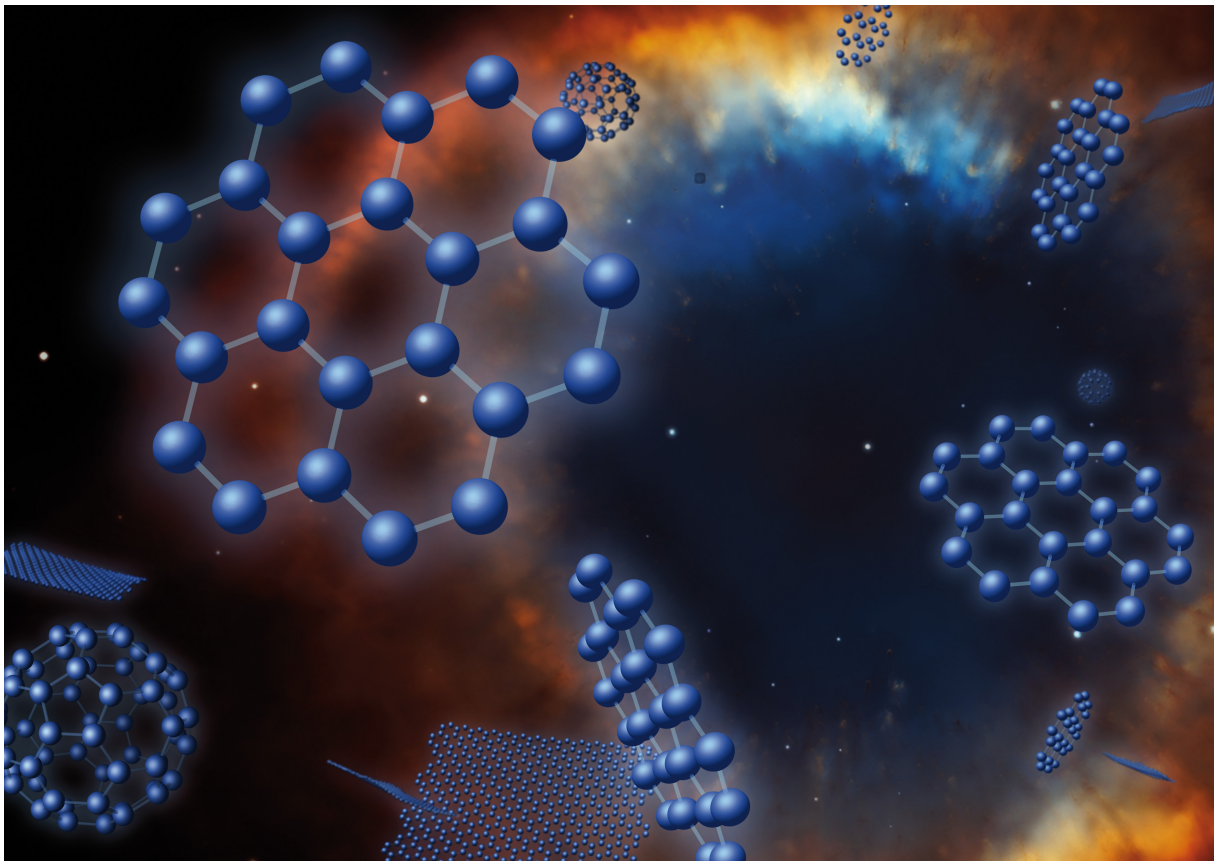
First Meeting of NanoSpace Working Group 2

Processing, reactivity and relaxation pathways of nC



Edinburgh, Scotland

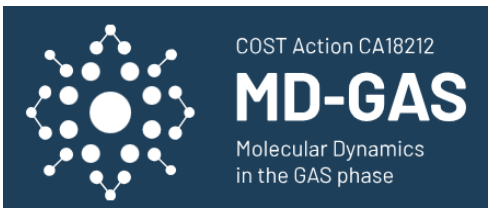
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	Tue	Wed	Thu	Fri
8:00				
	Registration and opening remarks	**Registration**		**Registration**
9:00	Puzzarini	Oomens	**Registration**	Hróðmarsson
			Hornekær	Campisi
10:00	Bull	Palotás		Asvany
	Coffee break	**Coffee break**	McCoustra	**Closing remarks**
11:00	Loru	Jusko	**Coffee break**	
	Zettergren	DeVine	Brown	
12:00	Fárník	Daly	Noble	
	Lunch	**Lunch**	**Lunch**	
13:00	Stockett	Gruber	Jacovella	
14:00	Berberan-Santos	Koch	Tanuma	
	Biennier	Piekarski	Bychkova	
15:00	**Coffee break**	Algarra	**Coffee break**	
	Simonsen	**Coffee break**	Maclot	
16:00	Rousseau	Glasse	Candian	
	Drink reception and poster session	Biller		
17:00				
18:00				
19:00				
20:00		**Dinner**		

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Hunting for interstellar molecules

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Understanding the chemical evolution of the universe is one of the main aims of Astrochemistry. The starting point to address this challenge is the knowledge of the molecular census and their corresponding abundance. In this context, rotational spectroscopy plays the central role. The astronomical observation of the spectroscopic features of a given molecule is the definitive, unequivocal proof of its presence in the astronomical environment under consideration, with the overwhelming majority of gas-phase chemical species being discovered via their rotational signatures. Consequently, the detection of a molecular species requires an accurate laboratory characterization.

This contribution presents the strategy (and its application) developed at the ROT&Comp lab (https://site.unibo.it/rotational-computational-spectroscopy/en). The strategy [1,2] starts from the interplay of experiment and theory. State-of-the-art quantum-chemical calculations are used to predict the relevant spectroscopic information required to guide the spectral recording, analysis and assignment. Rotational spectra measurements are then performed in the millimeter-/submillimeter-wave region. Subsequently, the spectral analysis leads to accurate spectroscopic parameters, which are then used for setting up accurate line catalogs for astronomical searches and detections [3-5]. The last step is the derivation of the molecular abundance within the local thermodynamic equilibrium (LTE) approximation by exploiting the rotational diagram method. However, going beyond the LTE approximation might be needed, thus requiring the knowledge of their collisional coefficients for the most abundant perturbing species [6].

Acknowledgements
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Cooling dynamics and stabilisation mechanisms of small PAH cations in space

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The recent discovery of small polycyclic aromatic hydrocarbon (PAH) molecules in space,[1-3] and infrared observations by the James Webb Space Telescope inferring the widespread distribution of PAHs as a class of molecules throughout the Milky Way (e.g. TMC-1) and other galaxies, is prompting a new era in laboratory investigations on PAH unimolecular dynamics. The dynamical properties of small PAHs, including radiative cooling, ultimately define their lifecycles and leads to their significantly higher-than-expected abundances than those predicted from traditional astrochemical models.[1] This talk will describe combined experimental and simulation studies on the energized naphthalene-azulene radical cation couple (Np^+ and Az^+) and the indenyl cation ($[In\text{-}H]^+$), occurring over the microsecond to seconds timescale using a cryogenic electrostatic ion storage ring affording "molecular cloud in a box" conditions ($P \approx 10^{-14}$ mbar, $T \approx 13$ K).

For the Np^+-Az^+ couple, measurement of the cooling dynamics and kinetic energy release distributions for neutrals formed through dissociation, until several seconds after hot ion formation, are consistent with the establishment of a rapid (sub-microsecond) $Np^+ \rightleftharpoons Az^+$ quasi-equilibrium. Consequently, dissociation by C_2H_2-elimination proceeds predominantly through common Az^+ decomposition pathways. Simulation of the isomerisation, dissociation, recurrent fluorescence, and infrared cooling dynamics using a coupled master equation combined with high-level potential energy surface calculations [CCSD(T)/cc-pVTZ], satisfactorily describe the experimental trends and infer that radiative cooling *via* recurrent fluorescence efficiently quenches dissociation for vibrational energies up to ≈1 eV above dissociation thresholds.

While we cannot use ion storage rings to study neutral PAHs, $[In\text{-}H]^+$ has a closed-shell electronic structure and possesses similar optical transitions to neutral PAHs. Furthermore, the parent indene molecule and the larger substituted derivative 2-cyanoindene have been identified in TMC-1;[3] $[In\text{-}H]^+$ is the main photoproduct of these molecules following interaction with 13.6 eV H-ionisation radiation. For $[In\text{-}H]^+$, we similarly find that recurrent fluorescence plays the pivotal role in stabilising energized cations, reducing the influence of destruction mechanisms (dissociation). Ultimately, our measurements confirm that small PAHs possess efficient radiative stabilisation and resilience mechanisms that should be incorporated into robust astrochemical abundance models.

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Unveiling the structure and stability of homogeneous PAH clusters through cutting-edge IR-UV ion dip spectroscopy

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Clusters of polycyclic aromatic hydrocarbons (PAHs) hold significant importance across various scientific fields, encompassing astrochemistry, environmental science, and material science. In astrochemistry, for instance, PAH clusters have been proposed as contributors to the aromatic infrared bands (AIBs), serving as a potential link between isolated molecules and carbonaceous grains.[1,2] Beyond their astrochemical relevance, PAH clusters also play an important role in the field of atmospheric chemistry. On earth, they can form upon combustion of organic materials and contribute to the formation of soot particles, a significant component of air pollution.

Motivated by the potential implication of PAH clusters across these multiple scientific fields, we have investigated the structure and stability of cluster of phenanthrene ($C_{14}H_{10}$), a prototypical PAH molecule. Employing mass-selective IR-UV ion dip spectroscopy and the free electron laser FELIX, we have identified clusters comprising of more than 10 phenanthrene molecules formed in a cold molecular beam and recorded their mid-IR spectra between 360 – 2000 cm^{-1}. In addition, time-resolved measurements were performed to delve into the relative stability of the clusters upon interaction with infrared radiation. These measurements also provided valuable insights into the preferred destruction pathways.

If combined with observations from the James Webb Space Telescope, our findings could help assessing the presence of clusters of PAHs in space. Additionally, the present study provides important information to assess the stability of the phenanthrene clusters as well as their survival probabilities in cold and isolated conditions mimicking those encountered in astrophysical environments.

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Charge and energy transfer in mutual neutralisation reactions

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Mutual neutralisation (MN) in collisions between oppositely charged ions is an important charge-recombination process in any environment where atomic or molecular anions are prominent carriers of negative charges, as in e.g. dense interstellar clouds [1]. In this talk, I will highlight recent studies of MN reactions carried out at the cryogenically cooled ion beam storage ring facility DESIREE (Double ElectroStatic Ion Ring ExpEriment). These include MN with atomic systems [2], small [3,4] and complex molecules such as fullerenes and PAHs, where we take full advantage of the unique DESIREE features [5,6] to measure the final state distributions at sub-eV center-of-mass collision energies and the amount of energy transferred to the molecular species in the collisions. An important aspect here is the ability to store and thereby cool molecular ions on extended timescales [7] such that they are prepared in narrow ranges of quantum states before they interact. The experimental results are key to benchmark theory and models for calculations of MN rates, which determine the charge balance that defines the chemistry in e.g. low temperature (interstellar) environments.

Acknowledgements
This work was performed at the Swedish National Infrastructure, DESIREE (Swedish Research Council Contract Nos. 2017-00621 and 2021-00155), and supported by the Knut and Alice Wallenberg Foundation (contract No 2018.0028) and the Swedish Research Council (individual project grant with contract No 2020-03437).

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Molecular beam experiments with nanometer-size $(PAH)_N$ clusters: Attachment of molecules and electrons

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Experiments with clusters in molecular beams can provide a detailed molecular-level insight into the elementary processes in free nanoparticles triggered by the interaction of the particles with gas phase molecules or photons and electrons of different energies [1-3].

Two different experiments with PAH clusters will be reported here: First, we have recently determined the relative uptake probabilities for different molecules on different PAH nanoparticles (1-2 nm average size) composed of benzene, naphthalene, anthracene, phenanthrene, pyrene, indene and fluoranthene. The molecules picked up by the nanoparticles included water (H_2O), methanol (CH_3OH), ethanol (CH_3CH_2OH) ammonia (NH_3), methane (CH_4), oxygen (O_2) and carbon dioxide (CO_2) [4,5].

Second, we concentrate on the electron attachment to the naphthalene clusters namely on the formation of the $(Np)_2^-$ dimer anion. As naphthalene poses a negative electron affinity, a stable Np^- anion cannot be generated in the gas phase, nevertheless, solvation can stabilize the anion, and already $(Np)_2^-$ dimer anion has been observed. However, we show that it cannot be generated directly in a low energy electron attachment to the gas phase naphthalene dimer but it needs a third body to stabilize the transient negative species; in the present case it is a rare gas atom evaporating from the mixed $(Ar)_m \cdot (Np)_2^-$ cluster ions. Thus, we conclude that the dimer anions $(Np)_2^-$ cannot be generated directly in low-density environments, where collisions are scarce, such as the interstellar molecular clouds.

Acknowledgements

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On the stability of interstellar molecules

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Polycyclic Aromatic Hydrocarbons (PAHs) have long been thought to be ubiquitous in the space, but it was only recently that astronomers began to identify specific PAHs by their rotational emission features [1], mostly in the Taurus Molecular Cloud TMC-1. The astroPAHs identified to date fail to meet any of the supposed requirements for stability in interstellar environments. They bear weakly bound functional groups, non-aromatic five-membered rings and/or nitrogen atoms. Indeed, state-of-the-art astrochemical models underpredict the observed abundances of the astroPAHs by 4-6 orders of magnitude.

Since their detection in TMC-1, several laboratory groups have investigated the stability of the astroPAHs, in particular cyanonaphthalene $C_{10}H_7CN$ (center of Fig. 1), in an effort to rationalize their anomalously high abundances. Experiments using the DESIREE ion beam storage ring revealed that Recurrent Fluorescence – optical photon emission from thermally excited electronic states – efficiently stabilizes cyanonaphthalene following collisional ionization [2,3]. Synchrotron radiation sources have been used to determine the dominant ionization mechanism of cyanonaphthalene when exposed to UV photons in the range produced by recombination of cosmic-ray ionized hydrogen [4,5]. The photostability and photo-reactions of protonated cyano-PAHs have also been investigated [6].

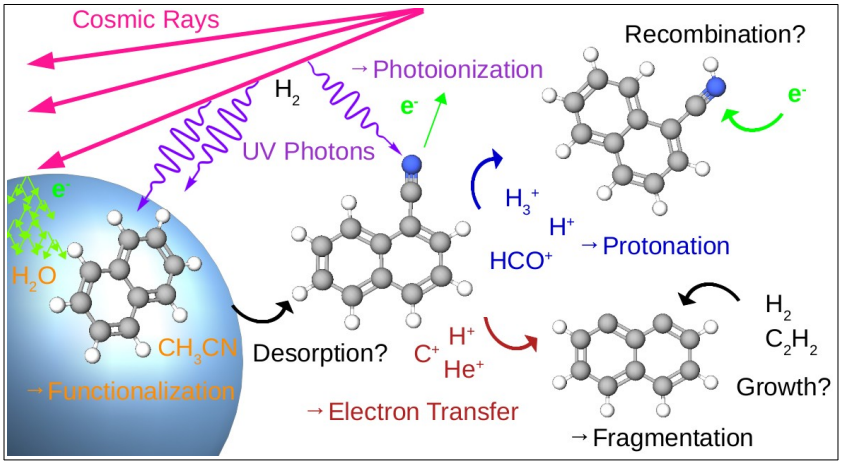


Figure 1: Hypothetical lifecycle of functionalized astroPAHs

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Some aspects of the photophysics of coronene

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Coronene is one of the PAHs present in the interstellar medium, both in the neutral and ionised forms [1]. Identification of the PAHs relies on their absorption and emission spectral signatures, namely in the UV, visible and infrared [1,2].

Here we review the photophysical properties of neutral coronene, with an emphasis on triplet-triplet absorption transitions [3,4] that may be of interest.

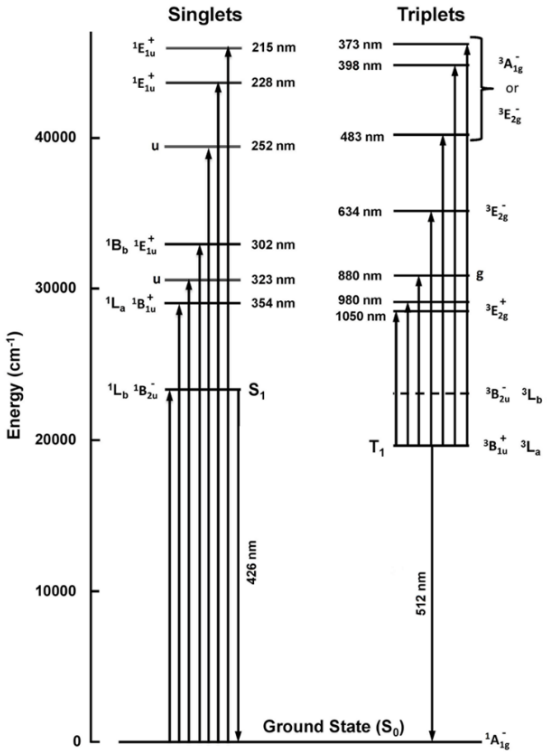


Figure 1: Important radiative processes in coronene involving transitions between electronic states [4].

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Laboratory investigation of shock-induced processing of carbons: astrophysical insights

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Astrophysical shocks participate to the chemical evolution of the interstellar medium. These violent events strongly alter dust grains and lead to the release of new molecular species in the gas phase. Only a few studies on the shock processing of cosmic analogues have been conducted so far.

We have explored in the laboratory the destruction of dust components using a shock tube associated to optical diagnostics. Shock tubes are commonly employed for fast thermal processing of gases and materials.

Our efforts have been first devoted to probe in situ the shock-induced decomposition of fullerene C_{60} at high temperatures (~4500 K) by optical emission spectroscopy [1]. The spectra point to the massive production of C_2 units. A broad underlying continuum was observed as well and was attributed to the collective visible emission of carbon clusters, generated similarly in large amounts. This proposed assignment was performed with the help of calculated emission spectra of various carbon clusters. Our laboratory experiments, supported by molecular dynamics simulations performed in the canonical ensemble, suggest that C_{60} is very stable, and that high-energy input is required to process it under interstellar low-density conditions and to produce C_2 units and an abundance of intermediate-sized carbon clusters.

Other cosmic dust analogues such as silicon carbide (SiC) particles have also been exposed and the solid carbonaceous residues examined by a variety of ex situ analytical techniques (X-ray diffraction, transmission electron microscopy). Shock processing of SiC dust leads to the formation of a wide variety of carbon allotropes.

These experiments provide some insights into the lifecycle of carbon in space. Our work illustrates the potential of shock tubes for laboratory astrophysics.

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Fragmentation patterns of PAHs and the complication of superhydrogenated edge termination

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Polycyclic aromatic hydrocarbons (PAHs) may exist in a partly superhydrogenated state in the interstellar medium (ISM) [1]. Superhydrogenation weakens the carbon skeleton of the PAH which not only promotes formation of smaller molecules through fragmentation [2], but also increases the catalytic properties towards e.g. H_2 formation on the surface of the PAH [3].

Here we examine the importance of their edge termination, superhydrogenation degree and molecular structure with respect to small molecule formation through fragmentation. With a focused data set of ionic- and neutral PAHs with different edge termination, we investigate their fragmentation patterns and tendencies to preserve or fracture its skeleton. The neutral PAHs were examined via temperature programmed desorption (TPD) and mass spectroscopy (MS) and the ionic PAHs were examined using both collision induced dissociation (CID), Molecular Dynamics (MD) and the Free electron Laser (FEL) at the FELIX laboratory.

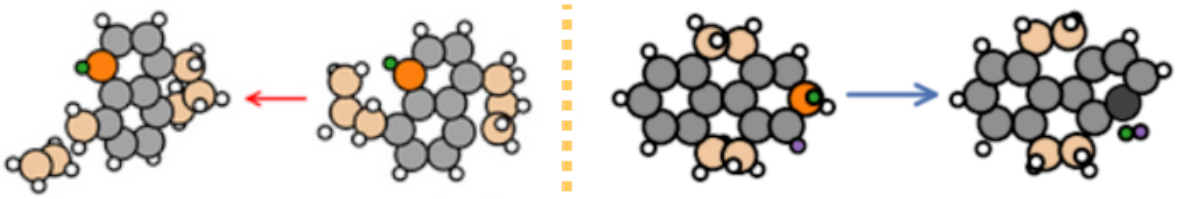


Figure 1: (left) Hexahydropyrene showing favourability towards fragmentation of the carbon skeleton. (right) Tetrahydropyrene showing favourability towards H_2 loss. Adapted from [2][4].

Acknowledgements

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Reactivity inside of molecular clusters induced by collisions with low-energy ions

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We are living in a molecular universe with more than 200 species identified in space. One can wonder what is the role on the molecular growth of the energetic processing of matter by radiation (photons, electrons, ions). Besides the two traditional approaches, namely bottom-up and top-down, we have shown that molecular growth can also occurred inside of molecular clusters of polycyclic aromatic hydrocarbons or fullerenes due to knock-out processes typical of low-energy ion collisions [1-2].

The formation of peptide bond is pivotal in the emergence of life. Using ion beams delivered by GANIL (Caen, France) and VUV photon beam produced at Synchrotron SOLEIL (Saint Aubin, France), we have studied the reactivity inside of amino acids clusters. In neutral clusters of β-alanine, polypeptide are formed after collisions with He^{2+} projectiles [3] while VUV excitation of protonated serine dimer leads to the formation of dipeptide [4].

Acknowledgements
This work is the result of fruitful collaborations with colleagues at Synchrotron SOLEIL, Stockholm University, Universidad Autonoma de Madrid, and Bar-Ilan University.

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IR spectroscopy of protonated fullerenes

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The presence of C_{60} and C_{70} in the interstellar medium had long been hypothesized, but was firmly established by spectroscopic evidence just over a decade ago [1-3]. It is then a small step to accept that also fullerene derivatives must be present, which was already proposed by Sir Harold Kroto himself in the 1980's [4]; protonated fullerenes were perhaps the most likely candidates. However, for a long time, decent laboratory spectra for these protonated fullerene derivatives have been unavailable. Interestingly, the symmetry-breaking effects of fullerene derivatization are – quite obviously – significant and are expected to be reflected in the spectra; computational spectra alone are therefore not sufficient and laboratory spectra are crucial.

Using the FELIX free-electron laser, we reported the first IR spectra of $C_{60}H^+$ and $C_{70}H^+$, using IR multiple-photon dissociation (IRMPD) spectroscopy in an ion trap mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) source [5,6]. Indeed, the attachment of a proton and the inherent symmetry lowering alter the IR spectra entirely as compared to their neutral analogues. With the experimental spectra in hand, we can evaluate the performance of DFT calculations in predicting the IR spectra, showing that the B3LYP functional reproduces the spectra accurately. Protonated fullerenes possess exactly one fundamental CH stretch band in the 3 μm spectral range that was experimentally inaccessible due to the limited pulse energy of FELIX, as well as of our OPO laser source. Recent upgrades of the FELIX laser have now enabled us to record this diagnostic IR band for $C_{60}H^+$ and $C_{70}H^+$. The band position deviates significantly from a value estimated from the scaled harmonic DFT frequency [5].

We contrast the laboratory IR spectra against astronomical spectra of objects featuring abundant emission of neutral C_{60}. In addition to the four well-known C_{60} bands, these objects show partly resolved emission bands that deviate clearly from typical PAH emission spectra and that may be due to protonated fullerenes and other low-symmetry fullerene derivatives [5,6].

Acknowledgements
We gratefully acknowledge funding from the EUROPAH MSCA network, the Dutch Astrochemistry Network and the Max Planck – Radboud University Center.

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Mid-infrared spectroscopy of cyano-PAH cations for astrochemical consideration

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The mid-IR spectra observed from different parts of the interstellar medium (ISM) are dominated by a set of IR features referred to as the unidentified infrared bands (UIBs). Although it has been accepted that these emission features originate from polycyclic aromatic hydrocarbon (PAH) molecules and their derivatives, the individual detection of the emitting species is challenging due to their similar IR fingerprint in the 5-15 um spectral region. [1]

Cyano-substituted PAHs were recently detected in the ISM based on their rotational spectra. [2,3] These species have dominant features (CH and CN stretch) in the less explored 1-5 um spectral region that can be diagnostic in further detection. However, there is still a lack of laboratory data to compare with the observed mid-IR spectra.

Here we present the low temperature gas-phase vibrational spectra of a set of ionised cyano-group containing PAHs in the mid-infrared region. Experimentally, the cyano-PAH ions are cooled below 10 K in a cryogenic ion trapping apparatus, tagged with He atoms and probed with tunable radiation. Quantum-chemical calculations are carried out at a density functional theory level. The spectra are dominated by the CN stretch around 4.5 um, with weaker CH modes near 3.2 um.

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IR pre-Dissociation Spectroscopy of Anion PAHs using FELIX

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The cryogenic trap, the FELion setup[1] at the FELIX Free electron laser (Nijmegen, NL), can be cooled down to 4 K, and therefor be used to attach He, Ne to the stored molecular ions of interest. The tunable IR radiation from the laser can consequently be used to dissociate the complex and provide spectroscopic information, e.g., for the cyc-$C_7H_7^+$ [2]. More recently, we were able to extend the same technique also to anions, by means of H_2. In our latest studies, we focused on the anionic species, simple PAHs, like cyc-$C_5H_5^{+/-}$, and on indenyl ($C_9H_7^{+/-}$) cation and anion and fluorenyl anion ($C_{13}H_9^-$). Together with the recent study on fluorenyl cation[3] the band positions of these species have now been localised.

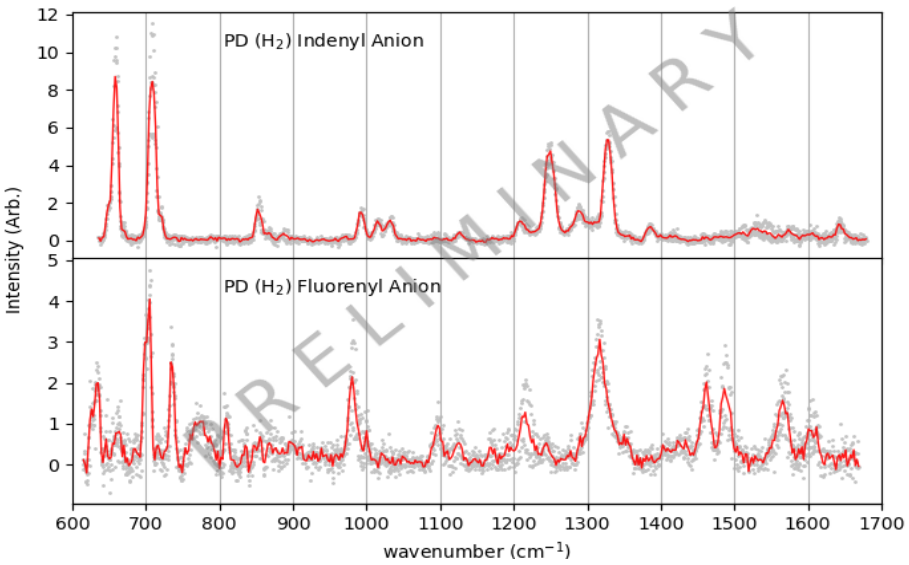


Figure 1: IR-PD Spectra (H_2 tag) of indenyl and fluorenyl anions recorded at FELion 22 pole cryogenic rf trap at FELIX.

Acknowledgements

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Vibrationally-Induced Chemistry in α-CO

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Solid-state reactions of CO which lead to C-C bond formation are of critical importance for production of complex carbon-rich molecules in astronomical environments. C-C bond formation has been routinely observed in laboratory analogs of astronomical CO ices, where bombardment with high-energy (10-100 keV) irradiation leads to production of a wide range of C_n, C_nO, and C_nO_2.[1] However, the harsh conditions of such experiments make it difficult to develop a state-specific mechanism by which these molecules form.

Vibrational excitation of CO crystals is known to induce vibrational energy pooling (VEP), where vibrational quanta are transferred between neighboring molecules through near-resonant processes described by

$$CO(v) + CO(w) \rightarrow CO(v+1) + CO(w-1).$$

We have found that the level of vibrational excitation achieved through VEP ($v \leq 37$)[2] are sufficient to induce chemical changes leading to production of equal amounts of CO_2 and C_3O_2, as evidenced by Fourier transform infrared spectroscopy. Exploration of the reaction pathway using density functional theory shows that the lowest-energy pathway to observed products requires a spin-forbidden transition into the triplet manifold of states; trajectories remaining on the singlet surface are not productive, but lead back to reactants plus heat (Fig. 1). Our results indicate that the required spin-flip occurs within a CO dimer that is consistent with the structural environment of α-CO, as well as energetic thresholds for states populated through VEP.

Acknowledgements
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Electronic Spectroscopy of 1-Cyanonaphthalene Cation for Astrochemical Consideration

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Polycyclic aromatic hydrocarbons (PAHs) are believed to be the carriers of the aromatic infrared bands (AIBs) and have been proposed as candidates to explain other astronomical phenomena such as diffuse interstellar bands (DIBs).[1,2] The first aromatic structures possessing more than one ring, 1- and 2-cyanonaphthalene (1-, 2-CNN), were recently detected by rotational spectroscopy in the dense molecular cloud TMC-1.[3] Laboratory investigations have indicated that due to fast and efficient relaxation through recurrent fluorescence, CNN^+ may be photostable in the harsh conditions of the lower density, more diffuse regions of the interstellar medium (ISM) exposed to ultraviolet radiation.[4] As a result, the widely held belief that small PAHs present in these regions are dissociated, may need to be revisited. If 1-CNN^+ is able to survive in the diffuse ISM it may contribute to the population of 1-CNN observed in TMC-1. To investigate the abundance of 1-CNN^+ in diffuse clouds, spectroscopic measurements are required. The present work concerns the gas-phase electronic spectroscopic experiments of 1-CNN^+, carried out using a cryogenic ion trapping apparatus at temperatures below 10 K through buffer gas cooling.[5] In this presentation, the electronic transitions $D_2 \leftarrow D_0$ and $D_3 \leftarrow D_0$ are discussed, complemented by time-dependant DFT calculations. The $D_2 \leftarrow D_0$ transition has a calculated oscillator strength of $f = 0.075$, dominated by its origin band. The origin band possesses a peak maximum at 7343 Å with a full width at half maximum of 28 Å, which is compared to observational data.[6]

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Advancements in cold ion spectroscopy

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Since the discovery of the buckminsterfullerene C_{60} in 1985, it has been speculated that fullerenes are abundant in space owning to their exceptional stability and the high cosmic abundance of carbon. A quarter of a century later, the identification of the fullerenes C_{60} and C_{70} in the IR spectrum of the young planetary nebula Tc1 confirmed this notion [1]. Meanwhile, C_{60} has been detected in many other planetary nebulae and interstellar clouds. From the very beginning, it has been discussed whether C_{60} analogues could serve as carriers of the diffuse interstellar bands. These bands describe a large set (~600) of relatively broad absorption bands in the visible and NIR range, the carriers of which are puzzling astronomers for a century. To date, only C_{60}^+ has been unequivocally assigned as a DIB carrier through the comparison of observational data with precise gas-phase laboratory measurements [2].

It is plausible to consider that, alongside C_{60}^+, other C_{60} analogues are DIB carriers. Promising candidates include C_{60} complexes with other cosmic abundant elements like H, H_2, Fe, Mg, Na, K, Ca, Si. Additionally, multiply-charged C_{60} analogues are of interest to study, as they can be formed under UV radiation in space. While these molecules are currently subjects of intensive research, technical limitations have confined their experimental studies to the infrared region. However, electronic spectra in the UV/Vis-NIR range are essential for unambiguous identification.

In this contribution, we will focus on a novel instrumental setup that facilitates messenger-type spectroscopy of various cold ions formed within the superfluid environment of multiply-charged helium nanodroplets [3]. A recent extension of this setup even enables the formation of multiply-charged dopant ions embedded in helium nanodroplets, opening new avenues for exploring the formation, stability, and spectroscopy of highly charged (metastable) species [4].

With this innovative setup, we have successfully replicated the near-infrared (NIR) spectrum of C_{60}^+. Furthermore, our ongoing investigations include spectroscopic studies of fullerene analogues such as $C_{60}H^+$, $C_{60}D^+$, $C_{60}H_2O^+$ and $C_{60}Mg^+$ in the VIS-NIR wavelength range. Our initial findings will be presented during the meeting.

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MeV-GeV ion irradiation combined with in-situ analysis for cosmic radiation simulation

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The M-branch at the GSI/FAIR facility provides a variety of ion beams from protons to uranium and specific energies ranging from 3.6 to 11.4 MeV per nucleon to an international user community. These beams are well suited to study the impact of cosmic radiation on materials, molecules, and carbon nanostructures, which is characterized using a broad selection of in-situ analysis techniques and in various experimental environments.

The M3 endstation features a vacuum chamber with a cryo stage (temperature down to 20 K) accessible to ion beams and spectroscopy methods like FTIR and Raman. The setups allow temperature-dependent analysis of the destruction and formation of molecules relevant to astrochemistry under ion irradiation[1]. The chamber's flexibility permits in situ preparation of different mixtures to mimic carbon species embedded in ice in molecular clouds. Moreover, it accommodates custom hardware and analysis tools like quadrupole mass spectrometry and ionoluminescence measurements.

The M1 endstation focuses on secondary ion mass spectroscopy (SIMS) and secondary neutrals mass spectroscopy (SNMS) measurements in ultra-high vacuum conditions using a time-of-flight (ToF) mass spectrometer for analyzing sputtered particles. Laser ionization of neutral secondary particles allows access to various emitted particles. Studies using this technique demonstrated the emission of large polycyclic aromatic hydrocarbons from interstellar dust analogues under ion irradiation[2]. In addition, the facility offers an in-situ scanning electron microscope with energy dispersive X-ray spectroscopy and a 3-circle X-ray diffractometer.

The local environment of a molecular species under irradiation is decisive for the creation of products in ion triggered reactions and at GSI is continously developed for implementing new ideas and experiments. This motivates the development of an upgraded spectroscopy platform with ultra high vacuum conditions. Beamtime with access to the different in-situ techniques is granted on a proposal basis.

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Reactivity and relaxation pathways of ionized C_4H_6 clusters

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Molecules embedded into clusters present an explicit environmental effect on encapsulated target molecules, especially when their reactivity is induced with e.g. highly-charged ions; such a protective effect due to the presence of an environment around the one excited molecule can stabilize a cluster [1]. This is explained by a redistribution of energy and charge between the different residues in the cluster. In addition, the presence of an environment can induce an additional reactivity within the cluster itself, such as hydrogen transfers [2] or molecular growth processes [3], that is not observed in the individual molecule fragmentation. Based on *ab initio* molecular dynamics and potential energy surface calculations we postulate that external (cosmic) radiation can induce Diels-Alder (**DA**) reactivity in the outer space, transforming the linear unsaturated clusters of 1,3-butadiene into more stable, long-lived cyclic species. Some of the observed products (m/z=68$^+$ and m/z=79$^+$) have been previously proposed as PAHs precursors, cyclic or bicyclic singly charged species, that have been observed in outer-space [4]. The observation of a long-live cyclic structure has been rationalized via **DA** mechanism for cationic and protonated species, allowing to easily form 4-vinylcyclohexene radical cation, the precursor of followed fragmentation products.

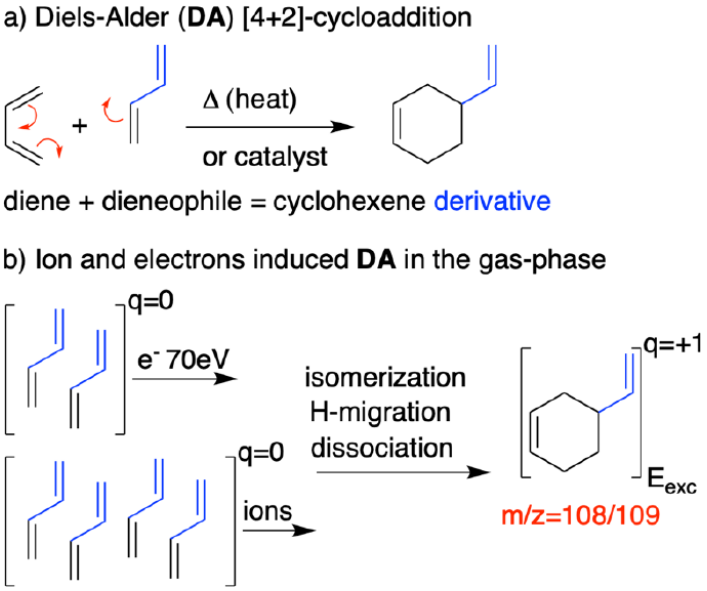


Figure 1: a) general scheme of Diels-Alder mechanism and b) our approach.

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Synthesis and Surface Characterization of Carbon Nanoparticles

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Nanotechnology presents a novel avenue for augmenting the production of nanoparticles (NPs), ranging in size from 1 to 50 nm. These days, carbon-based nanoparticles are among the most promising systems for a variety of uses, they have gained attention due to numerous applications such as energy storage, supercapacitors, chemical sensing, biosensing, solar cells, etc [1]. The focus of this presentation is how carbon nanoparticles, commonly known as Carbon dots, are formed.

The surface of the nanoparticles obtained will be analyzed since their composition will provide us with the functional groups (Figure 1), using XPS spectroscopy. What makes this type of system attractive is its emission, due to the phenomena of electronic transitions that originate in these surface groups. It will be presented, from a computational approach, how functional groups interact with different molecules, which makes their potential use, as is the case of spectroscopy [2], drug delivery [3] or photocatalyst [4].

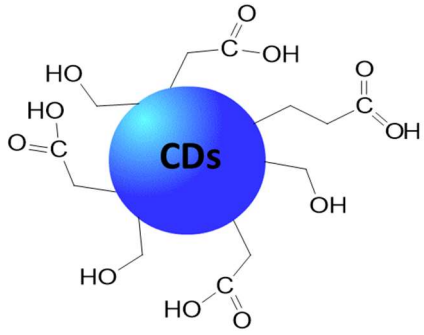


Figure 1: Scheme of the Surface Composition of Carbon Dots

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Recent Discoveries from the JWST

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We will describe a few of the recent discoveries from the James Webb Space Telescope, concentrating on exo-planet atmospheric characterisation. The role of the UKATC in leading the build, test and commissioning of one of its four instruments, the MIRI imager and spectrometer is discussed.

Understanding the Atmospheres of Directly Imaged Giant Planets and Brown Dwarfs with JWST

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Direct imaging will be a vital method to characterize a wide range of exoplanets in the next decades and may eventually determine whether "habitable zone" planets are truly habitable. Deep characterization of giant exoplanet atmospheres now is necessary to develop the expertise for similar studies of Earth-like exoplanets in future decades. The James Webb Space Telescope (JWST) represents a paradigm shift for this field, enabling imaging and spectroscopy of these objects (Teff=500-2000 K) for the first time ever at wavelengths beyond 5 um. The 5-20 um wavelength region provides novel probes for characterizing clouds, chemistry, and atmospheric structure of imaged planets. In addition, variability monitoring over the full rotation period of a planet or brown dwarf (~3-20 hours) probes the 3-d time-resolved structure of these atmospheres. I will discuss the first spectroscopy and variability monitoring results for directly imaged giant planets and brown dwarfs with JWST.

Polycyclic aromatic hydrocarbons as interstellar catalysts and reactants

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Interstellar space harbours a surprising chemical complexity in spite of the extremely low temperatures and pressures that characterize it. This chemical complexity is thought to be catalyzed by interstellar nanoscale dust grains and large carbonaceous molecules such as the Polycyclic aromatic hydrocarbons (PAHs). PAHs are ubiquitous in interstellar space, however, their impact on interstellar chemistry is still not thoroughly understood. Theoretical calculations and experimental measurements show that PAHs react readily with atomic hydrogen to form superhydrogenated species - e.g. PAH molecules like pentacene and coronene can be fully superhydrogenated with one excess H atom pr. carbon atom via H atom addition [1,2]. Once super-hydrogenated, PAH molecules can act as catalysts for molecular hydrogen formation and may participate in further reactions towards formation of a variety of hydrocarbon molecules. In the talk I present laboratory measurements of hydrogen and deuterium addition reactions on a selection of PAHs molecules with focus on resulting stable superhydrogenation configurations and cross-sections and isotope effects for H and D addition reactions. Density Functional Theory calculations provide insights into the underlying principles that guide the hydrogen functionalization pathways [1,2]. Furthermore, I discuss reactions towards more complex species via hydrogenation of pentacene-quinone and fragmentation of functionalized PAHs [3,4]. While we have obtained significant understanding of PAH interactions with both O and H/D atoms during recent years, a full understanding of fragmentation pathways and isotope effects in reaction rates, as well as the effect of functionalization beyond O and H atoms are still missing. I highlight the impact of this on our ability to interpret new JWST observations of PDRs and on ascertaining how complex chemistry we can reach in interstellar settings.

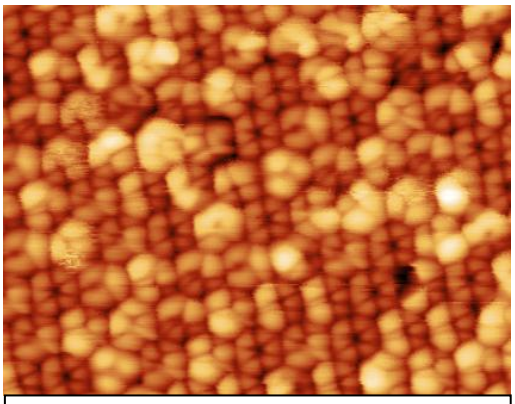


Figure 1: 5K STM image of super-hydrogenated Coronene molecules on a graphite surface.

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Heterogeneous Catalysis of Carbon Species Formation in Space

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The formation of primary nanocarbon materials (PAHs, fullerenes, CNT, *etc.*) in stellar outflows from carbon-rich stars is well-known and expected to follow gas-phase soot formation mechanisms akin to those observed in low-oxygen flames in the laboratory. However, there are other well-established chemistries that can produce such materials through catalytic processes involving small saturated (*e.g.*, [1]) and unsaturated (*e.g.*, [2]) hydrocarbons as a found in aged, cold dense environments. The catalytic centres in such chemistry are commonly first row transition elements, in particular iron and nickel clusters. Moreover, there are even reports of aromatic molecule formation from acetylene on simple olivine mimic surfaces [3] without any catalytic metal participation. There is therefore a strong case for investigations of the surface-promoted formation of these materials in relation to a range of astrophysical environments from warming cores and corinos, through protoplanetary disks to evolved stellar systems and exo-planetary atmospheres.

In this presentation, we will outline the activities planned in a new programme entitled *Astrocatalysis: In Operando Studies of Catalysis and Photocatalysis of Space-abundant Transition Metals* funded by the UK EPSRC exploring the role of transition metal catalysis in astrophysical environments. As part of that programme, we will integrate experimental surface science studies of nanocarbon formation on small atom number (1-3) molecular species and on larger metallic clusters in the Astrochemistry Group at Heriot-Watt University (HWU) with computational investigations on these systems through collaboration with the Rimola Group at the Universitat Autonoma de Barcelona.

Acknowledgements
JA acknowledges EPSRC for a DTP Studentship to support his PhD studies. VC and MRSM acknowledge the support of the EPSRC through responsive mode grant no. EP/W023024/1 *Astrocatalysis: In Operando Studies Of Catalysis And Photocatalysis Of Space-abundant Transition Metals*. AR is indebted to the EU Horizon 2020 research and innovation programme through the European Research Council (ERC) project "Quantum Chemistry on Interstellar Grains" (QUANTUMGRAIN, Grant No. 865657) and to the MICINN for the project PID2021-126427NB-I00.

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Surface science studies of model astrophysical ices

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To date, more than 300 different species have been identified in different regions of space in the gas phase. As well as gas phase species, molecules are also found frozen out on dust grains, forming icy mantles. The composition of these icy mantles depends on the region of space, but includes water ice, CO, CO_2 and a number of complex organic molecules (COMs). Molecular ices frozen out on dust grains act as an important reservoir for molecules in astrophysical environments, and the processing of these ices, thermally and via photons and electrons, leads to the formation of other molecules. Processing also leads to the desorption of the molecules into space where they can react to form more complex species. Astronomers have long speculated that surface processes on dust grains are important in the formation of various molecules in space.

Our group uses surface science techniques including temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and reflection absorption optical (RAO) spectroscopy to investigate the adsorption, desorption and processing of molecules found in interstellar ices on graphitic dust grain analogue surfaces. The aim of our investigations is to better understand surface processes that take place in space, and hence to provide data that can be used in astrophysical models.

This talk will describe studies of the adsorption and processing (thermal and non-thermal) of astrophysically relevant model ices containing a range of different COMs such as methyl formate, acetonitrile and acetaldehyde. Model astrophysical ices are grown on a graphitic dust grain analogue surface and TPD, RAIRS and RAO spectroscopy are used to investigate the processing of the ices.

UV photophysics of PAHs in ices and water complexes

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Polycyclic Aromatic Hydrocarbons (PAHs) are believed to account for a significant fraction of the carbon budget in the interstellar medium (ISM). This family of molecules is proposed to be among the carriers of the aromatic interstellar bands (AIBs), a set of strong infrared emission bands observed in diffuse regions of the ISM and used to trace local physical conditions. Much work has been done to determine molecular properties of PAHs in order to relate observed variations in the ratios between the AIBs to ionisation fraction, size distribution and chemical nature.

In dense environments, PAHs are likely to condense onto or integrate into the water-dominated ice mantles covering dust grains. The role of these ice-covered grains in regulating non-radiative relaxation pathways of PAHs including ionisation, fragmentation and reactivity, and thus in the generation of molecular complexity, is not yet fully constrained, despite decades of study though observations and associated laboratory astrophysics. We will review recent developments, focussing on a series of experimental and theoretical studies of PAH-water complexes and molecular solids where photoreactivity is induced by excitation of electronic excited states of PAHs by UV photons. In particular, we will discuss the role of ice structure and water-PAH interaction geometries in modifying the branching ratios between ionisation and reactivity.

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Vacuum ultraviolet photochemistry of interstellar PAHs

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The polycyclic aromatic hydrocarbons (PAHs) and their radical cations are suggested to be significant reservoirs of carbon matter in space and potential carriers of unidentified aromatic infrared bands (AIBs) [1] and diffuse interstellar bands (DIBs) [2]. Understanding their isomerization, photodissociation dynamics, and reactivity is crucial for explaining their presence in the interstellar medium (ISM). Most PAHs have isomerization barriers near or below their dissociation limits, leading to competition between these relaxation routes.

This presentation will concentrate on the chemical pathways activated by the photoabsorption of a vacuum ultraviolet (VUV) photon, as illustrated in the Figure. Specifically, it will delve into the reactivity following photoionization, photoisomerization, and dissociative photoionization. The discussion will be supported by studies of bare PAHs using a combination of mass spectrometry and tunable VUV photoionization, employing the chemical monitoring technique to track reactivity changes with varying photoionization energy. It will also include investigations into the fate of PAH derivatives, such as cyano-substituted and N-heterocyclic PAHs, particularly their protonated forms after VUV excitations. All these studies were conducted using the DESIRS VUV light from the SOLEIL synchrotron.

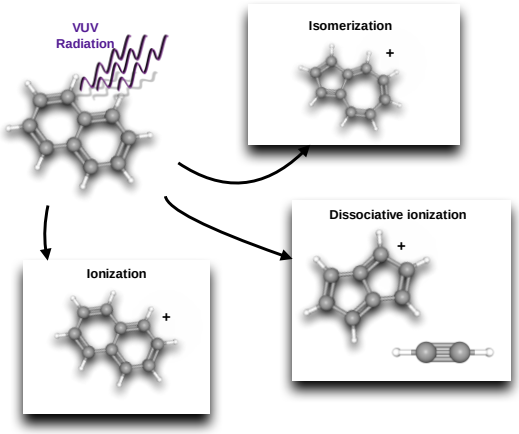


Figure 1 Processes investigated after absorption of a VUV photon.

Acknowledgements

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Stabilisation of Azafullerene Radicals in the Supra-Monolayer Phase on Au

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Azafullerene $C_{59}N$ is an organic radical, which is expected to be a qubit for the quantum circuit. In this study, azafullerene radicals $C_{59}N^{\bullet}$ were deposited on the Au(111) substrate for layer thicknesses between 0.35 and 2.1 monolayers (ML) and characterised by using X-ray photoemission (XPS) and X-ray absorption fine structure (NEXAFS) spectroscopy, low-temperature scanning tunnelling microscopy (STM), and by density functional calculations (DFT) [1].

We observed the singly unoccupied molecular orbital (SUMO) of $C_{59}N^{\bullet}$, which indicates the molecular radical state, by the N 1s XPS and NEXAFS. At ≤1 ML thickness, $C_{59}N$ molecules are stabilised with the C radical orbital next to the N atom oriented toward the substrate. As the 2nd layer formation starts, the $C_{59}N^{\bullet}$ SUMO peak intensity increases. This SUMO peak disappears as the 2nd layer completes, which indicates $C_{59}N^{\bullet}$ radical state is stabilised in a film thickness between 1 and 2 ML. We discuss the $C_{59}N^{\bullet}$ radical stabilisation of this supramonolayer on the passivating azafullerene contact layer to the substrate, which can be explored for molecular radical state stabilisation and positioning on solid substrates.

Acknowledgements
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Effect of swift ion irradiation on pyrene

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Polycyclic Aromatic Hydrocarbons (PAHs) are believed to represent 15% of all carbon in the ISM both in gas and in solid phases [1]. When PAHs are exposed to ionizing radiation, they can be destroyed. It is therefore important to study the resistance of PAHs to ionizing radiation and to predict their lifetime in space. We report the results of an experimental study of the irradiation of the PAH molecule pyrene at 20K. The experiments were performed at the Ice Chamber for Astrophysics-Astrochemistry [2] at the Tandetron facility of ATOMKI (Debrecen, Hungary). Fig. 1 shows the decrease of the pyrene 710 cm^{-1} IR band area as a function of deposited local dose for 11 projectiles.

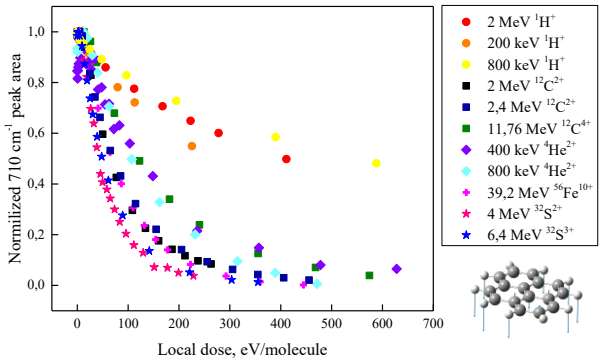


Figure 1: Normalized 710 cm^{-1} pyrene IR band as a function of local dose. Irradiations with 11.67 MeV C and 39.2 MeV Fe were performed at GANIL-IRRSUD

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Dissociation studies of ionized adamantane

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Adamantane ($C_{10}H_{16}$) is the prototypical diamondoid molecule, which due to their high stability are of high interest both in astrophysics, and nanotechnologies. A recent series of photoionisation experiments have been performed in various facilities to reveal the fragmentation dynamics of adamantane cations.

The initial experiment was done at Lund University (SE) using femtosecond XUV pulses produced via high-order harmonic generation and ion/electron spectroscopy [1]. As a main result we were able to show that the doubly charged adamantane molecule is metastable and will spontaneously dissociate. But, preceding dissociation, the cage structure will open and hydrogen migration(s) will occur.

Recently, we investigated the fragmentation dynamics of adamantane dications produced after core-ionization at the carbon edge followed by Auger decay using X-rays of the synchrotron SOLEIL (FR) [2,3]. The combination of high-resolution electron spectroscopy, energy-resolved electron-ion multi-coincidence spectroscopy and different theoretical models allows us to give a complete characterization of the processes involved after ionization. We show that energy- and site-sensitivity is observed even for a highly-symmetric molecule that lacks any unique atomic site. In addition, we performed time-resolved XUV-XUV experiments at the Free-electron laser FLASH2 (DE) as well as time-dependent photoabsorption spectroscopy at the cryogenic ring DESIREE (SE) where preliminary results will be presented.

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Unveiling the photochemical evolution of carbonaceous molecules: experimental and theoretical studies.

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The new stunning observations delivered by the James Webb Space Telescope are revolutionizing our view of the molecular universe, in particular when it comes to large carbon-containing species such as Polycyclic Aromatic Hydrocarbons (PAHs) and carbon cages. The infrared spectra show a treasure of spectroscopic features that change in response to the physical conditions in the astronomical object and thus speak of active photochemistry shaping the population of carbonaceous molecule [1,2].

The synergy between experiments, quantum chemistry calculations and modelling is fundamental to get insight on the behavior of molecules in the interstellar medium. In this talk I will present our latest efforts to constrain how the molecular properties of PAHs influence their photochemistry.

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High-resolution gas-phase photoionization of fullerenes: A meeting of multiple Jahn-Teller effects in the context of astrophysics

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Despite C_{60}^+ being the first molecular carrier of the diffuse interstellar bands (DIBs) to be identified, there is still ambiguity in the literature concerning its photophysics [1]. The ground state symmetry of the cationic ground state has been found to be D_{5d} in frozen matrices [2] which is also mirrored in the results of *ab initio* calculations that include various geometrical distortions due to Jahn-Teller effects [3]. However, previous gas phase photoionization measurements interpreted the C_{60}^+ ground state being D_{3d} symmetric [4]. We have recorded the first high-resolution threshold photoelectron spectrum (TPES) of C_{60} and in combination with molecular dynamics DFTB calculations and *ab initio* methods, we show that the C_{60}^+ ion also exhibits a D_{5d} symmetric ground state in the gas phase [5]. This allows us to further elucidate the photoexcitation mechanisms of the transitions that have been assigned to several DIBs in diffuse interstellar space and even predict other DIBs at shorter wavelengths. This makes for an interesting comparison to the first measured TPES of C_{70} which exhibits multitudes of weakly resolved bands [6].

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Oxygenation of Naphthalene: The break-Down Reaction

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Polycyclic aromatic hydrocarbons (PAHs) are common in space, holding about 15% of space carbon. If accessible, this carbon might aid in forming complex organic molecules (COMs) [1]. While COM formations often start from CO activation via hydrogenation, PAH breakdown could provide an alternative route [1].

Atomic oxygen, with an abundance of 10^{-4} with respect to atomic hydrogen, shows a 35% deficit in cold interstellar regions [2,3]. Binding with PAHs, oxygen might contribute to COM formation and explain the oxygen scarcity in cold ISM. While PAHs are known to react with atomic hydrogen becoming super-hydrogenated, their interaction with atomic oxygen lacks research [4].

Using density functional theory (DFT), I predicted intermediate formations due to atomic oxygen's reaction with naphthalene (Figure 1). Similar to PAH hydrogenation, DFT suggests oxygen attachment sequence. Once atomic O reacts with the first C atom of naphthalene, intersystem crossing (ISC) occurs from the triplet to the singlet spin state. Oxygen initially bridges carbons in naphthalene, catalyzing barrier-less breakdown of a C-C bond, forming a heterocyclic ring. Subsequent oxygenation break-down the PAH structure, crucial for understanding COM formation in star-forming regions—precursors for life's building blocks [1]. Thereby, these findings might clarify the 35% oxygen deficit observed in interstellar space [2,3].

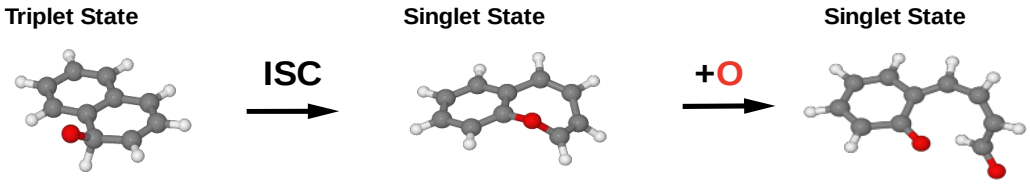


Figure 1: Oxygenation (in red) of naphthalene leading to opening the aromatic ring.

Acknowledgements

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Rotational Spectroscopy of Molecular Ions using a novel Double Resonance Approach

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A novel method of rotational spectroscopy of trapped, cold molecular ions is presented. It is a double resonance scheme, combining rotational excitation (in the mm-wave region) with rovibrational excitation (in the IR). The rovibrational excitation is detected by the recently developed leak-out spectroscopy (LOS) approach [1]. LOS is based on the vibrational-translational energy transfer process occurring during the collision of the IR-excited ion with a heavy noble gas atom (typically Ne), after which the ion may escape the trap (”leak out”) so that it can be counted by a detector. LOS and the rotational scheme based on it [2] are very sensitive and generally applicable to any cation or anion. This talk presents rotational spectra of molecular ions of astrophysical interest, e.g. $HCCCO^+$, c-$C_3H_2D^+$ and H_2CCCH^+. These investigations led to the detection of H_2CCCH^+ in the cold molecular cloud TMC-1, whereas only upper limits could be given for the column density of c-$C_3H_2D^+$ in the same source [3,4].

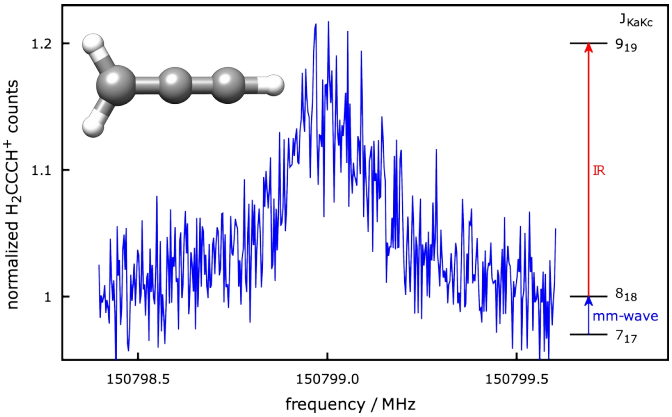


Figure 1: Rotational transition $8_{18} \leftarrow 7_{17}$ of H_2CCCH^+ recorded using a double resonance scheme [3].

Acknowledgements

This work has been supported by an ERC advanced grant (MissIons: 101020583), and the Deutsche Forschungsgemeinschaft (DFG) via SFB 956 (project ID 184018867), sub-project B2.

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Instrumentation for Photoinduced Action Spectroscopy of Anions in the Gas Phase

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Molecular anions are appealing targets for study because, compared with their neutral and cation counterparts, their spectroscopy and dynamics is more challenging to instigate from both experimental and theoretical perspectives. This poster details the first arm of a modular instrument at the University of East Anglia, designed to perform photoelectron and photodetachment spectroscopy of gas-phase anions (with provision for future isomer-specific or time-resolved spectroscopy). The modular framework of this instrument allows for the incorporation and adaptation of several ion sources, here demonstrated with plasma (electric) discharge sources providing variable hard to soft ion generation conditions. The generated anions are separated according to their mass-to-charge ratio through time-of-flight mass spectrometry and focused into a set of perpendicular velocity-map imaging (VMI) electrodes, where mass-selected anions are probed using wavelength-tunable light from a nanosecond laser. The successful operation of this instrument is demonstrated with photoelectron and photodetachment spectra for small, interstellar, carbon-based molecules such as C_4H^- and CH_2CN^-.

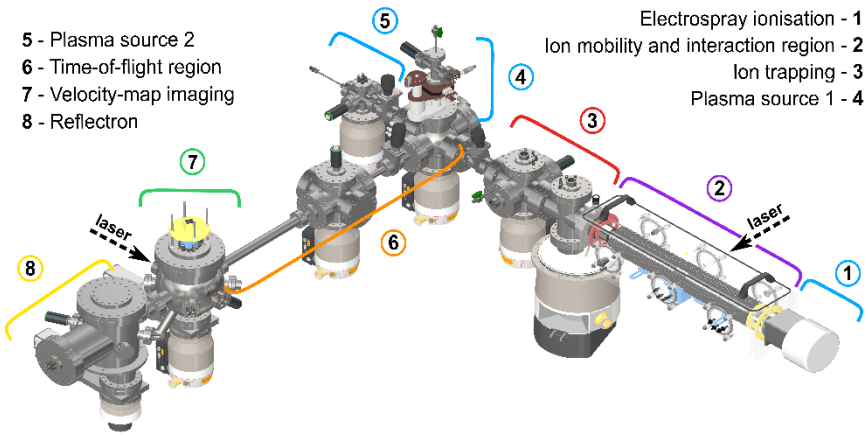


Figure 1: CAD schematic of the instrument at the University of East Anglia. Sections 1–3 and 8 are still a 'work-in-progress'.

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Engineering and Physical Sciences Research Council (EPSRC)

Graphene enhanced high-Q metamaterial bolometer

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Bolometers, which are highly sensitive detectors of infrared and THz radiation, are important for space applications due to the Earth's non-transparency at terahertz frequencies [1]. To address the limitations of cost and size associated with superconducting bolometers that require cryogenic temperatures, we propose the use of compact bolometers that operate at room temperature. These bolometers utilize a high-Q anapole metasurface and high absorptance graphene in the THz range, making integration with conventional electronics easier by detecting sub-THz or microwave photons resonant to the anapole metasurface. The anapole metamaterial is a high Q-factor resonator with localized electromagnetic energy in the near field, resulting from the interference of toroidal and electric dipole moments [2]. Graphene, with its broad absorption ability in the microwave and THz range, low heat capacity, and fast device response, is an ideal choice for a room-temperature or hot-electron bolometer absorber. The fast response of the resulting device and detection of single photons is facilitated by the low heat capacity, however, small losses in the system, such as an increase in resistivity caused by the absorption of a single THz photon, can significantly impact the anapole resonance of the metamaterial and alter its position and intensity [3, 4]. Simulations of the anapole metamaterial with introduced graphene pad (Figure 1) demonstrate the change in transmission of the metamaterial over graphene chemical potential. This allows one to detect THz heating of graphene pad via the change in metamaterial transmission spectrum.

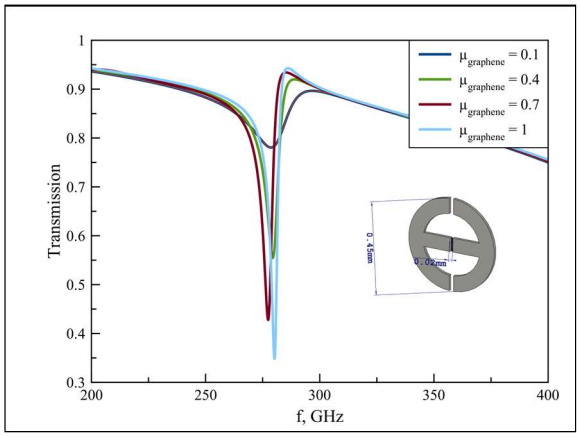


Figure 1: Transmission of proposed bolometer over graphene chemical potential

Acknowledgements

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Mid-IR Spectroscopy of 1-Cyanonaphthalene Cation for Astrochemical Consideration

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Polycyclic aromatic hydrocarbons (PAHs) are proposed to explain the unidentified infrared bands (UIBs), a series of IR emission lines first detected from various regions of the interstellar medium. Cyano-PAHs, such as 1- and 2-cyanonaphthalene, have recently been detected in the molecular cloud TMC-1 by radio astronomy and may contribute to PAH emission via emission from IR-active C-C, C-H and C-N modes. Here we present the gas-phase vibrational spectrum of ionised 1-cyanonaphthalene (1-CNN^+) in the mid-IR region. The ions are cooled below 10 K in a cryogenic ion-trap and tagged with helium for spectroscopic investigation. Quantum chemical calculations are presented at the density functional theory level to complement the laboratory observations.

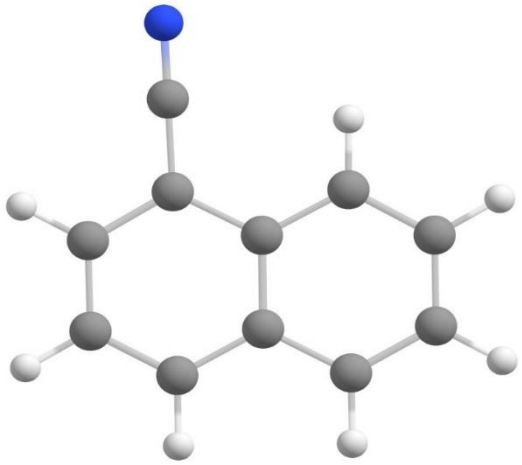


Figure 1: Optimised geometry of 1-cyanonapthalene cation (B3LYP/6-311+G)

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Formation of doubly- and triply-charged C_{60} dimers

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We present a new experimental method that enables the multiply-charging of ions embedded in superfluid helium nanodroplets (HNDs) by sequential ionization [1]. The setup was used to form multiply, positively charged $(C_{60})_n$ cluster ions and surprisingly, even doubly- and triply-charged C_{60} dimers could be detected [1]. Before, critical cluster sizes of n=5 and n=10 have been experimentally established for doubly- and triply-charged cationic $(C_{60})_n$ clusters, respectively [2]. In our setup, the efficient cooling within the superfluid environment of helium nanodroplets, and the step-by-step ionization scheme that populates covalently bound or physisorbed fullerene dimers allow resilience against Coulomb explosion [1].

The HNDs are formed within a supersonic jet expansion and are multiply-charged by electron impact ionization [3]. Subsequently, they pick up the C_{60} molecules that are brought into the gas phase by evaporation in an oven. Inside the droplets, the C_{60} molecules are ionized by charge transfer or Penning ionization from He^+ or metastable helium He*, respectively. Afterwards, the doped droplets are bombarded by a second electron beam, leading again to the formation of He^+ and He*. While He^+ will not approach and thus not ionize the $(C_{60})_n^+$ clusters due to Coulomb repulsion, He* can ionize $(C_{60})_n^+$ via Penning ionization. The formed multiply-charged C_{60} clusters are extracted from the HDN upon collisions with room-temperature helium gas and detected with a time-of-flight mass-spectrometer [1].

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Studies of cooling dynamics of PA(N)H cations at DESIREE.

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Synopsis Our aim in this study is to establish scaling laws for the internal energy dependent dissociation and radiative cooling rates as functions of the size of polycyclic aromatic hydrocarbons (PAHs) and their nitrogen substituted species. This kind of scaling laws could be used for modelling their survival probabilities in space.

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic molecules based on two or more fused hexagonal aromatic carbon rings with hydrogen atoms attached at their outer rims. They are found and formed in a wide variety of environments. In the case of extraterrestrial environments, PAHs are believed to be an important component in interstellar dust and gas and as such are responsible for infrared emission features that dominate the spectra of many galactic and extragalactic sources [1]. PAHs can be categorised as peri- or cata-condensed defined by the arrangement of those rings. Here, we choose to focus on catacondensed PAHs cations such as naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$) and tetracene ($C_{18}H_{12}$) but also nitrogen substituted PAHs (PANHs) such as acridine ($C_{13}H_9N$) and phenazine ($C_{12}H_8N_2$).

When exposed to high-energy photons, PAH molecules may be electronically excited; thus increasing their internal temperature considerably by rapidly redistributing the absorbed energy among all available vibrational states. On longer timescales, they can then relax, by either fragmenting or emitting photons. Emission of IR photons (vibrational de-excitations) is typically a very slow process occuring on timescales exceeding seconds, while Recurrent Fluorescence (RF) or so called Poincaré fluorescence have been shown to effectively stabilize internally hot PAHs on millisecond timescales [2, 3]. In the RF process, vibrational excitation is converted into electronic excitation (inverse internal conversion - IIC) followed by relaxation to the electronic ground state through photon emission.

For the catacondensed PAHs considered in the present study, the emitted photons are in the 1,5-2,5 eV range, which leads to an efficient cooling and a much higher survival probability than cooling via IR emission alone. Key ingredients determining the RF rate are the energy of the excited state being populated in IIC and the oscillator strength for the electronic transition. As these scales with the size of the catacondensed PAHs, we aim to find a simple scaling law for the RF rate by combining theoretical and experimental results from the literature and from novel studies carried out at electrostatic storage ring facilities in Lyon [4] and in Stockholm [5] by members of the present collaboration (see Fig.1). In a similar fashion, we aim to establish a scaling law for the dissociation rate. With these in hand, the survival probabilities for any catacondensed PAH may be determined as a function of internal energy and used in, e.g., astrophysical modelling.

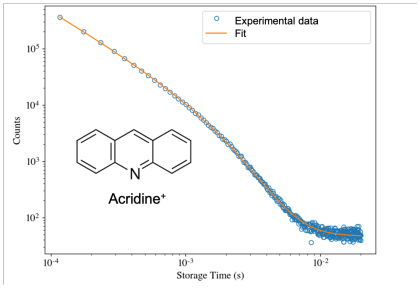


Figure 1. Spontaneous decay curve of acridine cations stored in DESIREE.

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Laboratory astrochemistry: electronic photoabsorption of interstellar functionalized PAHs

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Polycyclic aromatic hydrocarbons (PAHs) are found throughout the universe [1] and observed via their infrared emissions following absorption of starlight [2]. PAHs alongside multiple other candidates have been considered as potential carriers of the Diffuse Interstellar Bands (DIBs) [3], [4]. However, up to date no match has been found. This is often attributed to the large distribution of PAH species, which lead to too small populations of specific isomers to be observed [5]. Besides C_{60}^+ that has been identified as carrier, candidates closely related to these large carbon and hydrocarbon structures are proposed. We aim to investigate the less usual suspects, focusing on neutral functionalized species while seeking a deeper understanding of the electronic characteristics of PAHs. Our approach involves transitioning molecules to a gas phase, where they are rapidly cooled to 10K via a supersonic expansion in a high vacuum chamber [6]. This process creates a setting where molecules exist in cold, isolated conditions mirroring those James Webb Space Telescope (JWST) might encounter in its interstellar observations. Subsequently, by performing 1+1' Resonance Enhanced Multiphoton Ionization (REMPI) spectroscopy, we probe the high-resolution UV-visible absorption spectra to study their electronic behavior. We use Time Dependent Density Functional Theory (TDDFT) calculations as guide and for comparison with our experimental results. Our specific focus on functionalized PAHs aims to understand the influence of heteroatom(s) on PAH signatures, potentially shedding light on JWST's analysis of complex molecular structures in space. This investigation not only contributes to gaining insight into understanding the nature of DIB carriers but also advances our knowledge of PAHs' electronic behavior in the interstellar medium.

Acknowledgements

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Possible hydrocarbon chemical growth routes from l-C_3H^+ in space

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The cationic counterpart of propynylidyne (l-C_3H^+) has only been observed in interstellar regions that are highly exposed to UV radiation, towards the Horsehead photodissociation region (PDR) [1], the Orion Bar PDR [2] or Sgr B2(N) [3]. Given its key position in chemical networks in dense interstellar environments [4], understanding its reactivity with other small hydrocarbons is indeed important, as these serve as fundamental building blocks for the formation of larger carbonaceous species. These reaction pathways are particularly interesting as the reaction between l-C_3H^+ and H_2 is slow [5].

We used a tandem mass spectrometer coupled to the tunable vacuum-ultraviolet photoionization source of the DESIRS beamline of the SOLEIL synchrotron to study the reactivity of l-C_3H^+, generated from dissociative photoionization of allene and propyne, with small neutral target (propyne, allene and acetylene). Absolute reaction cross sections were measured and reaction constants were derived for comparison with kinetic databases such as the KInetic Database for Astrochemistry (KIDA) [6]. The ion-molecule reaction products were rationalized with the support of *ab initio* calculations.

Acknowledgements

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Direct measurement of recurrent fluorescence photons from PAH ions

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Recurrence fluorescence(RF) is the emission of optical photons from electronically excited states populated after the molecule undergoes inverse internal conversion. This process has recently been shown to be widely prevalent in polycyclic aromatic hydrocarbons (PAHs)[1] and in fact has been proposed as an alternate stabilization mechanism to infrared cooling which could explain the survivability of PAHs in harsh interstellar conditions[2]. To date, most experiments probing the effects of RF have only done so indirectly by modelling their lifetime curves, with only one group successfully detecting the photons[3] themselves of PAH ions. The spectra itself was only partially resolved in wavelength to a limited extent with the help of narrow-pass filters and a photomultiplier tube.

This poster presents the results of RF spectra in the wavelength range 200 nm - 1000 nm of different PAHs measured using a spectrograph coupled to an accelerator mass spectrometer at DESIREE, Stockholm. Internally hot PAH ions were produced from an electron cyclotron source and were then coupled to a beam line with a bending magnet for mass selection. The ions were dumped after a flight time of the order of microseconds. Near the dump, the ions pass through a cell from which the photons are collected through an optical window and are fed to the spectrometer. Preliminary spectra from measurements of naphthalene, cyano-naphthalene, quinoline etc were obtained. These results would help understand the RF process better and would also help in constraining astronomical models of these molecules.

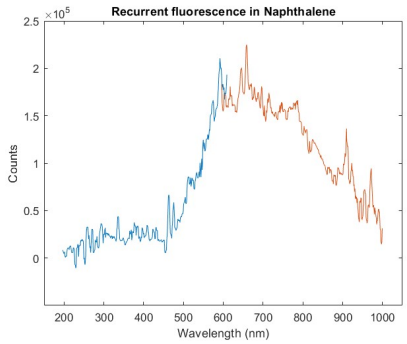


Figure 1: Recurrent fluorescence spectrum of naphthalene.

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Electronic Spectroscopy of Helium Tagged Polyacene Cations

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Messenger spectroscopy is a very useful tool in the search for carriers of diffuse interstellar bands (DIBs). Attaching messengers that only weakly interact with the molecule of interest ensures a small spectral shift induced by the tag. In our experimental setup we dope multiply charged helium nanodroplets (HNDs) with different polycyclic aromatic hydrocarbons (PAHs). The charged and doped droplets collide with a stainless-steel surface to obtain helium decorated ions which we detect using a reflectron-type time-of-flight mass spectrometer [1]. The helium tagged ions are irradiated with a tunable pulsed laser. Absorption spectra of helium tagged ions are obtained by tracing the change in the ion yield between mass spectra that were recorded after laser illumination and mass spectra without laser illumination for different wavelengths. We can determine the spectral shift caused by different numbers of attached helium atoms and compare our laboratory absorption spectra to astronomical observations.

In this study we compare the spectra of positively charged polyacenes, consisting of three [2], four [3], five and seven [4] benzene rings fused in a linear fashion. The two lowest optically allowed transitions shift to lower energies with increasing acene chain length.

Acknowledgements

This work was supported by the Austrian Science Fund, FWF, via projects I4130 and I6221.

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Interaction of free electrons with naphthalene clusters produced in supersonic expansion with various rare gases

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In our present study we focus on naphthalene clusters [1]. We generate the clusters in supersonic expansion of naphthalene with various buffer gasses (He, Ne, Ar, Kr) under different pressure conditions and probe via time-of-flight mass spectroscopy. After a low-energy electron attachment, Np_n^- anions ($n \geq 3$) are observed in the mass spectra. The monomer anion Np^- is not present at all, and the dimer is only observable in co-expansion with Ar and Kr at higher expansion pressures, when the mixed neutral clusters Np_nRg_m (Rg = Ar, Kr) are formed. This occurrence suggests the formation of the naphthalene dimer anion through the electron attachment to a mixed cluster and subsequent evaporation of the rare gas atoms.

Thus, we conclude that naphthalene dimer anion is not produced by the low-energy electron attachment directly, instead, it requires a stabilization process, e.g. the solvent-induced stabilization by Ar/Kr atoms in the mixed clusters, as in this case. The electron attachment to the large (up to nanometer size) naphthalene clusters (and the mixed Np_nRg_m species) will be discussed as well in the relevance to the astrochemistry.

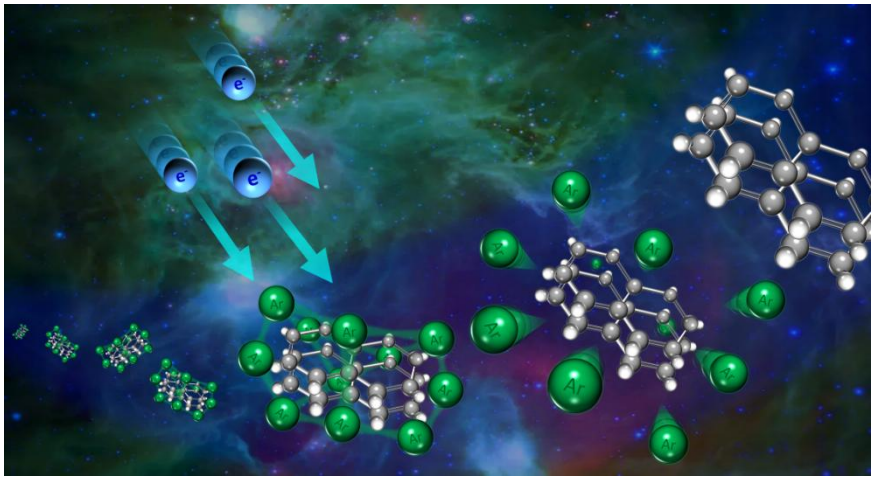


Figure 1: **Illustration of electron attachment to Np_2Ar_m clusters**

Acknowledgements

We acknowledge the Czech Science Foundation (GAČR) grant No.: 24-11390S.

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Atomistic Modelling of fullerene formation and destruction: Towards structural and spectroscopic identification

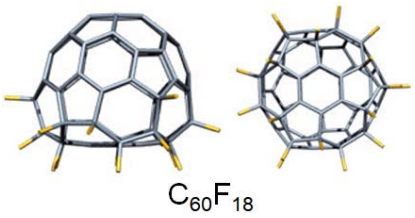
Y. Tanuma[1,2], R. Pinguet[1], B. Anezo[1], C. Ewels[*1]

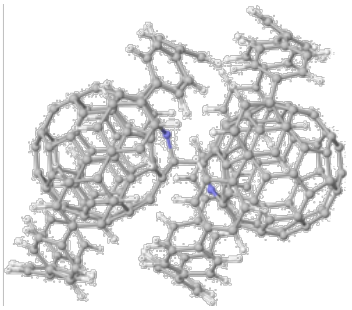
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We present our work over recent years using atomistic modelling techniques (primarily density functional theory, but also extended tight binding models such as xTB and empirical potential simulations using LAMMPS) of fullerene and azafullerene species. Using sequential addition and other approaches such as genetic algorithms, we have been able to successfully predict various stable "magic number" isomers of functionalized fullerenes (such as hydrogenated, fluorinated, and (CF_3) functionalized fullerenes and endofullerenes), as well as exploring hydrogen addition to smaller cage fullerenes (C_n, n=20→60). We explore how such approaches can also be used for the inverse, i.e. atom loss from fullerenes and fullerene derivatives. We discuss possible "next steps" and links we would like to explore with experimental groups.





Acknowledgements

We would like to acknowledge the COST Project NANOSPACE for support.

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Electron-induced Cage Shrinking of C_{60} on Cu(111) at Liq. He Temperature: Stone Wales Rearrangement and C_2 Evaporation

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When C_{60} (or any other fullerene) is excited in the gas phase via multiphoton laser excitation or relatively low energy collisional excitation, a typical fragmentation mass spectrum shows a series of smaller fullerene fragments, each separated by the mass of a C_2 molecule. The accepted inferred mechanism to form these smaller fullerene fragments is a Stone-Wales bond rearrangement to produce a less stable isomer with adjacent pentagons, providing a lower energy pathway for emitting (or absorbing) C_2. Here we provide evidence from STM/STS experiments for such a fragmentation process undergone by C_{60} deposited on a surface at liquid He temperature where the C_2 is emitted, leaving behind successively smaller fullerene cages on the surface. This may have consequences for understanding the origin of the wide range of fullerene species observed from the Almahata Sitta (AhS) polymict ureilite meteorite [1].

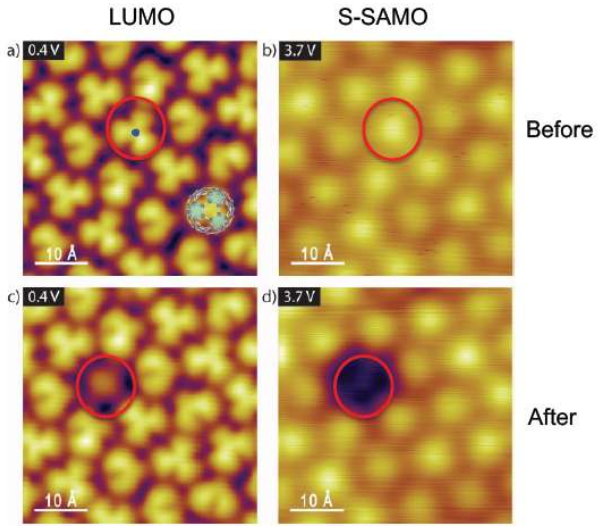


Figure 1. UHV STM images of C_{60} monolayer before (upper) and after (lower) decomposition of the targeted molecule (red circle) by ramping up STM current. The images are of the valence LUMO and Rydberg-like S-SAMO molecular orbital in both cases.

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Microbial Interactions with Fullerenes: Implications for the Impact of Extra-Terrestrial Organics on the Early Earth

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Fullerenes of extra-terrestrial origin may have been accessible as a carbon source for anaerobic microorganisms on the early Earth. Very little is known about how microorganisms respond to and utilise fullerenes and their soluble derivatives, particularly in anoxic environments. We present an investigation into the effects of fullerenes C_{60} and C_{70} and their hydroxylated fullerol derivatives on an environmentally relevant anaerobic community and microbial isolate. Anaerobic microorganisms were cultured in microcosms with suspensions of fullerenes with and without supplementary carbon under different levels of light exposure. Relevant early Earth environmental conditions were simulated by irradiating fullerene suspensions with 254nm UV light for two weeks in the absence of oxygen and the accessibility of the photodegradation products was assessed. We find that the anaerobic community is capable of utilising C_{60} as a sole carbon source, but that C_{70} is inhibitory, possibly due to the smaller aggregate size associated with fullerene biotoxicity. Additionally, we find that both C_{60} and C_{70} fullerol are inhibitory to the anaerobes in this study, which is contradictory to previous studies conducted under aerobic conditions.

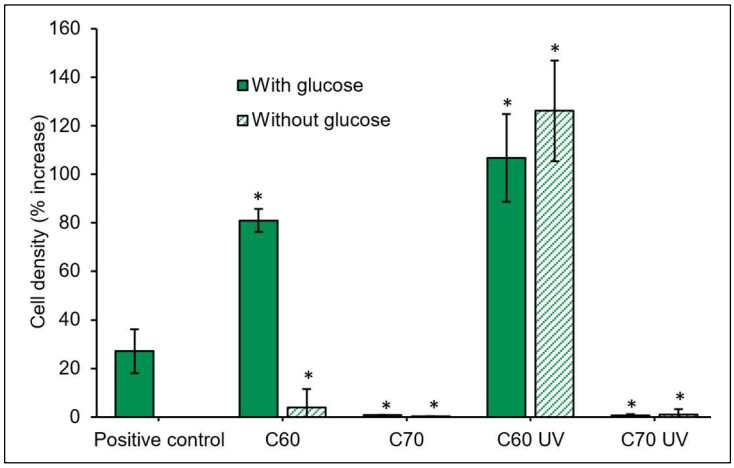


Figure 1. Effects of irradiated and non-irradiated fullerenes on growth of anaerobic isolate. The anaerobic isolate was cultured with C_{60} and C_{70} either in the native form or after UV irradiation, with and without additional glucose. Cell density (%) increase was measured on day 28 of growth. C_{60} and C_{70} UV were irradiated for 2 weeks before inoculation.