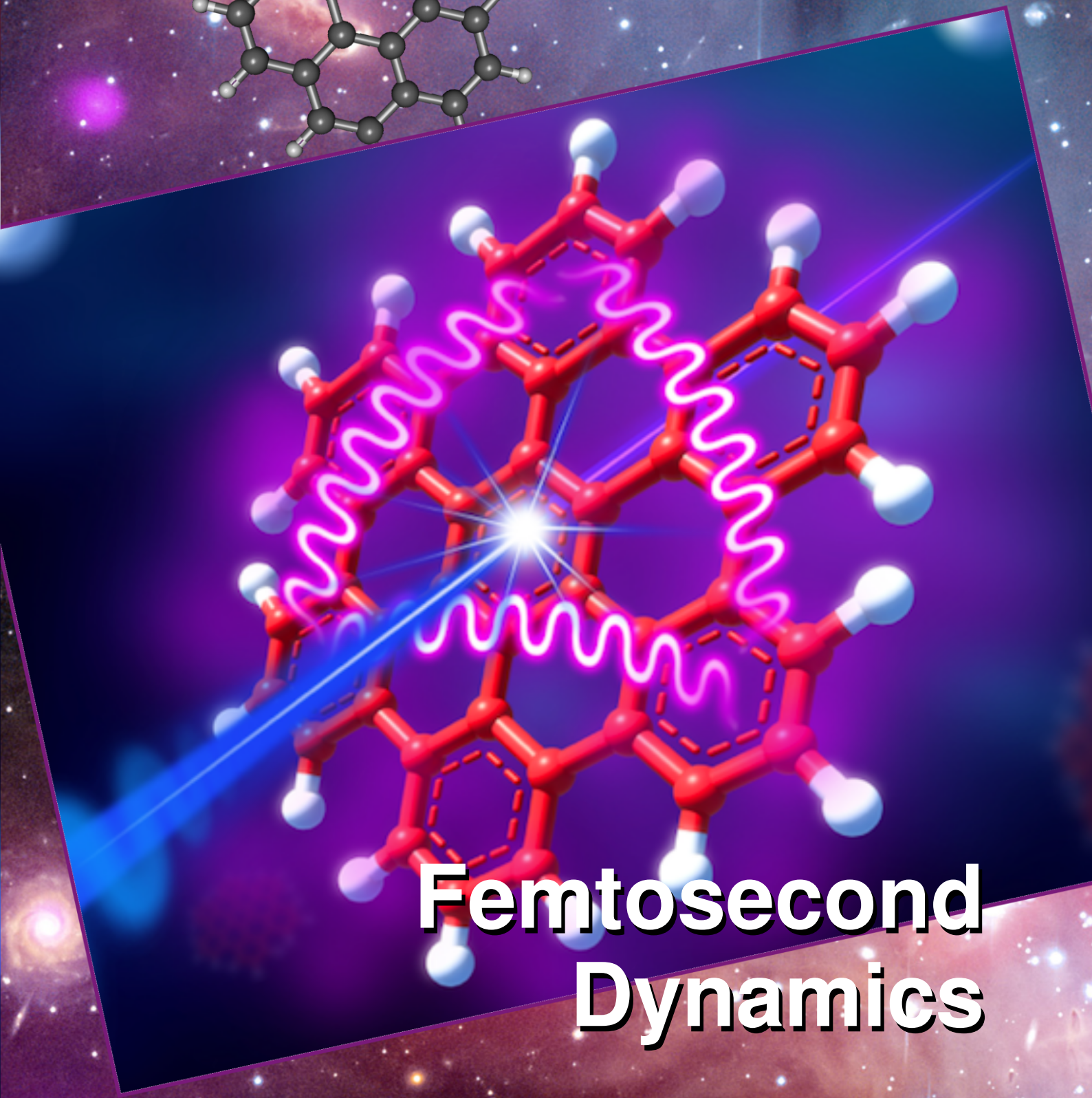
AstroPAH

A Newsletter on Astronomical PAHs

Issue 74 • December 2020



Femtosecond Dynamics

Editorial

Dear Colleagues,

Welcome to our 74^{th} AstroPAH volume, our last one for 2020! We hope all of you are healthy and doing well.

This month's cover picture represents an illustration showing that the irradiation of PAHs by energetic VUV/XUV photons resulting in unique femtosecond dynamics. More information on that along with many other recent PAH-blications can be found in the Abstract section.

Last month, we welcomed three new editors to our Editorial Board, so we are happy to have them introduce themselves in three interviews as part of our In Focus. Welcome again, Dona, Kelvin and Sandra!

We would also like to congratulate Dr. Christine Joblin on being awarded the Huy Duong Bui prize of the Académie des Sciences for her research on the laboratory astrophysics of PAHs and fullerenes!

Check out our Announcements for a PhD opportunity and Postdoctoral fellowship at the University of Hawaii at Manoa with Prof. Ralf Kaiser. We also advertise for the 2021 LAD Dissertation Prize. If you or anyone you might know is eligible, be sure to submit your complete application by the end of the month!

We hope you enjoy reading our newsletter, and we thank you for your dedication and interest in AstroPAH! In the meantime, please continue sending us your contributions, and if you wish to contact us, feel free to use our email. We will be taking our January break and see you in February of 2021!

Please be safe, stay healthy and happy holidays to all!

Enjoy reading our newsletter!

The Editorial Team

Next issue: 19 February 2021.
Submission deadline: 5 February 2021.

Contents

PAH Picture of the Month

Artistic illustration showing that irradiation of PAHs by energetic VUV/XUV photons triggers femtosecond dynamics that are governed by the quantum nature of the PAH. This new process has direct consequences on the description of interstellar PAHs under energetic irradiation, as it is general for all the PAH family. More information can be found in the abstract session.

Credits: Marius Hervé et al. (2020)

Contact us:

astropah@strw.leidenuniv.nl
http://astropah-news.strw.leidenuniv.nl
Click here to Subscribe to AstroPAH
Click here to Contribute to AstroPAH

This newsletter is edited in LaTeX. Newsletter Design by: Isabel Aleman. Image Credits: Background image in this page: NASA, ESA, and the Hubble Heritage Team (STScI/AURA). Headers background: X-ray and optical image composition. X-ray by Chandra: NASA/CXC/Univ.Potsdam/L.Oskinova et al; Optical by Hubble: NASA/STScI; Infrared by Spitzer: NASA/JPL-Caltech.

Interview with
Kin Long Kelvin Lee
New Member of the AstroPAH Editorial Board

I was born in Hong Kong, and spent most of my childhood in Auckland, New Zealand. My family moved to Sydney, Australia when I was just beginning high school. After graduating high school, I originally I wanted to become a high school teacher, but after the first two years at the University of Sydney I changed my priorities; I ended up completing my BSc in Chemistry and Plant Sciences, and completed an additional year of research for my Honours degree with Professors Scott Kable and Meredith Jordan. Afterwards, I moved onto a PhD at the University of New South Wales, again jointly supervised by Professors Kable and Jordan, on the photodissociation dynamics of small aldehydes studied using velocity-map ion imaging and quasi-classical trajectory simulations. I then moved to a postdoctoral position with Drs. Michael McCarthy and Carl Gottlieb at the Center for Astrophysics, Harvard & Smithsonian, where I initially worked on refractory species of relevance to dust formation in asymptotic giant branch stars. Over the three years I worked at the CfA, I spent a significant amount of time on open-source and reproducible research, combining quantum chemistry, high resolution spectroscopy, and machine learning to analyzing large volumes of astronomical and laboratory rotational spectra. Currently, I am working with Assistant Professor Brett McGuire at the Massachusetts Institute of Technology, where we are working broadly on topics of astrochemistry.

Can you tell us how you got into PAH-related research?

Professor Timothy Schmidt (first at University of Sydney, and now at the University of New South Wales) has a very extensive research program on PAHs, and while I was there, their relevance to the diffuse interstellar bands; a long standing and puzzling question in

astrophysics. I was fortunate enough to participate in some of the spectroscopic work on protonated naphthalene, and generally took a lot of interest in talks and laboratory work. More recently, I am involved as a member of the GOTHAM and ARKHAM collaborations—two large scale observations campaigns using the Green Bank Telescope in West Virginia (USA)—which seek to understand the intermediate molecules that bridge the gap between small radicals and carbon chains that are ubiqutious in space, and the large PAHs: how they form, their histories, and their distributions.

What are you working on right now?

I'm currently involved in a number of projects mainly in astrochemistry. Experimentally, we are currently building a new spectrometer at MIT, which will hopefully provide new data to guide astronomical observations. Computationally, I work on Bayesian and deep learning models for analyzing molecular spectra in new ways. From a quantum chemistry standpoint, I carry out first principles calculations of molecular structures and thermochemistry to guide experimental and observational work.

Which open question about PAHs would you like to see answered in the near future?

I would like to understand how they are linked with small molecules! Whether molecules like benzonitrile are formed under cold dark conditions, or via fragmentation of larger species like PAHs, or inherited!

What does it mean for you to be part of the AstroPAH editorial board?

I think it is a valuable opportunity to provide a service for the scientific community, both as a medium for research, as well as a platform or a voice for researchers.

What was the most important advice somebody gave you?

"You can grow to like a project, but it's harder to grow to like people." This was told to me in the context of looking for research groups to work with: for early-career researchers, this means talking to the members of a group and not just the PI about a research area that interests you. Hard work is made bearable with good people around you, while the inverse is not necessarily true.

What do you do outside of work?

As a nerd, I play a lot of video games. I also love traveling and eating my way around the world: I was fortunate enough to do a lot of that as a postdoc! My most memorable places are Saariselkä in Finland, and Banff National Park in Canada.

How has the COVID-19 pandemic impacted your professional and personal life?

On a personal level, one of the conferences I was looking forward to attending but was cancelled was in Sydney; I haven't visited Australia in three years and was beginning to miss friends, family, and the food. Professionally, the pandemic definitely changed my career plans: fewer places in academia and industry are hiring, and networking has become much more difficult.

How do you balance your personal and professional life?

My current advisor has given me quite a lot of good advice in doing so: to have strict rules to not expect work done on weekends; to draw boundaries where appropriate. Early on in my postdoc this balance was difficult to find, and after a while you learn that you can only do so much in a day, week, month, and year. On another note, only *you* know how you feel: you will have to make time to focus on yourself when you feel like you need it.

Interview with
Donatella Loru
New Member of the AstroPAH Editorial Board

My name is Donatella Loru. I was born and raised in a small town in the south of Sardinia (Italy). I obtained my BSc in chemistry at the University of Cagliari and then moved to the University of Bologna to complete an MSc in rotational spectroscopy under the supervision of Prof. Walther Caminati. In 2013, I joined the group of Maria Eugenia Sanz at King's College London as a PhD student. As part of my PhD project, I developed and set-up a broadband rotational spectrometer operating in the 2-8 GHz frequency range, which I then used to investigate the structure and conformations of several odorants, namely terpenoids, and their clusters with ethanol, with the aim of mimicking the intermolecular interactions occurring between odorants and olfactory receptors. In 2017, I defended my PhD thesis, for which I was awarded the Elsevier "Outstanding Thesis Prize". Afterwards, I decided to move further north, to the city of Hamburg, where I joined the group of Prof. Melanie Schnell, at the Deutsches Elektronen-Synchrotron (DESY), and I started my journey in the field of astrochemistry. In March 2019, I was awarded the Alexander von Humboldt Postdoctoral Fellowship. Using spectroscopic techniques, such as high-resolution rotational spectroscopy and IR-UV ion dip spectroscopy, my current research mainly focuses on PAHs, their clusters with themselves and with molecules detected in interstellar ice grains, and on their reactivity under the energetic conditions created by an electrical discharge source.

Can you tell us how you got into PAH-related research?

After my PhD, I wanted to keep working in the field of rotational spectroscopy; at the same time, I always wanted to explore different spectroscopic techniques and topics. When I joined the group of Prof. Melanie Schnell, I was offered the great possibility to become embedded in an astrochemistry project. A branch of this research exploits a multi-spectroscopic approach

to investigate the chemical processes that PAHs can undergo in different experimental conditions. Thus, a new topic and experimental techniques: a perfect match to what I was looking for after my PhD, indeed!

What are you working on right now?

Currently, my research mainly focuses on the reactivity of PAHs and of PAHs in mixture with other astrochemically relevant molecules under the energetic conditions generated by an electrical discharge source. I am particularly interested in understanding how the size, shape, and degree of aromaticity of PAHs influence, both qualitatively and quantitatively, their chemistry under similar experimental conditions. Under plasma conditions, previously unobserved molecules can also be formed, which can then be characterized and observed using radio- or IR-astronomy. In the laboratory experiments, the discharge products are formed with an electrical discharge nozzle and probed using cutting-edge spectroscopic techniques such as high-resolution microwave spectroscopy and mass-selective IR-UV ion dip spectroscopy. The two techniques are complementary to each other. The combination of IR-UV spectroscopy with mass spectrometry has the benefits of probing and characterizing the discharge species both via their mass as well as via their IR signatures. Microwave spectroscopy allows for the identification of molecules via their microwave spectra, known to be fingerprints of the molecules. Therefore, the latter allows the identification of species which cannot be unambiguously identified using IR-UV ion dip spectroscopy. Furthermore, molecular species without a permanent dipole moment are invisible to microwave spectroscopy but can be probed using mass-selective IR-UV ion dip spectroscopy. Using high-resolution microwave spectroscopy, I am also performing structural studies of complexes of PAHs with water. By looking at the microhydrated clusters of PAHs, we can obtain information which can potentially be used to disentangle the role of PAHs in the first steps of interstellar ice grains formation.

Which open question about PAHs would you like to see answered in the near future?

The presence and role of PAHs in the interstellar medium is quite puzzling and, of course, there are many open questions that I would like to see answered. For example, I would like to know about their formation mechanisms. Are PAHs formed via a top-down or a bottom-up approach? What is their role in the interstellar medium: how do PAHs influence the physics and chemistry of the interstellar environments in which they are detected?

What does it mean for you to be part of the AstroPAH editorial board?

Being part of the AstroPAH board gives me the wonderful opportunity to contribute to a research tool of great value for the astrochemistry community. It also provides an opportunity to get to know the community, which is especially important for me right now, being relatively “new” to field of astrochemistry.

What was the most important advice somebody gave you?

The most valuable advice that I have been given is “Be confident and believe in yourself”. Although sometimes I find hard to follow this advice, this helped me get through the different stages of my career so far.

What do you do outside of work?

I love photography. I recently bought a reflex camera and took a one-to-one photography class, which I enjoyed very much! I particularly like taking pictures of reflections on water at night. From this point of view, Hamburg is the perfect city. With its 2300 bridges, this city offers plenty of inspirations for pictures where dark, light, and reflections are the main protagonists. I am looking forward to exploring a bit more of this passion as soon as the pandemic will be over. During lockdown, I also discovered my passion for baking bread, which has now become one of my favorite hobbies! I also enjoy cooking, fresh pasta and pizza in particular - I guess this is not very surprising considering that I am Italian!

How has the COVID-19 pandemic impacted your professional and personal life?

My professional life has not been particularly affected by COVID-19. Hamburg was not hit so hard by it, at least during the first wave; therefore I have only experienced a “soft” lockdown. I still had the possibility to work in the lab and go to the office, if needed, always respecting the safety rules. What I understood during these unprecedented times is that I am not a “working-from-home” type of person. I like leaving the house in the morning and coming back home in the evening feeling that my working day is complete and that it is time to slow down, relax, and enjoy the rest of the day (at least when there are no deadlines approaching!). When I work from home, I find establishing a daily routine in which I can draw boundaries between my professional and personal life very challenging. Overall, I guess, my personal life is what has been affected the most. Living far from my family has been particularly challenging this year. This year will be the first time since I left Sardinia that I will not be able to spend the Christmas holidays with my family. Hopefully this will be over soon and we will be grateful for everything that we have been missing!

How do you balance your personal and professional life?

Drawing boundaries between personal and professional life can be difficult in academia. I always try, when possible, to have a few hours in the evening to do something that is not related to work and to work as little as possible on the weekends. I realized that taking a step back and having some quality time for me is often of great benefit to my health, but also to my productivity at work.

Interview with
Sandra Wiersma
New Member of the AstroPAH Editorial Board

My name is Sandra Wiersma, and did my PhD at the University of Amsterdam, in the group of Dr. ir. Annemieke Petrignani, one of the founding editors of the AstroPAH Newsletter. While I was scientifically embedded in Annemieke's group, I was stationed at the FELIX Laboratory in Nijmegen. There, I worked on the mid-infrared characterization of PAHs and PAH related molecules. I used an FT-ICR mass spectrometer which was placed inside the cavity of the infrared free-electron laser to have access to the highest possible IR fluences. This allows us to fragment even the most strongly-bound PAH with just IR photons, down to 100 μm! To make sense of my data in an astronomical context, I collaborated with astronomer and theorist Dr. Alessandra Candian, another founding editor of this newsletter. Last month, I moved to Toulouse, where I began a post-doc with Dr. Christine Joblin at the Institut de Recherche en Astrophysique et Planétologie (IRAP). Working with people who are just as happy and enthusiastic to learn new things every day is what makes this field such a dream to work in.

Can you tell us how you got into PAH-related research?

I have had very broad interests for as long as I can remember, and I have loved space and science ever since I watched *Star Trek: Voyager* with my dad and my brother when I was a little girl. The intersection of physics and chemistry has fascinated me since I was a bachelor student in physics at the Radboud University in Nijmegen. I used most of the elective space in my curriculum to take chemistry classes. I was also the head of the colloquium committee at the physics students club. We invited a new speaker from another university every month to give a lunch talk to our students. One of the speakers I invited was prof. Harold Linnartz. His talk introduced me to the concept of astrochemistry, and it left a mark. At that point in time, I was also very interested in inorganic chemistry, because chemically, metals behave

in such an erratic way. For my bachelor project, I worked on the production on gas-phase platinum clusters in a molecular beam at the FELIX Laboratory, under the supervision of Dr. Joost Bakker. During that project, I discovered just how much I love to work in a lab. Pushing hard to make an apparatus do what you want it to do, and then the rush when you get those results you've worked so hard for... I fail to see how you could like solving integrals more than working in a lab. I hadn't felt quite so good about myself and my abilities in a long time. For my master thesis, I moved to Ulm, Germany for a year, where I studied iron sulfide clusters and their reactivity towards small molecules, under the supervision of Dr. hab. Sandra Lang. This work wasn't just interesting from an industrial catalysis point-of-view, but also with regard to the origins of life, which was the cooler topic of the two to me. When Joost told me that they had two PhD openings at FELIX, one for him to work on copper clusters for CO_2 conversion, and one with Annemieke to do work on the infrared spectroscopy of PAHs, it was a tough choice, but you will all agree with me that astrochemistry was the right choice to make.

What are you working on right now?

I just started as a post-doc in Dr. Christine Joblin's group at the IRAP in Toulouse. Because I love to get my hands a little dirty and get intimately acquainted with the machine I work with, my first project here will be to get the new apparatus — PIRENEA-2 — to work. It uses a double laser vaporization source to bring clusters of various chemical compositions into the gas phase, which are then mass-selectively introduced into a cryogenic quadrupole ion trap. Inside the trap, the gases can be introduced to react with the clusters at different temperatures. The clusters are then pulsed out of the trap, into an FT-ICR mass spectrometer. This FT-ICR is also cryogenically cooled, and UV lasers can be coupled in to perform dissociation studies on the cluster complexes. At the moment, the source and the FT-ICR work independently, and I will work with Dr. Anthony Bonnamy to get all of these different parts to work together. Once the apparatus is operational, I will produce silicon carbides, and study their reactions with small, astrochemically relevant hydrocarbons. In a sense this project combines three things I love, experimental challenges, clusters, and astrochemistry. If I can get it to work with the simple hydrocarbons, I might even get back to studying PAHs.

Which open question about PAHs would you like to see answered in the near future?

I would really love it if JWST could find more clues on if and how PAHs absorb deuterium in the ISM. In my first paper (Wiersma, S. D. *et al.*, (2020). A& A, 635, A9.) we showed that deuterated PAHs are more much more likely to lose regular hydrogen than deuterium, far exceeding what would be expected from isotopic differences. We propose a scrambling mechanism along the rim of the molecule, through which PAHs can easily swap a lot of their regular hydrogens for deuterium. We believe that signs of these swaps can be found in the aliphatic/aromatic C-H/C-D stretching bands in the 3-5 μm spectral region. JWST will provide the necessary sensitivity to see these subtle ratios, and I hope there is an observational astrochemist who read my paper and considers this an interesting prospect as well!

What does it mean for you to be part of the AstroPAH editorial board?

I've been a loyal reader from the start of my PhD, and not just because Annemieke was my supervisor and I worked with Alessandra on every project. AstroPAH provides an invaluable service to the community, and I am really happy that I get to be a part of it. I am also grateful for the opportunity to expand my network and introduce myself to the readers at this point in my career.

What was the most important advice somebody gave you?

"You don't have to be the smartest person around to be successful, you just have to work your hardest." This is paraphrased from a much longer pep talk Joost gave me. I've often felt like I wasn't smart enough to be a scientist, because there are always people around who are able to understand things faster than I can, but it's really just a matter of trying harder and taking your time. Besides, this is an attitude that is especially useful when you work in a laboratory setting.

What do you do outside of work?

Cooking, and especially cooking for people is one of my favorite things. Seeing those I care about enjoy my food is almost as good as eating the food itself. I spend a huge amount of time thinking about food on a daily basis, which often made me a total weirdo in the "bread + cheese = lunch" Netherlands, but will probably make me fit in perfectly in France. Another good way to unwind for me is through sports. At my craziest, I used to do three different sports, and I wanted to be good at one of them at least. Three runs, at least two bouldering sessions and one Krav Maga class was my weekly routine. There are three very good reasons for this absurd schedule: 1) it allows me to eat whatever I want 2) it makes me leave work on time 3) if I plan it right, I can also socialize in the meantime.

How has the COVID-19 pandemic impacted your professional and personal life?

It was not as hard for me as it was for a lot of others because the crisis hit the Netherlands when I was supposed to turn into a thesis-hermit anyway. I can blame not having dinner parties, movie nights or Krav Maga on COVID, but these are things that would have disappeared from my life because of my thesis anyhow. I was very lucky to have just moved into a big house with a separate office when the crisis hit the Netherlands. This helped me keep my personal and my professional life separate. I did really miss having an office with others, especially because they became good friends and we had a good atmosphere. I was used to just bounce ideas at my coworkers, which made being all alone in the office very demoralizing. You can't just call someone to ask them "does this sentence sound pedantic to you?". My boyfriend moved into my house during my last month of writing, and joined me in the office. This was exactly what I needed to push through at the end.

How do you balance your personal and professional life?

Evidently, that balance was tilted a bit too much towards work. Right now, I'm trying to get back into a healthier routine, although that is difficult between finishing a PhD, getting used to a new job, and getting paperwork done during a lockdown. I try to work as little as possible on weekends, and I talk to my boyfriend every day. He will often tell me to take a break when I need one, and I find it easier to do that when someone else tells me to.

Abstracts

Dissociative Single and Double Photoionization of Biphenyl ($C_{12}H_{10}$) by Soft X-rays in Planetary Nebulae

Heidy M. Quitián-Lara[1], Felipe Fantuzzi[2,3,4], Ricardo R. Oliveira[2], Marco A. C. Nascimento[2], Wania Wolf[5] and Heloisa M. Boechat-Roberty[1]

[1] Observatório do Valongo, Universidade Federal do Rio de Janeiro, Ladeira Pedro Antônio 43, 20080090 Rio de Janeiro, Brazil.

[2] Instituto de Química, Universidade Federal do Rio de Janeiro, Av. Athos da Silveira Ramos 149, 21941909 Rio de Janeiro, Brazil.

[3] Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

[4] Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Emil-Fischer-Straße 42, 97074 Würzburg, Germany.

[5] Instituto de Física, Universidade Federal do Rio de Janeiro, Av. Athos da Silveira Ramos 149, 21941972 Rio de Janeiro, Brazil.

Biphenyl ($C_{12}H_{10}$), or phenylbenzene, is an important building block of polycyclic aromatic hydrocarbons (PAHs), whose infrared spectral features are present in a variety of galactic and extragalactic sources. In this work, we use synchrotron radiation coupled with time-of-flight spectrometry to study the photoionization and photodissociation processes of biphenyl upon its interaction with soft X-ray photons at energies around the inner-shell C1s resonance. These results are compared with our previous studies with benzene (C_6H_6) and naphthalene ($C_{10}H_8$), and discussed in the context of four planetary nebulae featuring PAH infrared emission: BD+30°3639, NGC 7027, NGC 5315, and NGC 40. We show that the mass spectrum of biphenyl before the C1s resonance energy is dominated by single photoionization processes leading to $C_6H_5^+$, $C_6H_4^{+\cdot}$, and $C_{12}H_{10}^{+\cdot}$, while after the resonance dissociation following multiple photoionization processes is dominant. The release of neutral C_6H_6 and $C_6H_5\cdot$ species accounts for one of the most relevant dissociation processes starting from the doubly ionized biphenyl, indicating that heterolytic charge separation of the two phenyl rings is also achieved. By using quantum chemical calculations, we show that the biphenylic structure is a high-lying isomer of the singly and doubly ionized $C_{12}H_{10}$ species, whose minimum energy geometries are related to the acenaphthene molecule, composed of a C_2-bridged naphthalene. Furthermore, we estimate the lifetime of biphenyl for 275 and 310 eV in photon-dominated regions of planetary nebulae. We discuss distinct processes that may enhance its lifetime and those of other small-sized PAHs in such astrophysical environments.

E-mail: heloisa@astro.ufrj.br

MNRAS, 499(4), 6066 (2020)

https://doi.org/10.1093/mnras/staa3181

Dependence upon charge of the vibrational spectra of small Polycyclic Aromatic Hydrocarbon clusters: the example of pyrene

Léo Dontot[1], Fernand Spiegelman[1], Sébastien Zamith[2], and Mathias Rapacioli[1]

[1] Laboratoire de Chimie et Physique Quantique (LCPQ/IRSAMC), UMR5626, Université de Toulouse (UPS) and CNRS, 118 Route de Narbonne, 31062 Toulouse, France

[2] Laboratoire Collisions Agrégats Réactivité (LCAR/IRSAMC), UMR5589, Université de Toulouse (UPS) and CNRS, 118 Route de Narbonne, 31062 Toulouse, France

Infrared spectra are computed for neutral and cationic clusters of Polycyclic Aromatic Hydrocarbon clusters, namely $(C_{16}H_{10})^{(0/+)}_{n=1,4}$, using the Density Functional based Tight Binding scheme combined with a Configuration Interaction scheme (DFTB-CI) in the double harmonic approximation. Cross-comparison is carried out with DFT and simple DFTB. Similarly to the monomer cation, the IR spectra of cluster cations are characterized by a depletion of the intensity of the CH stretch modes around 3000 cm^{-1}, with a weak revival for n = 3 and 4. The in-plane CCC modes in the region 1400-2000 cm^{-1} are enhanced while the CH bending modes in the range 700-1000 cm^{-1} are significantly weakened with respect to the monomer cation, in particular for n = 2. Finally, soft modes corresponding to diedral fluctuations of the monomers within the central stack of the ion structure, possibly mixed with monomer folding, are also observed in the region 70–120 cm^{-1}.

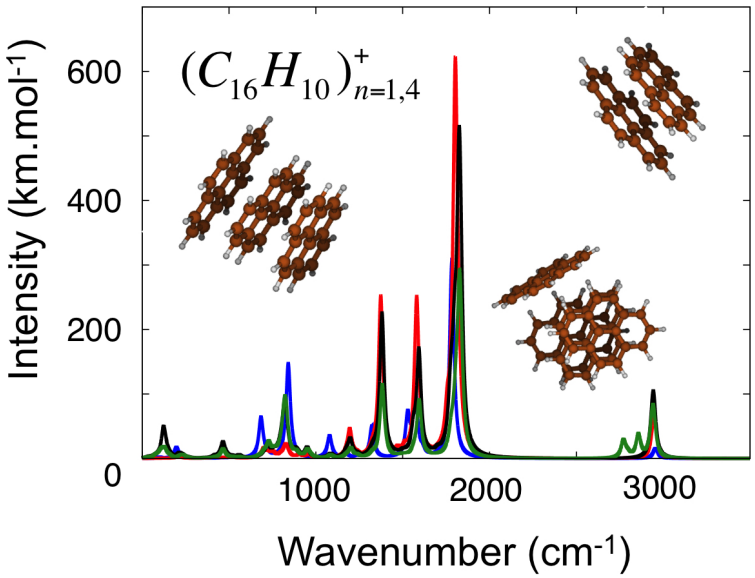


Figure 1: *IR spectra of cationic pyrene clusters. With kind permission of The European Physical Journal (EPJ).*

E-mail: mathias.rapacioli@irsamc.ups-tlse.fr

Eur. Phys. J. D, 74: 216 (2020)

https://epjd.epj.org/articles/epjd/abs/2020/11/d200081/d200081.html

Formation of Complex Organic Molecules (COMs) from Polycyclic Aromatic Hydrocarbons (PAHs): Implications for ISM IR Emission Plateaus and Solar System Organics

A. L. Mattioda[1], G. A. Cruz-Diaz[1,2], A. Ging[1], M. Barnhardt[1], C. Boersma[1,3], L. J. Allamandola[1,2], T. Schneider[4], J. Vaughn[4], B. Phillips[4] and A. Ricca[1,5]

[1] NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035, USA

[2] Bay Area Environmental Research Institute, P.O. Box 25, Moffett Field, CA 94035, USA

[3] San Jose State University Research Foundation, 210 North 4th Street, San Jose, CA 95112, USA

[4] NASA Marshall Space Flight Center, Huntsville, AL, 35824, USA

[5] SETI Institute, 189 Bernardo Ave, Suite 200, Mountain View, CA 94043, USA

The presence of complex organic molecules (COMs) in a variety of solar system objects has prompted various theories regarding their origins. This paper reports on a series of proton, electron, and UV radiation experiments, conducted singly and in combination, on polycyclic aromatic hydrocarbon (PAH) thin films to determine if PAH-related materials could be related to COMs. Fourier transform infrared (FTIR) and mass spectra reveal that the PAHs are fragmented and altered, producing new infrared features and a mass spectral pattern similar to those from small aliphatic and larger saturated hydrocarbon chain and ring systems. Mass spectra after proton and electron irradiation exhibit significant differences. The proton irradiation products appear to contain more oxygen-related species, possibly the result of higher H_2O concentrations in the vacuum chamber, whereas electron irradiation generates a more abundant, larger mass organic species mass spectral pattern. Combined irradiation produces a superposition of the proton and electron results, with some subtle differences. Mass spectral patterns resulting from electron and combined irradiation compare favorably to Cassini ion neutral mass spectrometer (INMS) measurements of particles falling from Saturn's inner rings into its upper atmosphere. FTIR results are compared to PAH emission from interstellar sources and absorption components in IR spectra observed toward low-mass young stellar objects (YSOs). Notably, some newly reported broad IR features appear very similar in structure to the plateaus underlying the astronomical 3.2-3.6, 6-9, and 10-15 μm emission plateaus and several of the absorption components found in spectra observed toward YSOs. The studies also indicate that the presence of other species, such as H_2O, may significantly impact the radiation products. These results point to the fact that a top-down synthesis of solar system COMs is possible via irradiative processing of PAHs.

E-mail: andrew.mattioda@nasa.gov

ACS Earth and Space Chemistry, accepted, 2020

https://dx.doi.org/10.1021/acsearthspacechem.0c00165

The NASA Ames PAH IR Spectroscopic Database: The Laboratory Spectra

A. L. Mattioda[1], D. M. Hudgins[2], C. Boersma[1], C. W. Bauschlicher Jr.[3], A. Ricca[1,4], J. Cami[4,5,6], E. Peeters[4,5,6], F. Sánchez de Armas[4], G. Puerta Saborido[4], and L. J. Allamandola[1]

[1] NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035, USA

[2] NASA Headquarters, MS 3Y28, 300 E St. SW, Washington, DC 20546, USA

[3] NASA Ames Research Center, MS 230-3, Moffett Field, CA 94035, USA

[4] Carl Sagan Center, SETI Institute, 189 N. Bernardo Avenue, Suite 200, Mountain View, CA 94043, USA

[5] Department of Physics and Astronomy, The University of Western Ontario, London, ON N6A 3K7, Canada

[6] The Institute for Earth and Space Exploration, The University of Western Ontario, London ON N6A 3K7, Canada

The astronomical emission features, formerly known as the unidentified infrared bands, are now commonly ascribed to polycyclic aromatic hydrocarbons (PAHs). The laboratory experiments and computational modeling performed at NASA Ames Research Center generated a collection of PAH IR spectra that have been used to test and refine the PAH model. These data have been assembled into the NASA Ames PAH IR Spectroscopic Database (PAHdb). PAHdb's library of computed spectra, currently at version 3.20, contains data on more than 4000 species and the library of laboratory-measured spectra, currently at version 3.00, contains data on 84 species. The spectra can be perused and are available for download at www.astrochemistry.org/pahdb/. This paper introduces the library of laboratory-measured spectra. Although it has been part of PAHdb since its inception, the library of laboratory-measured spectra lacked a proper description in the literature. Here, the experimental methods used to obtain the data are described in detail, an overview of the contents of the experimental library is given, and specific tools developed to analyze and interpret astronomical spectra with the laboratory data are discussed. In addition, updates to the website, documentation and software tools since our last reporting are presented. Software tools to work with the spectroscopic libraries are being developed actively and are available at GitHub. Lastly, a comprehensive demonstration showing how the laboratory-measured data can be applied to explore absorption features in observations toward embedded sources is presented. This demonstration suggests that PAHs very likely contribute to interstellar absorption spectra associated with dense clouds and underscores the need for further IR spectroscopic studies of PAHs trapped in water ice.

E-mail: andrew.mattioda@nasa.gov

Astrophys. J. Suppl. Ser., Volume 251, Issue 2, pp.22

https://doi.org/10.3847/1538-4365/abc2c8

Ultrafast dynamics of correlation bands following XUV molecular photoionization

Marius Hervé[1], Victor Despré[2], Pablo Castellanos Nash[3], Vincent Loriot[1], Alexie Boyer[1], Audrey Scognamiglio[1], Gabriel Karras[1], Richard Brédy[1], Eric Constant[1], Alexander G. G. M. Tielens[3], Alexander I. Kuleff[2] and Franck Lépine[1]

[1] Univ Lyon, Univ Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, Villeurbanne, France.

[2] Theoretische Chemie, PCI, Universität Heidelberg, Heidelberg, Germany.

[3] Leiden Observatory, Leiden University, Leiden, The Netherlands.

Modern ultrashort X-ray/XUV (extreme ultraviolet) sources provide unique opportunities to investigate the primary reactions of matter upon energetic excitation. Understanding these processes in molecules on ultrafast timescales is required to improve bespoke high-energy radiation detectors, nanomedicine schemes or to study the molecular composition of interstellar media. However, current experiments struggle to provide a general framework because of the uniqueness and complexity of each system. Here we show the universal role of correlation bands–features created by electron correlation. This is done by studying ultrafast energy relaxation of size-scalable two-dimensional molecules following ionization by an ultrashort XUV pulse. We observed long lifetimes that nonlinearly increase with the number of valence electrons. A general law based on solid-like electron–phonon scattering is proposed, which explains both our results and previously reported measurements. This offers new opportunities in attosecond science and high-energy photophysics.

E-mail: franck.lepine@univ-lyon1.fr

Nat. Phys., accepted (2020)

https://doi.org/10.1038/s41567-020-01073-3

Chemical modelling of dust-gas chemistry within AGB outflows III. Photoprocessing of the ice and return to the ISM

M. Van de Sande[1], C. Walsh[2] and T.J. Millar[3]

[1] Institute of Astronomy, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

[2] School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK

[3] Astrophysics Research Centre, School of Mathematics and Physics, Queen's University Belfast, University Road, Belfast BT7 1NN, UK

To explain the properties of dust in the interstellar medium (ISM), the presence of a refractory organic mantle is necessary. The outflows of AGB stars are among the main contributors of stellar dust to the ISM. We present the first study of the refractory organic contribution of AGB stars to the ISM. Based on laboratory experiments, we included a new reaction in our extended chemical kinetics model: the photoprocessing of volatile complex ices into inert refractory organic material. The refractory organic feedback of AGB outflows to the ISM is estimated using observationally motivated parent species and grids of models of C-rich and O-rich outflows. Refractory organic material is mainly inherited from the gas phase through accretion onto the dust and subsequent photoprocessing. Grain-surface chemistry, initiated by photodissociation of ices, produces only a minor part and takes place in a sub-monolayer regime in almost all outflows. The formation of refractory organic material increases with outflow density and depends on the initial gas-phase composition. While O-rich dust is negligibly covered by refractory organics, C-rich dust has an average coverage of 3-9%, but can be as high as 8-22%. Although C-rich dust does not enter the ISM bare, its average coverage is too low to influence its evolution in the ISM or significantly contribute to the coverage of interstellar dust. This study opens up questions on the coverage of other dust-producing environments. It highlights the need for an improved understanding of dust formation and for models specific to density structures within the outflow.

E-mail: marie.vandesande@kuleuven.be

MNRAS, accepted, 2020

https://arxiv.org/abs/2011.11563
https://doi.org/10.1093/mnras/staa3689

The Unsolved Issue with Out-of-Plane Bending Frequencies for C=C Multiply Bonded Systems

Timothy J. Lee[1] and Ryan C. Fortenberry[2]

[1] MS245-3, Planetary Systems Branch, Space Science Astrobiology Division, NASA Ames Research Center, Moffett Field, CA 94035, USA

[2] Department of Chemistry Biochemistry, University of Mississippi, University, MS, 38677-1848, USA

More than 30 years ago two groups independently identified a problem in the calculation of the out-of-plane bending (OPB) vibrational frequencies for the ethylene molecule using correlated electronic structure methods. Several studies have been done in the meantime to try and understand and resolve this issue. In so doing this problem has been found to be far more insidious than previously realized for acetylene-like and benzene-like molecules, which can become non-linear and non-planar, respectively. The one common feature that all molecules with this problem have is that they contain C=C multiple bonds, and so this has been called the "C=C multiple bond OPB frequency issue" or "the C=C OPB problem." Various explanations for this problem have been advanced such as basis set superposition error, basis set incompleteness error, linear dependences in the basis set, proper balancing of the basis set between saturation and inclusion of higher angular momentum functions, etc. and possible solutions have arisen from these suggestions. All of these proposed solutions, however, amount to one main point connecting them all: modifying the one-particle basis set in some way. None of the explanations that have been advanced, however, really fit all of the data for all of the molecules where this problem has been identified, and importantly, none of these diagnostic tests have been applied to similar molecules where this issue does not appear. In this review, the studies over the last 30 plus years are discussed and relevant data from each of these is compared and contrasted. Recent density functional theory studies on polycyclic aromatic hydrocarbons, that may or may not be connected to this issue, are also discussed. It is hoped that by collecting and analyzing the data from these studies a path forward to understanding and resolving this issue will become evident.

E-mail: Timothy.J.Lee@nasa.gov

pectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

https://doi.org/10.1016/j.saa.2020.119148

Molecular growth upon ionization of van der Waals clusters containing HCCH and HCN is a pathway to prebiotic molecules

Tamar Stein[1,2], Partha P. Bera[3,4], Timothy J. Lee[3] and Martin Head-Gordon[1,2]

[1] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

[2] Department of Chemistry, University of California, Berkeley, CA, USA

[3] Space Science and Astrobiology Division, NASA Ames Research Center, MS 245-6, Moffett Field, Mountain View, CA 94035, USA

[4] Bay Area Environmental Research Institute, NASA Research Park, Moffett Field, CA 94035, USA

The growth mechanisms of organic molecules in an ionizing environment such as the interstellar medium are not completely understood. Here we examine by means of ab initio molecular dynamics (AIMD) simulations and density functional theory (DFT) computations the possibility of bond formation and molecular growth upon ionization of van der Waals clusters of pure HCN clusters, and mixed clusters of HCN and HCCH, both of which are widespread in the interstellar medium. Ionization of van der Waals clusters can potentially lead to growth in low temperature and low-density environments. Our results show, that upon ionization of the pure HCN clusters, strongly bound stable structures are formed that contain NH bonds, and growth beyond pairwise HCN molecules is seen only in a small percentage of cases. In contrast, mixed clusters, where HCCH is preferentially ionized over HCN, can grow up to 3 or 4 units long with new carbon–carbon and carbon–nitrogen covalent bonds. Moreover, cyclic molecules formed, such as the radical cation of pyridine, which is a prebiotic molecule. The results presented here are significant as they provide a feasible pathway for molecular growth of small organic molecules containing both carbon and nitrogen in cold and relatively denser environments such as in dense molecular clouds but closer to the photo-dissociation regions, and protoplanetary disks. In the mechanism we propose, first, a neutral van der Waals cluster is formed. Once the cluster is formed it can undergo photoionization which leads to chemical reactivity without any reaction barrier.

E-mail: mhg@cchem.berkeley.edu

Physical Chemistry Chemical Physics

https://doi.org/10.1039/D0CP03350B

Characterization of Cosmic Grain Analogs Formed at Low Temperature from Small Hydrocarbon Precursors in the NASA Ames COSmIC Facility

Ella Sciamma-O'Brien and Farid Salama

Space Science and Astrobiology Division, NASA Ames Research Center, MS 245-6, Moffett Field, Mountain View, CA 94035, USA

Here, we present the results of the first solid-phase ex situ analysis of cosmic grain analogs produced at low temperature ($<$200 K) in the NASA Ames COsmic SImulation Chamber (COSmIC) from small hydrocarbon precursors, methane (CH_4) and acetylene (C_2H_2), seeded in an argon supersonic jet expansion and submitted to a plasma discharge. The plasma-induced chemical reactions, initiated between the precursor molecules and their atomic and molecular fragments, radicals and ions, produce larger molecules and eventually solid particles that are collected in situ under controlled conditions. Scanning electron microscopy (SEM) imaging was used to provide insight on the morphology and growth structure of the grains produced in COSmIC, and to investigate how the precursors used to produce the grains affect these parameters. This SEM study has shown that under identical experimental conditions with fixed physical and chemical parameters (precursor density, temperature, energy, and reaction time), heavier precursors in the initial mixture produce larger grains and in larger quantity, most likely as a result of a more complex chemistry: most of the grains produced in the Ar/CH_4 (95:5) gas mixture ranged from 15 to 385 nm in diameter with an average density of 2.1 grains μm^{-2}, while the grains produced in the Ar/C_2H_2 (95:5) gas mixture ranged from 40 to 650 nm with a density of 3.5 grains μm^{-2}. Changes in the morphology were also observed, with grains produced from acetylene (C_2H_2) precursors tending to be more spherical than grains produced from methane (CH_4) precursors. This change in morphology could be associated with different stages of growth formation at low temperature from a more "planar" growth at first, followed by coagulation into more spherical particles. This study demonstrates that the COSmIC experimental setup can be used to investigate carbon grain formation from small gas-phase molecular precursors at low temperature ($<$200 K), i.e., under a temperature regime that is representative of the dust condensation zone and outer region of circumstellar envelopes.

E-mail: ella.m.sciammaobrien@nasa.gov

The Astrophysical Journal

https://doi.org/10.3847/1538-4357/abc00d

Meetings

PATAS 2021

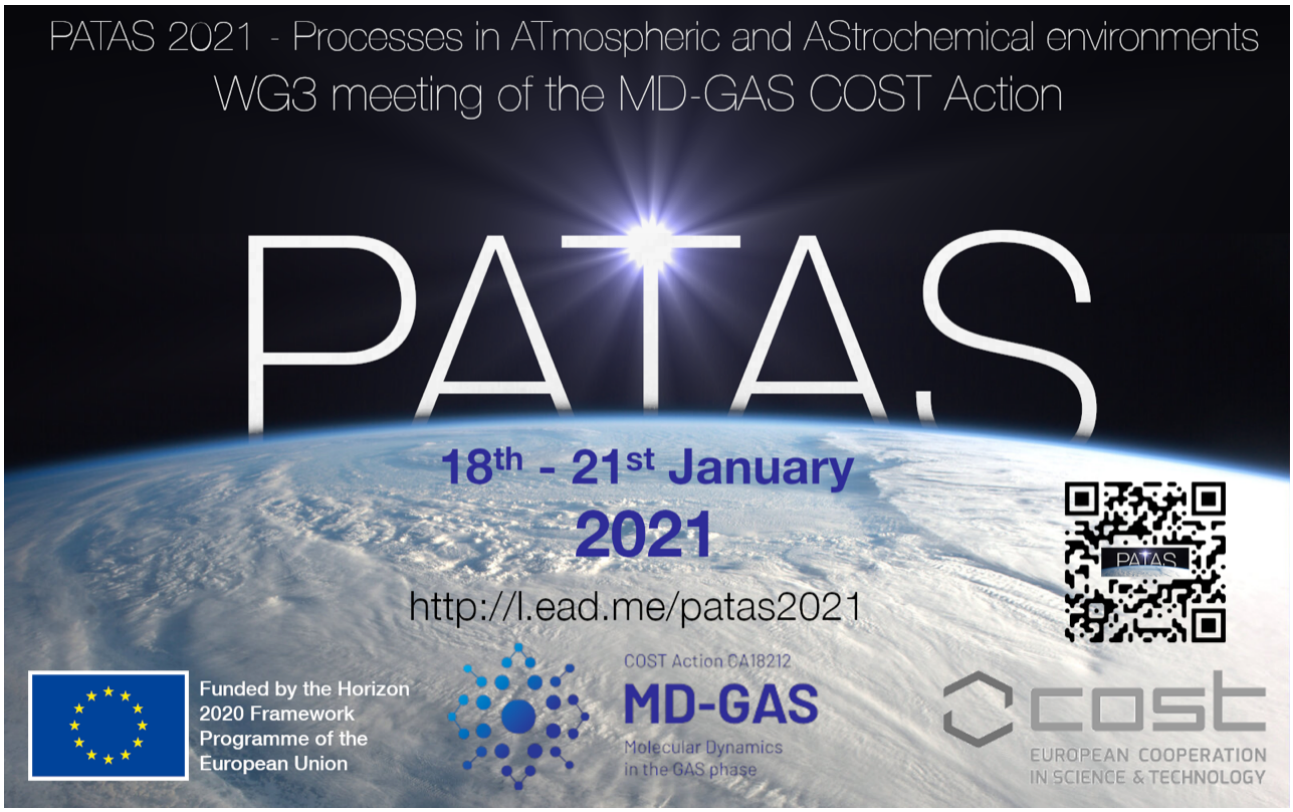
Processes in ATmospheric and AStrochemical environments

Virtual Conference

18-21 January 2021

http://l.ead.me/patas2021

Scope: This meeting is one of the activities proposed in the frame of working group 3 of the MD-GAS COST Action (CA18212), and it will focus in Processes in Atmospheric and Astrochemical Environments.
We will cover related topics such as charge and energy flow processes in atmospheric aerosols, hydration and solvation of molecules in the atmosphere, molecular encapsulation of gas-phase pollutants for air pollution control, deexcitation and/or molecular growth processes of relevant carbonaceous species in the interstellar medium, etc.



Deadlines:

- 1st December 2020 - Registration open
- 15th December 2020 - Abstract submission deadline
- 4th January 2021 - Registration deadline

E-mail for contact: Sergio Díaz-Tendero and Sylvain Maclot

Announcements

Ph.D. Studentship
University of Hawaii at Manoa
Astrochemistry & Astrobiology

Advertised by Prof. Ralf I. Kaiser

The W.M. Keck Research Laboratory in Astrochemistry at the University of Hawaii, Department of Chemistry, invites applications for Ph.D. Fellows in laboratory astrochemistry and astrobiology. The prime directive of our research program is to explore the fundamental mechanisms how complex organic, often astrobiologically relevant molecules are synthesized from the bottom up via single atoms, radicals, and small molecules in low temperature ices and in the gas phase. This requires state-of-the art, laser based detection systems exploiting REMPI and/or single photon ionization (four wave mixing, synchrotrons) and molecular beams experiments. Combined with astrochemical modeling and computational chemistry, the goals of these studies are to provide realistic, scientifically sound reaction pathways to organic molecules (of astrobiological relevance) in deep space. Currently, positions are open in the following research areas (https://www.uhmreactiondynamics.org):

1. Gas phase formation of (nitrogen-bearing) polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial environments exploiting molecular beams (ISM) and low temperature ices (Solar System).

2. Gas phase formation of silicon-bearing molecules as precursors to interstellar and circumstellar grains utilizing crossed molecular beams.

3. Surface science experiments exploring the synthesis of complex organics in interstellar ices by ionizing radiation in conjunction with analysis through single photon ionization – reflectron time of flight mass spectrometry (SPI-ReTOF-MS).

For Fall 2021 admission, international students are encouraged to apply by May 1, 2021. Qualified students will receive full tuition fee waivers along with a stipend and summer overload. Applicants holding a Master/Diploma degree can request credits of their Master/ Diploma course work toward their Ph.D. degree. Prior to any application, interested candidates should discuss and coordinate potential research areas with Prof. Dr. Ralf I. Kaiser, Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI 96822, USA (email: ralfk@hawaii.edu).

Postdoctoral Fellows
University of Hawaii at Manoa
Astrochemistry & Astrobiology

Advertised by Prof. Ralf I. Kaiser

The W.M. Keck Research Laboratory in Astrochemistry at the University of Hawaii, Department of Chemistry, invites applications for multiple postdoctoral positions in laboratory astrochemistry and astrobiology. The prime directive of our research program is to explore the fundamental mechanisms how complex organic, often astrobiologically relevant molecules are synthesized from the bottom up via single atoms, radicals, and small molecules in low temperature ices and in the gas phase. This requires state-of-the art, laser based detection systems exploiting REMPI and/or single photon ionization (four wave mixing, synchrotrons) and molecular beams experiments. Combined with astrochemical modeling and computational chemistry, the goals of these studies are to provide realistic, scientifically sound reaction pathways to organic molecules (of astrobiological relevance) in deep space. Currently, positions are open in the following research areas (https://www.uhmreactiondynamics.org):

1. Gas phase formation of (nitrogen-bearing) polycyclic aromatic hydrocarbons (PAHs) in extraterrestrial environments exploiting molecular beams (ISM) and low temperature ices (Solar System).

2. Gas phase formation of silicon-bearing molecules as precursors to interstellar and circumstellar grains utilizing crossed molecular beams.

3. Surface science experiments exploring the synthesis of complex organics in interstellar ices by ionizing radiation in conjunction with analysis through single photon ionization – reflectron time of flight mass spectrometry (SPI-ReTOF-MS).

For all positions, the appointment period is initially for one year, but can be renewed annually based on availability of funds and satisfactory progress. The salary is competitive and commensurate with experience. Successful applicants should have a strong background in one or more of the following: experimental reaction dynamics, molecular beams, UHV technology, combustion chemistry, UHV technology, pulsed laser systems, VUV light. Solid communication skills in English (written, oral), a publication record in internationally circulated, peer-reviewed journals, and willingness to work in a team are mandatory. Only self-motivated and energetic candidates are encouraged to apply. Please send a letter of interest, three letters of recommendation, CV, and publication list to Prof. Ralf I. Kaiser, Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI 96822, USA [ralfk@hawaii.edu]. The review of applications will start January 1, 2021, and continues until the positions are filled. A description of our current research group can be found at https://www.uhmreactiondynamics.org/

2021 LAD Dissertation Prize
American Astronomical Society (AAS)

Advertised by Rachel Smith

Dear colleagues,

This is a final reminder that the Laboratory Astrophysics Division (LAD) of the American Astronomical Society (AAS) is inviting nominations for the **2021 LAD Dissertation Prize due Dec 31, 2020!**

Be sure to submit your completed applications by this date (email to Rachel Smith at lad.secretary@aas.org as a single compiled PDF or separate PDFs, which can come separately as well). All files must be received by 11:59 pm ET on Dec 31, 2021, to be eligible.

The field of laboratory astrophysics encompasses all fundamental theoretical and experimental research into the underlying processes that drive the cosmos.

The Dissertation Prize is presented, normally on an annual basis, to recognize an outstanding theoretical or experimental doctoral dissertation (or the equivalent) in laboratory astrophysics. The prize is awarded to an individual who has completed their PhD or equivalent degree in any of the three calendar years immediately preceding the award year. The prize includes a cash award, a citation, and an invited lecture by the recipient at a meeting of the Division.

The recipients for each year will be announced in January/February of that year, and their presentations will be made at the annual LAD meeting. Currently, this meeting is scheduled to be held jointly with the 2021 AAS Summer meeting, June 6-10 in Anchorage, AK, although this could change depending on the ongoing COVID-19 pandemic. Any nominee not selected will be automatically considered in the next two consecutive years, or as long as the nominee is still eligible.

The Nomination package for the Dissertation Prize must include:

1. A nomination letter, including a one-sentence proposed citation. Only one signator is allowed.
2. Two letters of support. Additional letters will not be considered. Only one signator per letter is allowed. Note that each of the nomination letter and two support letters must be written by separate individuals.
3. A summary of the thesis (not to exceed 5 pages including figures and bibliography)
4. A statement from the nominee's university (Ph.D. or equivalent degree has been awarded)
5. A curriculum vitae
6. A publication list

Additional material (such as reprints, etc.) will not be considered.

Nominators, letter writers, and candidates need not be AAS or LAD members. Self-nominations are allowed and encouraged. The deadline for receipt of the nomination package and supporting letters for the Dissertation Prize is by 11:59:59 pm EST on December 31, 2020.

Attracting and serving a diverse and inclusive membership worldwide is a primary goal for LAD. In calling for nominations, we wish to remind you how important it is to give full consideration to qualified women, members of underrepresented minority groups, and scientists from outside the United States. All nomination material should be emailed as a single or multiple PDF(s) by the deadline directly to the LAD Secretary (lad.secretary@aas.org).

Website: https://lad.aas.org/prizes/dissertation-prize

Deadline: Dec 31, 2021 – 11:59 pm ET

AstroPAH Newsletter

http://astropah-news.strw.leidenuniv.nl Next issue: 19 February 2021

astropah@strw.leidenuniv.nl Submission deadline: 5 February 2021