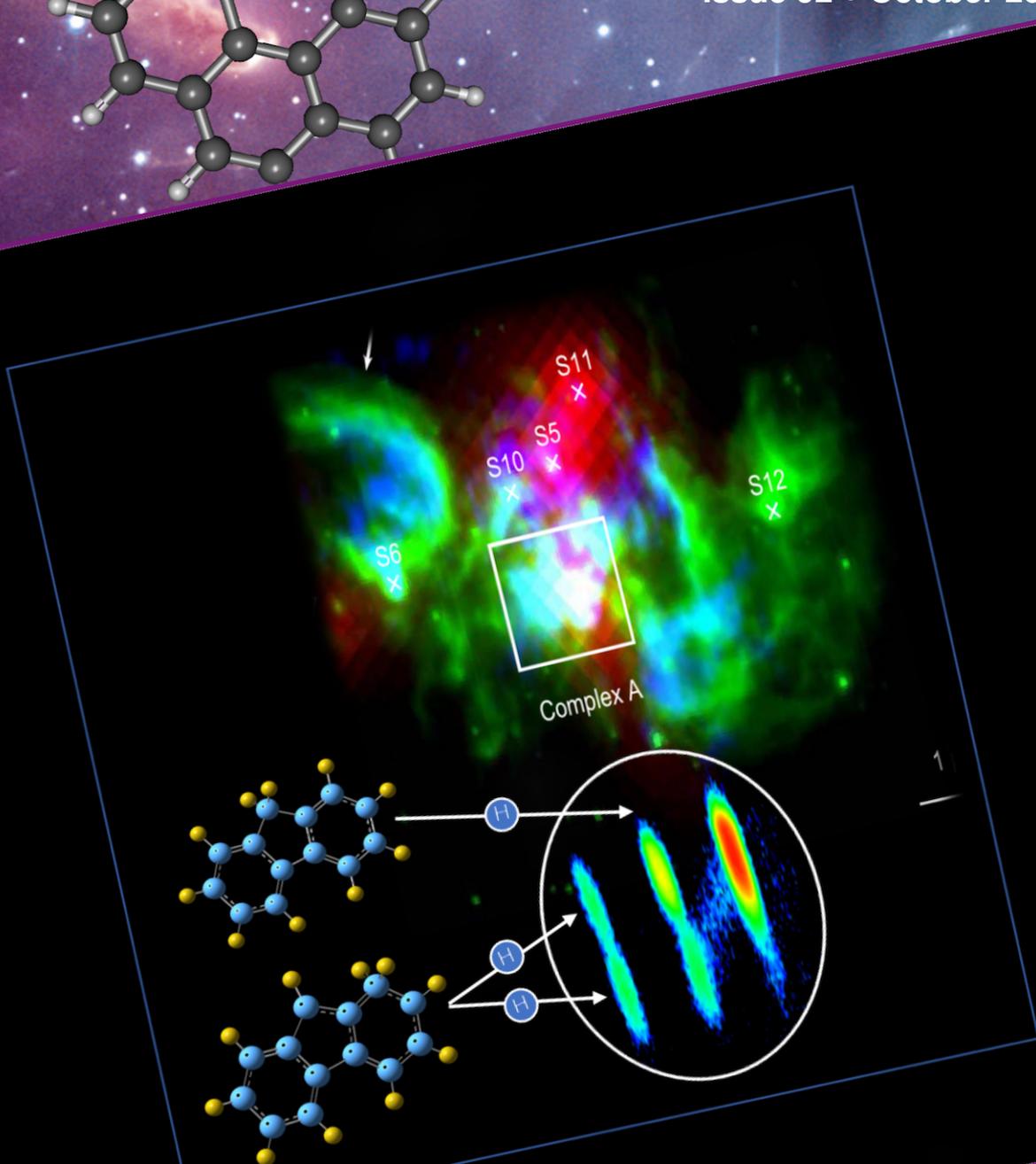


AstropAH

A Newsletter on Astronomical PAHs

Issue 92 • October 2022



Deciphering isomerisation in PAHs and PANHs



Editorial

Dear Colleagues,

Welcome to our new AstroPAH volume! We hope all of you are healthy and doing well!

First, we would like to congratulate Prof. Ewine van Dishoeck from Leiden University, Netherlands on receiving the Niels Bohr International Gold Medal. The medal was presented to her by Her Majesty the Queen Margrethe II during a dedicated event at the Carlsberg Academy in Copenhagen, on October 7, 2022. You can find more details about it here: <https://bohirmedal.com/>.

In this month's newsletter, our *In Focus* was written by Dr. Umesh Kadhane and presents a vast overview of his team's recent investigations on dissociative processes of PA(N)Hs. The *Picture of the Month* on the cover of our October issue illustrate the work done by the team to decipher isomerisation in PAHs and PANHs.

As always, many thanks to you for so many contributions this month. Check our *Abstracts* section for a set of papers published by groups from all across the globe presenting results of experimental, theoretical, and observational studies including PAH cooling rates, anharmonic spectra, formation pathways, synthesis, contribution in neutral gas heating in galaxies, and inclusion in cometary organic molecules.

We have three announcements in the *Meetings* section. The first one is an upcoming Astrochemistry Meeting on Dust, Ice and Gas (DIG), which will take place virtually in November 2022; the second one is an International Winter School on Laboratory Astrophysics that will take place in Les Houches, France in February 2023, and the third one is a Laboratory Astrophysics Workshop that will take place in Kauai, Hawaii in February 2024.

If you are on Instagram, be sure to check out our next [PAH of the Month!](#)

We hope you enjoy reading our newsletter, and we thank you for your dedication and interest in AstroPAH! Please continue sending us your contributions, and if you wish to contact us for a future In Focus, Picture of the Month or other ideas, feel free to use our [email](#).

The Editorial Team

**Next issue: 17 November 2022.
Submission deadline: 4 November 2022.**

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PAH Picture of the Month

Top right: Color-composite image of the IRAS 17160–3707 region. (*Blue*) ionized gas emission at 1.3 GHz from Giant Metrewave Radio Telescope (GMRT, India). (*Green*) warm dust emission as well as emission due to PAHs at 8 μm from NASA Spitzer-IRAC. (*Red*) cold dust emission at 870 μm from APEX Telescope Large Area Survey of the Galaxy (ATLASGAL). (*Nandakumar et al.*). *Bottom left:* Experimental evidence of fluorene (in cationic state) losing a single H atom directly, or 2H atoms after undergoing an H shift isomerization for a specific internal energy (*Vinitha et al.*).

Credits: Background picture by *Nandakumar et. al.* Molecular dynamics graphics by *Vinitha et. al.*

X-ray by Chandra: NASA/CXC/Univ.Potsdam/L.Oskinova et al; Optical by Hubble: NASA/STScI; Infrared by Spitzer: NASA/JPL-Caltech.

In search of unified reaction mechanisms in the radiation driven dissociation of PA(N)Hs: A tryst with isomerisation

by Umesh Kadhane

Introduction

The importance of polycyclic aromatic hydrocarbons (PAHs) and their hetero-atomic derivatives can hardly be overstated. Their ubiquitous presence in the universe and their sensitivity to the ambient radiation environment makes them excellent proxies for their surroundings^[1,2]. Powerful as they might appear, these “thermometers” of the prevailing astronomical environment are extremely non-linear and complex^[3,4]. A typical PAH molecule goes through numerous associative and dissociative processes intermingled with isomerisation as it evolves in the interstellar medium (ISM). There are two crucial aspects that govern the PAH evolution in the ISM. Firstly, extensive observations of various ionic and radical species and their associated dissociation barriers have conclusively demonstrated that the PAH population in the ISM is driven by kinetics rather than thermodynamics, with extreme ultraviolet (EUV) and other energetic radiations tipping the balance away from thermal equilibrium^[5]. Secondly, a pure associative model of reactions leading to the formation of larger molecular species often fails to explain the PAH population in the ISM. Instead, a mix of “top-down” or “trickle-down” effects with associative reactions is found to be more plausible in explaining the composition of the molecular inventory of PAHs in the ISM. This implies that dense carbon-rich stellar evolution injects large PAHs into the ISM, where they are further degraded into smaller molecular species and reactive fragments, which can then react to form larger molecules, resulting in a dynamic cycle^[6,7,8]. Recent studies, for example, have demonstrated the formation of up to four-membered ring PAHs starting exclusively from naphthalene^[9]. Previously, it was believed that only larger PAHs could survive the harsh conditions of space and that smaller PAHs would fragment immediately upon formation. However, recent studies reveal the presence of two-ringed PAHs in astronomical environments^[10,11], thus cementing the role of the entire class of PAHs in astrochemical evolution.

While dissociative reactions continue to be the focus of many laboratory-based studies on PAHs, another aspect of PAH evolution that has remained elusive is structural isomerisation^[12,13,14,15]. Structural rearrangement prior to dissociation may result in dissociative pathways that are not accessible from the initial structure. Isomerisation

also determines the structure of the daughters, which influences subsequent dissociation. Isomerisation could also connect PAHs with different structural properties to common structures, resulting in uniform dissociation schemes. However, it is challenging to identify and probe such effects in the stable as well as metastable species of PAHs directly using conventional instrumentation. Recently, for the case of naphthalene, IR spectroscopy utilising an ion trap mass spectrometer has helped experimentally establish the involvement of isomerisation to azulene before dissociation^[16].

PAHs are exceptionally stable in the harsh conditions of the ISM due to their peculiar molecular properties of symmetry and delocalisation. Laboratory studies of hetero-atomic derivatives of PAHs are thus crucial to understanding how the deviation from the symmetry and electronic delocalisation affects the radiation interactions with such derivatives. In the ISM, carbon chemistry is driven by PAHs or oxygen. Oxygenated PAHs would be the most likely candidates to investigate; however, the oxygen-driven astrochemistry is often too strong to let PAHs survive in their native environment^[2]. On the other hand, molecular species such as N₂, HCN/HNC, NH₃, and CN are often found to coexist with PAHs more symbiotically^[2]. Furthermore, recent discoveries of nitrogenated PAHs (PANHs) in the ISM have put a new perspective on the composition and evolution of organic inventory in the ISM, making them exciting candidates to investigate^[17,18,19]. Another strong reason for interest in investigating PANHs is their likely presence in Titan's dynamic, carbon-nitrogen-rich atmosphere^[20,21].

Indian Institute of Space Science and Technology (IIST) is the first Asian space university established in 2007 under the Department of Space, Government of India. The Atomic and Molecular Physics (AMP) lab at IIST exclusively focuses on uncovering fundamental molecular dynamic aspects of dissociative processes in a few prototypical PAHs and PANHs, with the ultimate goal of unravelling the underlying similarities and mechanistic commonalities across the PAH family and its diverse excitation processes. The excitation processes include ultraviolet (UV) multiphoton excitations, electron impact ionisation-dissociation, collision with heavy charged particles and extreme UV excitation. The experimental techniques involve time-of-flight (ToF) mass spectroscopy, energy-correlated ToF mass spectroscopy, photoelectron photoion coincidence spectroscopy, and velocity map imaging spectroscopy. There are four primary decay processes which span the statistical decay processes in PAHs and PANHs: single or multiple hydrogen loss, loss of acetylene (C₂H₂), loss of hydrogen cyanide (HCN) or its isomer (HNC), and the loss of methyl amidogen (HCNH)^[5]. Apart from this, several other minor channels are also of astronomical importance. Several times while conducting these studies, we encountered situations in which the observations were found to be inconsistent or could not be supported by computations unless the role of isomerisation is invoked. The primary goal of this article is to explain the inevitability of isomerisation in the energetic radiation processing of PA(N)Hs.

Methodology

Pursuing a goal of such magnitude demands focusing on a specific set of target molecules and diversification in the experimental approach. Such an endeavour needs a variety of capabilities which are impractical to find under one roof. Thus, creating a strong collaborative environment is as crucial as creating the necessary laboratory infrastructure at AMP lab, IIST.

The AMP infrastructure consists of three main instruments which were developed in-house over the last 12 years: i) a high-resolution energy correlated ToF mass spectrometer equipped with nanosecond optical parametric oscillator (OPO) laser (see Figure 1), ii) an electron impact energy selective electron-ion coincidence spectrometer and more recently iii) an electrospray ion (ESI) source with 14 pole Radio Frequency (RF) ion trap instrument (see Figure 5). These instruments together provide the capability of studying a wide variety of target molecules, not limited to the gas phase, under electron impact and photon-mediated ionisations. However, in order to access a broader range of internal energies than what is accessible by a tabletop laser, we also perform experiments using the synchrotron light source at Elettra Sincrotrone Trieste, Italy. The high flux tunable light source capable of accessing x-ray energy regimes required for core excitation has also allowed us to study multiply charged states. Finally, to completely cover a wide variety of radiation environments in space, the AMP group has also been performing high-energy proton collision experiments at the Inter-University Accelerator Center, Delhi, India (see Figure 2).

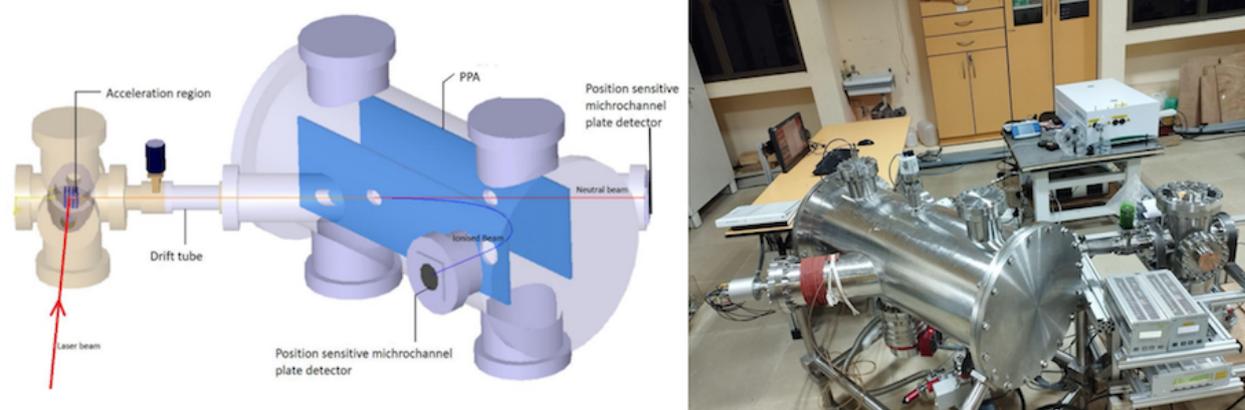


Figure 1 – Experimental setup for energy correlated time-of-flight mass spectrometry

Due to the very nature of statistical dissociation, it is possible to generalize fragmentation trends of a wide range of PA(N)Hs by studying a set of candidate molecules with different structural attributes. To that end, we started our experiments with the double-ringed naphthalene, the fundamental building block of all PAHs and its isomer, azulene. Quinoline and isoquinoline are the next targets currently being studied to understand the effect of nitrogen inclusion into the skeleton. Methyl quinoline and naphthalenamine are a natural progression towards substituted PAHs (PANHs), as they would reveal the role of substituents in the main ring in dissociation. We are also studying fluorene and anthracene to confirm if the trends generalize to higher ring members.

In order to truly understand the dynamics of the dissociative processes under study, we also use a variety of theoretical approaches. We use Outer Valence green's function theory to calculate the ionisation energies and electron affinities which are used in determining the ionisation pathways and assigning different peaks in the electron spectra^[22]. We also conduct potential energy surface explorations to help uncover the molecule's evolution prior to dissociation^[23,24]. This is done using the density function theory (DFT) calculations chosen due to their computational efficiency. To compare the experimental and theoretical breakdown curves, we use the Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular dissociation to calculate the rate constants, which are then used to solve the master equation using in-house codes^[24]. We perform these calculations to ascertain the experimentally observed decay channels among the various combinations possible. Finally,

we perform complementary ion optics and Monte Carlo simulations to explain any interesting decay features observed in experimental data^[25].

Charged Particle Impact with PA(N)Hs

In view of the astronomical and biological implications, particularly in the context of Titan's ionosphere, we studied energetic proton (25–150 keV) and high energy electron (0.25–2 keV) collisions with naphthalene, azulene, quinoline and isoquinoline^[26,27,28,29,30]. Figure 2 shows the schematic of the setups used. The magnetosphere of Saturn is known to guide solar protons with energies in the tens of keV onto Titan, thereby adding proton collision to the radiation processing in the upper atmosphere of Titan. For the charged particle interaction with the targets under study, the interaction of the projectile with electronic charge density dominates the energy loss at the energy scale studied. As a result, the energy loss cross-sections and average energy deposition are expected to be similar in these four targets. Therefore it is hardly surprising that all four targets showed similar recoil ion mass spectra for both ion and electron projectiles. Typically, the dominant parent ion peak is followed by C₂H₂/HCN equivalent loss, subsequent loss of C₂H₂ and often a very strong peak of parent dictation and its violent fragmentation.

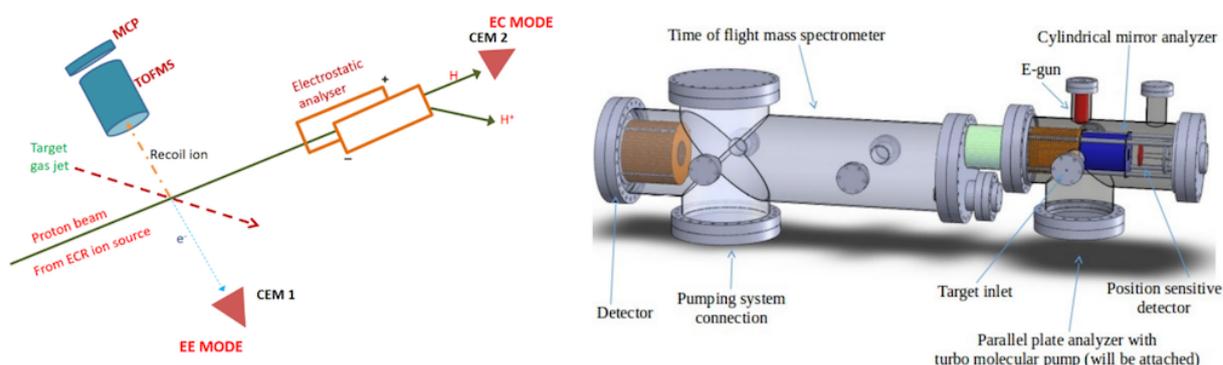


Figure 2 – Left: The experimental setup for proton collision experiments at the Inter-University Accelerator Center. Right: The experimental setup for electron collision experiments.

We further analysed the data for the ion yields, ion-ion correlation, and the released kinetic energy, and observed several interesting features. Specifically, we observed a significant commonality in the decay processes, particularly in the ion-ion correlation data. We found that collective excitation, also known as plasmon excitation, is the pathway for ionisation in all of the studied PAHs and PANHs. We modelled the collective excitation theoretically and confirmed that the single-mode excitation directly leads to single ionisation and the double excitation leads to double ionisation. The main difference between the otherwise identical mass spectra of naphthalene and azulene was observed at C₂H₂ loss peak and, to a lesser extent, at the H-loss peak. The observed qualitative and quantitative differences could not be explained without invoking the isomerisation process between naphthalene and azulene. This was our first direct encounter with isomerisation in PAHs and was crucial in our model of charged particle-driven naphthalene-azulene dissociation.

Dehydrogenation by multi step multiphoton ionisation-dissociation

The charged particle collision experiments prompted us to investigate the potential role of isomerisation in PAHs. For small PAHs, isomerisation thresholds are typically lower than dissociation thresholds^[15]. As a result, there was a need for an instrument that could cover a long time range of dissociation to facilitate dissociation studies at lower internal energies. Therefore, we developed a high-resolution kinetic energy correlated ToF mass spectrometer^[31]. With the help of a large parallel plate electrostatic analyser and a pair of position-sensitive Micro Channel Plate detectors, it is now possible to achieve mass resolution better than 4000 and energy resolution better than 500 (see Figure 1).

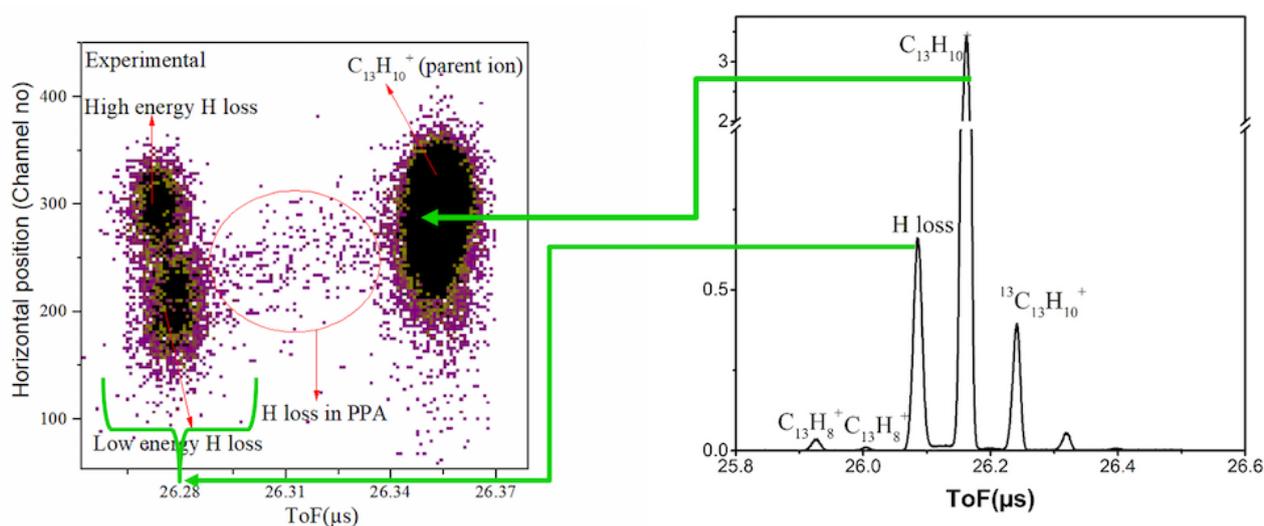


Figure 3 – 2D energy correlated ToF spectrum showing parent peak and first H loss.

A 2D energy correlated ToF spectrum allows us to deduce H-loss dissociation rate constants with the help of a concurrent Monte Carlo modelling of the instrument (see Figure 3). This technique covers dissociation time constant ranging from a few hundred nanoseconds to a few milliseconds, which is not easily accessible by all other available techniques. We use a tunable nanosecond OPO laser operating at UV wavelength to produce hot PAH ions. We demonstrated that the structural rigidity of PAHs can be exploited to produce a narrow and tunable internal energy ensemble of PAH cations using a single nanosecond tunable UV laser^[32,33]. Under this scheme, we studied three molecules, naphthalene, azulene, and fluorene. The capability of the instrument offered unprecedented clarity in the single and multiple H-loss processes in these test cases^[31,34]. It is now also possible to identify and quantify the contribution of molecular H₂ loss vis a vis sequential loss of two H-atoms. Our attempt to explain the observed H-loss sequence and the decay rates in the case of fluorene⁺ was possible only after including H-shift isomerisation. This helped in the structural identification of the relevant H-shift isomer of fluorene⁺ ^[31,34].

VUV PEPICO of PAHs and PANHs

The interaction of EUV/VUV radiation with PAHs and PANHs is a rich source of photochemistry. Hence, there is a strong need to understand and quantify various photodissociation processes and mechanisms in PANHs and PAHs. Furthermore, the resilience of PAHs and PANHs against direct VUV/EUV photo-damage allows great scope for molecular rearrangements, isomerisation, and statistical decay. To this extent, experiments are being performed on quinoline, isoquinoline, naphthalenamine, and methylquinoline using the PEPICO and VMI endstations at the gas phase and circular polarisation beam-lines at the Elettra Synchrotron Facility. Such experiments with the capability of event-by-event coincidence measurements enable us to study the internal energy dependence on the decay channels. At the same time, the VMI imaging detectors allow us to characterise the kinetic energy release distributions of different channels. These properties allow for direct experimental comparisons with our theoretical calculations, revealing several interesting dynamical aspects of dissociation, including the role of isomerisation^[23,24]. They have also helped us establish hierarchical decay chains, which reveal structural attributes such as the ring from which fragments are lost.

With the help of kinetic modelling based on extensive potential energy surface explorations, we found that quinoline can easily isomerise to 7-membered nitrogenated analogues (see Figure 4), mirroring its PAH counterpart naphthalene which isomerises to azulene prior to dissociation. Furthermore, RRKM modelling helped us establish that small fragments like HCN and C₂H₂ prefer to be lost from the 7-membered analogues rather than directly from the parent. In the case of naphthalene, isomerisation to 7-membered rings before dissociation has been verified, both theoretically^[15] and experimentally^[16]. Our findings with quinoline now provide a bridge between the well-studied PAH family and the often overlooked PANH family. Furthermore, our experiments with naphthalenamine and the preliminary DFT calculations show that the 7-membered isomerisation also occurs in this case and that such isomerisation may be required for further dissociation^[35]. These studies highlight the importance of 7-member ring isomerisation, which could pave the way for a common dissociating scheme for a wide variety of molecules.

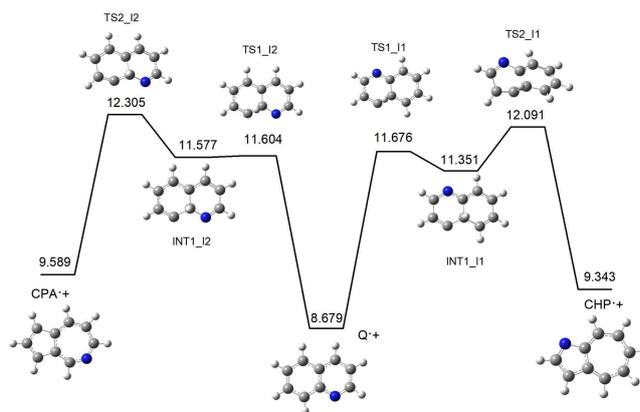


Figure 4 – Isomerisation of quinoline to cyclopenta[c]azepine cation and cyclohexa[b]pyrrole cation.

The way forward: going from less-known to unknown

Another allied goal that we are interested in is the dynamic molecular composition of different planetary atmospheres, for instance, Titan. The continuous dissociation of nitrogen and methane molecules caused by the strong interaction of Saturn's magnetosphere with Titan's upper atmosphere results in the production of small hydrocarbons and nitriles,

which then undergo further reactions to produce more complex molecules, such as PANHs. Additionally, the high abundance of HCN and HCNH in its upper atmosphere indicates that its molecular chemistry is rich in nitrogen. An important entity that is formed due to this complex nitrogen carbon chemistry is tholin, an orange-brown polymer known to ensheath the moon completely. Various mechanisms have been proposed to explain the formation of tholin involving a host of PA(N)H intermediates. Hence, our experience in handling PA(N)Hs is naturally extended to the dynamics of tholin formation.

Armed with information about Titan, we simulate its ionospheric conditions in the laboratory using our custom-built RF inductively coupled plasma reactor (see Figure 5 left). The tholins formed are further analysed using characterisation techniques like Atomic Force Microscope and Fourier Transform Infrared. Furthermore, mass spectroscopy of stable intermediates using a quadrupole mass analyser has led to valuable observations regarding its possible formation route^[36]. In order to fully characterise tholins, it is of utmost importance to study its non-volatile precursors, which is done using our in-house 14 pole ion trap equipped with an ESI source (see Figure 5 right).

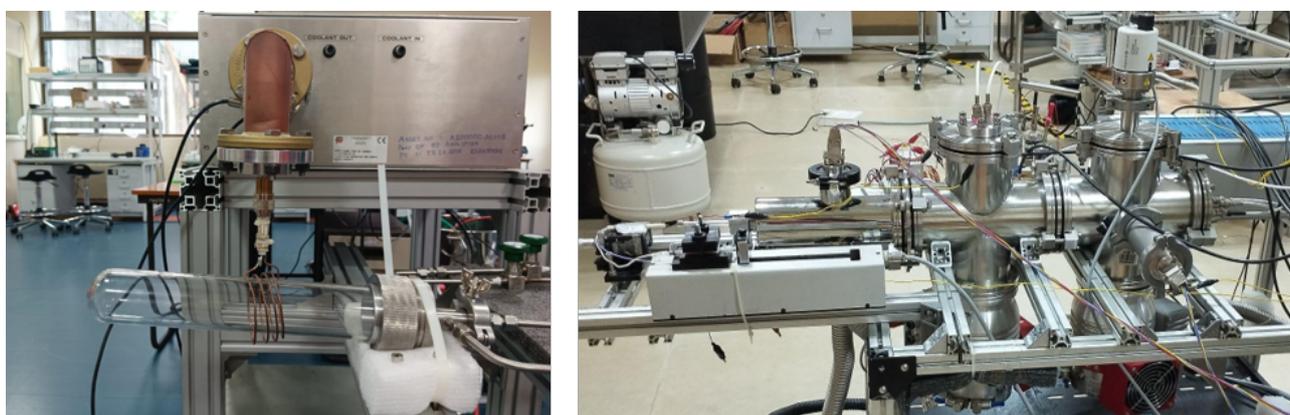


Figure 5 – Left: RF inductively coupled plasma reactor. Right: The ESI source integrated with 14 pole ion trap and other ion optics

Light at the end of the tunnel

Over the years, we keep stumbling across isomerisation directly or indirectly in our research expeditions. In particular, 7-member isomerisations and hydrogen migration appear to be omnipresent in statistical dissociation processes. The way ahead would be to verify the importance of these processes in different classes of molecules and generalise these trends. Such an effort would greatly help our understanding of the astrochemical evolution of space and would help bring about a complete picture instead of molecule-specific case studies. In addition, this will complement the ongoing research on identifying and quantifying structural isomers in astrochemical samples^[37].

Future prospects

Exploring unimolecular dissociations in PA(N)H is undoubtedly the most informative step in understanding their evolution in the universe. The AMP lab continues to tread the same path while expanding the target systems and methodologies. In coming years more investigations are planned using the homegrown ESI+Ion-trap+ToF instrument to perform action spectroscopy on PANHs specifically to understand the role of isomerisation and how these molecules can ultimately serve the purpose of molecule formation in space^[38]. Precise quantification of unimolecular dissociation pathways and unravelling of ring expansion mechanisms will be further investigated in double ring PA(N)H with substituents. While these investigations on pure samples are being executed, plans are afoot to produce tholin analogs using RF plasma discharge and to study the intermediates for their composition, isomeric structure and evolution to higher-mass polymers.

The AMP lab's primary affiliation with IIST, which is directly under the Dept. of Space, Govt. of India., has uniquely allowed it to actively pursue and participate in possible space exploration missions oriented towards organics in space. To this end, efforts are being made to bring the national astro-molecular physics community together with the Indian Space Research Organisation (ISRO) to initiate planning of future Indian space missions to explore organics in space. International collaborations are also being sought from the domain experts to achieve this long term goal.

Collaborators

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Dr. Umesh Kadhane completed his PhD in the field of ion-molecule collisions from TIFR, Mumbai followed by more than three years of experience with ion-storage devices and mass spectrometry at the Aarhus University, Denmark and the University of Paris Sud, Orsay, France. He started his academic career as a teacher at the Dept. of Physics, IIT Madras in Dec. 2008. Two years later, he moved to the newly formed Indian Institute of Space Science and Technology, Thiruvananthapuram. For the last decade, he has worked towards establishing the atomic and molecular physics laboratory. Apart from academics, he is also involved in multiple space research related activities. This includes substantial contributions in diagnostics systems, simulations and overall system development of Electric Propulsion Systems (EPS) being developed for the Indian space program. Presently he is the deputy project director for the High Thrust EPS for ISRO. He is also a principal investigator for three major payload activities at IIST including the plasma measurement instrumentation payload around Earth, Mars and Venus. He has also set up two more laboratories at IIST for space research which includes, the Electric Propulsion Diagnostics Laboratory (EPDL) and the Sensors and payload development laboratory for SSPACE (SPDL-S). He is an avid educator with a keen interest in disseminating scientific theory and ideas among the wider student community and public.

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Abstracts

Radiative cooling rates of substituted PAH ions

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The unimolecular dissociation and infrared radiative cooling rates of cationic 1-hydroxypyrene (OHPyr⁺, C₁₆H₁₀O⁺) and 1-bromopyrene (BrPyr⁺, C₁₆H₉Br⁺) are measured using a cryogenic electrostatic ion beam storage ring. A novel numerical approach is developed to analyze the time dependence of the dissociation rate and to determine the absolute scaling of the radiative cooling rate coefficient. The model results show that radiative cooling competes with dissociation below the critical total vibrational energies $E_c = 5.39(1)$ eV for OHPyr⁺ and $5.90(1)$ eV for BrPyr⁺. These critical energies and implications for radiative cooling dynamics are important for astrochemical models concerned with energy dissipation and molecular lifecycles. The methods presented extend the utility of storage ring experiments on astrophysically relevant ions.

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Gas-phase spectroscopy of photostable PAH ions from the mid- to far-infrared

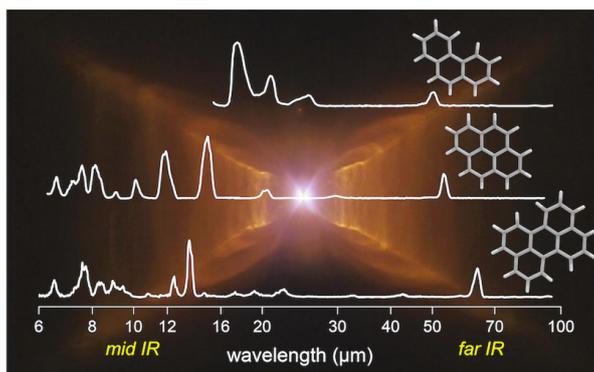
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We present gas-phase InfraRed Multiple Photon Dissociation (IRMPD) spectroscopy of cationic phenanthrene, pyrene, and perylene over the 100–1700 cm^{-1} (6–95 μm) spectral range. This range covers both local vibrational modes involving C–C and C–H bonds in the mid-IR, and large-amplitude skeletal modes in the far-IR. The experiments were done using the 7T Fourier-Transform Ion Cyclotron Resonance (FTICR) mass spectrometer integrated in the Free-Electron Laser for Intra-Cavity Experiments (FELICE), and findings were complemented with Density Functional Theory (DFT) calculated harmonic and anharmonic spectra, matching the experimental spectra well. The experimental configuration that enables this sensitive spectroscopy of the strongly bound, photoresistant Polycyclic Aromatic Hydrocarbons (PAHs) over a wide range can provide such high photon densities that even combination modes with calculated intensities as low as 0.01 km mol^{-1} near 400 cm^{-1} (25 μm) can be detected. Experimental frequencies from this work and all currently available IRMPD spectra for PAH cations were compared to theoretical frequencies from the NASA Ames PAH IR Spectroscopic Database to verify predicted trends for far-IR vibrational modes depending on PAH shape and size, and only a relatively small redshift (6–11 cm^{-1}) was found between experiment and theory. The absence of spectral congestion and the drastic reduction in bandwidth with respect to the mid-IR make the far-IR fingerprints viable candidates for theoretical benchmarking, which can aid in the search for individual large PAHs in the interstellar medium.



The mid- to far-infrared spectra of phenanthrene (top), pyrene (middle) and perylene (bottom). Credit for image of the Red Rectangle nebula to Hubble, NASA, ESA and Judy Schmidt.

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Monthly Notices of the Royal Astronomical Society, **516**, 4, 5216–5226 (2022)

<https://academic.oup.com/mnras/article/516/4/5216/6702436>

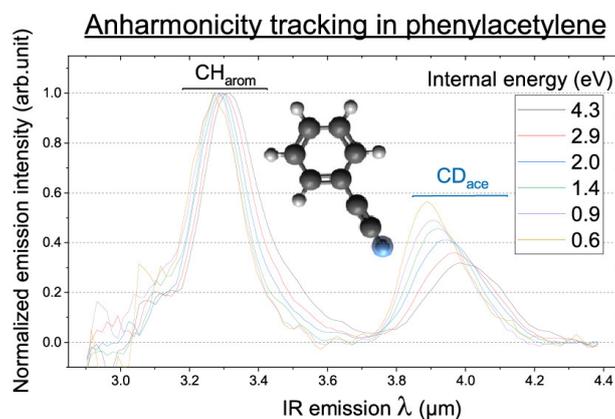
Aromatic and acetylenic C-H or C-D stretching bands anharmonicity detection of phenylacetylene by UV laser-induced vibrational emission

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To gain insight on Aromatic Infrared Bands and PAH-like carriers, a deeper understanding of anharmonicity effects are required. Questions related to PAH anharmonicity are more and more addressed in the cosmic PAH community both experimentally and theoretically. From an experimental viewpoint, anharmonicity effects of PAHs and their temperature-dependence have been studied via IR absorption. In this work, we investigate anharmonicity effects in phenylacetylene as a function of the total internal energy by detecting its vibrational emission induced by 193 nm UV excitation.



Internal energy-dependent emission spectra induced by 193 nm-excitation of phenylacetylene-d₁ (corrected by the response function of the apparatus). Reprinted with permission of the American Chemical Society.

The anharmonic infrared (IR) emission spectra of phenylacetylene C₆H₅CCH and an isotopologue C₆H₅CCD induced by 193 nm UV-excitation have been investigated in the gas phase. The study has been operated with a homemade IR spectrometer enabling to record time- and wavelength-resolved spectra between 2.5 and 4.5 μm, emitted all along the collisional cooling (cf. Figure). The analysis is supported by a kinetic Monte Carlo simulation in the vibrational harmonic approximation. For both species, the anharmonic shifts of the acetylenic C–H or C–D stretching modes and the aromatic C–H stretching modes are studied for band positions and bandwidths in terms of the total internal energy of phenylacetylene. For C₆H₅CCD, the internal energy dependence of the emission intensity band ratio is investigated and rationalized. This work demonstrates the potential of time-resolved IR emission spectroscopy to explore anharmonicity of astrophysically relevant molecules.

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<https://doi.org/10.1021/acs.jpca.2c01436>

Gas-phase synthesis of racemic helicenes and their potential role in the enantiomeric enrichment of sugars and amino acids in meteorites

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The molecular origins of homochirality on Earth is not understood well, particularly how enantiomerically enriched molecules of astrobiological significance like sugars and amino acids might have been synthesized on icy grains in space preceding their delivery to Earth. Polycyclic aromatic hydrocarbons (PAHs) identified in carbonaceous chondrites could have been processed in molecular clouds by circularly polarized light prior to the depletion of enantiomerically enriched helicenes onto carbonaceous grains resulting in chiral islands. However, the fundamental low temperature reaction mechanisms leading to racemic helicenes are still unknown. Here, by exploiting synchrotron based molecular beam photoionization mass spectrometry combined with electronic structure calculations, we provide compelling testimony on barrierless, low temperature pathways leading to racemates of [5] and [6]helicene. Astrochemical modeling advocates that gas-phase reactions in molecular clouds lead to racemates of helicenes suggesting a pathway for future astronomical observation and providing a fundamental understanding for the origin of homochirality on early Earth.

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Physical Chemistry Chemical Physics (2022) Advance Article

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On the formation of 2- and 3-cyanofurans and their protonated forms in interstellar medium conditions: quantum chemical evidences

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The literature is still poor in theoretical and experimental, including both spectroscopic and thermodynamic, data for protonated furan and protonated 2-cyanofuran and 3-cyanofuran (FH^+ , 2CFH^+ and 3CFH^+). These data are, however, crucial for astrophysicists and astrochemists in the detection of new species in interstellar medium (ISM), the discovery of these molecular species being not yet reported. It is in this perspective that a computational study based on quantum chemistry on FH^+ , 2CFH^+ and 3CFH^+ was undertaken. A series of properties including the proton affinity (PA) of furan and the two cyanofurans, the variations of enthalpy ($\Delta_r H$), entropy ($\Delta_r S$), and Gibbs free energy ($\Delta_r G$) for the reactions yielding cyanofurans (neutral and protonated forms), were studied at different temperatures (5 K, 10 K, 150 K and 298 K) and pressures ($P = 1\text{ atm}$ and $P = 10^{-5}\text{ atm}$) based on modern computational models (G2MP2, G3, G4MP2 and G4). While confirming that the protonation favors the α -position for furan, the PA values show that the protonation favors the nitrogen atom in cases of 2CFH^+ and 3CFH^+ . The $\Delta_r H$, $\Delta_r S$ and $\Delta_r G$ values revealed spontaneous reactions producing these species under ISM conditions of temperature and pressure. In addition quadrupole hyperfine structures and vibrational spectra which are essential tools for the characterization and the identification of interstellar molecular species are predicted, while the region where brightest lines fall for different temperatures is discussed. The results reported in this work are expected to assist astrophysicists and astrochemists, in the search for new chemical species in interstellar environments.

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<https://doi.org/10.1039/D2RA04351C>

<https://pubs.rsc.org/en/content/articlehtml/2022/ra/d2ra04351c>

Characterizing centrosymmetric two-ring PAHs using jet-cooled high resolution mid-infrared laser spectroscopy and anharmonic quantum chemical calculations

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The presence of Polycyclic Aromatic Hydrocarbon (PAH) molecules in the interstellar medium, recently confirmed by the detection of cyano-naphthalenes, renews the interest of extensive spectroscopic and physical-chemistry studies about such large species. The present study reports the jet-cooled rovibrational IR study of three centrosymmetric two-ring PAH molecules, naphthalene (C₁₀H₈), [1,5] naphthyridine (C₈H₆N₂) and biphenyl (C₁₂H₁₀) in the in-plane ring C–H bending (975–1035 cm⁻¹) and C–C ring stretching (1580–1620 cm⁻¹) regions. For the two most rigid PAHs, the accuracy of spectroscopic parameters derived in ground and several excited states (6 for naphthalene and 6 for [1,5] naphthyridine) has significantly improved the literature values. In addition, comparison between experiments and quantum chemical calculations confirms the predictive power of the corrected calculated rotational parameters. The more flexible structure of biphenyl makes particularly challenging the analysis of high resolution jet-cooled spectra of ν_{19} and ν_{23} modes recorded at about 1601 and 1013 cm⁻¹ respectively. The presence of three torsional vibrations below 120 cm⁻¹ together with small values of the rotational constants prevented us to determine the ground and $\nu_{19} = 1$ excited rotational constants independently. In the ν_{23} band region, the presence of two bands rotationally resolved and separated by only 0.8 cm⁻¹, raises the question of possible splittings due to a large amplitude motion, most probably the torsion of the aliphatic bond between the two phenyl rings.

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Vibrationally-Resolved X-ray Photoelectron Spectra of Six Polycyclic Aromatic Hydrocarbons from First-Principles Simulations

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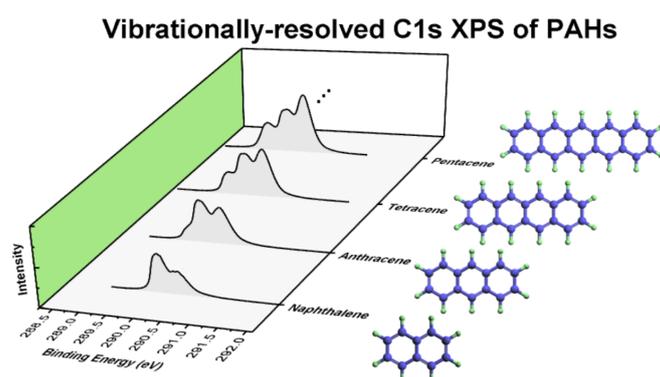
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Vibrationally-resolved C1s X-ray photoelectron spectra (XPS) of a series of six polycyclic aromatic hydrocarbons (PAHs; phenanthrene, coronene, naphthalene, anthracene, tetracene, and pentacene) were computed by combining the full core hole density functional theory and the Franck-Condon simulations with the inclusion of the Duschinsky rotation effect. Simulated spectra of phenanthrene, coronene, and naphthalene agree well with experiments both in core binding energies (BEs) and profiles, which validate the accuracy of our predictions for the rest molecules with no high-resolution experiments. We found that three types of carbons *i* (inner C), *p* (peripheral C bonded to three C atoms), and *h* (peripheral C bonded to an H atom) show decreasing BEs. In linear PAHs (the latter four), *h*-type carbons further split into *h1* or *h2* (on inner or edge benzene ring) subtypes with chemical shifts of ca. 0.2–0.4 eV. All major Franck-Condon-active modes are characterized to be in-plane vibrations: low-frequency ($< 800 \text{ cm}^{-1}$) C–C ring deformation modes play an essential role in determining the peak asymmetries; and for each *h*-type carbon a high-frequency (ca. 3600 cm^{-1}) C*–H stretching mode is responsible for the high-energy tail. We found that core ionization leads to reduction of all C*–C and C*–H bond lengths and ring deformation with a definite direction. Based on theoretical spectra of four linear PAHs, we found asymptotic relations and anticipated possible spectral features for even larger linear PAHs. Our calculations provide accurate reference spectra for XPS characterizations of PAHs, which are useful in understanding the vibronic coupling effects in this family.



Evolution of the vibrationally-resolved C1s X-ray photoelectron spectra of linear PAH molecules with increasing sizes.

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Low-temperature nitrogen-bearing polycyclic aromatic hydrocarbon formation routes validated by infrared spectroscopy

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Polycyclic aromatic hydrocarbons (PAHs) are abundant in many regions of the Universe, representing a major reservoir for cosmic carbon. However, their formation pathways in cold regions of space remain elusive. Recent astronomical detections show that current astrochemical models drastically underestimate the abundance of aromatic molecules and suggest that additional formation pathways such as ion–molecule reactions need to be considered. Here we reveal efficient low-temperature formation pathways towards nitrogen-containing PAHs via exothermic pyridine⁺ and acetylene ion–molecule reactions. The experimental approach combines kinetics with spectroscopic probing and unambiguously identifies key reaction intermediates and the final nitrogen-containing PAH product quinolizinium⁺, a structure that is thought to contribute to the 6.2 μm interstellar emission feature. This study not only provides competing formation pathways relevant in the chemistry of the interstellar medium and Titan’s atmosphere, but also delivers information to verify in-silico potential energy surfaces, astrochemical models and infrared observations.

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Contribution of polycyclic aromatic hydrocarbon ionization to neutral gas heating in galaxies: model versus observations

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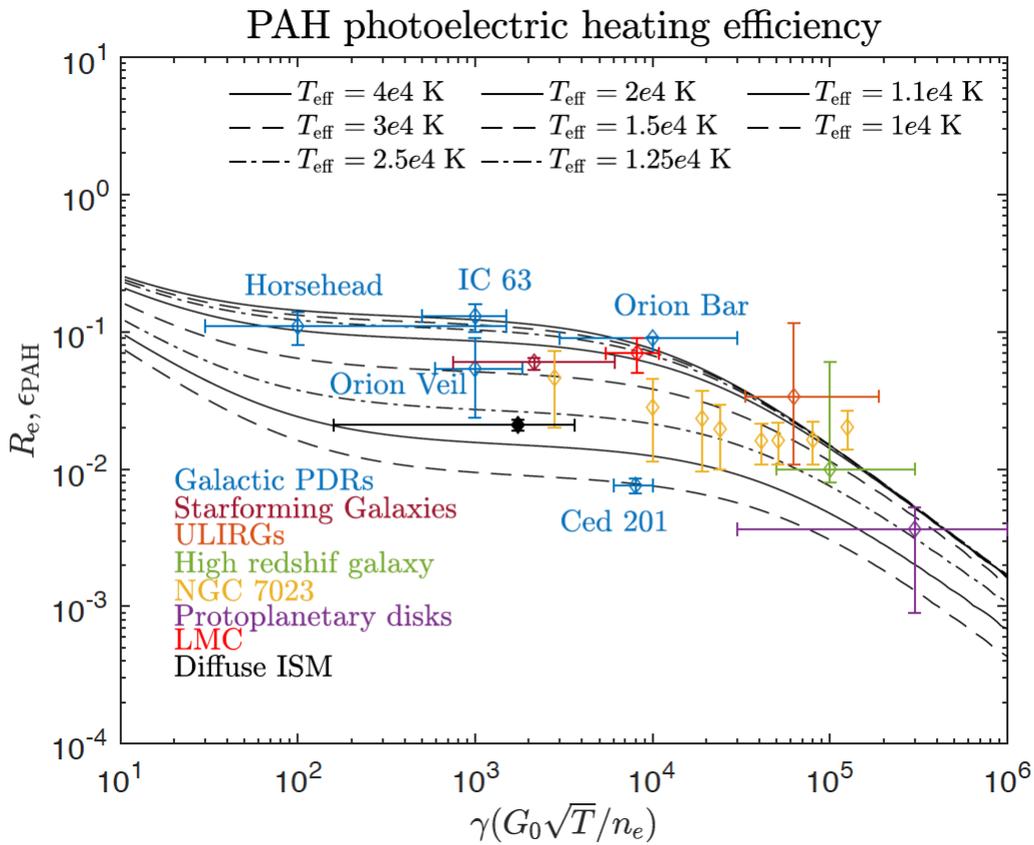
The ionization of polycyclic aromatic hydrocarbons (PAHs), by ultraviolet (UV) photons from massive stars is expected to account for a large fraction of the heating of neutral gas in galaxies. Evaluation of this proposal, however, has been limited by our ability to directly compare observational diagnostics to the results of a molecular model describing PAH ionization. The objective of this article is to take advantage of the most recent values of molecular parameters derived from laboratory experiments and quantum chemical calculations on PAHs and provide a detailed comparison between modeled values and observational diagnostics for the PAH charge state and the heating efficiency for PAHs. Despite the use of a simple analytical model, we obtain a good agreement between model results and observational diagnostics over a wide range of radiation fields and physical conditions, in environments such as star-forming regions, galaxies, and protoplanetary disks. In addition, we found that the modeled photoelectric heating rates by PAHs are close to the observed cooling rates given by the gas emission. These results show that PAH ionization is the main source of neutral gas heating in these environments. The results of our photoelectric heating model by PAHs can thus be used to assess the contribution of UV radiative heating in galaxies (*vs e.g. shock*). We conclude on the importance of implementing the physics of PAH ionization in astrophysical codes, which are developed, for example, for the evaporating surfaces of protoplanetary disks, the diffuse interstellar medium, and the photodissociation regions associated with star-forming regions in the local and distant universe. We provide the empirical formulas to calculate the heating rates and heating efficiencies for PAHs in this article.

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Astronomy and Astrophysics (accepted for publication August 2022)

<https://arxiv.org/abs/2208.08762>

<https://doi.org/10.1051/0004-6361/202243171>



Observed gas cooling to PAH emission ratio R_e and modeled photoelectric heating efficiency for PAHs, ϵ_{PAH} , as a function of the ionization parameter γ , for various stellar effective temperatures. The upper curve corresponds to $T_{\text{eff}} = 4 \times 10^4 \text{ K}$, and the lowest curve to $T_{\text{eff}} = 10^4 \text{ K}$. All models use $N_C = 54$ and a gas temperature of $T = 500 \text{ K}$.

PAH Growth in Flames and Space: Formation of the Phenalenyl Radical

Zachariah D. Levey¹, Benjamin A. Laws¹, Srivathsan P. Sundar², Klaas Nauta¹, Scott H. Kable¹, Gabriel da Silva², John F. Stanton³ and Timothy W. Schmidt⁴

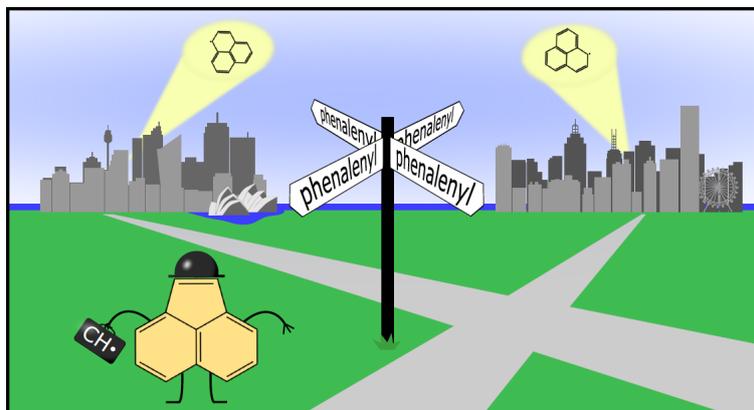
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Polycyclic aromatic hydrocarbons (PAHs) are intermediates in the formation of soot particles and interstellar grains. However, their formation mechanisms in combustion and interstellar environments are not fully understood. The production of tricyclic PAHs and, in particular, the conversion of a PAH containing a five-membered ring to one with a six-membered ring is of interest to explain PAH abundances in combustion processes. In the present work, resonant ionization mass spectrometry in conjunction with isotopic labelling is used to investigate the formation of the phenalenyl radical from acenaphthylene and methane in an electrical discharge. We show that in this environment, the CH cycloaddition mechanism converts a five-membered ring to a six-membered ring. This mechanism can occur in tandem with other PAH formation mechanisms such as hydrogen abstraction/ acetylene addition (HACA) to produce larger PAHs in flames and the interstellar medium.



The reaction of acenaphthylene + CH· – all roads lead to phenalenyl!!

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Identification and characterization of a new ensemble of cometary organic molecules

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In-situ study of comet 1P/Halley during its 1986 apparition revealed a surprising abundance of organic coma species. It remained unclear, whether or not these species originated from polymeric matter. Now, high-resolution mass-spectrometric data collected at comet 67P/Churyumov-Gerasimenko by ESA's Rosetta mission unveil the chemical structure of complex cometary organics. Here, we identify an ensemble of individual molecules with masses up to 140 Da while demonstrating inconsistency of the data with relevant amounts of polymeric matter. The ensemble has an average composition of $C_1H_{1.56}O_{0.134}N_{0.046}S_{0.017}$, identical to meteoritic soluble organic matter, and includes a plethora of chain-based, cyclic, and aromatic hydrocarbons at an approximate ratio of 6:3:1. Its compositional and structural properties, except for the H/C ratio, resemble those of other Solar System reservoirs of organics — from organic material in the Saturnian ring rain to meteoritic soluble and insoluble organic matter —, which is compatible with a shared prestellar history.

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Nature Communications, **13**, 3639 (2022)

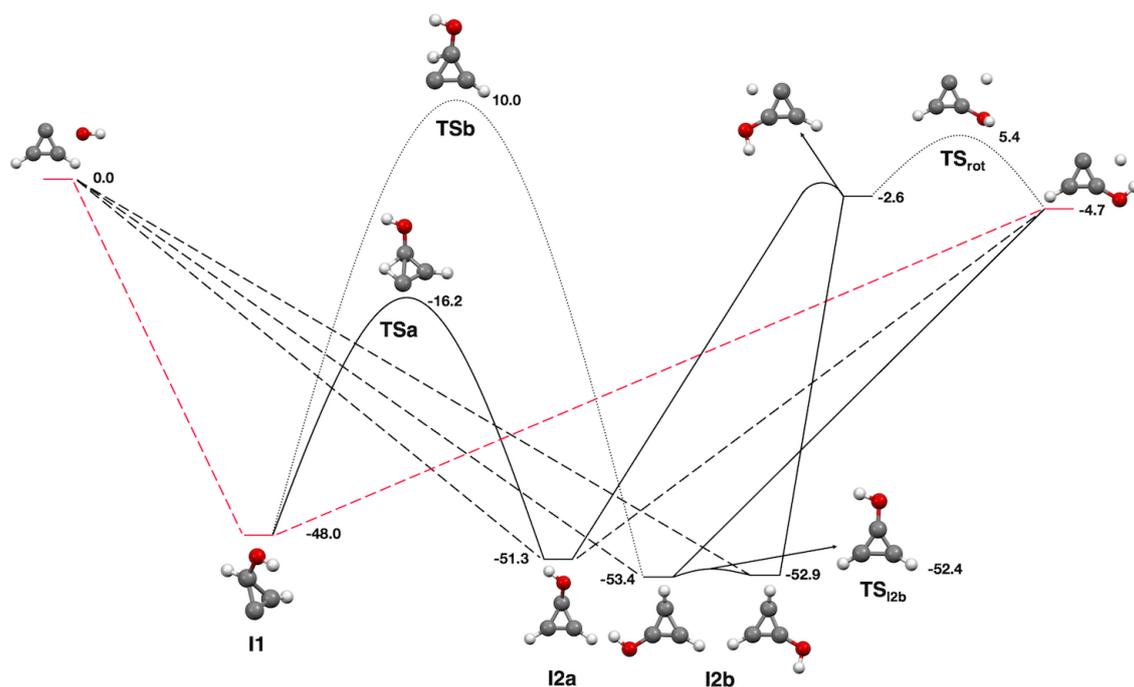
<https://doi.org/10.1038/s41467-022-31346-9>

The Formation of Monosubstituted Cyclopropenylidene Derivatives in the Interstellar Medium via Neutral-Neutral Reaction Pathways

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Five substituted cyclopropenylidene derivatives ($c\text{-C}_3\text{HX}$, $X = \text{CN}, \text{OH}, \text{F}, \text{NH}_2$), all currently undetected in the interstellar medium (ISM), are found herein to have mechanistically viable, gas-phase formation pathways through neutral-neutral additions of $\cdot X$ onto $c\text{-C}_3\text{H}_2$. The detection and predicted formation mechanism of $c\text{-C}_3\text{HC}_2\text{H}$ introduces a need for the chemistry of $c\text{-C}_3\text{H}_2$ and any possible derivatives to be more fully explored. Chemically accurate CCSD(T)-F12/cc-pVTZ-F12 calculations provide exothermicities of additions of various radical species to $c\text{-C}_3\text{H}_2$, alongside energies of submerged intermediates that are crossed to result in product formation. Of the novel reaction mechanisms proposed, the addition of the cyano radical is the most exothermic at $-16.10 \text{ kcal mol}^{-1}$. All five products are found to or are expected to have at least one means of associating barrierlessly to form a submerged intermediate, a requirement for the cold chemistry of the ISM. The energetically-allowed additions arise as a result of the strong electrophilicity of the radical species as well as the product stability gained through substituent-ring conjugation.



The calculated reaction mechanism for the formation of hydroxy cyclopropenylidene ($c\text{-C}_3\text{HOH}$).

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<https://doi.org/10.3847/1538-4357/ac8f4a>



Meetings

DIG (Dust, Ice and Gas) Astrochemistry

Virtual Meeting, India
17–18 November, 2022

<http://iases.org.in/dig-astrochem.html>

Using modern technologies and facilities, scientists unveiled the fingerprints of the chemicals in the interstellar medium down to stellar and planetary environments. High-sensitive and high-resolution telescopes like ALMA are providing amazing results by mapping the gas phase molecules down to the planetary scale. Further, JWST will complement chemical inventory by looking deep into the protoplanetary disk, planetary atmospheres, PDR, etc., and will investigate the ice compositions with a much deeper insight. Astrochemistry has now evolved as an emerging branch of many astrophysical fields, where molecules are used as a diagnostic tool to understand the physical and chemical properties of various astronomical objects. This webinar aims to bring together experimentalists, observers, and modelers to allow the astrochemical community to assemble and confer on recent accomplishments and upcoming challenges.

Registration is free.

Deadline: 8th November 2022.

Organized by:

- Institute of Astronomy Space and Earth Science (India),
- Physical Research Laboratory (India),
- Europlanet Society,
- Niigata University Quantum Research Center (Japan)

Conference chairs: Ankan Das and B. Sivaraman

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Laboratory Astrophysics

Tracking the evolution of cosmic matter towards molecular complexity

**International Winter School
Ecole des Houches, France**

5–10 February, 2023

<https://lab-astrophysic.sciencesconf.org/>

Following the last minute cancellation of the winter school on “Laboratory Astrophysics: tracking the evolution of cosmic matter towards molecular complexity” initially scheduled in 2022, we are pleased to confirm that a new session will be held in 2023. This session will take place at “Les Houches School of Physics”, located in the Chamonix valley in the French Alps in February 05–10 2023. Registration deadline is November 4th 2022.

Laboratory astrophysics is one the most powerful support to the interpretation of observation of baryonic matter in space. The development of high-performance ground-based and space telescopes observing the galactic and extra-galactic universe, together with large missions exploring the solar system are providing a wealth of information on complex molecular matter. The discovery of new exo-worlds together with the return of extra-terrestrial samples is very promising and exciting. Molecules exist in the Universe in a wide variety of environments and under a huge range of conditions, varying from ultra-low to ultra-high temperatures and densities. Laboratory Astrophysics aims to recreate these environments, to characterize the fundamental properties of matter and its evolution under specific controlled physical conditions. Scientists have to show great ingenuity to reproduce relevant conditions in the laboratory.

This school focuses on advanced techniques used to produce, analyze and investigate the properties and the evolution of extraterrestrial analogs in the laboratory, dedicated to improve our understanding of the origin and evolution of complex molecular matter observed in space, from dense molecular clouds up to the formation of new stars, planetary bodies and comets. The program will present a wide range of complementary and advanced methods developed in recent years in close connection to the most relevant astronomical observations. Emphasis will be put on the degree of chemical and/or structural complexity which can be achieved in the gas and solid phases and at their interface under space conditions. The methods used to characterize the physics of silicates and carbonaceous dust, and to investigate the formation/destruction processes of ices will be detailed. Techniques used to analyze matter from cometary and true-extra-terrestrial origins will also be presented.

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ICE 2024

Laboratory Astrophysics Workshop

**Sheraton Coconut Beach Resort
Kapaa, Kauai, Hawaii, USA**

February 19–22, 2024

<http://uhmreactiondynamics.org/ICE2024.html>

Significant new experimental techniques have been developed to investigate the interaction of ionizing radiation (UV, VUV, gamma rays, charged particles) and of neutrals (atoms, radicals, molecules, grains) with surfaces of solids (ices, minerals, carbonaceous compounds) in the Solar System and in the Interstellar Medium (ISM). These processes provide new fundamental insights — sometimes on the molecular level — into the processes that are critical to the chemistry in the ISM, of star and planet forming regions, and on/in icy objects in the Solar System from the formation of the simplest molecule (molecular hydrogen) to astrobiologically important species such as amino acids and sugars. There is an increasing convergence of interests of these fields, so a ‘united’ workshop is highly desired. Based on the successful workshops in 2013 and 2015, the third workshop will feature invited (senior and junior researchers) as well as contributed talks covering the interaction of (non)ionizing radiation (UV, VUV, gamma rays, charged particles) and neutrals (atoms, radicals, molecules, grains) with low temperature solids (ices, minerals, organics). The talks can be extended to observations, modeling, and electronic structure calculations, if these topics can be linked — as evident from the abstract — to laboratory experiments. The session chairs will adhere strictly to the allocated time limits of the presentations.

Accommodation: The workshop will take place in the Sheraton Coconut Beach Resort in Kapaa, Kauai, Hawaii, USA, starting with a reception and registration on February 18, 2024, at 6 pm (Sunday). Group rates on an allocated block of rooms are being negotiated. Additional hotels are within walking distance.

Transportation: Sheraton Coconut Beach Resort is a short drive (20 minutes) from the airport (LIH). LIH can be reached on non-stop flights from HNL, LAX, SFO, SEA, PHX, OAK.

Registration: Registration and abstract submission will begin July 1, 2023, with late registration beginning on November 1, 2023. No refunds will be given after November 1, 2023. This is an in-person conference only.

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AstroPAH Newsletter

<http://astropah-news.strw.leidenuniv.nl>

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Next issue: 17 November 2022

Submission deadline: 4 November 2022