

Program of International online seminar
“Origin and evolution of organic molecules in our Galaxy”
11 May 2023, 10.00 am (GMT+4)

Session 1.

Chair – Pavel A. Mikheyev; Moderators – Oleg V. Kuznetsov, Eugeny V. Fomin.

10.00 - 10.10 (GMT+4)	Opening Remarks. Ralf I. Kaiser (University of Hawaii at Manoa, Honolulu, USA)
10.10 - 11.00 (GMT+4)	Ralf I. Kaiser (University of Hawaii at Manoa, Honolulu, USA) <i>Untangling the Formation of Polycyclic Aromatic Hydrocarbons</i>
11.00 - 11.50 (GMT+4)	Gleb S. Fedoseev (Ural Federal University, Ekaterinburg, Russia) <i>Production of Carbonaceous Molecules by Accretion of C-Atoms on the Surface of Cosmic Dust During the Early Onset of Star System Formation</i>
11.50 - 12.20 (GMT+4)	Alexander P. Shevchenko (Lebedev Physical Institute, Samara Branch, Samara State Technical University, Samara, Russia) <i>Lithium coordination compounds on Earth and in space</i>
	Break

Session 2.

Chair – Marsel V. Zagidullin; Moderators – Eugeny V. Fomin, Oleg V. Kuznetsov.

16.00-16.50 (GMT+4)	Alexander M. Mebel ¹ , Alexander N. Morozov ¹ , and Michael Frenklach ² (¹ Florida International University, Miami, Florida, USA; ² University of California at Berkeley, Berkeley, California, USA) <i>On the Mechanism of Soot Nucleation</i>
16.50-17.20 (GMT+4)	Anatoliy A. Nikolayev (Lebedev Physical Institute, Samara Branch, Samara University, Samara, Russia) <i>The formation of the skeleton of pyrrole (C₄H₅N) as a result of acetylene(C₂H₂)+ethynamine(C₂H₃N) reactions involving radicals</i>
17.20-17.30 (GMT+4)	Closing Remarks. Valery N. Azyazov (Lebedev Physical Institute, Samara Branch, Samara University, Samara, Russia)

Connection link: <https://bbb.ssau.ru/b/mhq-pqf-dr9-hzb>

The link will be available 20 minutes before the start of the workshop.

UNTANGLING THE FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS

Ralf I. Kaiser

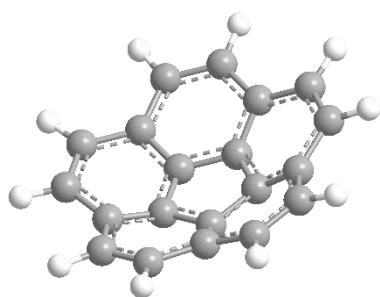
Professor & Director W.M. Keck Research Laboratory in Astrochemistry
Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA

<http://www.uhmreactiondynamics.org>

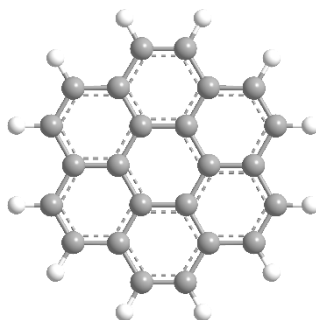
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For decades, polycyclic aromatic hydrocarbons (PAHs) – organic molecules containing fused benzene rings - have been invoked in fundamental molecular mass growth processes leading eventually to carbonaceous nanostructures in the interstellar medium (grains) and in combustion processes (soot). However, the elementary steps involved in low- and high-temperature growth mechanisms of these aromatics have remained essentially elusive until recently. Extracted from gas phase molecular beam studies on the molecular level (Hawaii) combined with isomer-selective photoionization mass spectrometry and electronic structure calculations (Advanced Light Source, Swiss Light Source), this talk presents a comprehensive mechanistical framework on key elementary reaction mechanisms synthesizing aromatic molecules in extreme environments culminating in the gas phase preparation of corannulene (1), coronene (2), and nano bowls (3).

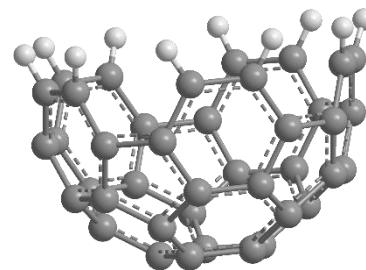
Facile low-temperature routes to complex aromatics signify a fundamental shift in the perception that PAHs can be only formed at high-temperature combustion and circumstellar conditions on electronic ground state surfaces with novel mechanisms comprising excited state dynamics, submerged barriers, and unconventional concerted reactions between aromatic radicals. An outlook is also presented on the synthesis of PAHs in low temperature, hydrocarbon-dominated solids upon interaction with (non)-ionizing radiation driven predominantly by non-adiabatic dynamics to PAHs as complex as nano bowls ultimately shedding light on the aromatic universe we live in.



(1)



(2)



(3)

PRODUCTION OF CARBONACEOUS MOLECULES BY ACCRETION OF C-ATOMS
ON THE SURFACE OF COSMIC DUST DURING THE EARLY ONSET OF STAR
SYSTEM FORMATION

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Complex organic molecules (COMs) have been observed in different evolutionary stages of star and planet formation, including along different lines of sight in dark and translucent clouds. Yet, understanding the formation of COMs in such clouds is far from complete, and can be partially explained by the lack of laboratory experiments that specifically target carbon atom addition reactions on icy surfaces of interstellar grains that are ubiquitous in star-forming regions.

This report presents the results of systematic laboratory studies, supported by theoretical results, showing that the carbon skeleton of oxygen-containing complex organic molecules (COMs) can efficiently form under extreme physical and chemical conditions typical for earliest stages of star formation, such as a translucent cloud and a dark molecular cloud from which protostars and protoplanetary disks are formed.

Besides presenting the results obtained for the common approach, where the COM carbon skeleton is formed by sequential enlargement from simplest atoms and molecules, i.e., the so-called "bottom-up" mechanism, the report also presents laboratory results confirming the possibility to form organic compounds by the "top-down" method. In this alternative approach, the role of the carbon skeleton for future organic compounds is played by the "carbon chains", with the backbone described by the general formulas $-(C\equiv C)_n-$ and $C-(C\equiv C)_n-$ with $n \geq 1$.

LITHIUM COORDINATION COMPOUNDS ON EARTH AND IN SPACE

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Lithium is one of the rare chemical elements on Earth, but it is in great demand as a coolant in nuclear reactors, a component of special types of glass in the form of an oxide, an important component of lithium batteries, etc. Lithium is formed during the radioactive decay of the unstable beryllium-7 isotope and is distributed unevenly throughout Universe. Some stars are distinguished by an anomalously high content of lithium atoms, compared to what is expected from the Big Bang theory, therefore a detailed study of the distribution of this element in the Universe, including through the detection of its chemical compounds by new methods, is of interest both for theory and for practice of astrochemistry. In order to understand in the form of which lithium compounds can be present in space ices, we considered the known crystal structures containing this metal and analyzed the values of their descriptors.

According to the data obtained, lithium prefers to coordinate 4, 3, and 5 atoms in 49%, 18%, and 12% of cases, respectively, which is in good agreement with the concepts known in crystal chemistry. The most frequently associated atoms are oxygen, nitrogen, and carbon contained in the ligands 12-Crown-4 $C_8H_{16}O_4$, tetrahydrofuran C_4H_8O , phthalocyaninat $C_{32}H_{16}N_8$, ethylenediamine $C_2H_8N_2$, cyclopentadienyl C_5H_5 , etc. Single structures with polycyclic aromatic hydrocarbons are known, such as bis(μ -2,2'',4,4'',5,5''-hexamethyl-1,1':3',1''-terphenyl-2'-yl)-di-lithium, bis(μ_2 - η^6 , η^6 -fluorene)-di-lithium. Lithium compounds with organic ligands are predominantly molecular structures (77% of their total number) with topological types in the standard representation quadrangle 2M4-1, linear 1M2-1 and in the form of a distorted cube 3M8-1, occurring in 40.7%, 11.6%, 8.3% of cases, respectively. Structural types CaF_2 (23.8%), PtS (13.9%), $SrAl_2$ (9.9%) correspond to the most frequent cases in three-periodic crystal structures. The revealed structural features of lithium-containing compounds are planned to be used in the selection of molecular samples for quantum chemical calculations.

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ON THE MECHANISM OF SOOT NUCLEATION

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Keywords: Polycyclic aromatic hydrocarbons (PAH), soot, nucleation, non-equilibrium dynamics, molecular dynamics

The mechanism of carbon particulate (soot) inception has been a subject of numerous studies and debates. We critically reviewed prior proposals, analyzed factors enabling the development of a meaningful nucleation flux, and then introduced new ideas that lead to the fulfillment of these requirements. In the new proposal, a rotationally-activated dimer is formed in the collision of an aromatic molecule and an aromatic radical; the two react during the lifetime of the dimer to form a stable, doubly-bonded bridge between them, with the reaction rooted in a five-member ring present on the molecule edge. Several such reactions were examined theoretically and the most promising one generated a measurable nucleation flux. The consistency of the proposed model with known aspects of soot particle nanostructure is discussed. The foundation of the new model is fundamentally the H-Abstraction-Carbon-Addition (HACA) mechanism with the reaction affinity enhanced by rovibrational excitation. In particular, by carrying out molecular dynamics simulations of dimerization of midsize polycyclic aromatic hydrocarbons (PAH), which is the presumed critical step in formation of carbonaceous particles in terrestrial and extraterrestrial environments, we have discovered non-equilibrium precursor mediated kinetics for reactions of gaseous molecules at high temperatures. The non-equilibrium precursor state originates from inelastic collisional dynamics of two PAH monomers, with low-frequency modes acting as a sink for translational energy in the reaction coordinate. Owing to the prolonged lifetime of the non-equilibrium physical dimer, the probability of chemical dimerization increases by an order of magnitude. This phenomenon brings us closer to a solution for the carbon-particle inception puzzle and should prove useful for the fundamental understanding of gas-phase chemical reactions involving large molecules.

References

Frenklach M, Mebel AM. On the mechanism of soot nucleation. *Phys Chem Chem Phys* 2020;22:5314-5331.

Morozov AN, Mebel AM, Frenklach M. Acceleration of a chemical reaction due to non-equilibrium collisional dynamics: Dimerization of polyaromatics. *J Phys Chem Lett* 2022;13:11528-11535.

THE FORMATION OF THE SKELETON OF PYRROLE (C₄H₅N) AS A RESULT
OF ACETYLENE(C₂H₂) + ETHYNAMINE(C₂H₃N) REACTIONS
INVOLVING RADICALS

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Keywords: Polycyclic aromatic nitrogen heterocycles (PANH), pyrrole, acetylene, chemical reactions

The cosmic abundance of the N atom is sufficiently high to be found in a huge variety of molecular forms, from the simplest species like CN, formamide (NH₂CHO) to most complex structures, such as polycyclic aromatic nitrogen heterocycles (PANHs), as some of which have been analyzed in Murchison meteorite samples. If the substituted N is located on the periphery of the PAH, the resulting PANH is quite reactive, which may lead to the production of other N-heterocycles, as pyrroles, pyridines, pyrimidines or purines [1]. This study of chemical reactions resulting in pyrrole formation reveals the first step of the way that PANHs may form. Various reactions of acetylene with ethynamine and its radicals are likely to obtain a five-membered hydrocarbon cyclic structure including nitrogen. Acetylene is an imperative building block assisting in forming lots of polycyclic aromatic hydrocarbons (PAHs), for instance via the hydrogen abstraction acetylene addition (HACA) mechanism. In addition, chemical reactions in the C₂H₂ ices are accompanied with the benzene formation [2]. The molecular compound pyrrole and its radicals formed in the work are the simplest N-heterocycle with four carbon atoms. Pyrrole and its derivatives can further lead to the formation of the bicyclic structure indole (C₈H₇N) comprising a six-membered benzene ring fused to a five-membered pyrrole ring. PANHs are especially relevant for astrochemistry and astrobiology as they serve precursors of DNA and RNA. The formation of N-heterocycles is one of the open questions in contemporary chemistry.

References

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