

<b>Title of Grant / Cooperative Agreement:</b>	Laboratory, Computational and In-Situ Investigations of Probable Extraterrestrial Materials
<b>Type of Report:</b>	Summary of Research
<b>Name of Principal Investigator:</b>	Robert W. Bergstrom
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<b>Name and Address of recipient's institution:</b>	BAY AREA ENVIRONMENTAL RESEARCH INSTITUTE 625 2 <sup>nd</sup> St Ste 209, Petaluma, CA 94952
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**Reference 14 CFR § 1260.28 Patent Rights**

The Recipient shall include a list of any Subject Inventions required to be disclosed during the preceding year in the performance report, technical report, or renewal proposal. A complete list (or a negative statement) for the entire award period shall be included in the summary of research.

Have any Subject Inventions / New Technology Items resulted from work performed under this Grant / Cooperative Agreement?	[X] NO	[ ] YES
If yes a complete listing should be provided here: Details can be provided in the body of the Summary of Research report.		

***Attach the Summary of Research text behind this cover sheet.***

**Reference 14 CFR § 1260.22 Technical publications and reports (December 2003)**

Reports shall be in the English language, informal in nature, and ordinarily not exceed three pages (not counting bibliographies, abstracts, and lists of other media).

A Summary of Research (or Educational Activity Report in the case of Education Grants) is due within 90 days after the expiration date of the grant, regardless of whether or not support is continued under another grant. This report shall be a comprehensive summary of significant accomplishments during the duration of the grant.

# **Final Report for NASA Cooperative Agreement NNX12AB89A**

## **Title: Laboratory, Computational, Observational, and In-situ Investigations of Probable Extraterrestrial Materials**

Submitted by email to:

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Period of Performance: 12/1/11 to 11/30/15

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**Summary:**

The output of this Cooperative Agreement in the period December 1, 2011 – November 31, 2015 includes 22 peer-reviewed publications. Titles, author lists, bibliographic information and abstracts for these papers are found below.

**Title: The Photochemistry of Pyrimidine in Realistic Astrophysical Ices and the Production of Nucleobases**

Authors: Nuevo, M., Materese, C. K., and Sandford, S. A.

Source: *Astrophys. J.*, 793, 125, Published 2014.

**Abstract:**

Nucleobases, together with deoxyribose/ribose and phosphoric acid, are the building blocks of DNA and RNA for all known life. The presence of nucleobase-like compounds in carbonaceous chondrites delivered to the Earth raises the question of an extraterrestrial origin for the molecules that triggered life on our planet. Whether these molecules are formed in interstellar/protostellar environments, in small parent bodies in the solar system, or both, is currently unclear. Recent experiments show that the UV irradiation of pyrimidine ( $C_4H_4N_2$ ) in  $H_2O$ -rich ice mixtures that contain  $NH_3$ ,  $CH_3OH$ , or  $CH_4$  leads to the formation of the pyrimidine-based nucleobases uracil, cytosine, and thymine. In this work, we discuss the low-temperature UV irradiation of pyrimidine in realistic astrophysical ice mixtures containing  $H_2O$ ,  $CH_3OH$ , and  $NH_3$ , with or without  $CH_4$ , to search for the production of nucleobases and other prebiotic compounds. These experiments show the presence of uracil, urea, glycerol, hexamethylenetetramine, small amino acids, and small carboxylic acids in all samples. Cytosine was only found in one sample produced from ices irradiated with a higher UV dose, while thymine was not found in any sample, even after irradiation with a higher UV dose. Results are discussed to evaluate the role of the photochemistry of pyrimidine in the inventory of organic molecules detected in meteorites and their astrophysical/astrobiological implications.

**Title: N- and O-heterocycles Produced from the Irradiation of Benzene and Naphthalene in  $H_2O/NH_3$ -containing Ices**

Authors: Materese, C. K., Nuevo, M., and Sandford, S. A.

Source: *Astrophys. J.*, 800, 116, Published 2015

**Abstract:**

Aromatic heterocyclic molecules are an important class of molecules of astrophysical and biological significance that include pyridine, pyrimidine, and their

derivatives. Such compounds are believed to exist in interstellar and circumstellar environments, though they have never been observed in the gas phase. Regardless of their presence in the gas phase in space, numerous heterocycles have been reported in carbonaceous meteorites, which indicates that they are formed under astrophysical conditions. The experimental work described here shows that N- and O-heterocyclic molecules can form from the ultraviolet (UV) irradiation of the homocyclic aromatic molecules benzene (C<sub>6</sub>H<sub>6</sub>) or naphthalene (C<sub>10</sub>H<sub>8</sub>) mixed in ices containing H<sub>2</sub>O and NH<sub>3</sub>. This represents an alternative way to generate aromatic heterocycles to those considered before and may have important implications for astrochemistry and astrobiology.

**Title: Ice Chemistry on Outer Solar System Bodies: Electron Radiolysis of N<sub>2</sub>-, CH<sub>4</sub>-, and CO-Containing Ices**

Authors: Materese, C. K., Cruikshank, D. P., Sandford, S. A., Imanaka, H., and Nuevo, M.

Source: *Astrophys. J.*, 812, 150, Published 2015

**Abstract:**

Radiation processing of the surface ices of outer Solar System bodies may be an important process for the production of complex chemical species. The refractory materials resulting from radiation processing of known ices are thought to impart to them a red or brown color, as perceived in the visible spectral region. In this work, we analyzed the refractory materials produced from the 1.2-keV electron bombardment of low-temperature N<sub>2</sub>-, CH<sub>4</sub>-, and CO-containing ices (100:1:1), which simulates the radiation from the secondary electrons produced by cosmic ray bombardment of the surface ices of Pluto. Despite starting with extremely simple ices dominated by N<sub>2</sub>, electron irradiation processing results in the production of refractory material with complex oxygen- and nitrogen-bearing organic molecules. These refractory materials were studied at room temperature using multiple analytical techniques including Fourier-transform infrared spectroscopy, X-ray absorption near-edge structure (XANES) spectroscopy, and gas chromatography coupled with mass spectrometry (GC-MS). Infrared spectra of the refractory material suggest the presence of alcohols, carboxylic acids, ketones, aldehydes, amines, and nitriles. XANES spectra of the material indicate the presence of carboxyl groups, amides, urea, and nitriles, and are thus consistent with the IR data. Atomic abundance ratios for the bulk composition of these residues from XANES analysis show that the organic residues are extremely N-rich, having ratios of N/C ~ 0.9 and O/C ~ 0.2. Finally, GC-MS data reveal that the residues contain urea as well as numerous carboxylic acids, some of which are of interest for prebiotic and biological chemistries.

**Title: Mid-infrared study of stones from the Sutter's Mill meteorite**

Authors: Nuevo, M., Sandford, S. A., Flynn, G. J., and Wirick, S.

Source: Meteoritical and Planetary Society, 49, 2017, Published 2014

**Abstract:**

The Sutter's Mill meteorite fell in northern California on April 22, 2012. Several fragments of the meteorite were recovered, some of them shortly after the fall, others several days later after a heavy rainstorm. In this work, we analyzed several samples of four fragments—SM2, SM12, SM20, and SM30—from the Sutter's Mill meteorite with two infrared (IR) microscopes operating in the 4000-650  $\text{cm}^{-1}$  (2.5-15.4  $\mu\text{m}$ ) range. Spectra show absorption features associated with minerals such as olivines, phyllosilicates, carbonates, and possibly pyroxenes, as well as organics. Spectra of specific minerals vary from one particle to another within a given stone, and even within a single particle, indicating a non-uniform mineral composition. Infrared features associated with aliphatic  $\text{CH}_2$  and  $\text{CH}_3$  groups associated with organics are also seen in several spectra. However, the presence of organics in the samples studied is not clear because these features overlap with carbonate overtone bands. Finally, other samples collected within days after the rainstorm show evidence for bacterial terrestrial contamination, which indicates how quickly meteorites can be contaminated on such small scales.

**Title: First results of the ORGANIC experiment on EXPOSE-R on the ISS**

Authors: Bryson, K. L., Salama, F., Elsasser, A., Peeters, Z., Ricco, A. J., and Foing, B. H.

Source: International Journal of Astrobiology, 14, 55, Published 2015

**Abstract:**

The ORGANIC experiment on EXPOSE-R spent 682 days outside the International Space Station, providing continuous exposure to the cosmic-, solar- and trapped-particle radiation background for fourteen samples: 11 polycyclic aromatic hydrocarbons (PAHs) and three fullerenes. The thin films of the ORGANIC experiment received, during space exposure, an irradiation dose of the order of 14 000  $\text{MJ m}^{-2}$  over 2900 h of unshadowed solar illumination. Extensive analyses were performed on the returned samples and the results compared to ground control measurements. Analytical studies of the returned samples included spectral measurements from the vacuum ultraviolet to the infrared range and time-of-flight secondary ion mass spectrometry. Limited spectral changes were observed in most cases pointing to the stability of PAHs and fullerenes under space exposure conditions. Furthermore, the results of these experiments confirm the known trend in the stability of PAH species according to molecular structure: compact PAHs are more stable than non-compact PAHs, which are themselves more stable than PAHs containing heteroatoms, the last category being the most prone to degradation in

the space environment. We estimate a depletion rate of the order of  $85 \pm 5\%$  over the 17 equivalent weeks of continuous unshadowed solar exposure in the most extreme case tetracene (smallest, non-compact PAH sample). The insignificant spectral changes (below 10%) measured for solid films of large or compact PAHs and fullerenes indicate a high stability under the range of space exposure conditions investigated on EXPOSE-R.

**Title: Low Temperature Formation of Nitrogen-substituted Polycyclic Aromatic Hydrocarbons (PANHs) - Barrierless Routes to Dihydro(iso)quinolones**

Authors: Parker, D. S. N., Yang, T., Bangi, B. B., Kaiser, R., Bera, P. P., and Lee, T. J.

Source: *Astrophys. J.*, 815, 115, Published 2015.

**Abstract:**

Meteorites contain bio-relevant molecules such as vitamins and nucleobases, which consist of aromatic structures with embedded nitrogen atoms. Questions remain over the chemical mechanisms responsible for the formation of nitrogen-substituted polycyclic aromatic hydrocarbons (PANHs) in extraterrestrial environments. By exploiting single collision conditions, we show that a radical mediated bimolecular collision between pyridyl radicals and 1,3-butadiene in the gas phase forms nitrogen-substituted polycyclic aromatic hydrocarbons (PANHs) 1,4-dihydroquinoline and to a minor amount 1,4-dihydroisoquinoline. The reaction proceeds through the formation of a van der Waals complex, which circumnavigates the entrance barrier implying it can operate at very low kinetic energy and therefore at low temperatures of 10 K as present in cold molecular clouds such as TMC-1. The discovery of facile de facto barrierless exoergic reaction mechanisms leading to PANH formation could play an important role in providing a population of aromatic structures upon which further photo-processing of ice condensates could occur to form nucleobases.

**Title: Properties of Polycyclic Aromatic Hydrocarbons in the Northwest Photon Dominated Region of NGC 7023. III. Quantifying the Traditional Proxy for PAH Charge and Assessing its Role**

Authors: Boersma, C., Bregman, J., and Allamandola, L. J.

Source: *Astrophys. J.*, 806, 121, Published 2015.

**Abstract:**

Polycyclic aromatic hydrocarbon (PAH) emission in the Spitzer/IRS spectral map of the northwest photon dominated region (PDR) in NGC 7023 is analyzed. Here, results from

fitting the 5.2-14.5  $\mu\text{m}$  spectrum at each pixel using exclusively PAH spectra from the NASA Ames PAH IR Spectroscopic Database ([www.astrochem.org/pahdb/](http://www.astrochem.org/pahdb/)) and observed PAH band strength ratios, determined after isolating the PAH bands, are combined. This enables the first quantitative and spectrally consistent calibration of PAH charge proxies. Calibration is straightforward because the 6.2/11.2  $\mu\text{m}$  PAH band strength ratio varies linearly with the ionized fraction (PAH ionization parameter) as determined from the intrinsic properties of the individual PAHs comprising the database. This, in turn, can be related to the local radiation field, electron density, and temperature. From these relations diagnostic templates are developed to deduce the PAH ionization fraction and astronomical environment in other objects. The commonly used 7.7/11.2  $\mu\text{m}$  PAH band strength ratio fails as a charge proxy over a significant fraction of the nebula. The 11.2/12.7  $\mu\text{m}$  PAH band strength ratio, commonly used as a PAH erosion indicator, is revealed to be a better tracer for PAH charge across NGC 7023. Attempting to calibrate the 12.7/11.2  $\mu\text{m}$  PAH band strength ratio against the PAH hydrogen adjacency ratio (duo+trio)/solo is, unexpectedly, anti-correlated. This work both validates and extends the results from Paper I and Paper II.

**Title: Ice chemistry on outer Solar System bodies: Carboxylic acids, nitriles, and urea detected in refractory residues produced from the UV photolysis of  $\text{N}_2:\text{CH}_4:\text{CO}$ -containing ices**

Authors: Materese, C.K., Cruikshank, D.P., Sandford, S.A., Imanaka, H., Nuevo, M., and White, D.W.

Source: *Astrophys. J.*, 788, 11, Published 2014

**Abstract:**

Radiation processing of the surface ices of outer solar system bodies may result in the production of new chemical species even at low temperatures. Many of the smaller, more volatile molecules that are likely produced by the photolysis of these ices have been well characterized by laboratory experiments. However, the more complex refractory material formed in these experiments remains largely uncharacterized. In this work, we present a series of laboratory experiments in which low-temperature (15–20 K)  $\text{N}_2:\text{CH}_4:\text{CO}$  ices in relative proportions 100:1:1 are subjected to UV irradiation, and the resulting materials are studied with a variety of analytical techniques including infrared spectroscopy, X-ray absorption near-edge structure spectroscopy, gas chromatography coupled with mass spectrometry, and high-resolution mass spectroscopy. Despite the simplicity of the reactants, these experiments result in the production of a highly complex mixture of molecules from relatively low-mass volatiles (tens of daltons) to high-mass refractory materials (hundreds of daltons). These products include various carboxylic acids, nitriles, and urea, which are also expected to be present on the surface of outer solar system bodies, including Pluto and other transneptunian objects. If these compounds occur in sufficient concentrations in the ices of outer solar system bodies, their characteristic bands may be detectable in the near-infrared spectra of these objects.

**Title: Photosynthesis and Photo-Stability of Nucleic Acids in Prebiotic Extraterrestrial Environments**

Authors(s): Sandford, S.A., Bera, P.P., Lee, T.J., Materese, C.K., and Nuevo, M.

Source: Topics of Current Chemistry, Chapter 14 of the book Photoinduced Phenomena in Nucleic Acids, eds. Barbatti, M., Borin, A.C., Ullrich, S. (Springer-Verlag: Berlin, Heidelberg), 499 Published 2014.

Abstract:

Laboratory experiments have shown that the UV photo-irradiation of low-temperature ices of astrophysical interest leads to the formation of organic molecules, including molecules important for biology such as amino acids, quinones, and amphiphiles. When pyrimidine is introduced into these ices, the products of irradiation include the nucleobases uracil, cytosine, and thymine, the informational sub-units of DNA and RNA, as well as some of their isomers. The formation of these compounds, which has been studied both experimentally and theoretically, requires a succession of additions of OH, NH<sub>2</sub>, and CH<sub>3</sub> groups to pyrimidine. Results show that H<sub>2</sub>O ice plays key roles in the formation of the nucleobases, as an oxidant, as a matrix in which reactions can take place, and as a catalyst that assists proton abstraction from intermediate compounds. As H<sub>2</sub>O is also the most abundant icy component in most cold astrophysical environments, it probably plays the same roles in space in the formation of biologically relevant compounds. Results also show that although the formation of uracil and cytosine from pyrimidine in ices is fairly straightforward, the formation of thymine is not.

**Title: Thymine and Other Prebiotic Molecules Produced from the Ultraviolet Photo-Irradiation of Pyrimidine in Simple Astrophysical Ice Analogs**

Authors: Christopher K. Materese, Michel Nuevo, Partha P. Bera, Timothy J. Lee, and Scott A. Sandford

Source: ASTROBIOLOGY, Volume 13, Number 10, Published 2013.

Abstract:

The informational subunits of RNA or DNA consist of substituted N-heterocyclic compounds that fall into two groups: those based on purine (C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>) (adenine and guanine) and those based on pyrimidine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>) (uracil, cytosine, and thymine). Although not yet detected in the interstellar medium, N-heterocycles, including the nucleobase uracil, have been reported in carbonaceous chondrites. Recent laboratory experiments and ab initio calculations have shown that the irradiation of pyrimidine in ices containing H<sub>2</sub>O, NH<sub>3</sub>, or both leads to the abiotic production of substituted pyrimidines, including the nucleobases uracil and cytosine. In this work, we studied the methylation and oxidation of pyrimidine in CH<sub>3</sub>OH:pyrimidine, H<sub>2</sub>O:CH<sub>3</sub>OH:pyrimidine, CH<sub>4</sub>:pyrimidine, and H<sub>2</sub>O:CH<sub>4</sub>:pyrimidine ices irradiated with UV photons under astrophysically-relevant conditions. The nucleobase thymine was



detected in the residues from some of the mixtures. Our results suggest that the abundance of abiotic thymine produced by ice photolysis and delivered to the early Earth may have been significantly lower than that of uracil. Insofar as the delivery of extraterrestrial molecules was important for early biological chemistry on early Earth, these results suggest that there was more uracil than thymine available for emergent life, a scenario consistent with the RNA world hypothesis.

**Title: Relative energies, structures, vibrational frequencies, and electronic spectra of pyrylium cation, an oxygen-containing carbocyclic ring isoelectronic with benzene, and its isomers**

Authors: Partha P. Bera, Martin Head-Gordon, and Timothy J. Lee

Source: J. Chem. Phys. 139, 174302, Published 2013

Abstract:

We have studied relative energies, structures, rotational, vibrational, and electronic spectra of the pyrylium cation, an oxygen-containing six-membered carbocyclic ring, and its six isomers, using ab initio quantum chemical methods. Isoelectronic with benzene, the pyrylium cation has a benzenoid structure and is the global minimum on the singlet potential energy surface of  $C_5H_5O^+$ . The second lowest energy isomer, the furfuryl cation, has a five membered backbone akin to a sugar, and is only 16 kcal mol<sup>-1</sup> above the global minimum computed using coupled cluster theory with singles, doubles, and perturbative triple excitations (CCSD(T)) with the correlation consistent cc-pVTZ basis set. Other isomers are 25, 26, 37, 60, and 65 kcal mol<sup>-1</sup> above the global minimum, respectively, at the same level of theory. Lower level methods such as density functional theory (B3LYP) and second order Møller-Plesset perturbation theory performed well when tested against the CCSD(T) results. The pyrylium and furfuryl cations, although separated by only 16 kcal mol<sup>-1</sup>, are not easily interconverted, as multiple bonds must be broken and formed, and the existence of more than one transition state is likely. Additionally, we have also investigated the asymptotes for the barrierless ion-molecule association of molecules known to exist in the interstellar medium that may lead to formation of the pyrylium cation.

**Title: The Titan Haze Simulation experiment on COSmIC: Probing Titan's atmospheric chemistry at low temperature**

Authors: Sciamma-O'Brien, E., Ricketts, C.L., and Salama, F.

Source: Icarus, 243, 325 Published 2014

Abstract:

The aim of the Titan Haze Simulation (THS) experiment is to contribute to a better understanding of aerosol formation in Titan's atmosphere through the study of the

chemical formation pathways that link the simpler gas phase molecules resulting from the first steps of the  $N_2$ - $CH_4$  chemistry, to the more complex gas phase precursors of aerosols; and more specifically, to investigate the role of polycyclic aromatic hydrocarbons (PAHs) and nitrogenated polycyclic aromatic hydrocarbons (PANHs), among other hydrocarbons, in this process. In the THS experiment developed at the NASA Ames Cosmic simulation facility (COSmIC), Titan's atmospheric chemistry is simulated by a pulsed plasma jet expansion at temperature conditions ( $\sim 150$  K) close to those found in Titan's atmosphere in regions where aerosols are formed. In addition, because of the very short residence time of the gas in the plasma discharge, only the initial steps of the chemistry occur, making the COSmIC/THS a unique tool to study the first and intermediate (when adding heavier precursors to the initial  $N_2$ - $CH_4$  mixture) steps of Titan's atmospheric chemistry at low temperature as shown in the study presented here. We further illustrate the potential of COSmIC/THS for the simulation of Titan's atmospheric chemistry by presenting very promising results from a preliminary comparison of the laboratory data to data from the Cassini Plasma Spectrometer-Ion Beam Spectrometer (CAPS-IBS) instrument.

**Title: Laboratory Investigations of PAH Formation and Destruction in the Circumstellar Outflow of Carbon Stars**

Authors: Contreras, C., and Salama, F.

Source: *Astrophys. J. Suppl. Ser.*, 208, 6, Published 2103.

**Abstract:**

The formation and destruction mechanisms of interstellar dust analogs formed from a variety of polycyclic aromatic hydrocarbon (PAH) and hydrocarbon molecular precursors are studied in the laboratory. We used the newly developed facility COSmIC, which simulates interstellar and circumstellar environments, to investigate both PAHs and species that include the cosmically abundant atoms O, N, and S. The species generated in a discharge plasma are detected, monitored, and characterized in situ using highly sensitive techniques that provide both spectral and ion mass information. We report here the first series of measurements obtained in these experiments which focus on the characterization of the most efficient molecular precursors in the chemical pathways that eventually lead to the formation of carbonaceous grains in the stellar envelopes of carbon stars. We compare and discuss the relative efficiencies of the various molecular precursors that lead to the formation of the building blocks of carbon grains. We discuss the most probable molecular precursors in terms of size and structure and the implications for the expected growth and destruction processes of interstellar carbonaceous dust.

**Title: Properties of polycyclic aromatic hydrocarbons in the northwest photon dominated region of NGC 7023. II. Traditional PAH analysis using k-means as a visualization tool.**

Authors: C. Boersma, J. Bregman, and L.J. Allamandola

Source: *Astrophysical Journal*, 795, 110, published 2014.

**Abstract:**

Polycyclic aromatic hydrocarbon (PAH) emission in the Spitzer-IRS spectral map of the northwest photon dominated region (PDR) in NGC 7023 is analyzed using the "traditional" approach in which the PAH bands and plateaus between 5.2-19.5  $\mu\text{m}$  are isolated by subtracting the underlying continuum and removing H<sub>2</sub> emission lines. The spectra are organized into seven spectroscopic bins by using k-means clustering. Each cluster corresponds to, and reveals, a morphological zone within NGC 7023. The zones self-organize parallel to the well-defined PDR front that coincides with an increase in intensity of the H<sub>2</sub> emission lines. PAH band profiles and integrated strengths are measured, classified, and mapped. The morphological zones revealed by the k-means clustering provides deeper insight into the conditions that drive variations in band strength ratios and evolution of the PAH population that otherwise would be lost. For example, certain band-band relations are bifurcated, revealing two limiting cases; one associated with the PDR, the other with the diffuse medium. Traditionally, PAH band strength ratios are used to gain insight into the properties of the emitting PAH population, i.e., charge, size, structure, and composition. Insights inferred from this work are compared and contrasted to those from Boersma et al. (first paper in this series), where the PAH emission in NGC 7023 is decomposed exclusively using the PAH spectra and tools made available through the NASA Ames PAH IR Spectroscopic Database.

**Title: Complementary and Emerging Techniques for Astrophysical Ices Processed in the Laboratory**

Authors: Allodi, M. A. and Baragiola, R. A. and Baratta, G. A. and Barucci, M. A. and Blake, G. A. and Boduch, P. and Brucato, J. R. and Contreras, C. and Cuyllé, S. H. and Fulvio, D. and Gudipati, M. S. and Ioppolo, S. and Kaňuchová, Z. and Lignell, A. and Linnartz, H. and Palumbo, M. E. and Raut, U. and Rothard, H. and Salama, F. and Savchenko, E. V. and Sciamma-O'Brien, E. and Strazzulla, G.

Source: *Space Science Reviews*, 180 (1-4), 101 ISSN 0038-6308, published 2013.

**Abstract:**

Inter- and circumstellar ices comprise different molecules accreted on cold dust particles. These icy dust grains provide a molecule reservoir where particles can interact and react. As the grain acts as a third body, capable of absorbing energy, icy surfaces in space have a catalytic effect. Chemical reactions are triggered by a number of possible processes; (i) irradiation by light, typically UV photons from the interstellar radiation field and Ly- $\alpha$

radiation emitted by excited hydrogen, but also X-rays, (ii) bombardment by particles, free atoms (most noticeably hydrogen, but also N, C, O and D-atoms), electrons, low energy ions and cosmic rays, and (iii) thermal processing. All these effects cause ices to (photo) desorb, induce fragmentation or ionization in the ice, and eventual recombination will make molecules to react and to form more and more complex species. The effects of this solid state astrochemistry are observed by astronomers; nearly 180 different molecules (not including isotopologues) have been unambiguously identified in the inter- and circumstellar medium, and the abundances of a substantial part of these species cannot be explained by gas phase reaction schemes only and must involve solid state chemistry. Icy dust grains in space experience different chemical stages. In the diffuse medium grains are barely covered by molecules, but upon gravitational collapse and darkening of the cloud, temperatures drop and dust grains start acting as micrometer sized cryopumps. More and more species accrete, until even the most volatile species are frozen. In parallel (non) energetic processing can take place, particularly during planet and star formation when radiation and particle fluxes are intense. The physical and chemical properties of ice clearly provide a snapshot to characterize the cosmological chemical evolution. In order to fully interpret the astronomical observations, therefore, dedicated laboratory experiments are needed that simulate dust grain formation and processing as well as ice mantle chemistry under astronomical conditions and in full control of the relevant parameters; ice morphology (i.e., structure), composition, temperature, UV and particle fluxes, etc., yielding parameters that can be used for astrochemical modeling and for comparison with the observations. This is the topic of the present manuscript. Laboratory experiments simulating the conditions in space are conducted for decades all over the world, but particularly in recent years new techniques have made it possible to study reactions involving inter- and circumstellar dust and ice analogues at an unprecedented level of detail. Whereas in the past “top-down scenarios” allowed to conclude on the importance of the solid state for the chemical enrichment of space, presently “bottom-up approaches” make it possible to fully quantify the involved reactions, and to provide information on processes at the molecular level. The recent progress in the field of “solid state laboratory astrophysics” is a consequence of the use of ultra high vacuum systems, of new radiation sources, such as synchrotrons and laser systems that allow extensions to wavelength domains that long have not been accessible, including the THz domain, and the use of highly sensitive gas phase detection techniques, explicitly applied to characterize the solid state such as fluorescence, luminescence, cavity ring-down spectroscopy and sophisticated mass spectrometric techniques. This paper presents an overview of the techniques being used in astrochemical laboratories worldwide, but it is incomplete in the sense that it summarizes the outcome of a 3-day workshop of the authors in November 2012 (at the Observatoire de Meudon in France), with several laboratories represented, but not all. The paper references earlier work, but it is incomplete with regard to latest developments of techniques used in laboratories not represented at the workshop.

**Title: Association mechanisms of unsaturated C2 hydrocarbons with their cations: acetylene and ethylene**

Author(s): Bera, P. P.; Head-Gordon, M.; Lee, T. J.

Source: Phys. Chem. Chem. Phys., 15, 2012, Published 2013.

Abstract: The ion–molecule association mechanism of acetylene and ethylene with their cations is investigated by *ab initio* quantum chemical methods to understand the structures, association energies, and the vibrational and electronic spectra of the products. Stable puckered cyclic isomers are found as the result of first forming less stable linear and bridge isomers. The puckered cyclic complexes are calculated to be strongly bound, by 87, 35 and 56 kcal mol<sup>-1</sup> for acetylene–acetylene cation, ethylene–ethylene cation and acetylene–ethylene cation, respectively. These stable complexes may be intermediates that participate in further association reactions. There are no association barriers, and no significant inter-conversion barriers, so the initial linear and bridge encounter complexes are unlikely to be observable. However, the energy gap between the bridged and cyclic puckered isomers greatly differs from complex to complex: it is 44 kcal mol<sup>-1</sup> in C<sub>4</sub>H<sub>4</sub><sup>+</sup>, but only 6 kcal mol<sup>-1</sup> in C<sub>4</sub>H<sub>8</sub><sup>+</sup>. The accurate CCSD(T) calculations summarized above are also compared against less computationally expensive MP2 and density functional theory (DFT) calculations for structures, relative energies, and vibrational spectra. Calculated vibrational spectra are compared against available experiments for cyclobutadiene cation. Electronic spectra are also calculated using time-dependent DFT.

**Title: Properties of Polycyclic Aromatic Hydrocarbons in the Northwest Photon Dominated Region of NGC 7023. I. PAH Size, Charge, Composition, and Structure Distribution**

Authors: Boersma, C., Bregman, J. D., and Allamandola, L. J.

Source: Astrophysical Journal, 769, 117, Published 2013.

Abstract:

Polycyclic aromatic hydrocarbon (PAH) emission in the Spitzer Infrared Spectrograph spectral map of the northwest photon dominated region (PDR) in NGC 7023 was analyzed exclusively using PAH spectra from the NASA Ames PAH IR Spectroscopic Database ([www.astrochem.org/pahdb](http://www.astrochem.org/pahdb)). The 5-15 μm spectrum at each pixel is fitted using a non-negative-least-squares fitting approach. The fits are of good quality, allowing decomposition of the PAH emission into four subclasses: size, charge, composition, and hydrogen adjacency (structure). Maps tracing PAH subclass distributions across the region paint a coherent astrophysical picture. Once past some 20 seconds of arc from HD 200775, the emission is dominated by the more stable, large, symmetric, compact PAH cations with smaller, neutral PAHs taking over along the lines-of-sight toward the more

distant molecular cloud. The boundary between the PDR and the denser cloud material shows up as a distinct discontinuity in the breakdown maps. Noteworthy is the requirement for PAH cations to fit the bulk of the 6.2 and 11.0  $\mu\text{m}$  features and the indication of PAH photo-dehydrogenation and fragmentation close to HD 200775. Decomposition of the spectral maps into "principal" subclass template spectra provides additional insight into the behavior of each subclass. However, the general applicability of this computationally more efficient approach is presently undetermined. This is the first time the spectra of individual PAHs are exclusively used to fit the 5-15  $\mu\text{m}$  region and analyze the spatial behavior of the aromatic infrared bands, providing fundamental, new information about astronomical PAH subpopulations including their dependence on, and response to, changes in local conditions.

**Title: The development of the Space Environment Viability of Organics (SEVO) experiment aboard the Organism/Organic Exposure to Orbital Stresses (O/OREOS) satellite**

Authors: Bramall, N. E., Quinn, R., Mattioda, A., Bryson, K., Chittenden, J. D., et al.

Publication: Planetary and Space Science, Volume 60, Issue 1, 121, Published 2012.

**Abstract:**

The Space Environment Viability of Organics (SEVO) experiment is one of two scientific payloads aboard the triple-cube satellite Organism/ORganic Exposure to Orbital Stresses (O/OREOS). O/OREOS is the first technology demonstration mission of the NASA Astrobiology Small Payloads Program. The 1-kg, 1000-cm<sup>3</sup> SEVO cube is investigating the chemical evolution of organic materials in interstellar space and planetary environments by exposing organic molecules under controlled conditions directly to the low-Earth orbit (LEO) particle and electromagnetic radiation environment. O/OREOS was launched on November 19, 2010 into a 650-km, 72°-inclination orbit and has a nominal operational lifetime of six months. Four classes of organic compounds, namely an amino acid, a quinone, a polycyclic aromatic hydrocarbon (PAH), and a metallo-porphyrin are being studied. Initial reaction conditions were established by hermetically sealing the thin-film organic samples in self-contained micro-environments. Chemical changes in the samples caused by direct exposure to LEO radiation and by interactions with the irradiated microenvironments are monitored in situ by ultraviolet/visible/near-infrared (UV/VIS/NIR) absorption spectroscopy using a novel compact fixed-grating CCD spectrometer with the Sun as its light source. The goals of the O/OREOS mission include: (1) demonstrating key small satellite technologies that can enable future low-cost astrobiology experiments, (2) deploying a miniature UV/VIS/NIR spectrometer suitable for in-situ astrobiology and other scientific investigations, (3) testing the capability to establish a variety of experimental reaction conditions to enable the study of astrobiological processes on small satellites, and (4) measuring the chemical evolution of organic molecules in LEO under conditions that can be extrapolated to interstellar and planetary environments. In this paper, the science and technology development of the SEVO instrument payload and its measurements are

described.

**Title: The ORGANIC experiment on EXPOSE-R on the ISS: Flight sample preparation and ground control spectroscopy**

Authors: [Bryson, K. L.](#), [Peeters, Z.](#), [Salama, F.](#), [Foing, B.](#), [Ehrenfreund, P.](#), [Ricco, A. J.](#), [Jessberger, E.](#), [Bischoff, A.](#), and [Breitfellner, M.](#)

Publication: *Advances in Space Research*, 48, 1980, Published 2011.

Abstract:

In March of 2009, the ORGANIC experiment integrated into the European multi-user facility EXPOSE-R, containing experiments dedicated to Astrobiology, was mounted through Extra Vehicular Activity (EVA) externally on the International Space Station (ISS). The experiment exposed organic samples of astronomical interest for a duration of 97 weeks (~22 months) to the space environment. The samples that were returned to Earth in spring 2011, received a total UV radiation dose during their exposure including direct solar irradiation of >2500 h, exceeding the limits of laboratory simulations. We report flight sample preparation and pre-flight ultraviolet-visible (UV-Vis) characterization of the ORGANIC samples, which include 11 polycyclic aromatic hydrocarbons (PAHs) and three fullerenes. The corresponding time-dependent ground control monitoring experiments for ORGANIC measured over ~19 months are presented and the results anticipated upon return of the samples are discussed. We present the first UV-Vis spectrum of solid circobiphenyl (C<sub>38</sub>H<sub>16</sub>). Further, we present the first published UV-Vis spectra of diphenanthro[9,10-b',10'-d]thiophene (C<sub>28</sub>H<sub>16</sub>S), dinaphtho[8,1,2-abc,2',1',8'-klm]coronene (C<sub>36</sub>H<sub>16</sub>), tetrabenzo[de,no,st,c'd']heptacene (C<sub>42</sub>H<sub>22</sub>), and dibenzo[jk,a'b']octacene (C<sub>40</sub>H<sub>22</sub>) in solid phase and in solution. The results of the ORGANIC experiment are expected to enhance our knowledge of the evolution and degradation of large carbon-containing molecules in space environments.

**Title: Initiating molecular growth in the interstellar medium via dimeric complexes of observed ions and molecules**

Authors: [Bera, P. P.](#), [Head-Gordon, M.](#), and [Lee, T. J.](#)

Publication: *Astronomy & Astrophysics*, 535, 74, Published 2011.

Abstract:

A feasible initiation step for particle growth in the interstellar medium (ISM) is simulated by means of ab initio quantum chemistry methods. The systems studied are dimer ions formed by pairing nitrogen containing small molecules known to exist in the ISM with ions of unsaturated hydrocarbons or vice versa. Complexation energies, structures of ensuing complexes and electronic excitation spectra of the encounter complexes are estimated using various quantum chemistry methods. Møller-Plesset perturbation theory

(MP2), Z-averaged perturbation theory (ZAPT2), coupled cluster singles and doubles with perturbative triples corrections (CCSD(T)), and density functional theory (DFT) methods (B3LYP) were employed along with the correlation consistent cc-pVTZ and aug-cc-pVTZ basis sets. Two types of complexes are predicted. One type of complex has electrostatic binding with moderate (7-20 kcal mol<sup>-1</sup>) binding energies that are nonetheless significantly stronger than typical van der Waals interactions between molecules of this size. The other type of complex develops strong covalent bonds between the fragments. Cyclic isomers of the nitrogen containing complexes are produced very easily by ion-molecule reactions. Some of these complexes show intense ultraviolet-visible spectra for electronic transitions with large oscillator strengths at the B3LYP,  $\omega$ B97, and equations of motion coupled cluster (EOM-CCSD) levels. The open shell nitrogen containing carbonaceous complexes especially exhibit a large oscillator strength electronic transition in the visible region of the electromagnetic spectrum. Appendix A is available in electronic form at <http://www.aanda.org>

**Title: Photochemistry and photophysics of *n*-butanal, 3-methylbutanal and 3,3-dimethylbutanal: Experimental and theoretical study**

Authors: Tadic, J. M., Moortgat, G. K., Bera, P. P., Lowenstein, M., Yates, E. L., and Lee, T. J.

Source: J. Phys. Chem. A, 116, 5830, Published 2012.

Abstract: Dilute mixtures of *n*-butanal, 3-methylbutanal, and 3,3-dimethylbutanal in synthetic air, different N<sub>2</sub>/O<sub>2</sub> mixtures, and pure nitrogen (up to 100 ppm) were photolyzed with fluorescent UV lamps (275–380 nm) at 298 K. The main photooxidation products were ethene (*n*-butanal), propene (3-methylbutanal) or *i*-butene (3,3-dimethylbutanal), CO, vinylalcohol, and ethanal. The photolysis rates and the absolute quantum yields were found to be dependent on the total pressure of synthetic air but not of nitrogen. At 100 Torr, the total quantum yield  $\Phi_{100} = 0.45 \pm 0.01$  and  $0.49 \pm 0.07$ , whereas at 700 Torr,  $\Phi_{700} = 0.31 \pm 0.01$  and  $0.36 \pm 0.03$  for 3-methylbutanal and 3,3-dimethylbutanal, respectively. Quantum yield values for *n*-butanal were reported earlier by Tadić et al. (*J. Photochem. Photobiol. A* **2001**143, 169–179) to be  $\Phi_{100} = 0.48 \pm 0.02$  and  $\Phi_{700} = 0.32 \pm 0.01$ . Two decomposition channels were identified: the radical channel  $\text{RCHO} \rightarrow \text{R} + \text{HCO}$  (Norrish type I) and the molecular channel  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO} \rightarrow \text{CH}_2\text{CHCH}_3 + \text{CH}_2=\text{CHOH}$  or  $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CHO} \rightarrow \text{CHC}(\text{CH}_3)\text{CH}_3 + \text{CH}_2=\text{CHOH}$ , (Norrish type II) having the absolute quantum yields of 0.123 and 0.119 for 3-methylbutanal and 0.071 and 0.199 for 3,3-dimethylbutanal at 700 Torr of synthetic air. The product ethenol  $\text{CH}_2=\text{CHOH}$  tautomerizes to ethanal. We have performed ab initio and density functional quantum (DFT) chemical computations of both type I and type II processes starting from the singlet and triplet excited states. We conclude that the Norrish type I dissociation produces radicals from both singlet and triplet excited states, while



Norrish type II dissociation is a two-step process starting from the triplet excited state, but is a concerted process from the singlet state.

**Title: The O/OREOS Mission: First Science Data from the Space Environment Viability of Organics (SEVO) Payload**

Authors: Mattioda, A., Cook, A., Ehrenfreund, P., Quinn, R., Ricco, A. J., Squires, D., Bramall, N., Bryson, K., et al.

Source: *Astrobiology*, 12, 841, Published 2012.

**Abstract:**

We report the first science results from the Space Environment Viability of Organics (SEVO) payload aboard the Organism/Organic Exposure to Orbital Stresses (O/OREOS) free-flying nanosatellite, which completed its nominal spaceflight mission in May 2011 but continues to acquire data biweekly. The SEVO payload integrates a compact UV-visible-NIR spectrometer, utilizing the Sun as its light source, with a 24-cell sample carousel that houses four classes of vacuum-deposited organic thin films: polycyclic aromatic hydrocarbon (PAH), amino acid, metalloporphyrin, and quinone. The organic films are enclosed in hermetically sealed sample cells that contain one of four astrobiologically relevant microenvironments. Results are reported in this paper for the first 309 days of the mission, during which the samples were exposed for 2210 h to direct solar illumination (1080 kJ/cm<sup>2</sup> of solar energy over the 124–2600 nm range). Transmission spectra (200–1000 nm) were recorded for each film, at first daily and subsequently every 15 days, along with a solar spectrum and the dark response of the detector array. Results presented here include eight preflight and 16 in-flight spectra of eight SEVO sample cells. Spectra from the PAH thin film in a water-vapor-containing microenvironment indicate measurable change due to solar irradiation in orbit, while three other nominally water-free microenvironments show no appreciable change. The quinone anthrarufin showed high photostability and no significant spectroscopically measurable change in any of the four microenvironments during the same period. The SEVO experiment provides the first in situ real-time analysis of the photostability of organic compounds and biomarkers in orbit.