Infrared action spectroscopy of doubly charged PAHs and their contribution to the aromatic infrared bands

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Polycyclic Aromatic Hydrocarbons (PAHs) are suspected to be the carriers of aromatic infrared bands observed in the spectra of galactic and extragalactic sources. Changes in the astronomically observed band strengths are attributed to different PAH charge states existing under different conditions in the interstellar medium [1]. To identify these PAHs, laboratory infrared gas phase spectra are necessary to be compared to the observed astronomical data. Many previous studies employed Infrared Multiphoton Dissociation (IRMPD) action spectroscopy by utilizing the intense IR radiation provided by free electron lasers (FELs), examples include a number of cationic, protonated, and anionic PAHs of varying sizes [2,3]. However, spectroscopic data on doubly-charged (dicationic) PAHs is very sparse [4].

Here we present the experimental gas-phase infrared spectra of the three PAH dications Naphthalene^{2+} ($C_{10}H_8^{2+}$), Anthracene^{2+} and Phenanthrene^{2+} ($C_{14}H_{10}^{2+}$) in the IR fingerprint region 500–1600 cm^{-1} using the widely tunable IR FELs at the FELIX Laboratory. The dications were readily produced by electron impact ionization (EI) of the corresponding vapors with 70 eV electrons. In our work the spectra were obtained not by IRMPD but by Infrared Predissociation (IRPD) action spectroscopy of the mass-selected ions complexed in-situ with Ne in a 22-pole cryogenic ion trap setup (FELion [5]) operated at T=15 K. The narrow linewidth experimental spectrum was compared to calculated anharmonic spectra at the B3LYP/6-311G(d,p) level of theory for singlet and triplet states, and for all species the singlet state was the one detected in our experiment. The relevance of anharmonic effects in the observed PAH dication spectra will be discussed.

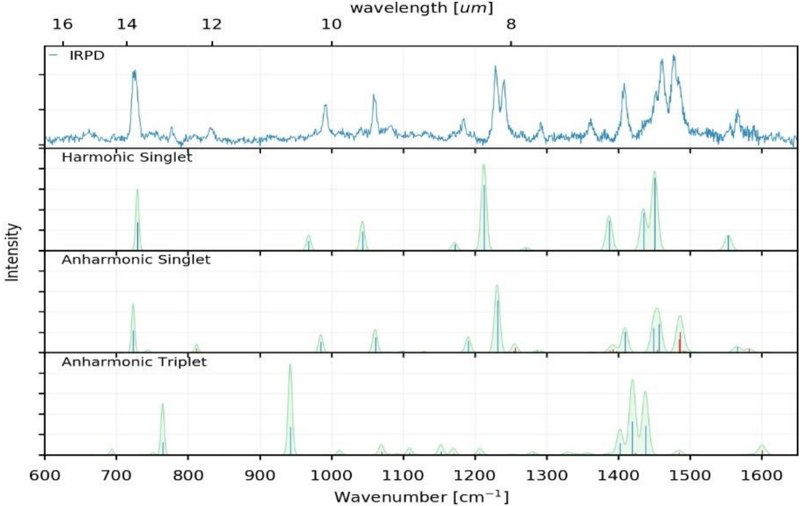

Figure 1: Experimental vibrational spectrum of rare gas complex of naphthalene dication with neon and DFT calculations on the singlet and triplet states of naphthalene dication.

References

1. A. Tielens, 2008, Annu. Rev. Astron. Astrophys, 46:289–337
2. J. Oomens, A. Tielens, B. Sartakov, G. Helden, and G. Meijer, 2003, ApJ 591:968–985
3. H. Knorke, J. Langer, J. Oomens, and O. Dopfer, 2009, ApJ 706: L66–L70
4. J. Zhen, P. Castellanos, J. Bouwman, H. Linnartz, and A. Tielens, 2017, ApJ 836 28
5. P. Jusko, S. Brünken, O. Asvany, S. Thorwirth, A. Stoffels, L. van der Meer, G. Berden, B. Redlich, J. Oomens, S. Schlemmer, 2019, Faraday Discuss., 217, 172

UV photolysis of acetylene ice as a possible formation pathway of PAHs

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The aromatic benzene molecule (C_6H_6) is a central building block of polycyclic aromatic hydrocarbon molecules (PAHs), commonly detected in the interstellar medium [1]. The formation of PAHs, alternative to the commonly accepted top-down scenario, was shown by cosmic-ray processing of low-temperature acetylene (C_2H_2) ices [2]. We investigate the role of UV photolysis of simple hydrocarbon ice (acetylene, C_2H_2) as a potential formation pathway towards larger hydrocarbons, possibly including aromatic species. In an ultra-high vacuum system acetylene ice is deposited and subsequently irradiated with UV photons, simulating the processing of cosmic ices by interstellar radiation field or secondary UV field. Laser desorption post ionization time-of-flight mass spectrometry was used to monitor the chemical evolution of the ices in situ. To enhance the sensitivity of the system towards large photoproducts, a nanosecond high voltage pulse is implemented on the detector. As a result of UV photolysis of acetylene ice at 20 K, we have detected formation of large hydrocarbons, up to $C_{10}H_X$.

References:

[1] Allamandola LJ, Tielens AG, Barker J. ApJ 290:L25-8 (1985).
[2] Zhou, L., Zheng, W., Kaiser, R.I., ApJ, 718(2) (2010).

The Interaction of PAHs and C_{60} with Forsterite: Machine Learning and DFT-D4 studies

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Polycyclic aromatic hydrocarbons (PAHs) and fullerenes (C_{60}) are interstellar carbon nanoforms ubiquitous in the universe locking up ~15% of the carbon in space. If this carbon can be made available it may play a role in the formation of so-called “complex organic molecules" (COMs)[1]. Forsterite (Mg_2SiO_4) is a mineral ubiquitous in all rocky bodies of our universe and provides surfaces where molecules have the time to gather and react. Here, we test if the interaction of PAHs with forsterite surfaces indeed plays a role in the freeing up of carbon from the PAHs, a first step in the formation of COMs in the universe [2].

In this study, we use periodic density functional theory employing the new PBE-D4 functional[3] (DFT-D4) along with a new surrogate machine learning model, using a scheme for global optimization with first-principles energy expressions (GOFEE)[4], to study four different {010} surfaces of forsterite (Mg_2SiO_4). The surfaces of {010} considered are the pristine, single Fe-doped, single Ni-doped, and with a MgO vacancy. The machine-learned surrogate model provides stable structures of MgO vacancy surface that would not be easily identified using only chemical intuition. Subsequently, using only the DFT-D4, a sample of PAHs and C_{60} are adsorbed on the considered forsterite surfaces. The outcome of this work is that PAHs strongly interact with all surfaces forming stable Si-C and O-C bonds with the carbons of quartet rings. Furthermore, the interaction with the mineral distorts the molecules and might trigger their fragmentation on the surface. Finally, our calculations reveal that larger PAHs such as benzocoronene suffer from major distortion on the surface that causes the breaking of a C-H bond. The latter is the first step to understand the link between PAHs and COMs in space and terrestrial zones and, hence, their role in the formation of building blocks of life.

[1] A.G.G.M. Tielens, Rev. Mod. Phys. 85, 1021-1081 (2013)
[2] F. L. Plows et al., Geochim. Cosmochim. Acta 67, 1429-1436 (2003)
[3] D. Campisi et al, J. Phys. Chem. A (2021), submitted
[4] M. K. Bisbo et al., Phys. Rev. Lett. 124, 086102 (2020)

Public engagement culture in Europah and the production of academic identities

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The ITN Europah introduced public engagement as a compulsory part of the training and production of knowledge for its 16 early-stage researchers. For two years, I followed how this choice was implemented and experienced, through participant observation and qualitative interviews. The social and material dimensions were investigated, paying attention to actions, narrations and discourses but also to what was left unsaid – tacit knowledge being a fundamental part of how expertise is forged (Collins, 2014).

Gherardi's theory of organisational learning (Gherardi, 2006) offered me a frame for thinking the ITN Europah as a temporary organisation where public engagement was *woven* through the *texture* of knowledge produced within the network. A range of diverse practices and cultures of public engagement existed in Europah and were the centre of discursive negotiations and rituals of accountability, while dealing with the continuities and discontinuities between several communities of practitioners.

This work across diverging cultures of engagement in research may call to a redefinition of how academic identities are produced, asking questions such as: how to conciliate academic autonomy with a culture of accountability? Is the commitment to engage with publics down to the researchers' individual morality or to their professional ethics? Does excellence in science research allow for inclusion?

Making engagement a compulsory part of how novice researchers become experts of their field entails a new culture of research as well as new paths for the production of academic identities. Transforming the relationships between science and society involves questioning elements of academic culture, such as excellence and autonomy.

References:

Collins, H. (2014). *Are we all scientific experts now?* Cambridge: Polity Press.

Gherardi, S. (2006). *Oragnizational Knowledge: the Texture of Workplace Learning*. Oxford: Blackwell Publishers.

The Influence of Configuration and Functionalisation on Interstellar PAH Reactivity

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In photodissociation regions of the ISM where UV photons dissociate molecules and grain surface reactions are less efficient, PAHs were postulated as catalysts for molecular hydrogen (H_2) formation [1]. Experiments and theoretical calculations, using coronene as the model PAH, indicated that superhydrogenated PAHs [2, 3] provide a route towards H_2 formation though the impact of the presence of other functional groups and PAH configuration on such routes remained unclear.

Using surface science techniques, mainly temperature programmed desorption (TPD) coupled with mass spectrometry, we studied the interaction of neutral PAHs - pentacene, 6, 13 – pentacenequinone and corannulene with H atoms, in order to understand the effect of configuration and functionalisation on the PAH reactivity.

Products with high degrees of superhydrogenation were seen for all three PAHs. Specific superhydrogenation degrees were found to be more stable than the others resulting in magic numbers in the hydrogenation sequence. Such magic numbers indicate barriers to addition as observed in experiments with coronene [4].The cross-section for the reaction, PAH + H → PAH, was obtained from the TPD data. For all three PAHs, the cross-sections were found to be higher than that for coronene, thereby providing evidence for the enhanced reactivity of zig-zag edges (pentacene), oxygen functional groups (PQ) and 5-membered rings (corannulene).

Interestingly, for PQ (mass 308 amu), the first species to form even at very short H atom exposures has a mass of 294 amu indicating the loss of an oxygen atom from PQ, potentially through the formation of H_2O or OH. Also, in contrast to pentacene and coronene, the fully superhydrogenated product does not dominate the mass distrbuiton at long H atom exposures for both PQ and corannulene.

References:

[1] Habart, E., et al. *Astronomy & Astrophysics* 397.2 (2003): 623-634.
[2] Rauls, E., and L. Hornekær. *The Astrophysical Journal* 679.1 (2008): 531.
[3] Thrower, J. D., et al. *The Astrophysical Journal* 752.1 (2012): 3.
[4] Jensen, Pernille A., et al. *Monthly Notices of the Royal Astronomical Society* 486.4 (2019): 5492-5498.

Laboratory IR spectra of protonated fullerenes

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With the detection of C_{60}, C_{70} and C_{60}^{+} [1,2,3], the fullerenes constitute by far the largest molecular species individually identified in the interstellar medium (ISM). Proton affinities of C_{60} and C_{70} are significant which support the hypothesis that protonated fullerenes may also be abundant in the ISM [4].

We present the experimental vibrational spectra of gaseous $C_{60}H^{+}$ and $C_{70}H^{+}$. Protonation of the highly symmetrical molecules causes a drastic symmetry lowering resulting in a rich vibrational spectrum. As compared to C_{60}, where all C-atoms are equivalent due to the icosahedral symmetry, C_{70} belongs to the D_{5h} point group and has five non-equivalent C-atoms, which are available as protonation sites. Combined analysis of the experimental spectrum and spectra computed at the density functional theory level enables us to evaluate the protonation isomers being formed. We compare the IR spectra of $C_{60}H^{+}$ and $C_{70}H^{+}$ to IR emission spectra from planetary nebulae, which suggests that a mixture of these fullerene analogues could contribute to their IR emission.

References:

[1] Cami, J., Bernard-Salas,J., Peeters,E. and Malek,S. E., Science **329**, 1180–1182 (2010).
[2] Sellgren, K. et al., Astrophys. J. **722**, L54 (2010)
[3] Campbell,E. K., Holz,M., Gerlich,D. and Maier,J. P., Nature **523**, 322–323 (2015)
[4] Kroto, H. W. and Jura, M., Astron. Astrophys. **263**, 275–280 (1992)

Structural investigation of doubly-dehydrogenated pyrene cations

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The vibrationally resolved spectra of the pyrene cation and doubly-dehydrogenated pyrene cation ($C_{16}H_{10}^{\bullet +}$; Py^+ and $C_{16}H_8^{\bullet +}$; $ddPy^+$) are presented. Infrared predissociation spectroscopy is employed to measure the vibrational spectrum of both species using a cryogenically cooled 22-pole ion trap. The spectrum of Py^+ allows a detailed comparison with harmonic and anharmonic density functional theory calculated normal mode frequencies. The $ddPy^+$ spectrum is dominated by absorption features from two isomers (4,5-$ddPy^+$ and 1,2-$ddPy^+$) with, at most, minor contributions from other isomers. These findings can be extended to explore the release of hydrogen from interstellar PAH species. Our results suggest that this process favours the loss of adjacent hydrogen atoms on the same ring.

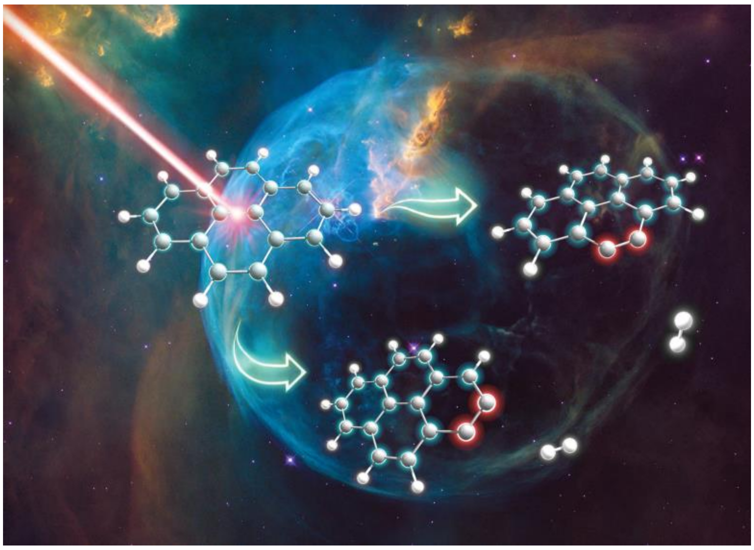

Figure 1: Graphical abstract showing the products formed upon double-dehydrogenation of pyrene following infrared absorption.

Atomic functionalization of C_{60} provides a route to form interstellar, dust-grain-mantle analogues

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Dust grains can form in the stellar outflows of AGB stars, where silicate and carbonaceous grains are injected to the interstellar medium [1]. A variety of thermal, radiative and functionalization processes can then impact the structure and composition of the dust grain surface. In their transition from more diffuse to more dense environments, the surface of the dust grains would be expected to form a mantle of carbonaceous nature [2]. Since important surface catalytic reactions are taking place on dust grains, the mantle composition and morphology is expected to contribute towards its catalytic properties. In this talk, I will discuss a way to produce an interstellar dust grain mantle analogue through atomic functionalization and thermal processing of C_{60} molecules.

A highly oriented pyrolytic graphite (HOPG) substrate, was cleaved, inserted into a UHV chamber with a base pressure of 5×10^{-10} mbar and then annealed to 1200 K. C_{60} powder was evaporated from a Knudsen cell evaporator, at 360°C and deposited on the HOPG, which was kept at a temperature of 320-340 K, to build 5-6 ML thick C_{60} films. Atomic functionalization of the as grown C_{60} films was performed at room temperature, by direct exposure of the film, separately, to deuterium or oxygen atoms, that we produced by thermal cracking molecular gases at 1950 and 1850 K respectively, using commercially available hydrogen and oxygen thermal cracking sources. Scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the functionalized species. Temperature programmed desorption was used to understand the desorption dynamics of the produced species and their mass distribution.

TPD data suggest that functionalized species, *i.e.* $C_{60}D_x$ and $C_{60}O_y$ were produced and the thermal desorption behaviour of these species will be discussed. Evidence suggests that a fraction of the functionalized species fragmented on the substrate upon annealing to temperatures above 800 K. STM and XPS revealed that a carbonaceous polymeric material grew on the substrate after several cycles of TPD measurements and this material proved to be thermally stable up to 1200 K. I propose that these carbonaceous materials could serve as a realistic dust mantle analogue. Functionalization of C_{60} molecules on this carbonaceous mantle led to a more efficient chemisorption of O atoms on C_{60} species, detected as a larger O/C ratio in XPS data, and also led to the formation of more complex chemical groups, when compared to the functionalization of C_{60} on a pristine HOPG substrate.

References:

[1] C.S. Contreras and F. Salama ApJS, **208**:6 (2013).
[2] A. P. Jones, M. Köhler, N. Ysard, M. Bocchio and L. Verstraete, A&A **602**, A46 (2017).

On application of Deep Learning to non-adiabatic molecular dynamics of phenanthrene

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Deep Learning is applied to simulate non-adiabatic molecular dynamics of phenanthrene based on Time-Dependent Density Functional based Tight Binding (TD-DFTB) [1] approach for excited states combined with mixed quantum-classical propagation. Starting with Tully's fewest-switches trajectory surface hopping [2] algorithm coupled to TD-DFTB, we examine the simplified treatment based on the Landau-Zener approximation and Deep Learning potentials for excited states. We first assess the accuracy of the TD-DFTB approach based on comparison with experimental and higher-level theoretical data. Using the recently developed SchNet [3,4] architecture for Deep Learning applications, we train several models and evaluate their performance. The main focus is given to the analysis of the electronic population of low-lying excited states computed with the aforementioned methods. We determine the relaxation timescales and compare them with experimental data. Our results show that the simplified approaches considered in this study do not yield accurate description of the electronic relaxation in phenanthrene as compared with the reference data. On the other hand, the SchNet performance allows high-throughput analysis at a negligible cost.

References:

[1] T. A. Niehaus, S. Suhai *et al.*, Phys. Rev. B **63**, 085108 (2001).

[2] S. Hammes-Schiffer, J. C. Tully, J. Chem. Phys. **101**, 4657 (1994).

[3] K. T. Schütt, P.-J.Kindermans *et al.*, J. Chem. Phys. **148**, 241722 (2018).

[4] K. T. Schütt, P. Kessel *et al.*, J. Chem. Theory Comput. **15**, 448 (2019).

Understanding Decalin Conformational Isomer Desorption from Silica Surfaces

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Trans- and *cis*-Decahydronaphthalene (decalin) are non-interconvertible conformations and are fused ring analogues of cyclohexane with different geometric positioning of hydrogen atoms at its ring junction. *Trans*-decalin is more energetically stable than the *cis*, because of reduced steric interactions. There are many catalytic studies of hydrogen (H_2) production during decalin dehydrogenation [1]. Adsorption and desorption of *cis*- and *trans*-decalins can be used to probe activation energies for C-H bond cleavage and non-specific dehydrogenation leading to surface carbon accumulation. A theoretical study has demonstrated that the first step of dehydrogenation, decalin to tetralin conversion is energetically preferred on Pt catalyst while on Pd the second dehydration step from tetralin to naphthalene is favoured. This suggests a lack of sufficient understanding in mechanistic and selectivity studies of decalin dehydrogenation [2]. Silica supported transition metal derivative catalytic studies have shown that naphthalene hydrogenation is 92.1% selectively to decalin and *cis*-decalin converted partly into *trans*-decalin under high temperature conditions employed [3]. Dehydrogenated decalin (naphthalene) has been tentatively detected in the interstellar medium. Further its protonated dehydrogenation intermediates or naphthalene hydrogenation intermediates are thought to contribute to the Unidentified Infrared emissions as protonated naphthalene itself is not a perfect match for the UIR spectra [4].

This study reports sub-monolayer and multi-layer desorption from silica surfaces of separately both trans and cis decalin. *Trans*-decalin exhibits a clear coverage dependence in its TPD in contrast to *cis*-decalin*.* This would be consistent with the former wetting the silica surface while the latter does not, implicating conformational significance with its interactions.

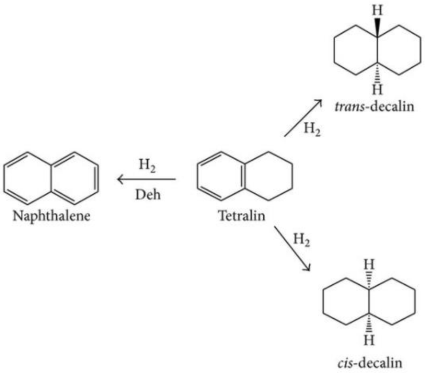

Figure 1: Tetralin dehydrogenation (deh) and Hydrogenation (H_2) connection with Decalin and Naphthalene [5].

References:
[1] Zhao, H., Bruce E. K., Surface Science. **573**, 473-425 (2004).
[2] Kyeounghak, K., Young, W. S., Catal. Sci Technol. **7**, 3728 (2017).
[3] Zhang, X., Changhai, L., Energy Fuels. **7**, 3796-3803, (2010).
[4] Ricks, A. M., Duncan, A. M., Astrophys J, **702**, 301 (2009).
[5] Upare, D. P., Byung, J., Lee, W. S., Nanomaterials J., **2013**, 1-2, (2014).

Time-related Alteration of Aqueous Phase Polycyclic Aromatic Hydrocarbon (PAH) Photoproducts Upon Interaction with TiO_2 Nanoparticles

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Polycyclic aromatic hydrocarbons (PAHs) and titanium dioxide (TiO_2) nanoparticles (NPs) are photoactive environmental pollutants that contaminate aquatic environments. Aqueous-phase interactions between PAHs and TiO_2-NPs are of interest due to their emerging environmental relevance, particularly with the deliberate application of TiO_2-NPs to remediate pollution events (e.g., oil spills). Our objective was to investigate photoproduct formation and transformation following ultraviolet A (UVA) irradiation of five representative PAHs in the presence and absence of TiO_2-NPs. PAH solutions were prepared alone or in combination with TiO_2-NPs, UVA irradiated, and either exposed to larval zebrafish or collected for chemical analyses of diverse hydroxylated PAHs (OHPAHs) and oxygenated PAHs (OPAHs). Expression profiles of genes encoding for enzymes involved in PAH metabolism showed PAH and time-dependent inductions that demonstrated changes in PAH and photoproduct bioavailability in the presence of TiO_2-NPs. Chemical analyses of PAH/NP solutions in the absence of zebrafish larvae identified diverse photoproducts of differing size and ring arrangements, which suggested photodissociation and photorecombination of PAHs occurred either during or following UVA irradiation. All PAHs demonstrated heightened oxidative potential following irradiation, but TiO_2-NP-related increases in oxidative potential were PAH-specific. The exploitation of multiple analytical methods from molecular biology and analytical chemistry provided novel insights into distinct PAH photoactivity; TiO_2-NP influence on photoproduct formation in a PAH-specific manner; and the significant role time plays in photoprocesses.

Dimerization of polycyclic aromatic hydrocarbons on graphene

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Dimerization of polycyclic aromatic hydrocarbons (PAHs) is important for soot formation, on-surface synthesis of graphene (nanoribbon) and growth of carbonaceous dust grain in interstellar medium. Pristine PAHs may dimerize to physically stacked larger PAHs due to the Van der Waals interaction. However, PAHs might loss hydrogen atoms and form reactive species under the harsh interstellar environments. Whether and how these dehydronated PAHs can form dimers on graphene (a dust grain analog) is the focus of our work.

Our work combines the global optimization and a machine learning potential to investigate the most stable dimer structures on graphene using dehydrogenated coronene and pentacene as seeds [1]. The mechanism of chemical dimerization of dehydrogenated coronene is revealed by density functional theory calculations. The hydrogen migration is occurring simultaneously with ring formation during the chemical dimerization.

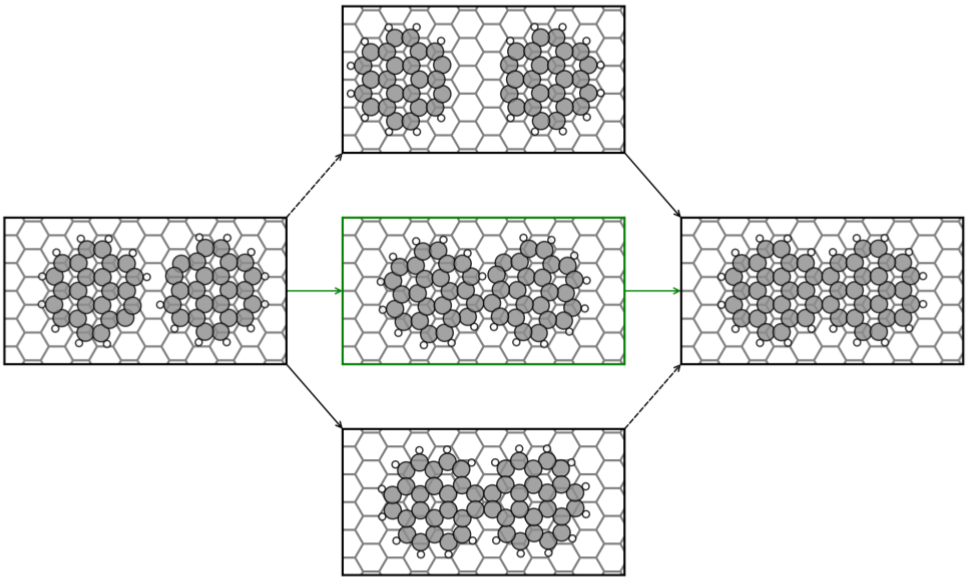

Figure 1: Dimerization of dehydrogenated coronene on graphene

References:
[1] Zeyuan Tang, Bjørk Hammer, In preparation.

Isomer diversity in the –H fragments of methylated PAHs

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Methylated PAHs are plausible carriers of the 3.4 µm emission band, a satellite of the 3.3 µm CH aromatic band. The aliphatic CH bonds are more fragile than the aromatic ones, which can account for the observed disappearance of the 3.4 µm band in photodissociation regions (PDRs) [1,2]. Theoretical studies have suggested that the –H fragment of methylated PAH cations could exhibit the same isomerization processes as those involved in the dissociative ionization of toluene, *i.e.*, species with a C_7 ring or with a CH_2 group [3]. In addition, an isomerization barrier of 3.5 – 4 eV was calculated between the two isomers of the fragment of the 1-methylpyrene cation ($C_{17}H_{11}^+$), namely $PyrC_7^+$ and $PyrCH_2^+$. This isomerization process might impact the chemical evolution of methylated PAHs in PDRs. Infrared predissociation (IRPD) spectroscopy of Ne tagged ions tagged has been established as a powerful tool to disentangle the cationic isomers that are formed in the dissociative ionization of toluene [4]. The here presented experiments were performed at the Free Electron Laser for Infrared eXperiments facility, FELIX, using IRPD spectroscopy at the FELion 22-pole cryogenic ion trap. We investigated the –H fragments occurring upon dissociative ionization of several methylated PAHs, namely the fragments of 2-methylnaphthalene ($C_{11}H_9^+$) and 2-methylanthracene ($C_{15}H_{11}^+$) in addition to $C_{17}H_{11}^+$ which has been investigated in a previous run [5]. For the latter, we obtained a high quality IRPD spectrum and were able to confirm the formation of $PyrCH_2^+$, but not $PyrC_7^+$. This could be rationalized by the fact that the former corresponds to the lower energy fragment according to DFT calculations [6] or that the formation of the C_7 ring is prevented due to strain effects. We tested this hypothesis by recording the IRPD spectra of the –H fragments of the acene species. Combining these results with quantum chemical calculations, the identification of both isomeric structures is evident for the $C_{11}H_9^+$. The case of $C_{15}H_{11}^+$ is more complicated and will be discussed here in detail.

References:
[1] C. Joblin *et al.*, Astrophys. J. **458**, 610 (1996).
[2] P. Pilleri *et al.*, Astron. Astrophys. **577**, A16 (2015).
[3] M. Rapacioli *et al.*, J. Phys. Chem. A **119**, 12845 (2015).
[4] P. Jusko *et al.*, ChemPhysChem **19**, 3182 (2018).
[5] P. Jusko *et al.*, Chem. Phys. Lett. **698**, 206 (2018).
[6] B. West *et al.*, J. Phys. Chem. A **122**, 4730 (2018).

Prediction of plasma reforming of naphthalene using a hybrid machine learning model

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Biomass has been highlighted as a key renewable feedstock to respond to the vital societal need for a step change in the sustainability of energy production which is required to combat climate change. Gasification of biomass wastes represents a major sustainable route to produce syngas (H_2 and CO) from a source which is renewable and CO_2-neutral. However, the formation of undesirable contaminates (e.g. tars, containing PAHs) in syngas remains a significant challenge to advance the gasification technology for large scale applications, and plasma has been regards as a promising method to solve this problem [1]. However, plasma reforming of tars is a complex process and the process performance is influenced by a wide range of processing parameters, and the investigation of the coupling effects of various parameters has been reported rarely so far.

In this work, a hybrid machine learning (ML) model was developed for the prediction and evaluation of a gliding arc plasma tar reforming process using naphthalene as a model tar compound from biomass gasification [2]. A linear combination of three well-known algorithms, including artificial neural network (ANN), support vector regression (SVR) and decision tree (DT) was established to deal with the multi-scale and complex plasma reforming process. The optimization of the hyper-parameters of each algorithm in the hybrid model was achieved by using the genetic algorithm (GA), which shows a fairly good agreement between the experimental data and the predicted results from the ML model. Based on this model, the importance of three key processing parameters was analyzed, and the steam-to-carbon ratio was the most important one for the conversion. Further, the coupling effects of different processing parameters on the key performance of the plasma reforming process was evaluated, and the plasma process was optimized to reach a better balance between reaction performance and energy efficiency.

References:
[1] S. Liu, D. Mei, L. Wang, X. Tu, **Chem. Eng. J.**, 307, 793-802 (2017).
[2] Y. Wang, Z. Liao, S. Mathieu, F. Bin, X. Tu, **J. Hazard. Mater.**, 404, 123965 (2021).