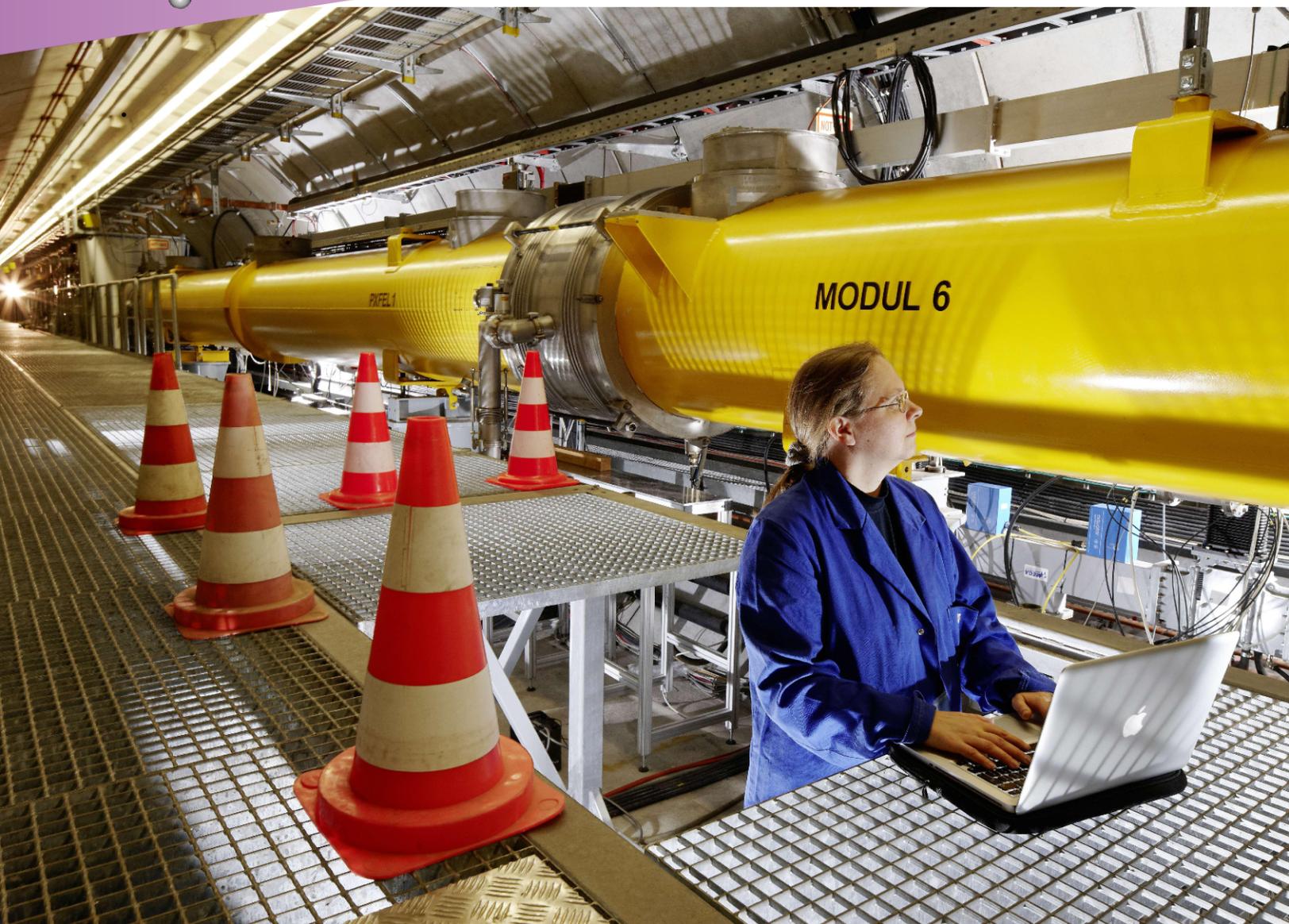


AstropAH

A Newsletter on Astronomical PAHs

Issue 36 | March 2017



FLASH

Editorial

Dear Colleagues,

It's spring again, and what better way to celebrate the vernal equinox than with a new issue of AstroPAH. The impressive installation featured on the cover is FLASH. No, not the fastest man alive, but the 'as fast as light' Free-electron-laser in Hamburg. FLASH is a beautiful and versatile user facility at the DESY research center, and you can now read all about it and the interest to PAH research in our In Focus.

The latest in PAH research is presented afterwards in the abstracts section and concerns PAH chemistry at eV internal energies, PAH reactions with carbon atoms, photochemistry of PAH:water complexes, the search for PAHs in outflows, and research on related species such as C_6^- , Titan's aerosols, and hydrocarbon interstellar dust analogs.

AstroPAH can help you promote your science. Visit our webpage or contact us for more information. You can send us your contributions anytime. For publication in April, see the deadlines below.

We thank you all for your contributions so far!

The Editorial Team

**Next issue: 18 April 2017.
Submission deadline: 7 April 2017.**

AstroPAH Newsletter

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PAH Picture of the Month

The Free-Electron Laser FLASH accelerating modules (<http://flash.desy.de>).

Credits: DESY/H. Müller-Elsner



The Free-Electron Laser FLASH at Deutsches Elektronen-Synchrotron (DESY) in Hamburg

Presented by Sébastien Gruet, Amanda Steber, and Melanie Schnell

In interstellar space, PAHs interact with intense ionizing radiation, but not much is known about the physics or photochemistry of these interactions. The molecular stability and photoinduced fragmentation dynamics of these PAHs under such conditions still hold open questions. While it is generally assumed that under UV irradiation PAHs will undergo complete dehydrogenation to form carbon clusters or even small graphene sheets, with a subsequent break up of carbon atoms if sufficient energy is provided^[1], the shorter wavelength spectral range is not well explored.

It has been experimentally observed that, after VUV and XUV excitation, there is a delicate interplay between different de-excitation pathways resulting in ionization and fragmentation, which largely depends on the molecular size^[2]. For small and medium-sized PAHs, fragmentation pathways resulting in loss of H and H₂ dominate over internal energy redistribution. For high excitation energies, loss of C₂H₂ (either neutral or charged) is also assumed. This situation is reversed for larger PAHs. The underlying mechanisms of this complex interplay between excitation of vibrational modes and fragmentation are not well understood. Answers to these fundamental questions can be given by performing both time-independent (static) and time-resolved laboratory spectroscopy experiments, mimicking the conditions in interstellar space.

Experiments have been previously performed that were interested in answering some of these questions, but time-resolved data is hard to come by. This is due to the fact that many sources do not have the ability to produce pulses short enough to monitor the evolution of the resulting processes^[3,4]. High Harmonics Generation (HHG) sources which create ultra-short pulses have been used for PAH research^[5]; however, these sources are not widely available. DESY's Free-Electron Laser (FEL) FLASH is a well-suited facility to study time-independent and time-resolved experiments involving PAHs, due to its high flux at relatively large photon-energy and ultra-short pulse durations. In the fall of 2016, we formed a larger consortium involving six international research groups and dedicated a measurement campaign to investigate the

photochemistry of three- and four-ring PAHs after XUV excitation in a XUV-UV pump-probe setup using FLASH. A more thorough explanation of the FLASH facility and its capabilities are presented below.

FLASH Overview

FLASH, the Free-Electron LASer in Hamburg, is a user facility that started its operation in summer 2005 as the first free-electron laser for VUV and soft X-ray radiation, and has since grown to drive two FEL light generating undulator lines with one accelerator. It currently covers a wavelength range from 4 nm to about 90 nm in the first harmonic with 1-5 GW peak power and ultra-short pulse durations between 10 fs and 200 fs. Figure 1 shows a schematic of the FLASH facility, and the operational parameters of the two FEL lines can be found in Table 1. FLASH is a high-gain FEL which achieves laser amplification and saturation within a single pass of a bunch of electrons through a long undulator. It does not require a mirror-based cavity which is needed in conventional lasers. The lasing process is initiated by the spontaneous undulator radiation (described in more detail below). The FEL is operated in the “self-amplified spontaneous emission” (SASE) mode without needing an external input signal. The SASE FEL radiation has similar properties as optical laser beams: it is transversely coherent and can be focused to tiny spots with an irradiance exceeding 10^{16} W/cm².

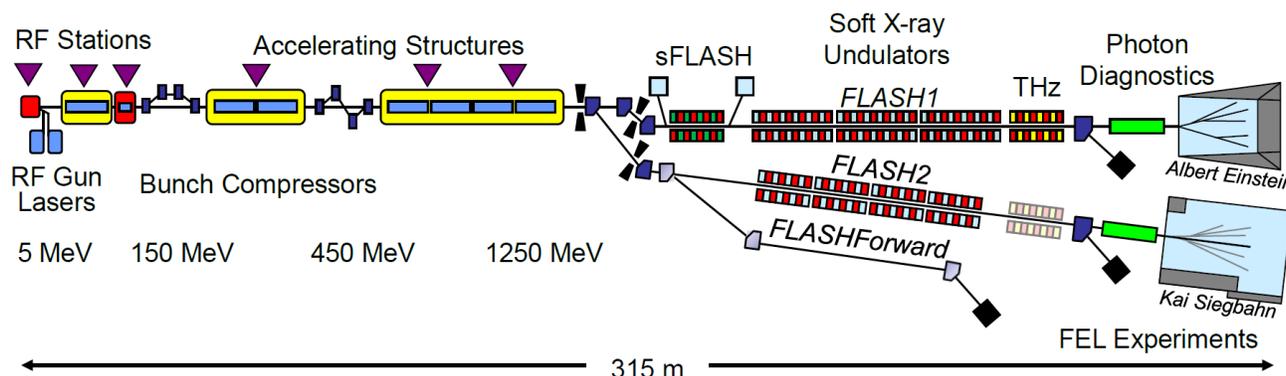


Figure 1: Schematic of the layout of the FLASH facility. Picture taken from http://flash.desy.de/index_eng.html

FLASH1 was the first user facility to be developed serving user groups in the FLASH experimental hall 'Albert Einstein'. It offers five beamlines for users: three beamlines utilizing the direct FEL pulses (BL1, BL2 and BL3), and two plane grating monochromator beamlines (PG1 and PG2) to select a narrower bandwidth from the FEL pulses for experiments requiring monochromatic radiation. The BL1, BL2 and BL3 beamlines focus the initial 3-5 mm FEL beam to spots of approximately 8 μ m, 20 μ m and 20 μ m, respectively. The BL2 and BL3 beamlines can also be used unfocused for experiments that do not require a high photon density or by research groups who prefer to install their own focusing optics. More information about BL1 can be found below, in particular on the permanent end-station CAMP where the PAH experiments were performed. The monochromator used for the PG1 and PG2 beamlines is tunable to allow for different wavelengths to be selected, for a user bandwidth that is approximately 1% of the

FEL bandwidth. An energy range from 20 eV to 1000 eV is covered. The spot size at PG2 is presently about 50 μm depending on wavelength and monochromator settings.

A second FEL undulator line, FLASH2, was built from 2011 to 2015 and has recently started operation for experiments in the new FLASH experimental hall ‘Kai Siegbahn’ adjacent to FLASH1. The long trains of electron bunches of FLASH are split in two - such that one part serves FLASH1, the other part FLASH2, both with the 10 Hz repetition rate of the accelerator. Thus, the FLASH facility at DESY currently comprises two separate and almost independent FEL sources. Because of this, the time for scientific experiments has practically doubled, significantly enhancing the capacities for XUV and soft X-ray FEL users at DESY. FLASH2 will eventually offer up to six experimental stations, with two initial beamlines FL24 and FL26 operational since April 2016.

Table 1: *FLASH parameters. Table taken from <http://flash.desy.de/accelerator/>*

| | | FLASH1 | FLASH2 |
|-----------------------------|---|---------------------|---------------------|
| Electron beam | | | |
| Energy | MeV | 0.35 - 1250 | 0.4 - 1250 |
| Peak Current | kA | 1 - 2.5 | 1 - 2.5 |
| Emittance, norm. (x,y) | $\mu\text{m rad}$ | 1.4 | 1.4 |
| Nb. of Bunches per Second | | 10 - 5000 | 10 - 5000 |
| Bunch Train Duration | ms | <0.8 | <0.8 |
| Rep. Rate | Hz | 10 | 10 |
| Energy Spread | keV | 200 | 500 |
| Undulators | | | |
| Period | cm | 2.73 | 3.14 |
| Gap | mm | 12 | 9 |
| Peak Magnetic Field | T | 0.48 | |
| K | | 1.2285 | 0.7 - 2.8 |
| Total Length | m | 6 * 4.5 | 12 * 2.5 |
| FEL Radiation | | | |
| Wavelength | nm | 4.2 - 51 | 4 - 90 |
| Single Pulse Energy | μJ | 1 - 500 | 1 - 1000 |
| Average Power | mW | <1000 | <1000 |
| Spectral Width (FWHM) | % | 0.7 - 2 | 0.5 - 2 |
| Pulse Duration (FWHM) | fs | <30 - 200 | <10 - 200 |
| Peak Power | GW | 1 - 5 | 1 - 5 |
| Photons per Single Pulse | | $10^{11} - 10^{14}$ | $10^{11} - 10^{14}$ |
| Peak Spectral Brilliance | photons/s/mrad ² /mm ² /(0.1% bw) | $10^{28} - 10^{31}$ | $10^{28} - 10^{31}$ |
| Average Spectral Brilliance | photons/s/mrad ² /mm ² /(0.1% bw) | $10^{17} - 10^{21}$ | |

A Quick Look at How FLASH Works

In a single pass/SASE free-electron laser, the special X-ray laser light is produced based on a sophisticated principle: during their slalom run through a periodic array of magnets (the undulator, cf. Fig. 2), the electron bunches emit synchrotron radiation (photons). The photon beam propagates in a straight line so that it overlaps with the electron bunch. This undulator “resonance” wavelength imprints its periodic structure on the electron bunch, so that the initially homogeneous charge density distribution becomes periodic - a chain of tiny individual charge “disks” regularly separated by a single wavelength. Now all the electron disks emit radiation in synchronism, and the light at this resonance wavelength can amplify itself to form high-intensity laser radiation - more than a million times more intense than the spontaneous undulator radiation.



Figure 2: *FLASH1* undulators. Picture taken from http://flash.desy.de/index_eng.html

A distinguishing feature of FLASH is the use of superconducting accelerator technology to propel the electrons to the required high energy. This pioneering technology was developed by DESY together with 50 institutes from 12 countries within the international TESLA Technology Collaboration. Unlike conventional facilities, the TESLA accelerator elements - the resonators/cavities - are of highly pure superconducting niobium: cooled to minus 271 degrees Celsius, they conduct electric current practically loss-free, so that almost all of the electric power they consume can be transferred to the particles - an extremely efficient acceleration method. What’s more, the superconducting resonators/cavities deliver a very thin and homogeneous electron beam of extremely high quality at a very high repetition rate. A particle beam with such special properties is a prerequisite to operate a free-electron laser in the X-ray region, which is why this technology is also used for the European XFEL.

The End-Station CAMP

The aforementioned PAH experiments were performed in the CAMP end-station at FLASH1 which is described in more detail below. Of the three BL beamlines on FLASH1, BL1 (cf. Fig. 3) has Kirkpatrick-Beaz (KB) focusing optics and the permanently installed multi-purpose chamber CAMP. This pair of nickel-coated KB mirrors allows focusing the FEL radiation over the entire wavelength range available at FLASH1 to a spot size of $6 \mu\text{m} \times 8 \mu\text{m}$ (hor/ver). The multipurpose end-station, CAMP, combines electron- and ion-spectroscopy, pump-probe, and imaging experiment capabilities. Its modular and flexible layout allows using many combinations of large-area, single-photon counting pnCCD photon-detectors with velocity map imaging (VMI)- and cold target recoil ion momentum spectroscopy (COLTRIMS)-type electron and ion

spectrometers, and various gas jets and particle injectors (available through collaborations). It also offers dedicated laser in-coupling optics and diagnostics for the FLASH pump-probe laser at the fundamental wavelength of 800 nm as well as the second (400 nm) and third (267 nm) harmonic.

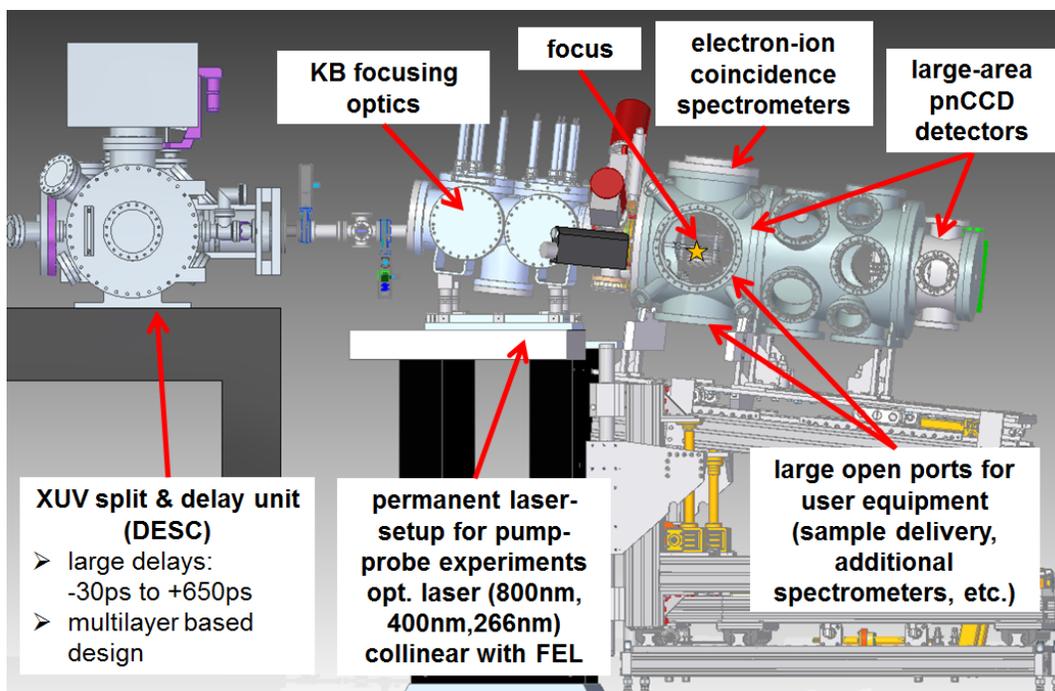


Figure 3: Layout of the BL1 front end including the Split-and-Delay unit DESC, the Kirkpatrick-Baez (KB) focusing optics, and the CAMP end-station. The picture was taken from http://photon-science.desy.de/facilities/flash/beamlines/bl_beamlines_flash1/camp/index_eng.html

Example of PAH Experimentation Using FLASH

At the end of 2016, the CAMP instrument at FLASH was used for the first time to investigate the photophysics of PAHs in the extreme ultraviolet (XUV). This ongoing project is led by Bastian Manschwetus and Melanie Schnell, and it involves collaborative work between six international laboratories/ groups: DESY and MPSD (Hamburg, Germany), Lund University (Sweden), Kansas State University (USA), University of Oxford (UK), and Aarhus University (Denmark).

This experiment aims to study the photoionization of neutral PAHs and their subsequent fragmentation pathways at 30.3 nm (40.8 eV) which is the fluorescence line of singly ionized helium (one of the strongest lines in the interstellar XUV radiation). The goal is to explore the molecular stability and the photoinduced fragmentation dynamics of PAHs under these conditions by identifying the timescales at which different fragmentation channels appear in a structure-dependent way. The femtosecond fragmentation dynamics after photoionization and fragmentation of small PAHs has been investigated through pump-probe experiments combining the XUV pulses from FLASH with UV pulses produced using a pump-probe femtosecond laser. A schematic of the

experiment conducted in late 2016 is shown in Fig. 4 using the example of naphthalene. The targeted molecules were phenanthrene and pyrene, two medium sized PAHs with three and four aromatic rings respectively. The results of this study will give insight into the ultrafast charge rearrangement and hydrogen loss processes of the molecules as well as provide information on how fast and efficiently the molecule can handle the additional energy after ionization.

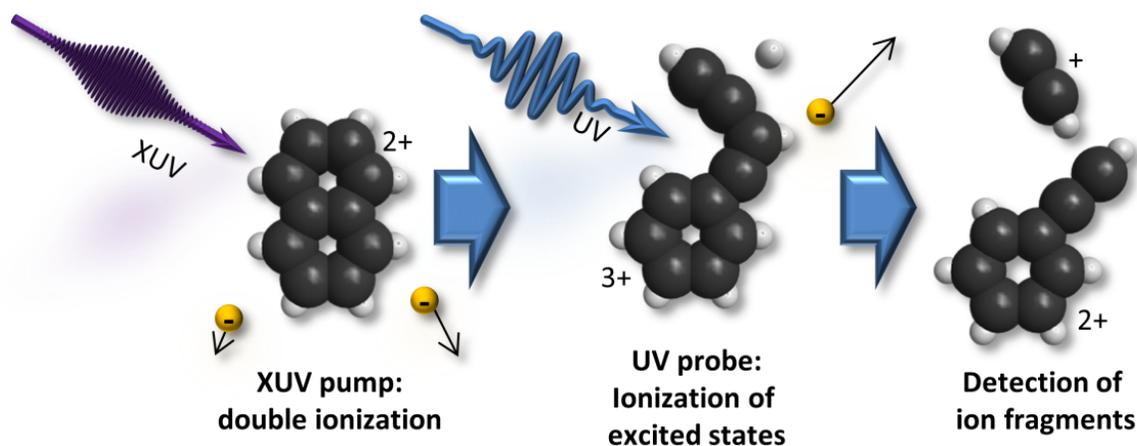


Figure 4: Scheme of a potential XUV pump UV probe mechanism: XUV excitation at 30.3 nm leads to double-ionization and excitation of naphthalene. The time-delayed UV probe pulse ionizes the excited state. The ion fragments are detected subsequently. Alternatively, the XUV pump might lead to ionization, directly followed by fragmentation into neutral and ionic fragments. The UV probe will then ionize the neutral fragments. Image credits: Bastian Manschwetus

As demonstrated here, the FLASH user facility offers the opportunity to study PAHs in a time-resolved manner that can answer many questions pertaining to the physics and photochemistry that could occur in interstellar environments. If you are interested in working at FLASH, proposals can be submitted in either April or November of each year. Information about submitting a proposal can be found at: http://photon-science.desy.de/users_area/user_guide/index_eng.html.

Acknowledgments

The authors would like to thank Dr. Thomas Zoufal (DESY PR) and Benjamin Erk (CAMP) for their contributions.

Information for the article was taken from the following websites and sister pages:

http://photon-science.desy.de/facilities/flash/index_eng.html

http://photon-science.desy.de/facilities/flash/beamlines/bl_beamlines_flash1/camp/index_eng.html

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Abstracts

PAH chemistry at eV internal energies 1. H-shifted isomers

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The PAH family of organic compounds (polycyclic aromatic hydrocarbons), involved in several fields of chemistry, has received particular attention in astrochemistry, where their vibrational spectroscopy, thermodynamic, dynamic, and fragmentation properties are now abundantly documented. This survey aims at drawing trends for low spin-multiplicity surfaces of PAHs bearing internal energies in the range 1-10 eV. It addresses some typical alternatives to the ground-state regular structures of PAHs, making explicit possible intramolecular rearrangements leading to high-lying minima. These isomerisations should be taken into consideration when addressing PAH processing in astrophysical conditions. The first part of this double-entry study focuses on the hydrogen-shifted forms, which bear both a carbene center and a saturated carbon. It rests upon DFT calculations mainly performed on two emblematic PAH representatives, coronene and pyrene, in their neutral and mono and multi-cationic states. Systematically searched for in neutral species, these H-shifted minima are lying 4-5 eV above the regular all-conjugated forms, and are separated by barriers of about one eV. General hydrogen-shifting is found to be easier for cationic species as the relative energies of their H-shifted minima are 1-1.5 eV lower than those for neutral species. As much as possible, classical knowledge and concepts of organic chemistry such as aromaticity and Clar's rules are invoked for result interpretation.

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Accepted for publication in Molecular Astrophysics

<http://dx.doi.org/10.1016/j.molap.2017.02.001>

<https://arxiv.org/abs/1702.04186>

PAH chemistry at eV internal energies. 2. Ring alteration and dissociation

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Recognized as important interstellar constituents, polycyclic aromatic hydrocarbons (PAHs) have been intensively studied in astrochemistry and their spectroscopy, thermodynamics, dynamics, and fragmentations are now amply documented. There exists typical alternatives to the ground-state regular planar structures of PAHs, as long as they bear internal energies in the range 1-10 eV. Resulting from intramolecular rearrangements, such high-lying minima on the potential-energy surfaces should be taken into consideration in the studies of PAH processing in astrophysical conditions. Resting upon DFT calculations mainly performed on two emblematic PAH representatives, coronene and pyrene, in their neutral and mono and multi-cationic states, this second survey addresses the following alternatives: (1) opened forms containing ethynyl or 2-butynyl groups, (2) vinylidene isomers, in which phenanthrene patterns are reorganized into dibenzofulvene ones, (3) twisted forms, where external CH=CH bonds can be partly twisted, and (4) bicyclobutane forms, in which the latter are integrated in saturated bicyclic forms. A few scenarios for elimination of fragments H, H₂, C₂H₂ and C₂H₄ are explored. As far as possible, familiar concepts of organic chemistry, such as aromaticity or Clar's rules, are invoked for interpretations.

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Accepted for publication in Molecular Astrophysics

<http://dx.doi.org/10.1016/j.molap.2017.02.002>

<https://arxiv.org/abs/1702.03826>

Formation and stabilization of C₆⁻ by radiative electron attachment

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Radiative electron attachment (REA) plays an important role in forming molecular anions in various astrophysical environments. In this work, we determined the rate coefficient for the formation of C₆⁻ by REA based on a detailed balance approach. C₆⁻ ions are stored in an electrostatic ion beam trap and are photoexcited above their adiabatic detachment energy (4.18 eV). Due to fast internal conversion and intramolecular vibrational redistribution, photoexcitation leads to the formation of temporary negative ions (TNIs), the same as those one formed by the electron attachment. Absolute vibrational autodetachment and recurrent (or Poincaré) fluorescence (RF) rate coefficients have already been reported [V. Chandrasekaran et al., J. Phys. Chem. Lett. 5, 4078 (2014)]. Knowing the branching ratios of the various competing rate

coefficients is decisive to the understanding of the formation probability of anions via REA. The radiative stabilization rate of C_6^- , shown to be dominated by RF, was determined to be $5 \times 10^4 \text{ s}^{-1}$ at the electron detachment energy, i.e., at least a factor of 100 faster than the stabilization by infrared transitions. The RF is found to very effectively stabilize the TNI formed by electron attachment. Using detailed balance to link the measured delayed detachment rate to the rate of electron attachment, we estimate the REA rate leading to the formation of C_6^- to be $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300 K in agreement with theory ($1.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ [R. Terzieva and E. Herbst, Int. J. Mass Spectrom. 201, 135 (2000)]). Such a high rate for REA to C_6 indicates that REA may play a prominent role in the formation of anions in the interstellar medium.

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The Journal of Chemical Physics 146, 094302 (2017)

<http://aip.scitation.org/doi/full/10.1063/1.4977059>

Growth and Destruction of PAH Molecules in Reactions with Carbon Atoms

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A very high abundance of atomic carbon in the interstellar medium (ISM), and the high reactivity of these species toward different hydrocarbon molecules including benzene, raise questions regarding the stability of polycyclic aromatic hydrocarbon (PAH) molecules in space. To test the efficiency of destruction of PAH molecules via reactions with atomic carbon, we performed a set of laboratory and computational studies of the reactions of naphthalene, anthracene, and coronene molecules with carbon atoms in the ground state. The reactions were investigated in liquid helium droplets at $T = 0.37 \text{ K}$ and by quantum chemical computations. Our studies suggest that all small and all large catacondensed PAHs react barrierlessly with atomic carbon, and therefore should be efficiently destroyed by such reactions in a broad temperature range. At the same time, large compact pericondensed PAHs should be more inert toward such a reaction. In addition, taking into account their higher photostability, much higher abundances of pericondensed PAHs should be expected in various astrophysical environments. The barrierless reactions between carbon atoms and small PAHs also suggest that, in the ISM, these reactions could lead to the bottom-up formation of PAH molecules.

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Astrophys. J. 836, 32, 2017

<http://stacks.iop.org/0004-637X/836/i=1/a=32>

Efficient photochemistry of coronene:water complexes

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The photochemistry of ices with polycyclic aromatic hydrocarbons (PAHs) has been extensively studied, but to date no investigation has been made of PAHs in interaction with low numbers ($n < 4$) of molecules of water. We performed photochemical matrix isolation studies of coronene:water complexes, probing the argon matrix with FTIR spectroscopy. We find that coronene readily reacts with water upon irradiation with a mercury vapour lamp to produce oxygenated PAH photoproducts, and we postulate a reaction mechanism via a charge transfer Rydberg state. This result suggests that oxygenated PAHs should be widely observed in regions of the ISM with sufficiently high water abundances, for example near the edges of molecular clouds where water molecules begin to form, but before icy layers are observed, that is at $A_V < 3$. In order to explain the low derived observational abundances of oxygenated PAHs, additional destruction routes must be invoked.

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A&A 599, A124 (2017)

<https://arxiv.org/abs/1612.03008>

<http://www.aanda.org/articles/aa/abs/2017/03/aa29613-16/aa29613-16.html>

Formation of coronene:water complexes: FTIR study in argon matrices and theoretical characterisation

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In this paper we report a combined theoretical and experimental study of coronene:water interactions in low temperature argon matrices. The theoretical calculations were performed with the mixed, Density Functional-based Tight Binding/Force Field approach. The results are discussed in the light of experimental matrix isolation FTIR spectroscopic data. We show that, in the solid phase $(C_{24}H_{12})(H_{20})_n$ ($n \leq 6$) σ -type complexes are formed, whereas in the gas

phase π -interaction is preferred. These σ -complexes are characterised by small shifts in water absorption bands and a larger blue shift of the out-of-plane $\gamma(\text{CH})$ deformation of coronene, with the shift increasing with the number of complexed water molecules. Such σ interaction is expected to favour photochemical reaction between water and coronene at the edges of the coronene molecule, leading to the formation of oxidation products at low temperature, even in presence of only a few water molecules and at radiation energies below the ionisation potential of coronene.

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Phys. Chem. Chem. Phys., 2017, Advance Article

<http://pubs.rsc.org/en/content/articlelanding/2017/cp/c6cp08559h#ldivAbstract>

Search for Polycyclic Aromatic Hydrocarbons in the Outflows from Dust-Producing Wolf-Rayet Stars

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A combined mid-IR spectrum of five colliding-wind, massive, dust-producing Population I Wolf-Rayet (WR) binaries shows a wealth of absorption and emission details coming from the circumstellar dust envelopes, as well as from the interstellar medium. The prominent absorption features may arise from a mix of interstellar carbonaceous grains formed in high- (e.g., 3.4, 6.8, 7.2 μm) and low-temperature (3.3, 6.9, 9.3 μm) environments. The broad emission complexes around ~ 6.5 , 8.0 and 8.8 μm could arise from ionized, small polycyclic aromatic hydrocarbon (PAH) clusters and/or amorphous carbonaceous grains. As such these PAH emissions may represent the long sought after precursors of amorphous Carbon dust. We also detect a strong ~ 10.0 μm emission in the spectra of WR48a and WR112, that we tentatively link to ionized PAHs. Upon examining the available archival spectra of prodigious individual WR dust sources, we notice a surprising lack of 7.7 μm PAH band in the spectrum of the binary WR19, in contrast to the apparent strength of the 11.2, 12.7 and 16.4 μm PAH features. Strong PAH emissions are also detected in the $\lambda > 10$ μm spectrum of another dust-producing system, WR118, pointing to the presence of large, neutral, presumably interstellar PAH molecules towards WR19 and WR118.

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Accepted for publication in MNRAS

<https://arxiv.org/abs/1703.01236>

The Titan Haze Simulation (THS) experiment on COSmIC. Part II. Ex-situ analysis of aerosols produced at low temperature

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This paper presents the first results of the solid phase analysis of the Titan tholins generated in the Titan Haze Simulation (THS) experiments. This study complements the gas phase analysis study that was presented in a previous publication introducing the THS capabilities. In the THS experiment, the chemistry is simulated by plasma in the stream of a supersonic jet expansion. With this unique design, the gas is jet-cooled to Titan-like temperature (~ 150 K) before inducing the chemistry by plasma, and remains at low temperature in the plasma discharge (~ 200 K). Here, we present and discuss the results of scanning electron microscopy and infrared spectroscopy studies of THS solid aerosols produced in the four gas mixtures already studied by mass spectrometry in the gas phase: N_2-CH_4 , $N_2-CH_4-C_2H_2$, $N_2-CH_4-C_6H_6$ and $N_2-CH_4-C_2H_2-C_6H_6$. Differences in the morphology of the grains and aggregates produced in the volume of the gas phase in the plasma cavity, depending on the initial precursors, have been observed by scanning electron microscopy, that appear to be linked to differences in the growth processes and might have an impact on microphysical models. The mid-infrared spectroscopic analysis highlights changes in the nitrogen chemistry, and the abundance of aromatic compounds, depending on the initial gas mixture. A preliminary study of the aging and degradation of the THS samples with time and exposure to air and light has shown the importance, for future studies of laboratory-generated planetary aerosol analogs, of collecting, storing and characterizing samples under controlled environment. A comparison to VIMS data shows that the THS tholins produced in simpler mixtures, i.e., with a higher level of nitrogen incorporation, are more representative of Titan's aerosols.

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Icarus 289, 214 (2017)

<http://www.sciencedirect.com/science/article/pii/S0019103516304791>

Structure and infrared spectra of hydrocarbon interstellar dust analogs

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A theoretical study of the structure and mid infrared (IR) spectra of interstellar hydrocarbon dust analogs is presented, based on DFT calculations of amorphous solids. The basic

molecular structures for these solids are taken from two competing literature models. The first model considers small aromatic units linked by aliphatic chains. The second one assumes a polyaromatic core with hydrogen and methyl substituents at the edges. The calculated spectra are in reasonably good agreement with those of aliphatic-rich and graphitic-rich samples of hydrogenated amorphous carbon (HAC) generated in our laboratory. The theoretical analysis allows the assignment of the main vibrations in the HAC spectra and shows that there is a large degree of mode mixing. The calculated spectra show a marked dependence on the density of the model solids, which evinces the strong influence of the environment on the strengths of the vibrational modes. The present results indicate that the current procedure of estimating the hydrogen and graphitic content of HAC samples through the decomposition of IR features into vibrational modes of individual functional groups is problematic owing to the mentioned mode mixing and to the difficulty of assigning reliable and unique band strengths to the various molecular vibrations. Current band strengths from the literature might overestimate polyaromatic structures. Comparison with astronomical observations suggests that the average structure of carbonaceous dust in the diffuse interstellar medium lies probably in between those of the two models considered, though closer to the more aliphatic structure.

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Phys. Chem. Chem. Phys., 2017, 19, 1352

<http://rsc.li/2mimXSX>

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Next issue: 18 April 2017
Submission deadline: 7 April 2017