exists with laser systems as available at the UvA (Prof. W.J. Buma) and Leiden (Sackler Laboratory for Astrophysics).
extension to the NIR and access to the 960 nm range (C₆₀⁺) is possible using other non-linear techniques, such as Raman shifting. Much expertise and support is available at the LCVU for all these laser techniques (Ivanov, et al. 2008; Salumbides et al. 2006; Zinkstok, et al. 2006). An overview of the available laser systems is given at www.lcvu.vu.nl (see LCVU access facilities).

These studies will provide the necessary input for future high resolution UV/Vis experiments on systems that appear as promising candidates for the DIBs. We envisage that gas-phase UV/Vis studies on mass selected UV photoproducts is possible using recently developed UV photodissociation spectroscopy methods in cryogenically cooled linear rf traps (Paul et al. 1995). These methods have been successfully applied to obtain UV spectra of mass-selected biological molecules (Boyarkin et al. 2006) and carbon chain species (Dzhonson et al. 2007). Laboratory spectroscopy studies of DIB candidates are a notoriously "high risk, high gain" game. Here, we mitigate this risk by focusing on species that are identified through our photochemistry and ion-bombardment studies as viable candidates. Moreover, even if identification with the DIBs remains elusive, understanding the electronic excitation process of these species still provides an important key to understand their role in the interstellar IR emission spectra.

In addition, these studies will investigate the UV photodissociation dynamics and reaction chemistry. The availability of an ion trap – where ions can be stored up to seconds if necessary – and widely tunable UV laser sources will allow for a detailed characterization of the dissociation dynamics, relating the UV photon energy, dissociation lifetime and fragmentation channel. Combined with the structural information on PAH fragments obtained via their IR spectroscopy (project 5.1), this is anticipated to yield a complete picture of the UV induced photochemistry of gas-phase PAH ions, thus expanding on the experiments of Jochims et al. (1999). Especially for the larger PAHs, it may be of interest to investigate the dynamics at still higher UV photon energies and we consider the possibility of performing similar experiments at the VUV beamline DESIRS (5 – 40 eV) at the synchrotron SOLEIL, where the installation of an ion trapping device is in progress.

Different detection techniques will be applied for neutral species; in particular, REMPI and LIF spectroscopy will be employed to record electronic excitation spectra that typically occur in the UV/VIS region, and extension to the near-IR is possible as well. The Molecular Photonics group at the University of Amsterdam (since recently associated with the Laser Center VU and part of the Amsterdam Institute for Laser Sciences & BioPhotonics) has extensive experience in high-resolution spectroscopy of a wide variety of molecular systems seeded and cooled into supersonic beams. Large species, that do not have appreciable vapor pressure, will be entrained into a supersonic beam by laser desorption, which will overcome size limitations involved in thermally evaporating PAHs (Rouillé et al. 2007). This method has been used in combination with REMPI detection for aromatic species (Meijer et al. 1990), but not for the large PAHs targeted here. This is a much more involved technique and for neutral species, the focus will therefore be on those stable intermediates – identified in the UV photolysis or ion-bombardment studies – that can be produced through organic synthesis techniques.

Finally, for some species ultrasensitive techniques will be required. Over the last two years, the Molecular Photonics group has set up an extensive collaboration with the group of Dr. Marcel Drabbels at the EPFL (Lausanne). Here, high-resolution spectroscopy of molecular species seeded into helium nanodroplets is performed. For neutral species, they have shown that unprecedented spectral resolution can be obtained, while recently also a new method has been developed that allows for regular IR and UV/VIS spectroscopy to be performed on ionic species with orders of magnitude higher sensitivities than possible so far.

In summary, over the first two years of the project, we propose to study the UV/Vis absorption spectra of key PAH fragment ions, identified in the UV and ion fragmentation studies. This study will likely reveal key candidates for DIBs that will then be followed up in subsequent years using higher spectral resolution techniques. In addition, in the second half of the project, the studies can be broadened to investigate the VUV behavior of relevant PAH fragments at SOLEIL.
Project 5.4: Astronomical implications

We propose to model the evolution of the interstellar PAH family due to ion-processing in interstellar shocks and due to irradiation with UV photons in the diffuse ISM. An essential part of this program will be to compare the measured spectral characteristics of dehydrogenated PAHs, graphitic sheets, fullerenes, cages, flats, rings and chains with IR emission spectra of PAHs in space and with the measured DIB spectrum. The focus of this study will be on determining the role of stable intermediaries identified in the laboratory studies in the interstellar PAH family. In addition, the role of PAHs in the origin of small hydrocarbons in PhotoDissociation Regions will be assessed. **We request one PhD position for this part of the project to be stationed primarily at Leiden Observatory but with involvement of the Pannekoek Institute at the University of Amsterdam.**

The response of PAH molecules to interstellar shocks has been modeled by Micelotta et al. (2010). In these models, the gas is rapidly stopped behind the shock as kinetic energy is converted into heat. Subsequently this gas cools rapidly radiatively and is further compressed. Because of their inertia, PAHs are slowly decelerated by collisions with gas atoms. These energetic collisions also transfer internal energy to the PAHs through electronic excitation that rapidly flows to the vibrational manifold through internal conversion. The resulting vibrationally highly excited PAH may then fragment, depending on the amount of energy transferred and the dissociation kinetics. At low collision energies, direct nuclear interaction may also be of importance directly ’knocking out’ an atom from the PAH. These two mechanisms are expected to have very different fragmentation products (Micelotta et al. 2010).

Previous studies of PAH processing by interstellar shocks focused on determining the lifetime of PAHs in the interstellar medium. In this, they treated PAHs as generic species with parameters which were largely guessed at. Here, we propose to build upon this by considering the actual chemical routes for the fragmentation and the isomerization processes and the fate of specific, individual PAH species (Fig. 5.1). These will follow directly from the experimental studies described under project 5.2. The focus will be on following the chemical fragmentation process predicting the abundances of key stable intermediary products (cages, fullerenes) as well as the abundance of small hydrocarbons (eg., rings, chains, C2H2 and daughter products) for different shock parameters. In this, we will adopt the shock models developed for the processing of interstellar PAHs developed by Micelotta et al. (2010). Using models for the shock frequency distribution in the interstellar medium (cf., Jones et al. 1994), predictions can be made for the abundance of these species in the ISM. Using the results on the IR and visible spectroscopic characteristics of these species, these results can be compared to existing observations of the IR emission and visible absorption spectra of different regions in the ISM.

The destruction of PAHs by UV photons has been modeled by Le Page et al. (2003) and Tielens (2005) focusing, again, largely on the lifetime of (generic) PAHs in the ISM. Also here, the molecular parameters involved were largely guessed at, based upon limited experimental studies on a few very small PAHs (eg., anthracene). Here, we will extend these studies by studying the processing of (specific) PAHs in PhotoDissociation Regions (PDRs), gas and dust illuminated by the intense radiation field of nearby massive stars. In these regions, penetrating UV photons will excite PAHs electronically. Internal conversion leaves the PAH highly vibrationally excited and fragmentation can ensue. The studies described under project 5.1 will provide the basic parameters and fragmentation products for specific, astrophysically relevant PAHs. For the PDR models, we will use the numerical codes originally developed by Tielens and Hollenbach (1985) and extended by Wolfire et al. (1990) and Kaufman et al. (1999) that follow the penetration of UV photons and the resulting physical and chemical response of the gas. These models will be updated to include the latest chemistry involving PAHs (cf., Tielens 2008) and to ensure that they are complete in the chemistry of small hydrocarbons. In this way, predictions can be made for the abundance of stable intermediates and small hydrocarbons as a function of the physical characteristics of the PDRs (eg., density, incident UV field). Using the results on the IR and visible spectroscopic characteristics of these species, these results can be compared to existing observations of the IR emission spectra of PDRs. In addition, the abundance of small hydrocarbons can be compared to those observed through their rotational,
submillimeter spectra (e.g., Pety et al. 2005). In addition, these models can also be applied to diffuse interstellar clouds (cf., Wolfire et al. 2003; 2008) and the role of different species as putative carriers of the DIBs can be quantitatively assessed.

Finally, an observational study of the DIBs is an essential part of this astronomical program. This will include a systematic survey of DIBs in the far-red and near-infrared. Very little has been done in searches for DIBs in this wavelength regime. Yet, Foing and Ehrenfreund (1997) discovered two DIBs around 960 nm that they tentatively attributed to C_60^+. In a general sense, electronic absorption features shift systematically to the red as PAHs, cages, or carbon chains and rings increase in size and this wavelength regime is likely a rich ‘hunting ground’ for astronomically relevant sizes. The ESO Very Large Telescope provides a unique set of instruments that allow detailed spectroscopic studies of DIBs. The full optical and near-infrared wavelength range is accessible, both at medium and high spectral resolution. Since October 2009, the first second-generation instrument on the VLT, X-shooter, is available for medium-resolution (R ~ 10,000) spectroscopy at optical and near-infrared wavelengths for the faintest targets accessible to the VLT. It is the most powerful spectrograph in the world and covers the wavelength region from 300 to 2500 nm in one shot. The instrument has been partly built in the Netherlands (PI Kaper) and we have access to the guaranteed time program. The optical spectrograph, UVES, or near-infrared spectrograph, CRIRES (1-5 micron) are available for higher spectral resolution (up to R ~ 100,000).

In summary, in the first two years, the PhD student will adept existing models for the photochemical and ion-processing evolution of PAHs under astrophysically relevant conditions (e.g., PDRs and shocks). These will be used to determine the implications in terms of the IR spectra and fragmentation products that can be observed in the sub-mm in the 3rd year. These studies will be guided by the experimental results on fragmentation products as they become available (near the end of year 2 of those studies). For the 4th year of his PhD, the student will perform a systematic study of the DIBs in the far-red and near-IR using the guaranteed time on X-shooter. In the actual timeline, rather than located at the end of the PhD, this latter study may actually be interwoven with the more theoretically oriented studies.
5.4 Overview of the projects

The projects are summarized below. Each project has a lead scientist who will carry overall responsibility for the project. A number of other institutes contribute to each and every project, resulting in a deeply interwoven program. Key scientists from the different institutes are also indicated in the table. We request 4 PhD students for this program (see table 5.1). These students will be stationed at the lead institute indicated and their studies will be supervised by local advisors.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Short name</th>
<th>PI</th>
<th>Requested</th>
<th>Key personnel</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>PAH Photochemistry</td>
<td>Oomens (FOM Rijnhuizen)</td>
<td>1 PhD student</td>
<td>Linnartz (UL), van der Zande (RU), Tielens (UL)</td>
</tr>
<tr>
<td>5.2</td>
<td>PAH ion interaction</td>
<td>Schlatholter (KVI Groningen)</td>
<td>1 PhD student</td>
<td>Oomens (FOM Rijnhuizen), Ubachs (VU), Tielens (UL)</td>
</tr>
<tr>
<td>5.3</td>
<td>PAH UV/VIS spectroscopy</td>
<td>Buma (UvA)</td>
<td>1 PhD student</td>
<td>Ubachs (VU), Linnartz (UL), Tielens (UL)</td>
</tr>
<tr>
<td>5.4</td>
<td>Interstellar PAHs</td>
<td>Tielens (UL)</td>
<td>1 PhD student</td>
<td>Kaper (UvA)</td>
</tr>
</tbody>
</table>

5.5 PAH samples

Figure 5.5. Molecular structures of some of the PAH samples that will be investigated. These structures range from very open structures to very compact structures. Compact structures such as C_{78}H_{26} are thought to be particularly relevant for astrophysics. These PAHs have been specifically synthesized for laboratory astrophysics purposes.

The IR spectroscopic and UV photochemical and ion-bombardment studies will initially focus on compact PAHs with sizes up to 80 C-atoms that are generally considered most relevant for interstellar space. Figure 5.5 shows molecular structures of such PAHs in our possession. These were specifically synthesized in gram quantities for astrophysical studies. In our initial studies, we will supplement these with small compact PAHs (e.g., pyrene (C_{16}H_{10}), coronene (C_{24}H_{12}), ovalene (C_{32}H_{14})) which are commercially available. The results of these studies will also guide us in follow up studies. PAHs for such follow-up studies can also be specifically synthesized for this purpose and this will be funded under an approved Advanced-ERC program (with the goal of measuring their IR spectroscopic properties in the gas phase). Particularly promising and
stable PAH fragmentation products identified in our studies can also be synthesized for this program. In the program proposed here, we will study the photochemistry of these species and the characteristics of their reaction products. We fully expect that larger PAHs can also be synthesized; up to 100 C-atoms, including supercompact PAHs, such as circumcoronene (C_{54}H_{18}) and circumcircumcoronene (C_{96}H_{24}). Existing matrix studies and DFT calculations suggest that while there are many isomers particularly for the larger PAHs, only the supercompact PAHs have spectra consistent with the observed interstellar spectra. Likely, the superaromaticity and resulting stability, associated with their compact molecular structure make these specific species particularly relevant for harsh environment and long exposure times of the ISM and they will be one focus of this program.

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6. The prebiotic Universe

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6.1 Background

Carbon is a key element in the evolution of prebiotic material. Astronomical observations have shown that carbonaceous compounds in the gas or solid state, refractory or icy are ubiquitous in our and distant galaxies (van Dishoeck & Blake 1998; Ehrenfreund & Charnley 2000; Pendleton & Allamandola 2002, van Dishoeck 2004, Tielens 2008). Interstellar molecular clouds and circumstellar envelopes are factories of complex molecular synthesis (Kwok 2004). During the formation of the solar system, this interstellar organic material (gas and dust) was chemically processed and integrated in the solar nebula from which planets and small solar system bodies formed. Small solar system bodies represent the remaining population of planetesimals not incorporated into planets. These comets and asteroids (and their fragments meteorites and interplanetary dust particles) impacted the young planets in the early history of the solar system and with particularly high frequency during the late heavy bombardment phase 3.9 billion years ago (Gomes et al. 2005). A surprisingly high number of biomolecules and molecules that are used in contemporary biochemistry on Earth are found in the interstellar medium, planetary atmospheres and surfaces, comets, asteroids and meteorites as well as interplanetary dust particles. Planet Earth was formed through a hot accretion process that allowed only the rocky material from the inner solar system to survive. Ices were sublimed and existing carbon material (volatile and refractory) combusted. Therefore, organic molecules found on terrestrial planets must have formed after the planetary surface cooled, or were delivered via impacts by small bodies in the young solar system. All terrestrial planets have been seeded with organic compounds through the impact of small bodies during solar system formation. Part of this material may have been important starting material for life (Chyba et al. 1990; Ehrenfreund et al. 2002). Understanding the evolution of organic molecules during incorporation into the solar system is essential to probe their role in the emergence of life on Earth and possible on other habitable worlds.

Organic compounds observed or sampled from our solar system, such as planetary surfaces/atmospheres, comets, and interplanetary dust, hold clues to processes that occurred during the origin of our solar system (Ehrenfreund & Charnley 2000; Cruikshank et al. 2005; Sephton & Botta 2005; Raulin 2008). More than 50 molecules have been identified in cometary comae (Crovisier et al. 2009). Many small organic molecules observed in cometary comae probably originate wholly or partially from the decomposition of larger molecules or particles, indicating that large polymers such as polyoxymethylene and HCN-polymers are present in comets (Cottin & Fray 2008). Carbonaceous meteorites contain a substantial amount of carbon (up to 3 % by weight) and exhibit evidence of thermal and aqueous alteration believed to have occurred on their parent bodies. In the soluble fraction of the Murchison meteorite, more than 70 extraterrestrial amino acids have been identified in addition to many other organic compounds, including N-heterocycles, carboxylic acids, sulfonic and phosphonic acids, and aliphatic and aromatic hydrocarbons (Cronin et al. 1993; Sephton 2002; Sephton & Botta 2005; Martins et al. 2007, 2008). The insoluble fraction in meteorite samples is composed of a aromatic macromolecular network (e.g. see Alexander 2005). Prebiotically-significant organic molecules identified in meteorites are likely formed within the solar system in radiation shielded environments and in the presence of liquid water (Martins et al. 2007; Glavin & Dworkin 2009). However, interstellar precursor material may have played an important role in their formation process. Life on Earth is based on amino acids that are left-handed. An L-excess of several meteoritic amino acids has been measured indicating that chirality for some biomolecules may have been predetermined (Glavin & Dworkin 2009). The inorganic matrix of meteorite parent bodies has undoubtedly played an important role in the formation and evolution of solar system
organics (Hazen et al. 2001). The high abundance of aromatic material in meteorites led to the hypothesis of the "aromatic world" that describes PAH-based transitions from non-living to living matter as an interesting alternative to traditional origin of life models (Ehrenfreund et al. 2006).

6.2 Objectives

It is generally agreed that life began relatively rapidly after conditions on the surface of the Earth allowed it, at least 3.5 billion years ago, although the evidence from the geological record is still under debate (Derenne et al. 2008). Because very few data are available regarding the atmospheric, oceanic, or geological conditions on the pre-biological Earth, it is difficult to determine conclusively whether terrestrially synthesized organic material or extraterrestrial molecules were more significant for life’s origin. Likely a combination of both sources led to the first pool of biological precursor molecules (Bada & Lazcano 2002). A fundamental question remains as to how simple molecules of terrestrial or extraterrestrial origin assembled into larger functional units under plausible geochemical conditions and then into replicating structures. The self-assembly of life’s precursor molecules from a pool of solid and volatile structures is a challenge under hostile early Earth conditions. To solve many of the outstanding questions in the origin of life on Earth an interdisciplinary approach to interface state of the art knowledge in astrochemistry, prebiotic chemistry, and artificial life research is required. This section of the Dutch Astrochemistry Network describes 4 proposals that focus on the following key questions:

- What is the inventory of biomolecules in star and planet forming regions?
- What are the formation routes of meteoritic and cometary organics?
- How can precursor molecules delivered via comets and asteroids have assembled to key components for life?
- How is chirality of biomolecules determined in space environment?

The listed team of scientists will investigate the four projects concerning the formation of biomolecules in space, their chirality and assembly capabilities as described:

Dr. Wesley Browne University Groningen, RUG Laboratory studies
Prof. Carsten Dominik Astronomical Institute, UvA Theory, modelling
Prof. Pascale Ehrenfreund Leiden Institute of Chemistry, UL Observations, laboratory studies
Prof. Ben Feringa University Groningen, RUG Laboratory studies
Dr. Dmitry Filippov Leiden Institute of Chemistry, UL Laboratory studies
Dr. Suzy Harutyunyan University Groningen, RUG Laboratory studies
Dr. Alexander Kros Leiden Institute of Chemistry, UL Laboratory studies
Prof. Harold Linnartz Leiden Observatory, UL Laboratory studies
Prof. Gijs vd Marel Leiden Institute of Chemistry, UL Laboratory studies
Prof. Alexander Tielen Leiden Observatory, UL Laboratory studies
Dr. Alexander Vlieg Radboud University Nijmegen, RU Laboratory studies

References


Project 6.1: The building blocks of life in interstellar ice - a combined astrophysical and biochemical laboratory study
H. Linnartz, H. Overkleeft, G. vd Marel

Goal: To investigate the stability of biomolecules in interstellar ice analogs under astronomical conditions and to monitor chemical processes in real time upon VUV irradiation.

Introduction: In recent years it has become clear that icy dust grains around young stellar objects act as catalytic sites for the formation of complex molecules. Chemical processing, through atom and electron bombardment, VUV irradiation, and thermal effects, subsequently results in the formation of species that are considered to be of pre-biotic interest. Experiments simulating inter- and circumstellar ice conditions in the laboratory indeed show that molecules, such as methanol, can be formed upon hydrogenation reactions of CO ice [Fuchs et al. 2009] and that subsequent VUV irradiation – simulating the cosmic radiation field - results in the generation of more complex species such as ethanol, methylformate, acetic acid, glycol aldehyde and ethylene glycol [Öberg et al. 2009a]. These studies are based on a long research tradition in Leiden and follow experiments by Greenberg and coworkers who irradiated astronomical ice equivalents with a VUV broadband light source for many days and identified gas chromatographically amino acids in the resulting organic refractory [Caro et al. 1999]. These experiments have set the tone and recent progress in optical solid state detection techniques now allows to study (also very complex) reaction products in situ and in real time with a unprecedented level of sensitivity.

Description of research project: The project we propose within this astrochemistry call is to use a recently constructed sensitive optical solid state absorption spectrometer [Bouwman et al. 2009, 2010] in the Sackler Laboratory for Astrophysics, to study inter- and circumstellar ice analogues in a top-down rather than bottom-up scenario, i.e. not focussing on the generation of more complex species starting from simple precursors, but to include real biological systems in the ice and to study their photostability. This can be ideally studied with the new experimental setup that is capable of recording optical (i.e. electronic) solid state spectra in situ and with millisecond time resolution and, consequently, to monitor chemical processes in real time upon VUV irradiation. A special discharge lamp is used that peaks at 121.6 nm (Ly alpha) and that simulates the interstellar radiation field. The setup has been used recently very successfully to study the spectroscopic and dynamical properties of highly diluted (1/10000) PAHs (pyrene, anthracene, benzo[ghi]perylene) in water ice. Here it was shown that these PAHs are easily ionized and that ion-mediated chemistry may play a more prominent role than assumed so far in the astrochemical models [Bouwman et al. 2010].

The project will be performed in close collaboration with the bioorganic synthesis group at the Leiden Institute for Chemistry (LIC). Biological systems that will be included in water ice within this proposal are ribonucleotides and their biosynthesis precursors. The purine ribonucleotides adenosine and guanosine are synthesized in nature starting from the common precursors 5-phosphoribosyl-1-pyrophosphate (PRPP) and glutamine, whereas the pyrimidine ribonucleotides cytosine and uridine are derived from orotate. In both series the final nucleobase heterocycles are derived from ribosylated precursors. However, it may well be that in the early stages of evolution the nucleobases adenine, guanine, cytidine and uracil emerged as the first building blocks. In this project we will introduce into our system relevant precursors (for instance, glutamine, glutamate, phosphorylated glycine) en route to the assembly of 5-aminoimidazole ribonucleotide, which is a common intermediate in the biosynthesis of both AMP and GMP. This project will provide information on the stability of ribosylated intermediates. A challenge will be to bring these species in the gas phase (through evaporative heating) and to deposit them into the ice in a controlled way. The setup offers this possibility through etalon monitoring following the ice growth with a HeNe laser.

We further will investigate the behavior of some reagents and intermediates (carbamoyl phosphate, carbonylated phosphate, aspartate) featuring in the biosynthesis of orotate, the
common precursor in the synthesis of UMP and CMP. The expertise in the bioorganic synthesis group on nucleic acid chemistry ensures that those precursors not commercially available will become available within the timeframe of the project. See also [van der Heden et al. 2008, Gold et al. 2008].

The spectra and photochemistry of these building blocks of life will be studied under astronomical conditions, providing both spectroscopic and dynamical information. The most relevant question that will be answered within this project is whether or under which conditions (read ice constituents, ice morphology, temperatures, VUV fluences) such species (or some of such species) may survive the harsh conditions in a solid state astrophysical environment. This is necessary to understand whether biologically relevant molecules indeed formed in the ice (and life was brought to the Earth through meteorites and comets) or whether such species substantially fragment or dissociate upon VUV irradiation. The expertise of the biosyn group is needed to characterize potential reaction channels.

The project serves as a pilot project to derive the feasibility of the proposed solid state study. Therefore only one year of postdoc is requested.

Network collaborations: The SLA has much experience in this research filed of ice analog chemistry and the setup intended for this work is fully operational. Recent collaborations comprise an intense project with NASA AMES. Once successful, the project has the full potential to carry a long term scientific commitment, i.e. a regular PhD project, for the proposed studies (not requested here). The initial focus will be on commercially available species and extended by studies on precursors and intermediates that have to be synthesized. The work is directly related to the solid state part of this proposal (Rudolf, Bickelhaupt, Kroes, Cuppen) and holds the potential to link aromatics and prebiotic species.

Working plan: The working plan comprises one year of active research by a postdoctoral fellow on a fully operational setup. The first focus will be on incorporating biological systems into the ice in a controlled way and obtaining optical absorption spectra, the second stage involves the VUV photoprocessing of the ice. Modelling of the time resolved data (in collaboration with Cuppen) will provide information on the efficiency of eventual destruction channels and consequently stability criteria.

References


Project 6.2: Formation of Protocells formed from PAHs and fatty acids
A. Kros

**Goal:** This project will investigate if (oxidized) polycyclic aromatic hydrocarbons (PAH), or in combination with fatty acids are able to self-assemble in a controllable manner resulting in vesicle-like aggregates mimicking the formation of early cell membranes (protocells). Furthermore, the photochemical-behavior of the PAHs will be investigated.

**Introduction:** It is generally accepted that the early forms of life must have been much simpler compared to life as we know it today, but at least had some functionalities in common (Ehrenfreund et al. 2006). Although minimal life is notoriously difficult to define, a molecular system can be considered alive if it turns resources into building blocks, replicates, and evolves. The hostile environmental conditions on the young Earth, including extreme temperatures and radiation, may have led to protocells self-assembled from components different from those used in modern biochemistry. Primitive life may have consisted of a compartmentalized genetic system coupled with an energy-harvesting mechanism. How these prebiotic building blocks self-assembled and transformed themselves into a minimal living system can be divided into two major questions: (1) How can prebiotic building blocks form vesicular type containers as the minimal requirements for membrane formation are important for evolutionary processes leading to the origin of cellular life on the early Earth (2) How can these components cooperatively organize to form a protocell that satisfies the minimal requirements for a living system?

Bilayer vesicles were observed to form from organics in the Murchison carbonaceous chondrite (Deamer 1985), presumably from carboxylic acid based compounds which are relatively abundant in the meteorite. It seems plausible that early membranes could form from such simple components and provide bilayer barrier functions for the earliest forms of cellular life. Fatty acids and their corresponding alcohols and glycerol monoesters are attractive candidates for the components of protocell membranes because they are simple amphiphiles that form bilayer membrane vesicles that retain encapsulated oligonucleotides and are capable of growth and division (Deamer et al. 2005, Szostak et al. 2001).

Aromatic macromolecules are the dominant organic material in space (Ehrenfreund et al. 2006, Tielens 2008). Aromatic material, in the form of gaseous polycyclic aromatic hydrocarbon as well as solid aromatic structures, comprises most of the carbon in the interstellar medium, comets and meteorites. Aromatic material is extremely stable and quite versatile and PAHs and aromatic macromolecular carbon were among the most abundant materials delivered to the early planets by meteoritic infall (Ehrenfreund et al. 2002). Thus, PAHs are excellent target molecules and assemblies based on aromatic hydrocarbons have been proposed to be the most abundant, flexible, and stable organic materials on the primitive Earth.

**Description of the project:**

1. Protocells composed of PAHs and carboxylic acids

We propose that assemblies based on aromatic hydrocarbons may have been the most abundant flexible and stable organic materials on the primitive Earth and discuss their possible integration into a minimal life form. In this project we attempt to combine current knowledge of the composition of prebiotic organic material of extraterrestrial and terrestrial origin, and put these in the context of possible prebiotic scenarios. We will perform laboratory experiments that might help clarify the transition from nonliving to living matter using the abundantly present aromatic materials. However, due to the extreme hydrophobic nature of PAHs it is impossible to form well-defined aggregates in aqueous environments. But combined with the fatty acids, which were also abundant on the young earth, it should be possible to form protocells. Studying the organization and interaction of PAHs in these mixed membrane systems is important in order to gain knowledge about the stability, dynamics and permeability of these bilayers.

For this study we will use several PAHs differing in their number of aromatic rings (anthracene, pyrene, benzo[a]pyrene, benzo[g,h,i]perylene and coronene, etc) combined with a number of fatty acids and alcohols to study the formation of these protocells. The functional integration of
these components is a difficult puzzle that requires cooperation among all the aspects of protocell assembly, including division and fusion.

The self-assembly behavior in aqueous environments of a library of mixtures (PAH, fatty acid, alcohol) will be studied with a variety of techniques like optical microscopy, electron microscopy, dynamic light scattering, differential scanning calorimetry, UV and fluorescence spectroscopy. DSC will be used to monitor the uptake process of a compound by a model membrane surface that is modulated by the compound lipophilicity and water solubility, as well as by the membrane composition. These studies combined will give information of the physico-chemical properties of these PAH based protocells. The permeability of these vesicles will be studied by encapsulating a dye and studying its release as a function of membrane composition. All these studies should give us a better understanding whether the formation of protocells based on the abundant PAHs is feasible.

2. Self-assembly properties of oxidized PAHs
It has been shown that the photodegradation of polycyclic aromatic hydrocarbon pyrene by iron oxide in solid phase leads to the oxidation of these compounds turning the PAHs in more hydrophilic compounds (Wang et al. 2009, Woo et al. 2009). Therefore, we also would like to study how these oxidized compounds assemble with or without fatty acids and how the photodegradation of the PAHs is influenced when the PAHs are co-assembled into vesicles. Previous studies suggest that the photodegradation of pyrene leads to the formation of an intermediate compound, pyreno, which subsequently leads to the formation of alcohols and quinones, which in turn leads to solubilization of the PAHs. Furthermore, the electron acceptor properties of quinones could lead to the development of a premature form of a light harvesting system.

3. A Miller-Urey type experiment for PAHs
We intend to perform a "Miller-Urey" type experiment to see what products form in the presence of inorganic catalysts (e.g. TiO₂, Fe₂O₃, SiO₂, CaO₂ oxides). Obviously there should be an "oxygen source" present, either pure oxygen or otherwise CO, CO₂. Metal oxides will also be tested as oxygen source. It would be fantastic if we would prove in this way a possible route to a) controlled self-assembly of PAHs in aqueous media and b) a premature form of a light harvesting system (e.g. quinone formation, which is known to reversibly accept-donate electrons). The product formation/degradation of the PAHs will be analyzed using mass-spectroscopy (GC-MS and LD-MS), FT-IR, UV- and fluorescence spectroscopy. In summary, the original Miller-urey experiment has shown that conditions simulating the early life could give rise to the synthesis of amino acids. The proposed experiment will provide insights into whether these conditions also could give rise to the formation of vesicles (i.e. primitive cell structure) based on the abundant polycyclic aromatics with or without the presence of fatty acids.

Workplan:
- Vesicle formation using PAHs and fatty acids and characterization
- Vesicle formation using oxidized PAHs
- Miller –Urey type experiment for vesicle formation

Network collaborations: This project will be a collaboration of the LIC and the Leiden Observatory in order to link the laboratory to the context of astronomical observations of PAHs. All required equipment is available either within the LIC or at the LUMC. Furthermore, we will collaborate with the Meijer/Palmans group (TUE) who already has a Miller-Urey set-up available. Initially we will use relatively small PAHs like pyrene, coronene, and ovalene in these studies. Co-I’s: Prof. A. Tielens, P. Ehrenfreund, Dr. Karen Sliedregt.

References
**Project 6.3: Amino-acid Formation Controlled by Chiral Template**

E. Vlieg

**Goal:** To find a possible route towards formation of chirally-enriched amino-acids and eventually small peptides under space conditions (ice, water, PAHs, inorganic matrices, micropores).

**Introduction:** As comets and meteorites delivered large quantities of carbon rich materials to the young Earth (approx. 4 billion years ago) significant amounts of chiral materials might have their origin in extraterrestrial sources. Most probably also small oligomers and other condensation products have been formed and delivered by meteorites. Although Earth-bound synthesis in Miller-Urey, Fischer-Tropsch or ion-molecule reaction settings remain important pathways to prebiotic molecules, the fact that the Murchison meteorite contains a large number of amino acids suggests indeed the alternative possibility that seeding from space could have been a factor in the rise of life on Earth.\(^1\) While 20 proteinogenic (\(\alpha\)-H) amino acids are the most common amino acids on Earth, over 80 different amino acids have been identified in the parent bodies of carbonaceous meteorites Murchison and Murray including the abundant \(\alpha\),\(\alpha\)-dialkylated amino acids Aib and Iva which are extremely rare on Earth. In contrast to the metabolic origin of the terrestrial amino acids, the complex mixture of extraterrestrial amino acids was suggested to have been the result of a Strecker-cyanohydrin and Mannich syntheses from precursors (aldehydes, ketones, HCN, NH\(_3\) and H\(_2\)O) which were present (or formed) in the protosolar nebula, and later incorporated into the asteroidal parent body. Aqueous alteration processes led to the formation of amino acids on the parent body. Oxygen isotopic ratios indicate that aqueous alteration occurred over a range of temperatures from \(\sim 20^\circ\)C on the Murchison parent body to \(\sim 140^\circ\)C on that of the Orgueil meteorite thus at the same conditions wherein the Strecker amino acid synthesis could have taken place. Experimental support for this hypothesis was supplied by the detection of synthetic intermediates like hydroxyl- and imino acids.

Interestingly, in Murchison a large L-enantiomeric excess (ee) on Iva was found, while the proteinogenic amino acids are racemic (D,L).\(^2\) This observation is easily understood by the fact that in contrast to proteinogenic amino acids, \(\alpha\),\(\alpha\)-dialkylated amino acids are resistant to racemization even at the harsh space conditions. In spite of many studies, nothing is known yet about the origin of the ee of amino acids in carbonaceous chondrite meteorites. Enantioselective photolytic destruction by circularly polarized light (CPL) seems unlikely due to the fact that the amino acids were found within the interior of the meteorite parent body, thus shielded from CPL. Since Pizzarella\(^3\) found a possible correlation between the magnitude of the ee of L-Iva in Murchison and the relative abundance of hydrous silicate minerals, the question arises about the possibility of an enantioselective Strecker synthesis of the \(\alpha\)-amino nitrile that is catalyzed by reaction on a chiral inorganic surface. On the other hand it seems unlikely to achieve enantiopure products in this manner unless coupled to a strong ee amplification.

**Description of the research project:** Although the Strecker reaction (see Scheme) of amino acids is already known for a long time little is known about the reaction mechanism in relation to the reaction condition. Earlier, we have found this reaction to be strongly dependent on the environment due to unstable reaction intermediates.\(^4\) High yields of \(\alpha\),\(\alpha\)-dialkylated amino acids were only obtained by using immiscible hydrophobic/hydrophilic solvent systems. While the addition reaction of the cyanide to the enamine takes place at the water phase, unstable intermediate products are preserved in hydrophobic solvent. Isotope tracing experiments showed that, although at a low yield, the amino acid can even be formed in the absence of NH\(_3\), indicating that under certain conditions the nitrogen of HCN might be the single donor for both the nitrile and amine groups of the amino nitrile. In this proposal we will address the following questions:

1. *What is the formation route of \(\alpha\)-amino acids in relation to meteoric environments?*
2. *How is the chirality of amino nitriles, amino acids as well as their polymers (homochiral peptides) determined in the solar nebula environment?*
3. *What are the chiral amplification methods which are most likely to occur under these conditions?*
To answer these questions the Strecker reaction will be systematically studied under conditions restricted to those which are presently known to occur in space environments (water filled micropores of phyllosilicates, PAHs and other surface adsorbed organic material) under different conditions (phase, environment, pH, temperature, pressure and molar ratios of starting materials). The relevance of the laboratory synthesis to those in solar nebula environment will be evaluated by measuring the isotope effect of this reaction to explain the C\textsubscript{13}/C\textsubscript{12} ratios which were previously observed in samples of extraterrestrial origin. To allow extrapolation of the obtained experimental data to the more extreme space conditions the thermodynamics, kinetics will be studied.

In achiral environments, a chemical synthesis will yield only a racemic mixture of enantiomers. Very small ee values have been reported for proteinogenic amino acids by enantioselective adsorption on chiral surfaces of \textit{d}-, and \textit{l}- inorganic materials (quartz, calcite)\textsuperscript{5}, but information about asymmetric synthesis of amino nitriles is still lacking. Recently, two effective but different chiral amplification methods have been reported by the Nijmegen and Groningen groups. Autocatalysis might be another mechanism by enantiomeric reproduction. Whether these methods can be applied to chiral amplification of \textit{\alpha,\alpha}-dialkylated as well as proteinogenic amino acids is an important subject of investigation in the context of the current astrochemistry program.

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Proposed asymmetric Strecker reaction showing the prochiral enamine adsorbed at the chiral inorganic surface and the asymmetric attack of the cyanide from one side yielding a chiral amino nitrite. In the next steps the amino nitrite is hydrolyzed to amino acid (Iva: \( R_1 = \text{CH}_3\text{CH}_2, \ R_2 = \text{CH}_3 \) as well as \( \alpha-\text{H} \) amino acids, \( R_2 = \text{H} \)) followed by amplification of the ee of the final product (amino acid, homochiral peptide).

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Chiral amplification through crystal formation and grinding, and controlled using circularly polarized light. From ref. [9].
The presence of chiral surfaces in a meteorite leads to symmetry breaking and can thus produce an ee with a handedness that is dictated by the surface chirality. The ee can occur because the surface acts as a heterogeneous catalyst. Alternatively, the chiral surface acts as a storage of oriented molecules (in the form of 2D or 3D crystals) that subsequently react in a chirality-preserving fashion. We will test this on chiral inorganic surfaces like quartz, calcite and mesoporous silica. Similar chiral surfaces are found in meteorites.

The enantiomeric excess, however, resulting from the proposed mechanism will be too small to explain the experimentally observed values and thus an amplification mechanism is required. Possibilities are dissolution and sublimation\textsuperscript{7}, but a more effective mechanism could involve the formation of crystals in separated left- and right handed forms (a so-called racemic conglomerate). We recently found that under the right conditions, 100% ee can be achieved and that very mild chiral symmetry breaking, including CPL, can completely determine the final state handedness, see figure\textsuperscript{8,9}. In the proposed research a similar approach will be followed, but using instead the concept of asymmetric catalysis of Strecker and oxazolone syntheses of chirally pure amino acids and dipeptides (Scheme).

**Working plan (1 PhD student):**

**Year 1:** Investigation of the Strecker synthesis under different conditions.

**Year 2:** Study of thermodynamics, kinetics and isotope effects of the reactions.

**Year 3:** Asymmetric syntheses using chiral inorganic surfaces like d, or l-chiral surfaces of quartz, calcite or chiral mesoporous silica (prepared by polymerization of SiO\textsubscript{2} using chiral templates).

**Year 4:** Chiral amplification (enantioselective crystallization combined with racemization of the in the solution remaining enantiomer), writing and defend of the thesis.

**Network of participating groups and their roles into the project:**

- Radboud University Nijmegen: Prof. dr. Elias Vlieg, **prime applicant**, solid state chemistry: chiral interactions and chiral amplification. Prof. dr. Floris Rutjes, asymmetry catalysis and environmental conditions. Prof. dr. Carsten Dominik (also staff member of UvA), **astrophysicist**: expertise solar nebula conditions.
- Leiden University: Dr. Jan Raap, organic chemist; **advisor**, amino acid synthesis, isotope tracing, isotope effects. Prof. dr. Pascale Ehrenfreund, astrochemist: **coordinator**, network.

References

**Project 6.4: Formation of Chiral Meteoritic Prebiotic Molecules**
B. Feringa

**Goal:** The goal of this project is to achieve chiral amplification under astrophysically relevant conditions and to transfer chiral information via (auto-)catalytic and replication schemes as well as in confined (gel) environments. The key questions to be answered are: can sublimation be used to generate a strong homochiral bias? How can this be coupled to condensation/oligomerization to generate chiral gels and templates for autocatalysis/replication? What is the role of mineral/ice chemistry to accelerate these transformations and to achieve selectivity/chiral selection? Can the amino acids operate as chiral organocatalysts to form optically active sugars via asymmetric condensation of aldehydes?

**Description of research project:**
Homochirality of its essential molecules is considered a ‘signature of life on Earth’ and arguably a marker of possible extraterrestrial life. The origin of the homochirality found throughout nature is one of the great unsolved scientific mysteries. Equally challenging is the amplification of a small chiral bias and the expression of chirality in primitive replicators and ‘information rich’ (macro-)molecule that might be relevant for chemiobiogenesis. As part of the ongoing research program of the Groningen group on fundamental aspects of chirality like chemiobiogenesis autocatalysis have been studied1-5. In particular an astrophysically relevant mechanism of chiral amplification of amino acids was discovered (Figure)6. Furthermore it was shown that simple low-molecular weight gelator molecules provide a fascinating way to achieve confined (chiral) materials in a fully reversible manner and exceptionally strong chiral amplification5,7. Due to the simple nature of the building blocks and the conditions for these phenomena to operate they seem highly relevant in extraterrestrial environments and in prebiotic chemistry.

**Origin of Chirality and Chiral amplification**
Based on our recent preliminary results on the amplification of chirality of amino acids through simple sublimation the sequential sublimation of tiny enriched samples of mono- and dialkylated amino acids will be studied. The extent of amplification under a variety of environmental conditions will be examined. Small enriched samples will be used generated by performing an asymmetric Strecker reaction and related (Mannich) condensations of aldehydes. An exciting alternative approach comprises prochiral molecules adsorbed to surfaces employing a combination of a magnetic and electric field (or a magnetic surface in combination with an electric field)8,9. Barron has analyzed the possibility of reaching an enantiomeric excess in a magnetic field as long as no-thermodynamic equilibrium is established or when molecules are partially aligned on a surface, interface or in a crystal. Rikken and Raupach demonstrated chiral enrichment in photochemistry in the presence of a magnetic field11. To reach absolute asymmetric synthesis under astrophysically and possible prebiotic conditions remains a major challenge4,10. Particularly challenging is the condensation-oligomerization of the sublimed and enriched amino acids on mineral surfaces and possibly ice to generate homochiral diketopiperazines and small oligopeptides. The latter ones are templates for replication and act as gelators12 while the diketopiperazines are both catalysts for e.g. the Strecker synthesis as well as excellent gelator molecules to generate a confined chiral space.

**Transfer of Chirality**
The dimer formation is a simple condensation with extrusion of water and provides a rather rigid template molecule with the propensity to form multiple hydrogen bonds and a scaffold for the binding of simple substrate molecules as well as orientation of functional groups. The first property is key to formation of higher aggregates e.g. gels, and fibers13. Simple linear and in particular cyclic amino acid dimers (like diketopiperazines) have the propensity to form gels. This means larger aggregates are formed at low concentration of the amino acid dimer in a
highly reversible manner. The gel fibers provide a confined space, can encapsulate other organic compounds, act as templates for inorganic crystal growth or silica formation and show strong non-linear (amplification) effects in molecular recognition\textsuperscript{12}. Chiral low-molecular weight based microgels are particularly fascinating as they provide confined space (without the requirement of e.g. a primitive cell membrane), opportunities for strong amplification and excellent chiral recognition, are fully reversible but can frequently stand a range of conditions and can readily be formed also in an inorganic matrix.

Asymmetric catalysis and template directed selection
The second property of the amino acid dimerization products e.g. the diketopiperazines, allows these molecules to act as an enantioselective organocatalysts as it is chiral, induces binding of reactants and orients groups for cooperative function. Diketopiperazines, formed by amino acid dimerization, have already been shown to act as chiral catalysts in the addition of HCN to aldehydes providing (after hydrolysis) a hydroxyl acid or amino acid\textsuperscript{14}. This scheme will be investigated in detail as it provides a direct simple condensation route from enriched amino acids via dimers (diketopiperazines) to more advanced chiral (prebiotic) products like amino acids (Strecker) hydroxyl acids (HCN addition to aldehyde) and sugars (aldol condensation of aldehydes).

The second important question is: how is the chiral information transferred from amino acids to other prebiotic molecules? In other words can the amino acids, in particular dialkylated amino acids, act as organocatalyst for the asymmetric condensation of aldehydes to sugars (formaldehyde, hydroxycetaldehyde condensations). Examples of asymmetric synthesis of D-sugars by catalyzed by L-amino acids have been reported\textsuperscript{15}. This requires the study of a range of condensations in which small amounts of enriched amino acids are used to catalyze the aldol type condensations. An alternative chirality and information transfer mechanism is via small oligomers. Also the role of carbon disulfide in the oligomerization process and particular chiral selection might be examined (c.f. recent work by Orgel and Ghadiri). The formation of small homochiral oligomers, their use as templates for amplification of chirality and in particular chiral crystal surface growth is an intriguing aspect in the context ‘origin and amplification of chirality’ in view of recent work by Lahav and coworkers at the Weizmann Institute. Special attention will be given to the role of water and ice in the approaches outlined here.

Recently it has been found by the Sharpless group\textsuperscript{16} that on water reactions result in dramatic accelerations and it is intriguing to study the role of on water and on and in ice matrices in the condensation-amplification mechanism discussed here. It is particular fascinating to examine if stereoselective condensations (like Strecker synthesis but also dimerization) and amino acid based asymmetric organocatalysis will be accelerated on ice or when encapsulated in ice matrices.

The scheme proposed is initially based on amino acids but can be extended to other relevant molecules. The entire system from the generation of a small chiral bias, chiral enrichment via sublimation, dimerization (diketopiperazines) to form gels and organo catalysis (by amino acids and diketopiperazines) for subsequent chiral amplification and autocatalysis and finally the formation of small information rich oligo’s is integrated in this proposal.

Working plan (1 PhD student):
Year 1: Exploration of the sublimation mechanism for chiral amplification with alpha and dialkylated amino acids. Preliminary studies of condensation reactions under magnetic/electric fields of surface adsorbed prochiral molecules
Year 2: Asymmetric catalysis with enriched amino acids of particular aldol reactions to transfer chirality to other prebiotic molecules. Sublimation coupled to small oligopeptide formation. Condensations on/in ice.
Year 3: Diketopiperazine studies and chiral gelation asymmetric autocatalysis toward amino acids (Strecker); templating studies with small chiral oligo’s.
Year 4: Extension of transfer of chirality to other prebiotic molecules (hydration, Mannich), completion of thesis.
Network of participating groups and their roles into the project:
University of Groningen: Prof. dr. Ben Feringa, prime applicant, chirality and asymmetric synthesis: chiral sublimation, gelation studies, chirality transfer, in/on ice chemistry. Dr. S. Harutyunyan, autocatalysis and chiral amplification. Dr. W.R. Browne, chiral spectroscopy, asymmetric induction in electric/magnetic fields. On the aspects of self-assembly (capsule formation) and on-ice chemistry we will collaborate with the groups of Kros (University Leiden) and Linnartz (UL) as well as Ehrenfreund (astrochemistry expertise, coordinator) in the context of the subprogram Prebiotic Universe. Raap will be involved as an advisor with expertise in amino acid synthesis and close cooperation is foreseen with Vlieg (University Nijmegen) on chiral amino acid formation and amplification. The complementary expertise in the Vlieg (RUN) (solid state chemistry, chiral crystallization) and Feringa (asymmetric synthesis, supramolecular chemistry) (RUG) groups will be highly beneficial to these projects. For the surface assembly aspects we will take advantage of our intense and ongoing cooperation with the Rudolf group (surface physics,RUG).

References
1. P. Bos, J. Teichert, B.L. Feringa, European Chembiogenesis program & Cost cm0703, Systems Chemistry.
## 6.4 Overview of the projects

The Table below summarizes the projects including requested positions.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Short name</th>
<th>PI(s)</th>
<th>Requested</th>
<th>Background</th>
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<td>Linnartz (UL)</td>
<td>1 y PD</td>
<td>Laboratory</td>
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<tr>
<td>6.2</td>
<td>Formation of Protocells formed from PAHs and fatty acids</td>
<td>Kros (UL)</td>
<td>1 PhD student</td>
<td>Laboratory</td>
</tr>
<tr>
<td>6.3</td>
<td>Amino-acid Formation Controlled by Chiral Templates</td>
<td>Vlieg (RU)</td>
<td>1 PhD student</td>
<td>Laboratory</td>
</tr>
<tr>
<td>6.4</td>
<td>Formation of Chiral Meteoritic Prebiotic Molecules</td>
<td>Feringa (RUG)</td>
<td>1 PhD student</td>
<td>Laboratory</td>
</tr>
</tbody>
</table>
7. The Dutch Astrochemistry Network

The field of molecular astrophysics is a highly interdisciplinary field where molecular physics, laboratory spectroscopy, surface science, theoretical chemistry, astrochemistry, astronomical observations, and astronomical modeling intersect. Each of these science areas is characterized by the use of different techniques and methods and no single individual scientist or even single institute covers all these areas to the depth required. Section 8 summarizes relevant expertise of key staff at the different institutes in molecular astrophysics in the Netherlands. In the past, collaborations involving members of these teams have successfully addressed key questions within molecular astrophysics. However, the next step will have to come from a wide ranging, coherent, and integrated program on the basic physical and chemical processes driving astrochemistry. This program will have to bring together experts and institutes from all of these scientific disciplines. In that way, Dutch science can be expected to reap the full benefit of the new developments in the field of chemical physics and molecular physics and prepare adequately for the exciting, new, observational opportunities on the horizon. Because relevant expertise is spread over so many different institutes, coordination is best done at the national level through an integrated Dutch Astrochemistry Network. Indeed, the objectives and work program (sections 3-6) that form the core of the scientific goals of the network fully demonstrate the inherent interwoven nature of this field of research. In this way, the very distinguished Dutch record in the area of molecular astrophysics – evident, for example, at international conferences – can be extended into the next decade.

7.1 Appointments

The research in the network has been divided into four global science themes. Each of these topics will be covered “end-to-end”; e.g., will cover the topic from astronomical data and modeling to molecular experiment, modeling and data. Hence, for successful completion, each of these themes requires contribution from the physics, chemistry, and astronomy groups in this network. These contributions have been split out as specific projects and the main team and leader responsible for that project have been identified. However, in general, all teams contribute their specific expertise and experience to a science theme and these teams will have to collaborate for a successful completion of the objectives of their theme.

Work on specific projects will be supported through the appointment of PhD students and/or postdocs. We envision that the research by these PhD students and postdocs will be highly interdisciplinary. Specifically, we expect that each PhD student in chemistry will be involved in the astronomical side as well and will have at least one “astronomical” chapter in his/her thesis and vice versa. Publications will be in leading astronomical and chemical physics/spectroscopy journals. The appointments will be made at the home institute of the project leader and this project leader will be responsible for the supervision of the work by the appointed fellow. The local institute where the fellow is appointed will manage the financial aspects of each appointment and this appointment will be funded directly by NWO at the local institute.

7.2 Network organization

Each science theme has a Coordinator who will be responsible for coordinating the activities in this area. Interaction and coordination between the different science themes will be the responsibility of the network Chair. The network Chair is responsible for the overall scientific progress of the network and provides the point of contact to the larger scientific community as well as NWO. The network Chair will be supported by a Program Secretary, appointed by NWO. The Program Secretary will be responsible for the programmatic aspects of the network. The four science theme Coordinators together with the network Chair and the Program Secretary form the executive committee of the network. The executive committee will be responsible for allocating the funding that is kept at the network level.
An international board of outside experts in the field of molecular astrophysics will review the overall functioning of the network and progress towards the goals and objectives of the network every two years. The advice from the board will be made available to NWO. At the end of the contract, the board will review the accomplishments of the network and advise NWO on continuation.

The network may coordinate and integrate its activities with international groups active in molecular astrophysics. This may include exchange of team members and/or students and postdocs. It may also involve organization of joint meetings. The network Chair will be responsible for the coordination of these international activities. Funding will be set aside at the network level to support these activities.

The science theme Coordinators and the network Chair will be selected from the network members at the network kick-off meeting. The appointment of the network Chair will have to be confirmed by NWO.

7.3 Network activities

The science of this network is highly interdisciplinary between the fields of physics, astronomy, and chemistry. The key to success for this network will therefore reside in a high degree of collaboration between the individual teams at the working level to ensure cross-fertilization between the disciplines. Indeed, the strength of the network will reside in the way it will be able to create informal and formal interactions and exchange of information and ideas between the different science disciplines involved in astrochemistry. Communication within the network will be facilitated through a Twiki page for informal discussions as well as a “living space” for working documents. In this environment, all members of the network will be able to deposit and modify documents. The website will provide access to progress reports, intermediate results, and the final results of the research involving this network. The network will also maintain a website open to the community in which they will report their progress and that will also serve as outreach to the general public.

Each of the science themes will organize team meetings, at least once a year. These meetings will serve to report progress on the individual projects, discuss any challenges, and exchange information on new results. These meetings represent one major way to cross fertilize between the projects in a theme. In order to further promote the exchange of information at the project level, over the four years of their graduate studies, PhD students are expected to be involved in research aspects associated with more than one discipline. Specifically, astronomy students are expected to be involved in a more chemically research project while chemistry students are expected to be involved in a more astronomically oriented research project. Besides furthering the exchange of information at the working level between the groups involved, this will also provide unique training for the students involved and position them well for a research career in astrochemistry. At the network level, cross-fertilization will be centered around workshops that will be organized annually. At these workshops, the overall progress of the network will be reviewed. In addition, this annual meeting will be used to bring in external experts to brief the teams on new developments in the science disciplines involved in astrochemistry, including discussions on promising new experimental or theoretical techniques or new observational opportunities.

At the end of the contract, the NWO and the network will organize an international conference to present the results to the larger community. Funding will be set aside by NWO outside this program to support attendance of foreign experts at these meetings. The network will organize a summer school each year – taught by team members and outside experts – to train the appointed PhD students and postdocs in all of the techniques and methods relevant to molecular astrophysics.

The network will actively promote participation of international visitors in its research projects through small travel grants. The network will also fund working visits of its members to
institutes abroad in support of the network goals and of key importance for one of the research projects. Funding will be kept at the network for these purposes. Visitor grants will also be available through the regular NWO Visitor Travel Grant program. Requests for visitor and travel grants will have to be recommended by the Executive Committee and approved by the Chair and the Program Secretary. However, travel funds will be specifically allocated to the appointed PhD students and postdoc as part of their appointment fees and these are kept at the institutes where they are appointed.

7.4 Budget

The total budget for the network is 2.8 million euros over 5 years. An indicative budget for the network is summarized in Table 7.1. The grant is envisioned to support 13 PhD students for four years. These costs include their salary, benefits, as well as an individual travel allowance and bench fee for each student. Instead of PhD students, postdocs can be employed, where it should be kept in mind that a 3-yr postdoc is equivalent to a 4-yr PhD student. The other budget costs are included to support the networking actions (see section 7.3). Funding for appointments is directly provided by NWO to the appointing institute and will be managed at the institute level. The other funds are kept at the network level. Reallocation of funding between the other budget items has to be recommended by the executive committee and approved by the Chair and the Program Secretary.

Table 7.1. Indicative budget in M€

<table>
<thead>
<tr>
<th>Yearly</th>
<th>Total</th>
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<tr>
<td>Appointment of PhD students or postdocs(^a)</td>
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<tr>
<td>Visitor grants, travel grants for network members</td>
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\(^a\)includes bench fee and travel for the appointed fellows.
8. Expertise of the network

Table 8.1 summarizes the expertise of the teams in the different disciplines that span up the network. We also attached short CVs of key personnel.

<table>
<thead>
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<th>Key staff</th>
<th>Molecular Physics</th>
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<th>Surface science</th>
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8.1 Short CV of key personnel (Alphabetically)

**Prof. dr. A.G.G.M. Tielens** leads a group at Leiden Observatory on the origin, evolution, and role of large PAH molecules in the Universe. He was among the first to recognize the importance of such large molecules in space. He has also made important contributions to the study of interstellar ices, interstellar grain surface chemistry, processing of interstellar dust, and the physics and chemistry of gas in photodissociation regions. Over the past 10 years, prof. Tielens has supervised 17 PhD theses. He is the Project Scientist of HIFI, the heterodyne instrument on board of the Herschel Space Observatory (1997-present) and was NASA Project Scientist of the Stratospheric Observatory for Infrared Astronomy (SOFIA) (2005-2007), and Coordinator of “The Molecular Universe”, a Marie Curie Research and Training Network funded under the European Commision Framework Program #6 (2004-2008). Prof Tielens has authored or co-authored 319 refereed papers with 19,500 citations; (ADS), 15 papers with more than 200 citations; 55 papers with more than 100 citations; H-index 77; author of the text book “Physics and Chemistry of the Interstellar Medium (University of Cambridge Press); editor of 4 conference proceedings; 13 invited reviews over the last 5 years.


**Prof. dr. ir. A. van der Avoird** obtained his Ir. and Ph.D. degrees from the Technical University Eindhoven, in 1964 and 1968. He worked at the Battelle Institute in Geneva (1964{1967) and the Unilever Research Laboratory in Vlaardingen (1967{1971). In 1968 he became part-time professor of Theoretical Chemistry at the University of Nijmegen, in 1971 full professor, and in 2008 emeritus. He held visiting professorships at Yeshiva University, New York (1970), at the University of California in Berkeley (1992), and at the University of Bielefeld (1996). In 2007 he received an Alexander von Humboldt Research Award. He is a member of the Netherlands Royal Academy of Arts and Sciences and of the International Academy of Quantum Molecular Sciences. About 30 Ph.D. degrees were obtained under his supervision and he (co-)authored about 250 scientific publications.


**Prof. dr. F. M. Bickelhaupt** has a chair and leads a group in applied theoretical chemistry in the department of theoretical chemistry at VU University Amsterdam of which he will be the head starting early 2010. He is interested in developing chemical theories and methods for rationally designing molecules, nano-structures and materials as well as chemical processes toward these compounds, based on quantum mechanics and advanced computer simulations. The project comprises four main directions of research that are intimately connected and reinforce each other: (1) Structure and Chemical Bonding in Kohn-Sham Density Functional Theory (DFT), (2) Molecular Recognition and Theoretical Biochemistry, (3) Elementary Chemical
Reactions (including environment effects, e.g., solvation) and (4) Fragment-oriented Design of (Bio-)Catalysts. For astrochemistry, the expertise in areas 1 and 3 (comprising structure, bonding and reactivity) is of particular relevance. Over the past 10 years, prof. Bickelhaupt has supervised 8 PhD theses. He is winner, among others, of the VICI award 2002, chairman of the board of the Holland Research School of Molecular Chemistry (HRSMC) and secretary of the board of the division Spectroscopy and Theory of NWO/CW. Prof Bickelhaupt has authored or co-authored 150 refereed papers with 4080 citations; H-index 33.


Prof. Dr. W.J. Buma holds the chair of Molecular Spectroscopy at the University of Amsterdam. The Molecular Photonics group aims to advance the fundamental knowledge of the dynamics of excited states in molecules and nano-sized objects, and to contribute with its expertise to applications of the photosciences. Over the past years we have made a substantial contribution to the field of high-resolution spectroscopy of large, complex molecular systems. Prof. Buma has (co)supervised 9 PhD theses. He has been Coordinator of EC-funded Networks (Training and Mobility of Researchers (TMR), Marie Curie Training Site (2001-2004), and Specific Targeted Research or Innovation Project). He has authored 99 refereed papers with 1,329 citations; H-index 22. He was member of the SynNanoMotors team that was awarded the 2008 EU Descartes Prize for Transnational Research.


Dr. E. Costantini is a research scientist at the Dutch Space Agency, SRON. One of her fields of expertise is the observation and modeling of scattering and absorption of interstellar dust in the X-ray band.


Prof. Dr. E.F. van Dishoeck is professor of molecular astrophysics at Leiden Observatory and leads a group on the physics and chemistry of interstellar molecules particularly in regions of...
star and planet formation. She has also made important contributions to our understanding of the basic molecular processes that play a role in the origin and evolution of molecules in space. She is the scientific director of the Netherlands Research School for Astronomy, NOVA, a member of the ALMA board and chair of the ALMA Science Advisory Committee, and a co-PI of the European JWST-MIRI consortium. She is also president of the IAU working group on Astrochemistry, responsible for organizing the major world-wide conference in the field, and vice-president of IAU Commission 14 on Atomic and Molecular Data. She has supervised 28 PhD theses and authored or coauthored some 300 refereed papers with ~13700 citations (ADS) and an h-index of 61.


Prof. dr. C. Dominik studies the formation of stars and the structure and evolution of protoplanetary disks, with particular focus on the growth and processing of dust. He has been involved in theoretical studies and modeling of H3+ in protoplanetary disks, and in studying and explaining the microphysics of dust aggregation. Carsten Dominik has co-supervised about 15 PhD students and published 86 papers in refereed journals. He is involved in two HERSCHEL key programs, studying star formation regions.


Prof. dr. P. Ehrenfreund is lead investigator of the NASA Astrobiology Institute (Node Wisconsin) and led the Astrobiology Laboratory at Leiden Institute of Chemistry since 2001, funded by NWO. She has made important contributions to interstellar chemistry (galactic and extragalactic), organic molecules in interstellar space, planetary surfaces, comets and meteorites as well as life detection on Mars and the origin of life. She is the Project scientist of NASA’s O/OREOs satellite the first missions of the NASA Astrobiology Small Payload program and the Vice President of the European Astrobiology Network Association EANA. She has managed space projects as Principal Investigator in Low Earth Orbit and on the International Space Station ISS (Biopan, O/OREOS, Organics/EXPOSE/ISS), Deputy Principal Investigator (Urey-Exomars), Teamleader (Miller/ISS), and contributes as Co-Investigator (Cassini-Hygens, Rosetta, SMART-1, Exomars) to space missions. She developed a full program for space laboratory simulations in the framework of leading the Mars Express Recognized Laboratory Mex-RCL for Geochemistry & Exobiology. Prof Ehrenfreund has authored or co-authored more than 300 publications (150 refereed papers) and edited 11 books.

Prof. Dr. B.L. Feringa is Jacobus van 't Hoff Distinguished Professor of Molecular Sciences at the University of Groningen and holds a KNAW chair. He is director of the Stratingh Institute for Chemistry and the Centre for Systems Chemistry. The group studies fundamental aspects of chirality and the research program includes asymmetric catalysis, replication, synthesis, supramolecular chirality, molecular motors and switches and self-assembly. He is recipient of the Spinoza award, the ACS Norrish award for physical organic chemistry and the Paracelsus award for life time achievement in chemistry. His work in stereochemistry was recently recognized with the international Chirality medal. He is author of more than 500 publications, supervised 68 PhD thesis and has an h-index of 66.

Dr. ir. G.C. Groenenboom is associate professor and interim group leader of the Theoretical Chemistry group in Nijmegen. He worked on ab initio electronic structure calculations of weakly interacting complexes, radicals, and electronically excited states and he performed quantum dynamical studies of bound states, inelastic- and reactive scattering and of photodissociation. His recent work in the field of cold and ultracold molecules has astrophysical applications. Groenenboom was a fellow of the Royal Dutch Academy of Science, received two NWO-CW Young Chemist and an NWO-CW ECHO grant. He has (co)supervised 7 PhD thesis and (co)authored 87 refereed publications and 6 book chapters and his current H-index is 21. He was the director of the Han-sur-Lesse winter-school on "Theory and Spectroscopy" for 10 years.

Dr. I. Kamp leads a group at the Kapteyn Astronomical Institute on the evolution of protoplanetary disks to planetary systems. She developed chemo-physical models of protoplanetary disks which enable a study of the complex interplay between gas chemistry,
heating/cooling and dust physics in the surfaces of protoplanetary disks and their implication for observable diagnostics such as SEDs, gas line emission and imaging. Her expertise ranges from stellar atmospheres to gas-phase chemical networks and radiative transfer. She is currently supervising two PhD theses and has supervised in the past three master theses. Dr. Kamp is co-PI of the Herschel Open Time Key Program GASPS (Gas Evolution in Protoplanetary Systems, PI Bill Dent). She organized, co-organized and participated in public outreach activities such as astronomy masterclasses, IR-workshops, Akademisch Jaarpreis 2008. She authored or co-authored 40 refereed papers with 671 citations (ADS), 3 of them with more than 60 citations; H-index 16; 5 invited review talks.


Prof. dr. L. Kaper leads a research group at the Astronomical Institute Anton Pannekoek at the University of Amsterdam. His main research interest is the formation, evolution and fate of massive stars, with emphasis on observational astronomy. In his PhD thesis (1993, University of Amsterdam, cum laude) he demonstrated that the cyclical variability in the stellar winds of the most massive stars is likely due to the presence of surface magnetic fields; these have recently been detected with spectropolarimetric measurements. He has studied massive stars and their compact remnants (neutron stars and black holes) in high-mass X-ray binaries and determined the mass of the most massive neutron star, thereby constraining the equation of state of matter at supra-nuclear densities. He was involved in the discovery of a supernova signature in the afterglow spectrum of GRB030329 establishing the link between gamma-ray bursts and the violent death of massive stars. He contributed to the observational study of diffuse interstellar bands in the Milky Way and beyond. He is the NL-PI of X-Shooter, a very efficient, wide-band spectrograph, installed on the ESO Very Large Telescope in 2009, and co-PI of the phase A study of OPTIMOS-EVE, a multi-object spectrograph for the European Extremely Large Telescope. He has supervised 6 PhD students and 11 master students. He is author or co-author of 217 scientific publications (3506 citations), of which 90 in refereed journals and co-author of 5 books (conference proceedings).


Prof. dr. W. Kegel holds a chair in ‘self-organizing systems’ at the Van ‘t Hoff Laboratory for Physical and Colloid Chemistry at Utrecht University, since June 2006. The van’t Hoff Laboratory is part of the Debye Institute for Nanomaterials Science, where groups from the chemistry and physics departments work together. Kegel has been a fellow with the Dutch Academy of Science (KNAW fellow) and in 2005 received a NWO -VICI grant. Over the last decade, Kegel published 2 papers in Science, 9 in Phys. Rev. Lett., 1 in PNAS, 1 in Angew. Chem. and 1 in JACS. In total he published 71 papers that have been cited 1410 times. His h-index is 22. Kegel is interested in novel finite-size objects that are thermodynamically stable or metastable. Current research topics in his group are (1) inorganic macromolecules (polyoxometalates) that reversibly form large (order tens to hundreds of nanometers) shells; (2) formation of colloidal molecules, i.e., well-defined clusters formed by colloids with liquid protrusions; (3) thermodynamically stable
emulsion drops covered by a monolayer of nanoparticles; (4) clusters of macromolecules or colloids, stabilized by long-ranged electrostatic repulsion and short-ranged attraction (5) virus capsids. Topics 1 – 4 are investigated by means of experiments and theory. Topic (5), up to now, by theory only, in collaboration with Paul van der Schoot.


Dr. A. Kros at Leiden University. After obtaining his PhD degree with Prof. Roeland Nolte at Radboud University, Nijmegen, he moved to the California Institute of Technology for a postdoctoral stay in the group of Prof. Dave Tirrell studying the self-assembly of conducting polymers at the surface of giant vesicles and fibers. Dr. Kros is an associate professor and heads the experimental section of the Soft Matter Research group consisting of 3 postdocs, 8 PhD students and 2 technicians. He is (co)author of more than 40 peer-reviewed publications. In 2009 he was awarded by the European Research Council with an ERC-starting grant. Current research is focused on the supramolecular chemistry of amphiphilic peptides and polymers, drug delivery systems and hydrogels based on polymers.


Prof. dr. H. Linnartz is the head of the Sackler Laboratory for Astrophysics at Leiden Observatory. He has a special chair in ‘Molecular Laboratory Astrophysics’ at the Laser Center Vrije Universiteit, Amsterdam. His research focuses on the characterization of inter- and circumstellar molecules and processes, both in the gas phase and in the solid state, with the aim to guide and interpret astronomical observations and to provide the numbers that are necessary to characterize astrochemical processes through modeling. In the last 10 years he has developed and operated state-of-the-art experiments to quantitatively characterize solid state astrochemical processes and to study molecular transients of astrophysical interest. Prof. Linnartz has (co)authored 90 refereed papers, has (co)supervised 18 PhD theses (4 ongoing) over the past 15 years. is the research coordinator of LASSIE, a FP7 interdisciplinary training network in the field of solid state astrochemistry, is the editor-in-chief of CAMOP, and has organized 5 international meetings in recent years.

Prof. dr. J. Oomens leads the in-house user group at the FELIX free electron laser facility at the FOM Institute for Plasma Physics 'Rijnhuizen' in Nieuwegein. His group seeks to apply the IR radiation produced by FELIX in spectroscopic studies mainly on species of astrophysical, biomolecular, mass-spectrometric and catalytic interest. He pioneered the use of the free electron laser to obtain gas-phase infrared spectra of mass-selected molecular ions. He published various papers on the gas-phase infrared spectroscopy of cationic PAHs. In collaboration with researchers from Florida and with funding from NSF, he constructed a Fourier-transform mass spectrometer, which is now widely applied for ion spectroscopy by external users of the FELIX facility. He collaborates with a large number of international scientists from the fields of mass spectrometry, physical chemistry and astrochemistry. He is Foreign Counterpart Investigator in an NSF sponsored exchange program (PIRE). In 2009, he was appointed professor of 'Action Spectroscopy' by special appointment of the Stichting Physica at the University of Amsterdam. Oomens has (co)authored 105 refereed journal papers and his current H-index is 26.


Prof. dr. D.H. Parker is head of the Molecular and Laser Physics group at the Institute for Molecules and Materials (IMM) at the Radboud University Nijmegen. His main expertise is in velocity map imaging of uni- and bimolecular dynamics processes with applications in atmospheric physics and astrophysics. His main research topics are photodissociation of small molecules and imaging measurements of state-to-state doubly differential scattering cross sections involving rotational energy transfer. Currently, he leads the EU-ITN Network ICONIC with 15 partner institutions. He has supervised 25 PhD theses and 7 current PhD students and co-authored 150 refereed publications with 3,966 citations and has a current H-index of 36.


Dr. J. Raap obtained his PhD degree with promotores: Prof. van Boom, Leiden University and Prof. Hilbers, Radboud University. He is associate professor at Leiden Institute of Chemistry and specialized in chemistry and spectroscopy of isotope and spin labelled amino acids, peptide and proteins. Over the past decade he was the coordinator of several international projects in collaboration with Russian (NWO Dutch-Russian cooperation program), French and Italian groups. Research topic "Self-assemble of ion-channel forming peptides". He has (co)supervised 10 PhD theses and is (co)author of 116 papers (H-index of 26).

**Prof. dr. P. Rudolf** holds the chair of Experimental Solid State Physics at the University of Groningen and heads the Surfaces and Thin Films group of the Zernike Institute for Advanced Materials. Her investigations focus on the growth of nanostructures and the morphology of surfaces or thin films, as well as on their electronic and vibrational properties. Current research themes are crystalline organic thin films, functional molecules and molecular motors on surfaces, graphene and nanocomposites. Prof. Rudolf has (co)supervised 17 PhD theses. She has been Coordinator of a EC-funded Networks (Training and Mobility of Researchers (TMR) on Composites of Augmented Strength: Study of Intercalates of Uniquely Structured Clays, and participated in other 7 EU Projects. She has authored 139 refereed papers with 3,027 citations (H-index 28). She was member of the SynNanoMotors team that was awarded the 2008 EU Descartes Prize for Transnational Research.


**Dr. F. van der Tak** leads a research group at the Netherlands Institute for Space Research (SRON) and the Kapteyn Astronomical Institute in Groningen on the physics of the interstellar medium and the formation of stars. His research interests include molecular spectroscopy, radiative transfer and interstellar chemistry. He has made important contributions to the fields of high-mass star formation, the astrochemistry of hot molecular cores and dark pre-stellar cores, radiative transfer and molecular data; and has discovered several new interstellar molecules. He has written 68 papers in peer-reviewed journals, 18 of which as first author, with 1561 citations (ADS). His H-index is 24 and he has written 5 single-author invited review papers. He is currently supervising 2 PhD students and 2 postdocs, and has co-supervised 9 other PhD students. He has served on several international review boards and program committees, including once as Chair.


**Prof. dr. W.M.G. Ubachs** is Director of the Laser Centre VU University Amsterdam, which is a major research infrastructure embedded in LASERLAB-Europe. There he leads a group in Atomic, Molecular and Laser Physics. His main expertise is in the generation of coherent radiation in the extreme ultraviolet wavelength range, and its application in astrophysics and atmospheric physics, in particular on the photo-dissociation of CO and N2 molecules. Currently he is also involved in ultra-precision laser studies aiming at detection of possible variation of fundamental constants for which he has also made several observation runs at the Very Large Telescope. Further he leads a FOM-funded program on "Metrology with Frequency Comb Lasers", and is involved in cavity-ring down spectroscopy. He has supervised 13 PhD theses in the past 10 years and co-authored 182 refereed publications.

**Prof.dr. E. Vlieg** is head of the Solid State Chemistry group in the Institute for Molecules and Materials (IMM) at the Radboud University Nijmegen and director of the IMM (since 2009). The group studies the fundamentals of crystal growth, for which a wide range of experimental, computational and theoretical methods are applied to a wide range of crystals. A major research topic is chirality and the generation of materials of single chirality through crystallisation. Prof. Vlieg has (co-)supervised 26 PhD theses, (co-)authored more than 200 papers and has an H-index of 36.


**Dr. C.P de Vries** is instrument scientist at SRON, working X-ray spectroscopic instruments. He is currently working on calibration and operations of the Reflection Grating Spectrometer on XMM-Newton and is involved in the Soft X-ray Spectrometer design onboard the planned Japanese ASTRO-H mission. Apart from the instrumental work he is working on X-ray absorption studies of the interstellar medium, in particular interstellar dust.


**Prof. dr. L.B.F.M. Waters** studies the cycle of dust in galaxies with emphasis on the refractory dust component. He has been involved in the identification of solids in space using astronomical observations and laboratory measurements, and made major contributions to this field using spectra taken with the Infrared Space Observatory. He has also studied the light scattering properties of dust in the laboratory. He is involved in HERSCHEL studies of dust in evolved stars and in proto-planetary disks. Waters has supervised more than 20 PhD students and published more than 200 papers in refereed journals.