

# AstroChemical Newsletter #94

September 2023

You can access the full abstracts by clicking the paper titles. Submit your abstracts before the 25th of each month for inclusion in the following newsletter.

## Abstracts

### Water in the terrestrial planet-forming zone of the PDS 70 disk

**G. Perotti, V. Christiaens, Th. Henning, B. Tabone, L. B. F. M. Waters, I. Kamp, G. Olofsson, S. L. Grant, D. Gasman, J. Bouwman, M. Samland, R. Franceschi, E.F. van Dishoeck, K. Schwarz, M. Güdel, P.-O. Lagage, T.P. Ray, B. Vandenbussche, A. Abergel, O. Absil, A. M. Arabhavi, I. Argyriou, D. Barrado, A. Boccaletti, A. Caratti o Garatti, V. Geers, A. M. Glauser, K. Justannont, F. Lahuis, M. Mueller, C. Nehmé, E. Pantin, S. Scheithauer, C. Waelkens, R. Guadarrama, H. Jang, J. Kanwar, M. Morales-Calderón, N. Pawellek, D. Rodgers-Lee, J. Schreiber, L. Colina, T. R. Greve, G. Östlin, G. Wright**

Terrestrial and sub-Neptune planets are expected to form in the inner ( $< 10$  AU) regions of protoplanetary disks. Water plays a key role in their formation, although it is yet unclear whether water molecules are formed in-situ or transported from the outer disk. So far Spitzer Space Telescope observations have only provided water luminosity upper limits for dust-depleted inner disks, similar to PDS 70, the first system with direct confirmation of protoplanet presence. Here we report JWST observations of PDS 70, a benchmark target to search for water in a disk hosting a large ( $\sim 54$  AU) planet-carved gap separating an inner and outer disk. Our findings show water in the inner disk of PDS 70. This implies that potential terrestrial planets forming therein have access to a water reservoir. The column densities of water vapour suggest in-situ formation via a reaction sequence involving O, H<sub>2</sub>, and/or OH, and survival through water self-shielding. This is also supported by the presence of CO<sub>2</sub> emission, another molecule sensitive to UV photodissociation. Dust shielding, and replenishment of both gas and small dust from the outer disk, may also play a role in sustaining the water reservoir. Our observations also reveal a strong variability of the mid-infrared spectral energy distribution, pointing to a change of inner disk geometry.

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### A global view on star formation: The GLOSTAR Galactic plane survey VIII. Formaldehyde absorption in Cygnus-X

**Y. Gong, G. N. Ortiz-León, M. R. Rugel, K. M. Menten, A. Brunthaler, F. Wyrowski, C. Henkel, H. Beuther, S. A. Dzib, J. S. Urquhart, A. Y. Yang, J. D. Pandian, R. Dokara, V. S. Veena, H. Nguyen, S.-N. X. Medina, W. D. Cotton, W. Reich, B. Winkel, P. Müller, I. Skretas, T. Csengeri, S. Khan, A. Cheema**

Cygnus X is one of the closest and most active high-mass star-forming regions in our Galaxy, making it one of the best laboratories for studying massive star formation. As part of the GLOSTAR Galactic plane survey, we performed large scale simultaneous H<sub>2</sub>CO (11,0-11,1) spectral line and radio continuum imaging observations toward Cygnus X at  $\lambda \sim 6$  cm with the Karl G. Jansky Very Large Array and the Effelsberg-100 m radio telescope. Our Effelsberg observations reveal widespread H<sub>2</sub>CO (11,0-11,1) absorption with a spatial extent of  $\geq 50$  pc in Cygnus X for the first time. On large scales of 4.4 pc, the relative orientation between local velocity gradient and magnetic field tends to be more parallel at H<sub>2</sub> column densities of  $\geq 1.8 \times 10^{22}$  cm<sup>-2</sup>. On the smaller scale of 0.17 pc, our VLA+Effelsberg combined data reveal H<sub>2</sub>CO absorption only toward three bright HII regions. Our observations demonstrate that H<sub>2</sub>CO (11,0-11,1) is commonly optically thin. Kinematic analysis supports the assertion that molecular clouds generally exhibit supersonic motions on scales of 0.17-4.4 pc. We show a non-negligible contribution of the cosmic microwave background radiation in producing extended absorption features in Cygnus X. Our observations suggest that H<sub>2</sub>CO (11,0-11,1) can trace molecular gas with H<sub>2</sub> column densities of  $\geq 5 \times 10^{21}$  cm<sup>-2</sup>. The ortho-H<sub>2</sub>CO fractional abundance with respect to H<sub>2</sub> has a mean value of  $7.0 \times 10^{-10}$ . A comparison of velocity dispersions on different linear scales suggests that the dominant  $-3$  km s<sup>-1</sup> velocity component in the prominent DR21 region has nearly identical velocity dispersions on scales of 0.17-4.4 pc, which deviates from the expected behavior of classic turbulence.

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## The diverse chemistry of protoplanetary disks as revealed by JWST

**E.F. van Dishoeck, S. Grant, B. Tabone, M. van Gelder, L. Francis, L. Tychoniec, G. Bettoni, A.M. Arabhavi, D. Gasman, P. Nazari, M. Vlasblom, P. Kavanagh, V. Christiaens, P. Klaassen, H. Beuther, Th. Henning, I. Kamp**

Early results from the JWST-MIRI guaranteed time programs on protostars (JOYS) and disks (MINDS) are presented. Thanks to the increased sensitivity, spectral and spatial resolution of the MIRI spectrometer, the chemical inventory of the planet-forming zones in disks can be investigated with unprecedented detail across stellar mass range and age. Here data are presented for five disks, four around low-mass stars and one around a very young high-mass star. The mid-infrared spectra show some similarities but also significant diversity: some sources are rich in CO<sub>2</sub>, others in H<sub>2</sub>O or C<sub>2</sub>H<sub>2</sub>. In one disk around a very low-mass star, booming C<sub>2</sub>H<sub>2</sub> emission provides evidence for a "soot" line at which carbon grains are eroded and sublimated, leading to a rich hydrocarbon chemistry in which even di-acetylene (C<sub>4</sub>H<sub>2</sub>) and benzene (C<sub>6</sub>H<sub>6</sub>) are detected (Tabone et al. 2023). Together, the data point to an active inner disk gas-phase chemistry that is closely linked to the physical structure (temperature, snowlines, presence of cavities and dust traps) of the entire disk and which may result in varying CO<sub>2</sub>/H<sub>2</sub>O abundances and high C/O ratios  $> 1$  in some cases. Ultimately, this diversity in disk chemistry will also be reflected in the diversity of the chemical composition of exoplanets.

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## Gas Sources from the Coma and Nucleus of Comet 46P/Wirtanen Observed Using ALMA

M. A. Cordiner, N. X. Roth, S. N. Milam, G. L. Villanueva, D. Bockelée-Morvan, A. J. Remijan, S. B. Charnley, N. Biver, D. C. Lis, C. Qi, B. P. Bonev, J. Crovisier, and J. Boissier

Gas-phase molecules in cometary atmospheres (comae) originate primarily from (1) outgassing by the nucleus, (2) sublimation of icy grains in the near-nucleus coma, and (3) coma (photo)chemical processes. However, the majority of cometary gases observed at radio wavelengths have yet to be mapped, so their production/release mechanisms remain uncertain. Here we present observations of six molecular species toward comet 46P/Wirtanen, obtained using the Atacama Large Millimeter/submillimeter Array during the comet's unusually close ( $\sim 0.1$  au) approach to Earth in 2018 December. Interferometric maps of HCN, CH<sub>3</sub>OH, CH<sub>3</sub>CN, H<sub>2</sub>CO, CS, and HNC were obtained at an unprecedented sky-projected spatial resolution of up to 25 km, enabling the nucleus and coma sources of these molecules to be accurately quantified. The HCN, CH<sub>3</sub>OH, and CH<sub>3</sub>CN spatial distributions are consistent with production by direct outgassing from (or very close to) the nucleus, with a significant proportion of the observed CH<sub>3</sub>OH originating from sublimation of icy grains in the near-nucleus coma (at a scale length  $L_p = 36 \pm 7$  km). On the other hand, H<sub>2</sub>CO, CS, and HNC originate primarily from distributed coma sources (with  $L_p$  values in the range 550–16,000 km), the identities of which remain to be established. The HCN, CH<sub>3</sub>OH, and HNC abundances in 46P are consistent with the average values previously observed in comets, whereas the H<sub>2</sub>CO, CH<sub>3</sub>CN, and CS abundances are relatively low.

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## The Automated Reaction-Pathway Search reveals the Energetically Favorable Synthesis of Interstellar CH<sub>3</sub>OCH<sub>3</sub> and HCOOCH<sub>3</sub>

Y. Komatsu, K. Furuya

Recent astronomical observations have shown that interstellar complex organic molecules (COMs) exist even in cold environments ( $\sim 10$  K), while various interstellar COMs have conventionally been detected in the hot gas ( $\geq 100$  K) in the vicinity of high-mass and low-mass protostars. However, the formation pathway of each interstellar COM remains largely unclear. In this work, we demonstrate that an automated reaction path search based on transition state theory, which does not require predetermined pathways, is helpful for investigating the formation pathways of interstellar COMs in the gas phase. The exhaustive search within electronic ground states helps elucidate the complex chemical formation pathways of COMs at low temperatures. Here we examine the formation pathways of dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>) and methyl formate (HCOOCH<sub>3</sub>), which are often detected in the cold and hot gas of star-forming regions. We have identified a barrierless and exothermic formation path of CH<sub>3</sub>OCH<sub>3</sub> by reaction between neutral species; CH<sub>3</sub>O + CH<sub>3</sub>  $\rightarrow$  H<sub>2</sub>CO  $\cdots$  CH<sub>4</sub>  $\rightarrow$  CH<sub>3</sub>OCH<sub>3</sub> is the most efficient path in the large chemical network constructed by our automated reaction path search and is comparable with previous studies. For HCOOCH<sub>3</sub>, we obtain complex pathways initiated from reactions between neutral species; HCOO and CH<sub>3</sub> generate HCOOCH<sub>3</sub> and its isomers without external energy. However, we also identified the competing reaction branches producing CO<sub>2</sub> + CH<sub>4</sub> and CH<sub>3</sub>COOH, which would be more efficient than the formation of HCOOCH<sub>3</sub>. Then the gas-phase

formation of HCOOCH<sub>3</sub> through reactions between neutral species would not be efficient compared to the CH<sub>3</sub>OCH<sub>3</sub> formation.

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## Protostellar Interferometric Line Survey of the Cygnus-X region (PILS-Cygnus) -- The role of the external environment in setting the chemistry of protostars

**S. J. van der Walt, L. E. Kristensen, H. Calcutt, J. K. Jørgensen, R. T. Garrod**

(Abridged) Molecular lines are commonly detected towards protostellar sources. However, to get a better understanding of the chemistry of these sources we need unbiased molecular surveys over a wide frequency range for as many sources as possible to shed light on the origin of this chemistry, particularly any influence from the external environment. We present results from the PILS-Cygnus survey of ten intermediate- to high-mass protostellar sources in the nearby Cygnus-X complex, through high angular resolution interferometric observations over a wide frequency range. Using the Submillimeter Array (SMA), a spectral line survey of ten sources was performed in the frequency range 329-361 GHz, with an angular resolution of  $\sim 1.''5$ , ( $\sim 2000$  AU, source distance of 1.3 kpc). Spectral modelling was performed to identify molecular emission and determine column densities and excitation temperatures for each source. We detect CH<sub>3</sub>OH towards nine of the ten sources, CH<sub>3</sub>OCH<sub>3</sub> and CH<sub>3</sub>OCHO towards three sources, and CH<sub>3</sub>CN towards four sources. Towards five sources the chemistry is spatially differentiated (different species peak at different positions and are offset from the peak continuum emission). The chemical properties of each source do not correlate with their position in the Cygnus-X complex, nor do the distance or direction to the nearest OB associations. However, the five sources located in the DR21 filament do appear to show less line emission compared to the five sources outside the filament. This work shows how important wide frequency coverage observations are combined with high angular resolution observations for studying the protostellar environment. Based on the ten sources observed here, the external environment appears to only play a minor role in setting the chemical environment on these small scales ( $< 2000$  AU).

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## Quantum mechanical modeling of the grain-surface formation of acetaldehyde on H<sub>2</sub>O:CO dirty ice surfaces

**J. Perrero, P. Ugliengo, C. Ceccarelli, A. Rimola**

Acetaldehyde (CH<sub>3</sub>CHO) is one of the most detected interstellar Complex Organic Molecule (iCOM) in the interstellar medium (ISM). These species have a potential biological relevance, as they can be precursors of more complex species from which life could have emerged. The formation of iCOMs in the ISM is a challenge and a matter of debate, whether gas-phase, grain-surface chemistry or both are needed for their synthesis. In the gas-phase, CH<sub>3</sub>CHO can be efficiently synthesized from ethanol and/or ethyl radical. On the grain-surfaces, radical-radical recombinations were traditionally invoked. However, several pitfalls have been recently identified, such as the presence of energy barriers and competitive side reactions (i.e., H abstractions). Here

we investigate a new grain-surface reaction pathway for the formation of acetaldehyde, namely the reaction between CH<sub>3</sub> and a CO molecule of a dirty water/CO ice followed by hydrogenation of its product, CH<sub>3</sub>CO. To this end, we carried out ab initio computations of the reaction occurring on an ice composed by 75% water and 25% CO molecules. We found that the CH<sub>3</sub> + CO(ice) reaction exhibits barriers difficult to overcome in the ISM, either adopting a Langmuir-Hinshelwood or an Eley-Rideal mechanism. The subsequent hydrogenation step is found to be barrierless, provided that the two reacting species have the correct orientation. Therefore, this pathway seems unlikely to occur in the ISM.

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## Interaction of H<sub>2</sub>S with H atoms on grain surfaces under molecular cloud conditions

**J. C. Santos, H. Linnartz, K.-J. Chuang**

Hydrogen sulfide (H<sub>2</sub>S) is thought to be efficiently formed on grain surfaces through the successive hydrogenation of S atoms. Its non-detection so far in astronomical observations of icy dust mantles thus indicates that effective destruction pathways must play a significant role in its interstellar abundance. While chemical desorption has been shown to remove H<sub>2</sub>S very efficiently from the ice, in line with H<sub>2</sub>S gas-phase detections, possible solid-state chemistry triggered by the related HS radical have been largely disregarded so far -- despite it being an essential intermediate in the H<sub>2</sub>S + H reaction scheme. We aim to thoroughly investigate the fate of H<sub>2</sub>S upon H-atom impact under molecular cloud conditions, providing a comprehensive analysis combined with detailed quantification of both the chemical desorption and ice chemistry that ensues. Experiments are performed in an ultrahigh vacuum chamber at temperatures between 10--16 K. The changes in the solid phase during H-atom bombardment are monitored in situ by means of reflection absorption infrared spectroscopy (RAIRS), and desorbed species are measured with a quadrupole mass spectrometer (QMS). We confirm the formation of H<sub>2</sub>S<sub>2</sub> via reactions involving H<sub>2</sub>S + H, and quantify its formation cross section under the employed experimental conditions. Additionally, we directly assess the chemical desorption of H<sub>2</sub>S by measuring the gas-phase desorption signals with the QMS, providing unambiguous desorption cross sections. Chemical desorption of H<sub>2</sub>S<sub>2</sub> was not observed. The relative decrease of H<sub>2</sub>S ices by chemical desorption changes from ~85% to ~74% between temperatures of 10 and 16 K, while the decrease as the result of H<sub>2</sub>S<sub>2</sub> formation is enhanced from ~5% to ~26%, suggesting an increasingly relevant sulfur chemistry induced by HS radicals at warmer environments. The astronomical implications are further discussed.

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## Experimental and Theoretical Investigation of the Reaction of NH<sub>2</sub> with NO at Very Low Temperatures

**K. M. Douglas, D. Lucas, C. Walsh, M. A. Blitz, D. E. Heard**

The first experimental study of the low-temperature kinetics of the gas-phase reaction between NH<sub>2</sub> and NO has been performed. A pulsed laser photolysis-laser-induced fluorescence technique was used to create and monitor the temporal decay of NH<sub>2</sub> in the presence of NO. Measurements were carried out over the temperature range of

24–106 K, with the low temperatures achieved using a pulsed Laval nozzle expansion. The negative temperature dependence of the reaction rate coefficient observed at higher temperatures in the literature continues at these lower temperatures, with the rate coefficient reaching  $3.53 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $T = 26 \text{ K}$ . Ab initio calculations of the potential energy surface were combined with rate theory calculations using the MESMER software package in order to calculate and predict rate coefficients and branching ratios over a wide range of temperatures, which are largely consistent with experimentally determined literature values. These theoretical calculations indicate that at the low temperatures investigated for this reaction, only one product channel producing  $\text{N}_2 + \text{H}_2\text{O}$  is important. The rate coefficients determined in this study were used in a gas-phase astrochemical model. Models were run over a range of physical conditions appropriate for cold to warm molecular clouds (10 to 30 K;  $10^4$  to  $10^6 \text{ cm}^{-3}$ ), resulting in only minor changes ( $<1\%$ ) to the abundances of  $\text{NH}_2$  and  $\text{NO}$  at steady state. Hence, despite the observed increase in the rate at low temperatures, this mechanism is not a dominant loss mechanism for either  $\text{NH}_2$  or  $\text{NO}$  under dark cloud conditions.

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## Parsec scales of carbon chain and complex organic molecules in AFGL 2591 and IRAS 20126

**P. Freeman, S. Bottinelli, R. Plume, E. Caux, C. Monaghan, B. Mookerjee**

There is a diverse chemical inventory in protostellar regions leading to the classification of extreme types of systems. Warm carbon chain chemistry sources, for one, are the warm and dense regions near a protostar containing unsaturated carbon chain molecules. Since the presentation of this definition in 2008, there is a growing field to detect and characterise these sources. The details are lesser known in relation to hot cores and in high-mass star-forming regions—regions of great importance in galactic evolution. To investigate the prevalence of carbon chain species and their environment in high-mass star-forming regions, we have conducted targeted spectral surveys of two sources in the direction of Cygnus X—AFGL 2591 and IRAS 20126+4104—with the Green Bank Telescope and the IRAM 30m Telescope. We have constructed a Local Thermodynamic Equilibrium (LTE) model using the observed molecular spectra to determine the physical environment in which these molecules originate. We map both the observed spatial distribution and the physical parameters found from the LTE model. We also determine the formation routes of these molecules in each source using the three-phase NAUTILUS chemical evolution code. We detect several lines of propyne,  $\text{CH}_3\text{CCH}$ , and cyclopropenylidene,  $c\text{-C}_3\text{H}_2$  as tracers of carbon chain chemistry, as well as several lines of formaldehyde,  $\text{H}_2\text{CO}$ , and methanol,  $\text{CH}_3\text{OH}$ , as a precursor and a tracer of complex organic molecule chemistry, respectively. We find excitation temperatures of 20–30 K for the carbon chains and 8–85 K for the complex organics. The  $\text{CH}_3\text{CCH}$  abundances are reproduced by a warm-up model, consistent with warm carbon chain chemistry, while the observed  $\text{CH}_3\text{OH}$  abundances require a shock mechanism sputtering the molecules into the gas phase.

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## Water ice: temperature-dependent refractive indexes and

## their astrophysical implications

W. R. M. Rocha, M. G. Rachid, M. K. McClure, J. He, and H. Linnartz

Interstellar ices are largely composed of frozen water. It is important to derive fundamental parameters for H<sub>2</sub>O ice such as absorption and scattering opacities for which accurate complex refractive indexes are needed. The primary goal of this work is to derive ice-grain opacities based on accurate H<sub>2</sub>O ice complex refractive indexes and to assess their impact on the derivation of ice column densities and porosity in space. We use the optool code to derive ice-grain opacities values based on new mid-IR complex refractive index measurements of H<sub>2</sub>O ice. Next, we use those opacities in the RADMC-3D code to run a radiative transfer simulation of a protostellar envelope containing H<sub>2</sub>O ice. This is used to calculate water ice column densities. We find that the real refractive index in the mid-IR of H<sub>2</sub>O ice at 30K is ~14% lower than previously reported in the literature. This has a direct impact on the ice column densities derived from the simulations of embedded protostars. We find that ice porosity plays a significant role in the opacity of icy grains and that the H<sub>2</sub>O libration mode can be used as a diagnostic tool to constrain the porosity level. Finally, the refractive indexes presented here allow us to estimate a grain size detection limit of 18~ $\mu$ m based on the 3 $\mu$ m band whereas the 6 $\mu$ m band allows tracing grain sizes larger than 20~ $\mu$ m. Based on radiative transfer simulations using new mid-IR refractive indexes, we conclude that H<sub>2</sub>O ice leads to more absorption of infrared light than previously estimated. This implies that the 3 and 6 $\mu$ m bands remain detectable in icy grains with sizes larger than 10~ $\mu$ m. Finally, we propose that also the H<sub>2</sub>O ice libration band can be a diagnostic tool to constrain the porosity level of the interstellar ice, in addition to the OH dangling bond, which is routinely used for this purpose.

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## Announcements

### PhD in Astrophysics

The International Max Planck Research School on Astrophysics at the Ludwig Maximilians University Munich.

We are the joint International Max-Planck Research School (IMPRS) on Astrophysics of the Max Planck Institute for Extraterrestrial Physics (MPE), the Max Planck Institute for Astrophysics (MPA), the University Observatory Munich at the Ludwig Maximilians University (LMU/USM), the European Southern Observatory (ESO).

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## **PhD and Postdoctoral Positions within the Dutch Astrochemistry Network (DAN-III)**

The launch of the James Webb Space Telescope (JWST) in 2022 opened a new window for the study of astrochemistry. JWST observes with unprecedented resolution different astronomical environments, thus permitting to study the ice composition in dense molecular clouds and protoplanetary disks but also the cycle of carbon through the phases of star and planet formation. Interpreting this novel data requires an interdisciplinary collaboration between astronomers, physicists and chemists to systematically collect and use key molecular data, such as gas and ice spectroscopy, collisional rate constants and/or reaction pathways.

Building on existing/long-standing successful collaborations of Dutch astronomers, laboratory/experimental and theoretical researchers - that led to the Dutch Astrochemistry Network (DAN) - we announce a focused research programme of 7 highly interwoven projects that aim to address the following astrochemical questions tightly linked to the new JWST data:

- A) Inheritance versus Reset: How do ice and gas-molecules evolve together and get processed from molecular clouds to disks?
- B) Carbon Cycle: How is carbon cycled through small gas-phase hydrocarbons and carbonaceous dust in different cosmic environments?

More information about the Dutch Astrochemistry Network can be found at <https://www.nwo.nl/en/researchprogrammes/astrochemistry>.

We are advertising seven PhD and postdoc projects within this network to address the above questions. More details about each position can be found at the respective institutes vacancy webpages and/or by contacting the main supervisors.

- 1) Probing spatially variable ice processing with radiative transfer  
3-yr postdoc position with Melissa McClure (Leiden University), Inga Kamp (University of Groningen), Stephanie Cazaux (TU Delft) and Rens Waters (Radboud University Nijmegen)
- 2) Bridging the gap: modeling molecular ice abundances at the micro- and macro level  
4-yr PhD position with Thanja Lamberts (Leiden University), Herma Cuppen (Radboud University Nijmegen) and Serena Viti (Leiden University)
- 3) Laboratory ice data in support of JWST ice observations  
1.5-yr postdoc position with Harold Linnartz and Koju Chuang (both Leiden University)
- 4) Energetic processing of ices  
1.5-yr postdoc position with Britta Redlich (Radboud University Nijmegen), Herma Cuppen (Radboud University Nijmegen) and Thanja Lamberts (Leiden University)
- 5) Rovibrational emission spectra of small linear organics  
4-yr PhD position with Floris van der Tak (SRON/University of Groningen), Gerrit Groenenboom (Radboud University Nijmegen), Inga Kamp (University of Groningen),

Ewine van Dishoeck (Leiden University) and Ad van der Avoird (Radboud University Nijmegen)

6) PAH spectroscopy for UV irradiated environments

4-yr PhD position with Sandra Bruenken, Jos Oomens (both Radboud University Nijmegen), Wybren Jan Buma and Alessandra Candian (both University of Amsterdam)

7) The contribution of PAHs to interstellar carbon chemistry

4-yr PhD position with Alessandra Candian, Wybren Jan Buma (both University of Amsterdam) and Inga Kamp (University of Groningen)