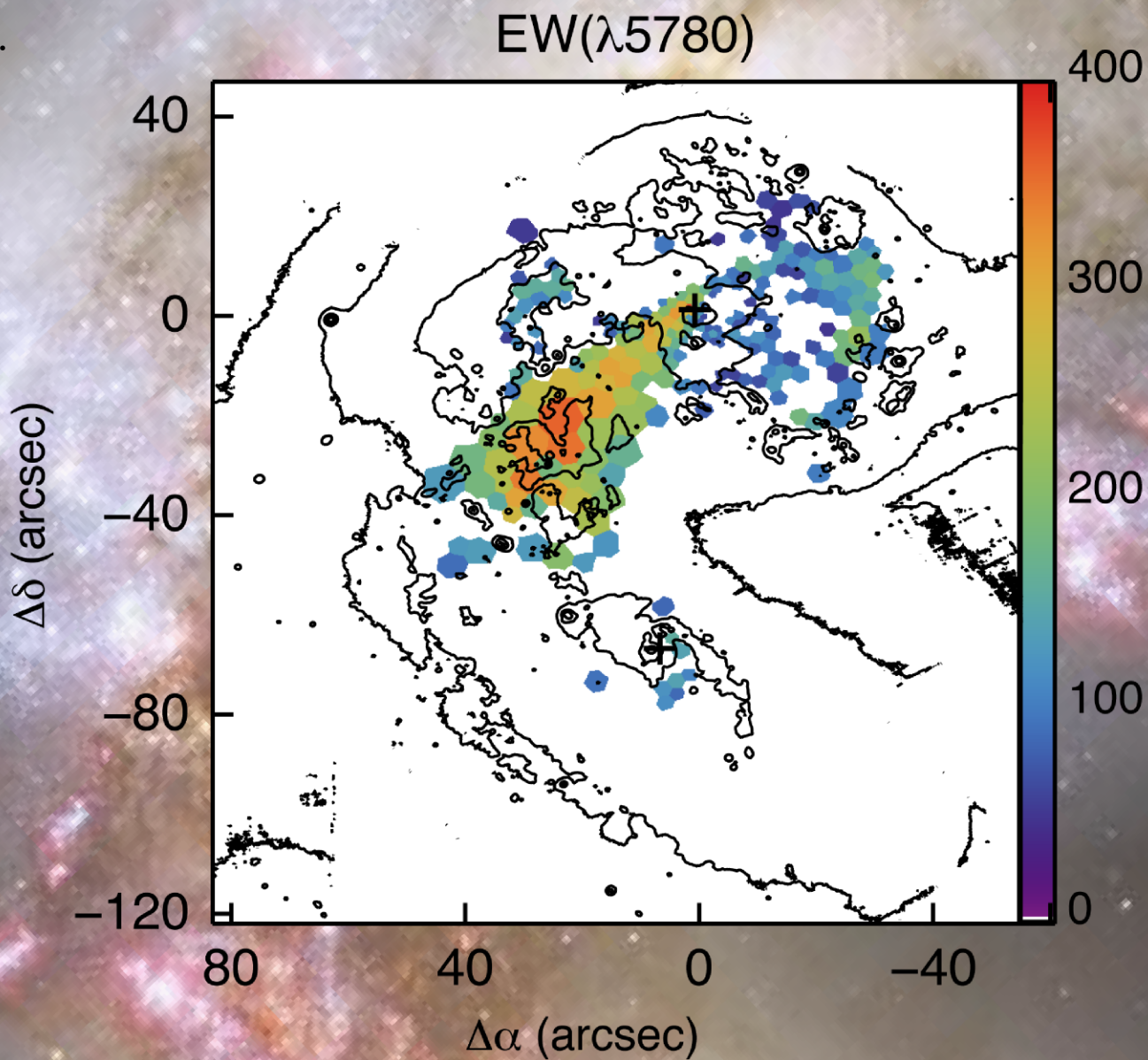


# AstropAH

A Newsletter on Astronomical PAHs

Issue 46 | Mar 2018



# Editorial

**Dear Colleagues,**

This spring issue features on the cover the first mapping of Diffuse Interstellar Bands in a galaxy outside the Local Group. Curious? Please take a look at our collected paper abstracts section.

This collection features interesting topics, on probing the Galactic wind environment with PAHs, nanoparticles in space, the extragalactic DIB research as featured on the cover, PAH-ice interaction, the photostability of super-hydrogenated PAHs, isomerisation of a carbon-cluster, and on microhydration as well as IR spectroscopy of hydrated PAH ions. We specifically would like to point out the presented update of the NASA Ames PAH IR Spectroscopic database.

Note also the last announcement of the NASA LAW meeting in the Meetings Section. The deadlines are closing today (22 March) and tomorrow; this is your last chance to submit your abstract and register!

Please also take a look at the Announcements section and distribute the vacancy for a PhD position in Leiden amongst possible interested students.

You might have noticed the lack of an In Focus this month. This could have been your spot! But no worries, you can always send your contribution for another issue. For publication in the next AstroPAH, see the deadlines below. We encourage you to send in your abstracts, In Focus suggestions, and other contributions. We look forward to it!

**The Editorial Team**

**Next issue: 19 April 2018.  
Submission deadline: 6 April 2018.**

# AstroPAH Newsletter

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## PAH Picture of the Month

Map of equivalent width (in  $m\text{\AA}$ ) of the 5780  $\text{\AA}$  Diffuse Interstellar Band recorded in the Antennae Galaxies (NGC 4038/NGC 4039, in the background) by the MUSE instrument on the Very Large Telescope (VLT). This is the first time that the DIBs are mapped in a Galaxy outside the Local Group. More information can be found in the paper by [A. Monreal-Ibero et al.](#) in the Abstracts section.

**Credits:** Background. NASA, ESA, and B. Whitmore (STScI); Composition. A. Candian



# Abstracts

## Polycyclic Aromatic Hydrocarbon Emission Toward the Galactic Bulge

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We examine polycyclic aromatic hydrocarbon (PAH), dust, and atomic/molecular emission toward the Galactic bulge using *Spitzer Space Telescope* observations of four fields: C32, C35, OGLE, and NGC 6522. These fields are approximately centered on  $(l, b) = (0.0^\circ, 1.0^\circ)$ ,  $(0.0^\circ, -1.0^\circ)$ ,  $(0.4^\circ, -2.4^\circ)$ , and  $(1.0^\circ, -3.8^\circ)$ , respectively. Far-infrared photometric observations complement the *Spitzer*/IRS spectroscopic data and are used to construct spectral energy distributions. We find that the dust and PAH emission are exceptionally similar between C32 and C35 overall, in part explained due to their location – they reside on or near boundaries of a 7 Myr old Galactic outflow event and are partly shock-heated. Within the C32 and C35 fields, we identify a region of elevated H emission that is coincident with elevated fine-structure and [O IV] line emission and weak PAH feature strengths. We are likely tracing a transition zone of the outflow into the nascent environment. PAH abundances in these fields are slightly depressed relative to typical ISM values. In the OGLE and NGC 6522 fields, we observe weak features on a continuum dominated by zodiacal dust. SED fitting indicates that thermal dust grains in C32 and C35 have temperatures comparable to those of diffuse, high-latitude cirrus clouds. Little variability is detected in the PAH properties between C32 and C35, indicating that a stable population of PAHs dominates the overall spectral appearance. In fact, their PAH features are exceptionally similar to that of the M82 superwind, emphasizing that we are probing a local Galactic wind environment.

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The Astrophysical Journal, 855, 32 (2018)

<http://iopscience.iop.org/article/10.3847/1538-4357/aaae06>

# Tetrahedral hydrocarbon nanoparticles in space: X-ray spectra

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It has been proposed, or confirmed, that diamond nanoparticles exist in various environments in space: close to active galactic nuclei, in the vicinity of supernovae and pulsars, in the interior of several planets in the Solar system, in carbon planets and other exoplanets, carbon-rich stars, meteorites, in X-ray active Herbig Ae/Be stars, and in the interstellar medium. Using density functional theory methods we calculate the carbon K-edge X-ray absorption spectrum of two large tetrahedral nanodiamonds: C<sub>26</sub>H<sub>32</sub> and C<sub>51</sub>H<sub>52</sub>. We also study and test our methods on the astrophysical molecule CH<sub>4</sub>, the smallest C-H tetrahedral structure. A possible detection of nanodiamonds from X-ray spectra by future telescopes, such as the project *Arcus*, is proposed. Simulated spectra of the diffuse interstellar medium using Cyg X-2 as a source show that nanodiamonds studied in this work can be detected by *Arcus*, a high resolution X-ray spectrometer mission selected by NASA for a Phase A concept study.

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Accepted for publication in MNRAS

<https://arxiv.org/abs/1803.01185>

# Diffuse interstellar bands $\lambda 5780$ and $\lambda 5797$ in the Antennae Galaxy as seen by MUSE

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Diffuse interstellar bands (DIBs) are faint spectral absorption features of unknown origin. Research on DIBs beyond the Local Group is very limited and will surely blossom in the era of the Extremely Large Telescopes. However, we can already start paving the way. One possibility that needs to be explored is the use of high-sensitivity integral field spectrographs.

Our goals are twofold. First, we aim to derive reliable mapping of at least one DIB in a galaxy outside the Local Group. Second, we want to explore the relation between DIBs and other properties of the interstellar medium (ISM) in the galaxy.

We use MUSE data for the Antennae Galaxy, the closest major galaxy merger. High signal-to-

noise spectra were created by co-adding the signal of many spatial elements with the Voronoi binning technique. The emission of the underlying stellar population was modelled and subtracted with the STARLIGHT spectral synthesis code. Flux and equivalent width of the features of interest were measured by means of fitting to Gaussian functions.

To our knowledge, we have derived the first maps for the DIBs at  $\lambda 5780$  and  $\lambda 5797$  in galaxies outside the Local Group. The strongest of the two DIBs (at  $\lambda 5780$ ) was detected in an area of  $\sim 0.6$  arcmin<sup>2</sup>, corresponding to a linear scale of  $\sim 25$  kpc<sup>2</sup>. This region was sampled using  $>200$  out of  $\sim 1200$  independent lines of sight. The DIB  $\lambda 5797$  was detected in  $>100$  independent lines of sight. Both DIBs are associated with a region of high emission in the HI 21 cm line, implying a connection between atomic gas and DIBs, as the correlations in the Milky Way also suggest. Conversely, there is mild spatial association between the two DIBs and the molecular gas, in agreement with results for our Galaxy that indicate a lack of correlation between DIBs and molecular gas. The overall structures for the DIB strength distribution and extinction are comparable. Within the system, the  $\lambda 5780$  DIB clearly correlates with the extinction, and both DIBs follow the relationship between equivalent width and reddening when data for several galaxies are considered. This relationship is tighter when comparing only with galaxies with metallicities close to solar. Unidentified infrared emission bands (UIBs, likely caused by polycyclic aromatic hydrocarbons (PAHs)) and the  $\lambda 5780$  and  $\lambda 5797$  DIBs show similar but not identical spatial distributions. We attribute the differences to extinction effects without necessarily implying a radically different nature of the respective carriers. The results illustrate the enormous potential of integral field spectrographs for extragalactic DIB research.

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Astronomy & Astrophysics (2018), in press

<http://adsabs.harvard.edu/abs/2018arXiv180110162M>

<https://doi.org/10.1051/0004-6361/201732178>

## The NASA Ames PAH IR Spectroscopic Database: computational version 3.00 with updated content and introduction of multiple scaling factors

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Version 3.00 of the library of computed spectra of the NASA Ames PAH IR Spectroscopic Database (PAHdb) is described. Version 3.00 introduces the use of multiple scale factors, instead of the single scaling factor used previously, to align the theoretical harmonic frequencies with the experimental fundamentals. The use of multiple scale factors permits the use of a variety of basis sets; this allows new PAH species to be included in the database, such as those containing oxygen, and yields an improved treatment of strained species and those containing nitrogen. In addition, the computed spectra of 2,439 new PAH species have been added. The impact of these changes on the analysis of an astronomical spectrum through database fitting

is considered and compared with a fit using Version 2.00 of the library of computed spectra. Finally, astronomical constraints are defined for the PAH spectral libraries in PAHdb.

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The Astrophysical Journal Supplement Series, 234 32, 2018

<https://doi.org/10.3847/1538-4365/aaa019>

## Adsorption of PAHs on interstellar ice viewed by classical molecular dynamics

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Polycyclic Aromatic Hydrocarbons (PAHs) are a family of molecules which represent the best candidates for explaining the observation of two sets of features in the Interstellar Medium (ISM): the Aromatic Interstellar Bands (AIBs) and the Diffuse Interstellar Bands (DIBs). In dense molecular clouds, PAHs may condense onto interstellar grains, contributing to the complex chemistry occurring in their icy mantles, composed essentially of water. In this context, the adsorption of various PAH molecules, from benzene to coronene, on different ices, both amorphous and crystalline, is investigated by means of classical molecular dynamics simulations. Initially, a systematic parametrization of the electronic charges on the chosen PAHs in these environments is carried out, and benchmarked with reference to free energies of solvation in liquid water. We go on to propose a new, rigorous methodology, transferable to any other PAH or molecular species, for evaluating the charges to be applied to the molecule in the gas phase, at interfaces, or in liquid water. Ultimately, the adsorption energies calculated for the various PAHs are used to derive a function predicting the adsorption energy of any PAH on a given ice surface as a function of the number of C and H atoms it contains. For all PAHs studied, the highest adsorption energies are found on the hexagonal crystalline ice surface (Ih). Binding energy maps constructed for each PAH-ice pair give valuable insight into adsorption site densities and the barriers to surface diffusion. One key result is that the amorphous surface offers a smaller number of adsorption sites compared to that of hexagonal ice. A direct correlation between the location of energetically favourable adsorption sites and the presence of dangling H bonds is also demonstrated using these maps, showing that PAHs adsorb preferentially on sites offering dangling H bonds. The present work represents a complete description of PAH-ice interaction in the ground electronic state and at low temperature, providing the binding energies and barrier heights necessary to the ongoing improvement of astrochemical models.

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Phys. Chem. Chem. Phys., 2018, Advance Article

<http://pubs.rsc.org/en/content/articlelanding/2018/cp/c8cp00593a#ldivAbstract>

# Hydrogenated Benzene in Circumstellar Environments: Insights into the photostability of Super-hydrogenated PAHs

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Polycyclic aromatic hydrocarbons (PAHs), comprised of fused benzene ( $C_6H_6$ ) rings, emit infrared radiation (3-12  $\mu m$ ) due to the vibrational transitions of the C-H bonds of the aromatic rings. The 3.3  $\mu m$  aromatic band is generally accompanied by the band at 3.4  $\mu m$  assigned to vibration of aliphatic C-H bonds of compounds such as PAHs with excess of peripheral H atoms ( $H_n$ -PAHs). Herein we study the stability of the fully hydrogenated benzene (or cyclohexane,  $C_6H_{12}$ ) under impact of stellar radiation in the photodissociation region (PDR) of NGC 7027. Using synchrotron radiation and time-of-flight mass spectrometry we investigated the ionization and dissociation processes at energy ranges of the UV (10-200 eV) and soft X-rays (280-310 eV). Density Functional Theory (DFT) calculations were used to determine the most stable structures and the relevant low-lying isomers of singly charged  $C_6H_{12}$  ions. The Partial Ion Yield (PIY) analysis evidences the higher tendency of dissociation of cyclohexane in comparison to benzene. However, because of the high photoabsorption cross section of benzene at the C1s resonance edge, its photodissociation and photoionization cross sections are enhanced, leading to a higher efficiency of dissociation of benzene in the PDR of NGC 7027. We suggest that a similar effect is experienced by PAHs in X-ray photon-rich environments, which ultimately acts as an auxiliary protection mechanism of super-hydrogenated polycyclic hydrocarbons. Finally, we propose that the single photoionization of cyclohexane could enhance the abundance of branched molecules in interstellar and circumstellar media.

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The Astrophysical Journal, 854, 61 (2018)

<https://doi.org/10.3847/1538-4357/aaa977>

## Ultraslow isomerization in photoexcited gas-phase carbon cluster $C_{10}^-$

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Isomerization and carbon chemistry in the gas phase are key processes in many scientific



studies. Here we report on the isomerization process from linear  $C_{10}^-$  to its monocyclic isomer.  $C_{10}^-$  ions were trapped in an electrostatic ion beam trap and then excited with a laser pulse of precise energy. The neutral products formed upon photoexcitation were measured as a function of time after the laser pulse. It was found using a statistical model that, although the system is excited above its isomerization barrier energy, the actual isomerization from linear to monocyclic conformation takes place on a very long time scale of up to hundreds of microseconds. This finding may indicate a general phenomenon that can affect the interstellar medium chemistry of large molecule formation as well as other gas phase processes.

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NATURE COMMUNICATIONS (2018) 9:912

<https://doi.org/10.1038/s41467-018-03197-w>

## Microhydration of PAH<sup>+</sup> cations: evolution of hydration network in naphthalene<sup>+</sup>-(H<sub>2</sub>O)<sub>n</sub> clusters ( $n \leq 5$ )

Kuntal Chatterjee, Otto Dopfer

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The interaction of polycyclic aromatic hydrocarbon molecules with water ( $H_2O = W$ ) is of fundamental importance in chemistry and biology. Herein, size-selected microhydrated naphthalene cation nanoclusters,  $Np^+ \cdot W_n$  ( $n \leq 5$ ), are characterized by infrared photodissociation (IRPD) spectroscopy in the C-H and O-H stretch range to follow the stepwise evolution of the hydration network around this prototypical PAH<sup>+</sup> cation. The IRPD spectra are highly sensitive to the hydration structure and are analyzed by dispersion-corrected density functional theory calculations (B3LYP-D3/aug-cc-pVTZ) to determine the predominant structural isomers. For  $n = 1$ , W forms a bifurcated  $CH \cdots O$  ionic hydrogen bond (H-bond) to two acidic CH protons of the bicyclic ring. For  $n \geq 2$ , the formation of H-bonded solvent networks dominates over interior ion solvation, because of strong cooperativity in the former case. For  $n \geq 3$ , cyclic  $W_n$  solvent structures are attached to the CH protons of  $Np^+$ . However, while for  $n = 3$  the  $W_3$  ring binds in the  $CH \cdots O$  plane to  $Np^+$ , for  $n \geq 4$  the cyclic  $W_n$  clusters are additionally stabilized by stacking interactions, leading to sandwich-type configurations. No intracluster proton transfer from  $Np^+$  to the  $W_n$  solvent is observed in the studied size range ( $n \leq 5$ ), because of the high proton affinity of the naphthyl radical compared to  $W_n$ . This is different from microhydrated benzene<sup>+</sup> clusters,  $(Bz \cdot W_n)^+$ , for which proton transfer is energetically favorable for  $n \geq 4$  due to the much lower proton affinity of the phenyl radical. Hence, because of the presence of polycyclic rings, the interaction of PAH<sup>+</sup> cations with W is qualitatively different from that of monocyclic  $Bz^+$  with respect to interaction strength, structure of the hydration shell, and chemical reactivity. These differences are rationalized and quantified by quantum chemical analysis using the natural bond orbital (NBO) and noncovalent interaction (NCI) approaches.

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Chem. Sci., 2018,9, 2301-2318

<http://pubs.rsc.org/en/content/articlelanding/2018/sc/c7sc05124g#!divAbstract>

# Infrared spectroscopy of hydrated polycyclic aromatic hydrocarbon cations: naphthalene<sup>+</sup>-water

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Polycyclic aromatic hydrocarbons (PAHs) are suggested to occur in interstellar media and ice grains. It is important to characterize hydrated PAHs and their cations to explore their stability in interstellar and biological media. Herein, the infrared photodissociation (IRPD) spectrum of the naphthalene<sup>+</sup>-H<sub>2</sub>O radical cation (Np<sup>+</sup>-H<sub>2</sub>O) recorded in the O-H and C-H stretch range is analysed by dispersion-corrected density functional theory calculations at the B3LYP-D3/aug-cc-pVTZ level to determine its structure and intermolecular bonding. Monohydration of Np<sup>+</sup> in its 2A<sub>u</sub> ground electronic state leads to the formation of a bifurcated CH<sup>+</sup>⋯O ionic hydrogen bond (H-bond), in which the lone pairs of H<sub>2</sub>O bind to two adjacent CH proton donors of the two aromatic rings. The frequency-dependent branching ratios observed for IRPD of cold Np<sup>+</sup>-H<sub>2</sub>O-Ar clusters allows the estimation of the dissociation energy of Np<sup>+</sup>-H<sub>2</sub>O as  $D_0 \sim 2800 \pm 300 \text{ cm}^{-1}$ . The monohydration motif of Np<sup>+</sup> differs qualitatively from that of the benzene cation in both structure and binding energy, indicating the strong influence of the multiple aromatic rings on the hydration of PAH<sup>+</sup> cations. This difference is rationalized by natural bond orbital analysis of the ionic H-bond motif. Comparison with neutral Np-H<sub>2</sub>O reveals the large change in structure and bond strength of the hydrated PAHs upon ionization. While neutral Np-H<sub>2</sub>O is stabilized by weak  $\pi$  H-bonds (OH<sup>+</sup>⋯ $\pi$ ,  $\pi$ -stacking), strong cation-dipole forces favour a planar bifurcated CH<sup>+</sup>⋯O ionic H-bond in Np-H<sub>2</sub>O.

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Phys. Chem. Chem. Phys., 2017, 19, 32262-32271, HOT Article

<http://pubs.rsc.org/en/content/articlelanding/2017/cp/c7cp06893j#!divAbstract>

# Meetings

## 2018 NASA Laboratory Astrophysics Workshop

University of Georgia, Athens, GA, USA

8-11 April 2018

The purpose of the NASA Laboratory Astrophysics Workshop (LAW) 2018 is to identify and prioritize the critical laboratory astrophysics data needs to meet the demands of NASA's current and near-term astrophysics missions. This meeting will also provide a forum within which the community can present and review the current state of knowledge in laboratory astrophysics and identify challenges and opportunities for the field. The agenda will include 16 invited talks, contributed talks, posters, panel discussions, and break-out sessions. Registration is \$250 with a reduced rate of \$125 for students and those who received their Ph.D. after April 1, 2016.

### Important Deadlines

- Registration: March 23, 2018, 11:59pm EDT (extended)
- Abstracts: March 22, 2018, 11:59pm EDT
- Student travel assistance: Friday, March 23, 11:59pm EDT

### Confirmed Invited Speakers

Keith Arnaud (NASA GSFC)  
Peter Bernath (Old Dominion U.)  
Nancy Brickhouse (CfA/SAO)  
Steven Federman (U. Toledo)  
Adam Foster (CfA/SAO)  
Harshal Gupta (NSF)  
Natalie Hell (LLNL)  
Taisuke Nagayama (Sandia NL)  
Els Peeters (U. Western Ontario)  
Robert Petre (NASA GSFC)  
Klaus Pontoppidan (STScI)  
Farid Salama (NASA Ames)  
Kimberly Ennico Smith (NASA Ames/SOFIA)  
Frank Timmes (Arizona State U.)  
Susanna Widicus-Weaver (Emory U.)  
Laurent Wiesenfeld (U. Grenoble)

**Scientific Organizing Committee**

Phillip Stancil (UGA), co-chair  
Doug Hudgins (NASA HQ), co-chair  
Gary Ferland (U. Kentucky)  
Bill Latter (NASA HQ)  
Stefanie Milam (NASA GSFC)  
David Neufeld (Johns Hopkins U.)  
Ella Sciamma-O'Brien (NASA Ames)  
Alan Smale (NASA GSFC)  
Randall Smith (SAO)  
Artemis Spyrou (Michigan State U.)  
Lisa Storrie-Lombardi (JPL)  
Glenn Wahlgren (STScI)

*The workshop is supported by the NASA Astrophysics Division, the Joint Institute for Nuclear Astrophysics, the UGA Franklin College of Arts and Sciences, and the UGA Office of Research.*

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Webpage: <http://www.physast.uga.edu/workshops/law>

# Announcements

## PhD student position at Leiden Observatory

**Advertised by Dr. Jordy Bouwman**

A 48 month fully funded PhD student position in the field of laboratory and computational astrochemistry is available at the Sackler Laboratory for Astrophysics, Leiden University, the Netherlands.

The project entails a combined experimental and computational study of gas phase radical-neutral chemical reactions that lead to complex organic molecules under interstellar conditions. The main goal is to supply isomer specific identifications and branching information that are crucial for astrochemical modeling and to gain fundamental insight into the reaction mechanisms at play. To achieve this, chemical reactions will be characterized by means of an imaging photoelectron photoion coincidence spectrometer connected to a synchrotron. Supplementary quantum chemical computations will be performed. The research will be performed in close collaboration with beamline scientists (Drs. Bodi & Hemberger) at the Vacuum Ultraviolet Beamline of the Swiss Light Source at Paul Scherrer Institute and frequent visits to the synchrotron facility are integral part of the project. See also <http://home.strw.leidenuniv.nl/~bouwman/index.html>.

Candidates with a background in (physical) chemistry and strong affinity with astronomy/astrochemistry are strongly encouraged to apply. Basic knowledge in the direction of quantum chemical computations is beneficial.

The PhD student will be appointed at the Sackler Laboratory for Astrophysics (<http://www.laboratory-astrophysics.eu>) within Leiden Observatory at the Faculty of Science of Leiden University. The project is part of the research within the framework of a VIDI grant funded by the Dutch Organization for Scientific Research.

For applications, please send a cover letter, a resume, and contact information of two persons willing to provide a letter of support to Dr. Jordy Bouwman ([bouwman@strw.leidenuniv.nl](mailto:bouwman@strw.leidenuniv.nl)). This is also the address where additional information can be obtained.

**Application deadline: June 1st, 2018.**

**Contact: Dr. Jordy Bouwman**

E-mail: [bouwman@strw.leidenuniv.nl](mailto:bouwman@strw.leidenuniv.nl)

## AstroPAH Newsletter

<http://astropah-news.strw.leidenuniv.nl>  
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Next issue: 19 April 2018  
Submission deadline: 6 April 2018