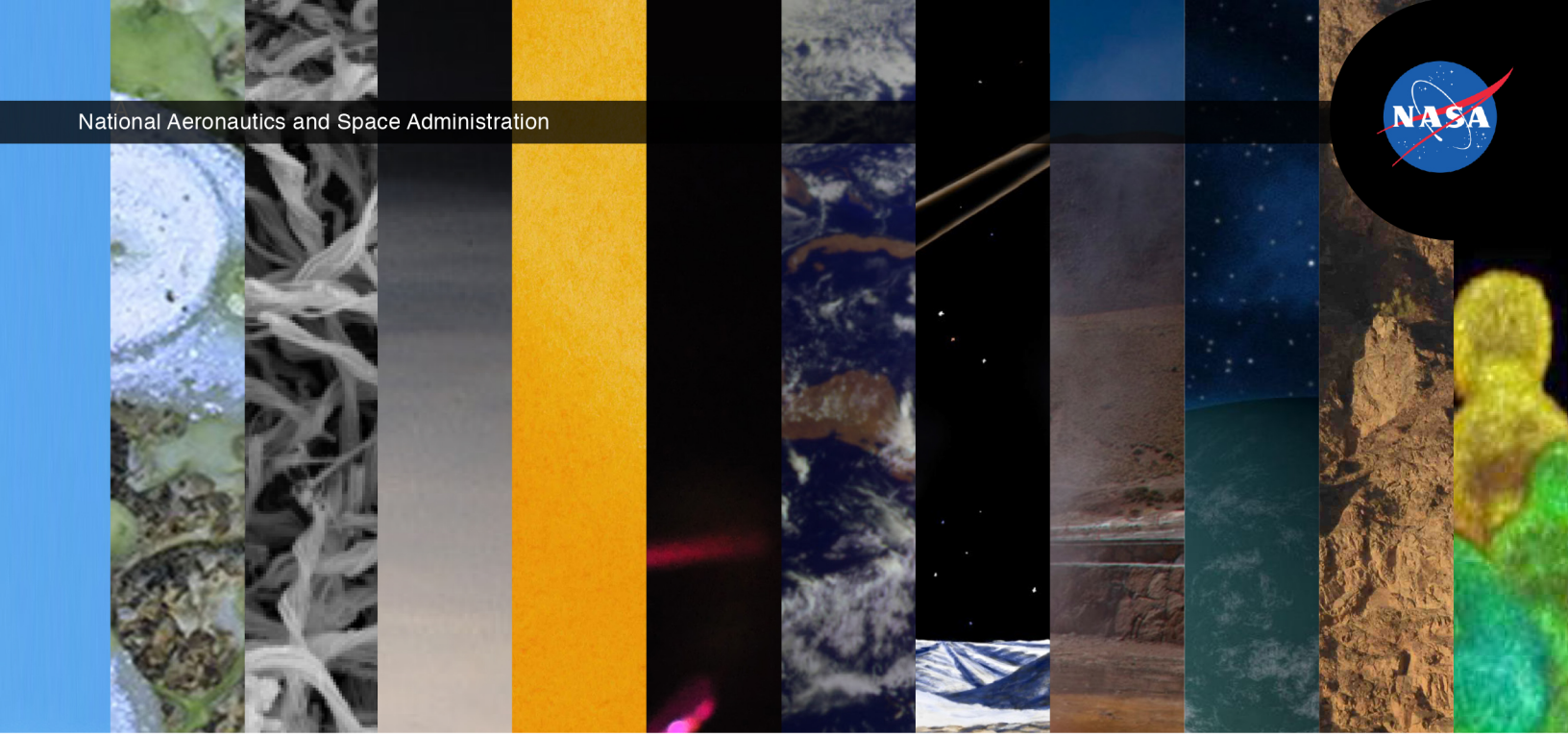
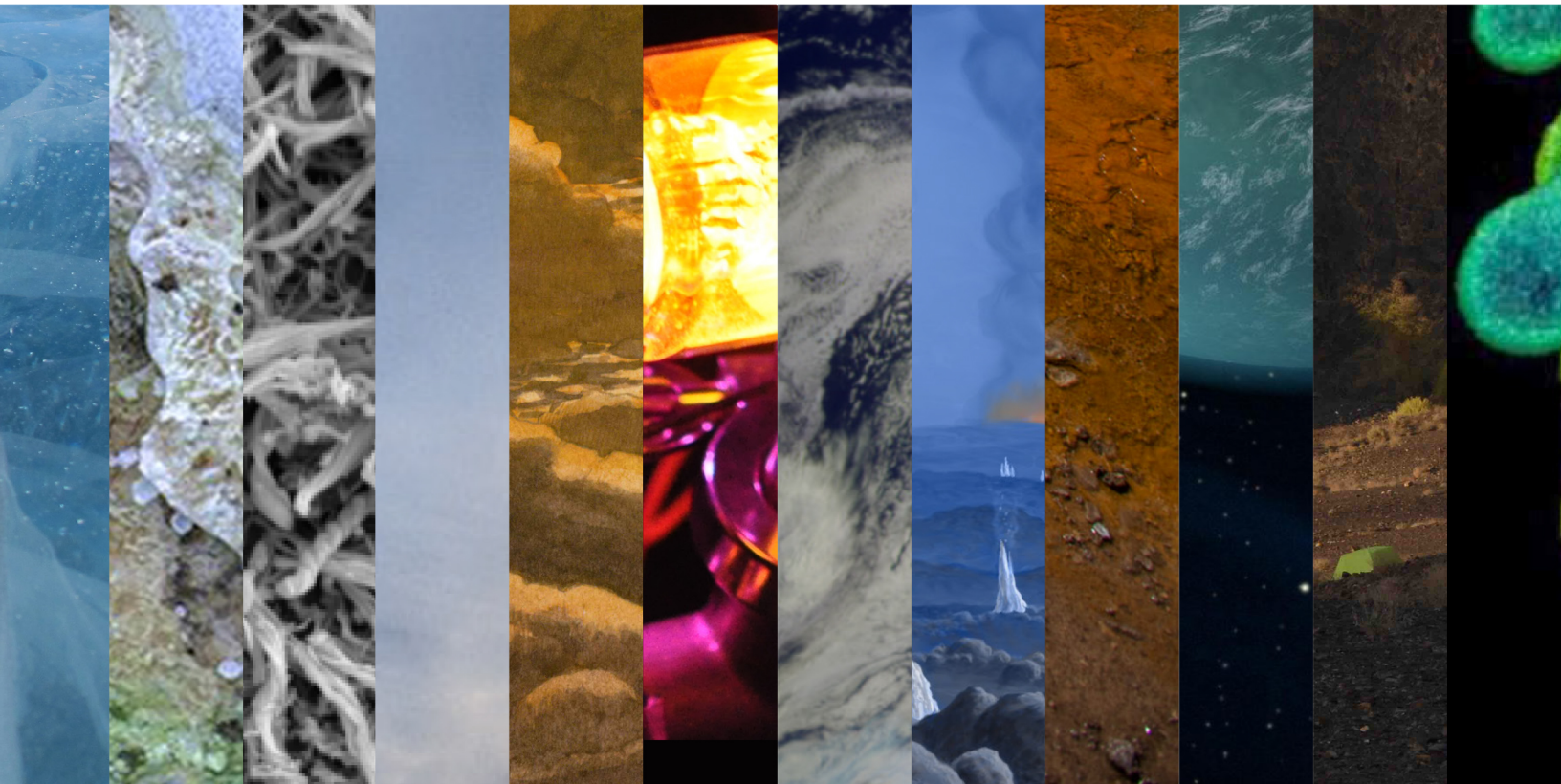


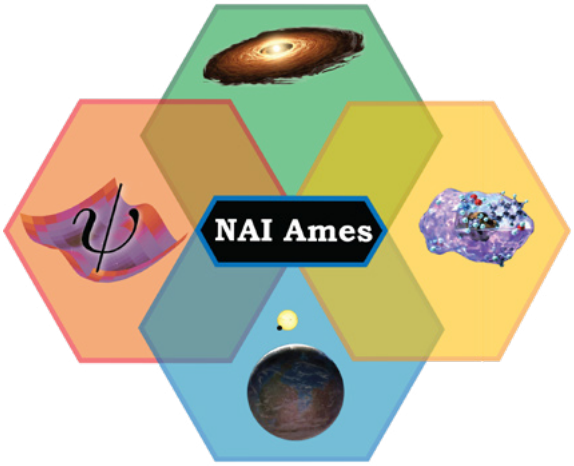
NASA Astrobiology Institute

2017 Annual Science Report

The Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disks and Primordial Planets

NASA Ames Research Center





The Evolution of Prebiotic Chemical Complexity
and the
Organic Inventory of Protoplanetary Disks and Primordial Planets

Lead Institution:
NASA Ames Research Center

Principal Investigator:
Scott Sandford

Team Overview

The Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disks and Primordial Planets Team seeks a greater understanding of the chemical processes occurring at every stage in the evolution of organic chemical complexity, from quiescent regions of dense molecular clouds, through all stages of disk and planet formation, and ultimately to the materials that rain down on planets. The effort is an integrated, coherent program involving the interaction of a number of well-integrated research projects:

- Modeling and Observations of Protoplanetary Disks
- Modeling and Observations of Exoplanets
- Laboratory Studies of Gas-Grain Chemistry
- Laboratory Studies of Ice Photolysis
- Computational Quantum Chemistry

These projects interact closely with each other so that each benefits from advances made in the others and helps guide future work. For example, the modeling of the chemistry that takes place in protostellar disks benefits from inputs provided by spectral, physical, and chemical properties of molecules determined by the laboratory and computational projects, but also provides guidance for key areas of future computational and laboratory work. Similarly, the computational studies can be used to help interpret laboratory results and extend them to additional materials or environments, while the lab results can provide confirmation of computational reaction paths.

Team Website: http://amesteam.arc.nasa.gov

2017 Executive Summary

During 2017 our team made significant progress on all aspects of our combined research. Highlights are described below and more details can be found in our individual project reports.

Disk Modeling - Progress on the modeling of protoplanetary disks was made on three fronts. First, we have incorporated a 3-phase chemical network that distinguishes between the surface and the bulk of grains for reactions and diffusion. This allows the network to track grain surface chemistry. Second, we are incorporating gas-grain chemistry into the disk modeling network to study the formation, destruction, and transport of ices. Finally, we are incorporating photochemical destruction rates into the models to study the survival times of organics within the disk. We find that organics are not completely destroyed on grain surfaces as they travel inwards, although a fraction of them are significantly processed (Fig. 1).

Exoplanets - Extrasolar planets represent an emerging frontier for life in the universe and an elucidation of the galactic planetary census, along with an understanding of how planets form and evolve, is a core tenet of astrobiology. Our team has made major strides in this area. We have announced the discovery of interesting new planetary systems, using both the photometric and radial velocity detection techniques, and we have published the definitive catalog of Doppler velocities taken over two decades with the Keck Telescope. We also made progress in statistically characterizing exoplanetary systems, with the discovery that individual system members tend to display startling uniformity in mass among their constituent planets.

Laboratory Studies of Gas-Grain and Ice Photolysis Chemistry - Significant progress has been made in several areas of our laboratory research. A modified Harrick Praying Mantis Diffuse Reflectance apparatus and low-temperature cell are being used to study the gas-grain chemistry of polycyclic aromatic hydrocarbons (PAHs) on mineral grains. We find that the gas-grain interactions result in mineral-dependent PAH hydrogenation without the need for any additional energy input. We have also completed studies of the abiotic production of nucleobases, sugars, and their sugar derivatives during the photolysis of simple ice mixtures. The work on nucleobases was highlighted on the cover of the August 2017 issue of *Astrobiology* (Fig. 2).

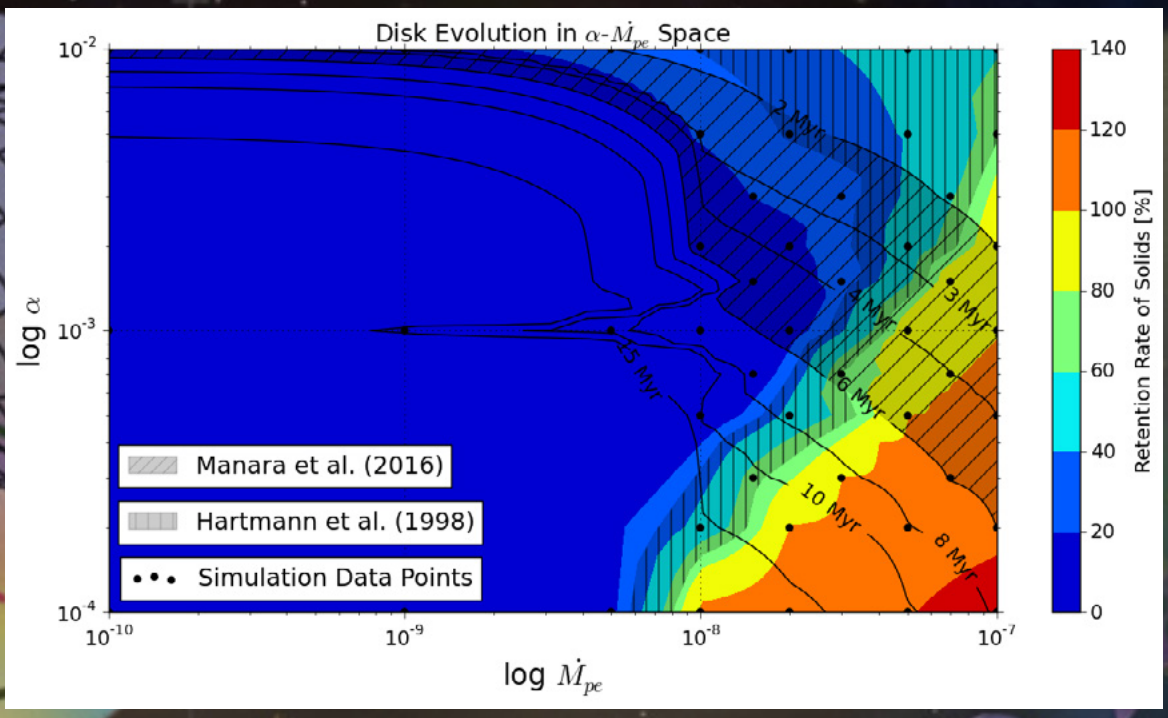
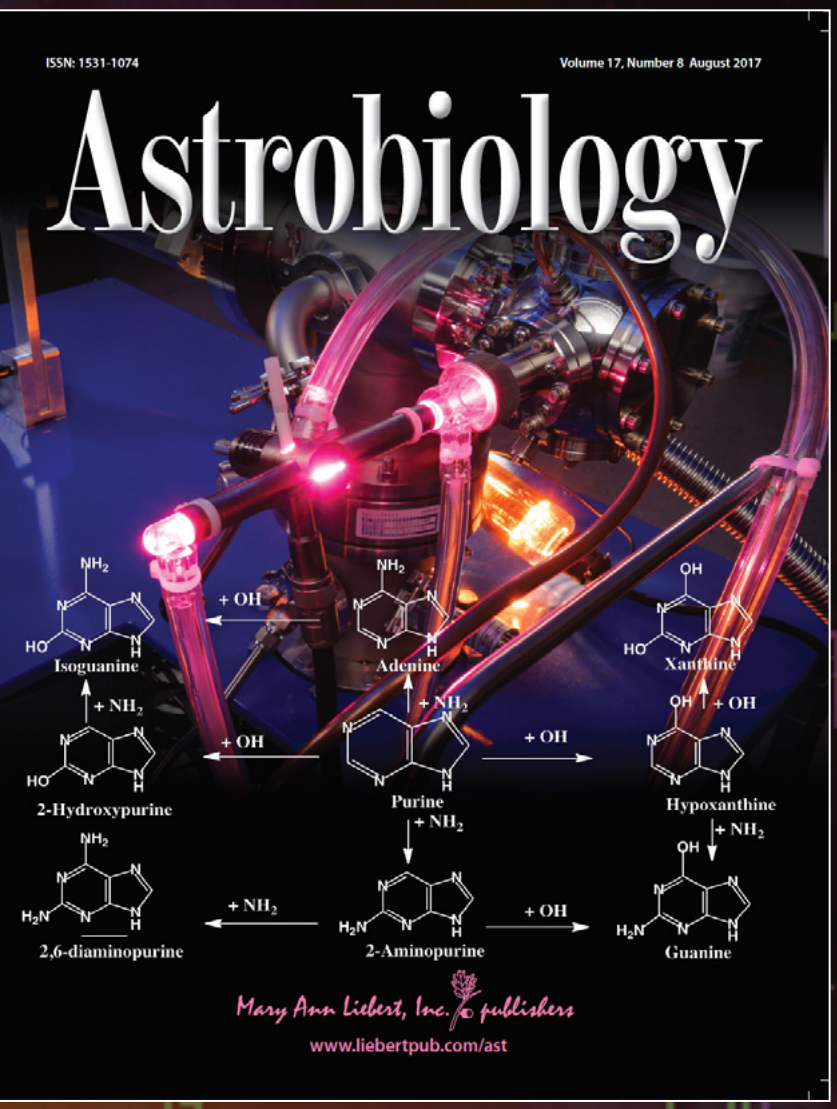


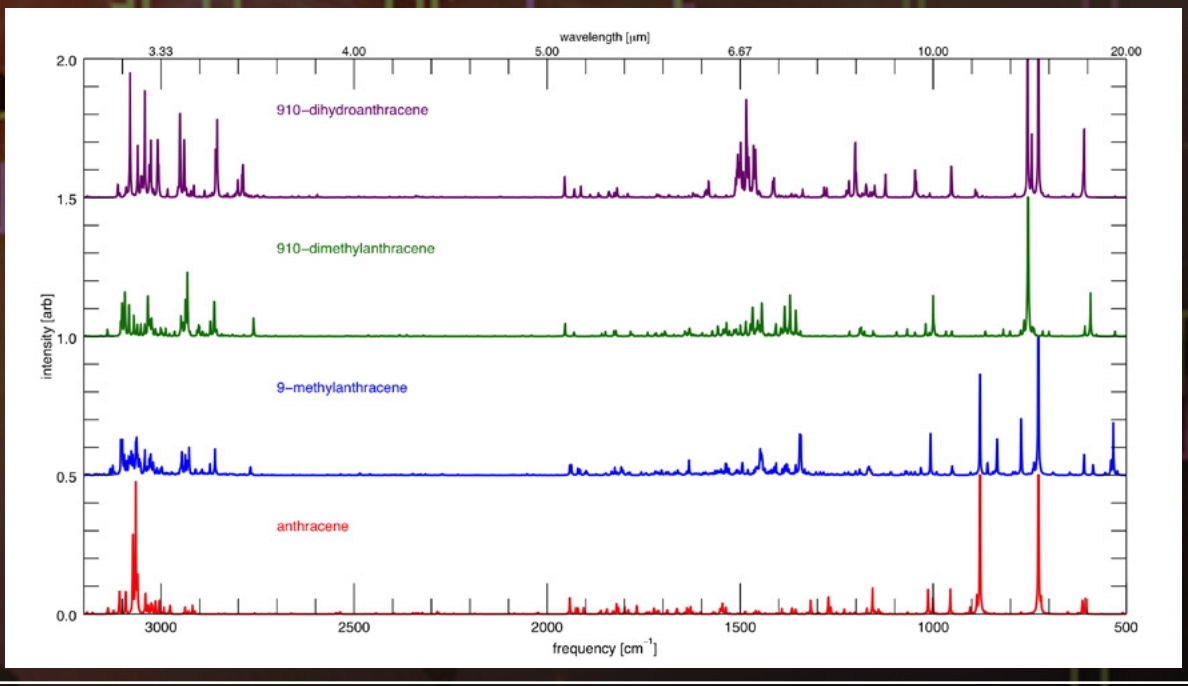
Fig. 1. The retention fraction of solids is shown in the mass loss rate – viscous parameter plane, with the contour lines indicating disk lifetimes from models. The viscous parameter determines the radial drift of solids, while the mass loss rate determines how quickly gas is removed from the system. The hashed region shows the region of parameter space (limited by various observations) that allows the formation of planetesimals prior to disk dispersal. Credit: Saunders, W., & Gorti, U. (2018) Impact of Ice on Evolution of Protoplanetary Disks and Formation of Planetary Systems. American Astronomical Society Meeting, Abstract #231, 231, 437.04.



Computational Quantum Chemistry - Quantum chemistry work was performed to unravel the formation mechanism of the purine-based nucleobases adenine, guanine, and their isomers in gas-phase and condensed-phase environments (Fig. 2). The calculations reveal that the formation of nucleobases is energetically and kinetically favorable via dominantly cationic routes that require the assistance of an H_2O matrix. We also conducted a combining experimental and theoretical study of molecular carbon growth arising from the ionization of neutral acetylene clusters that shows how ion-molecule reactions involving small unsaturated organics can lead to the benzene cation. Lastly, we carried out ab initio calculations on $[m\text{HCCH} + n\text{HCN}]^+$ (m, n=1, 2, 3) to understand how nitrogenated heterocyclic molecules form in space and continued our collaboration with the Dutch Astrochemistry Network (DAN II) on the computation of the infrared spectra of PAHs (Fig. 3).

Fig. 2. (Left) The exposure of mixed molecular ices to ionizing radiation yields a complex population of more complex organics, including many molecules of astrobiological interest like sugars and the nucleobases adenine and guanine. Details of experimental and quantum chemical calculation studies of the production of the purine-based nucleobases appeared in the August issue of Astrobiology journal in two companion papers. Credit: Cover, Astrobiology, Volume 17, Number 8, August 2017. This cover is associated with two of the papers that appear in the issue: Materese, C. K., Nuevo, M., & Sandford, S. A. (2017) The Formation of Nucleobases from the Ultraviolet Photoirradiation of Purine in Simple Astrophysical Ice Analogues. Astrobiology, 17 (8): 761-770 (DOI: 10.1089/ast.2016.1613), and Bera, P. P., Stein, T., Head-Gordon, M., & Lee, T. J. (2017) Mechanisms of the Formation of Adenine, Guanine, and their Analogs in UV Irradiated Mixed H_2O:NH_3 Ices Containing Purine. Astrobiology, 17 (8): 771-785. DOI: 10.1089/ast.2016.1614.

Fig. 3. (Below) Anharmonic vibrational spectra, including intensities, of a number of anthracene-containing polycyclic aromatic hydrocarbons. Credit: Mackie, C. J., Candian, A., Huang, X., Maltseva, E., Petrignani, A., Oomens, J., Buma, W. J., Lee, T. J., & Tielens, A. G. G. M. (2018) The Anharmonic Quartic Force Field Infrared Spectra of Hydrogenated and Methylated PAHs. Phys. Chem. Chem. Phys., 20: 1189-1197. DOI: 10.1039/C7CP06546A.



Project Reports

Modeling and Observations of Protoplanetary Disks

Our recent progress on disk modeling includes (i) chemical network refinements that incorporate grain surface chemistry, (ii) ice transport and its impacts on planetesimal formation, and (iii) the evolution of organics on grain surfaces as they move through the disk.

Chemical network: A 3-phase gas-grain chemical network is being included that distinguishes between reactions occurring on the surface and in the bulk of grains (Fig. 4). Thermal diffusion, quantum tunneling, and thermal/chemical/photo-desorption processes are all considered. Photochemistry by both X-rays and UV photons are considered and the photo-cross sections and reaction rates have been re-computed to be appropriate for disk models. This code has been tested and is now being used to reproduce line emission from disks for verification.

Ice transport: Gas-grain chemistry is being incorporated into the models to study ice transport. Gas-phase molecules preferentially freeze onto small grains, which have greater total cross-sectional area, and the resulting ices change the threshold for destructive collisions between grains. We modeled the disk around a young M3 star of mass 0.25 M_{sun} to investigate the range of possible viscous parameter values (α) and photoevaporation mass loss rates ($\dot{M}_{pe}$) that could mitigate radial drift of dust. We determined there is a range of α and $\dot{M}_{pe}$ values for which disks can produce planetesimals totaling tens of Earth masses.

Organics: Photodestruction rates of organics determined by our laboratory team members are being incorporated into the models to study the survival time of organics within disks. Our simulations indicate that molecules like PAHs are not completely destroyed on the surface of grains as they migrate inwards. Indeed, only a small fraction (<8%) of organic material gets exposed to surface irradiation during inward drift, although this fraction gets significantly processed. However, materials returned to the gas phase can subsequently re-condense and participate in additional chemistry.

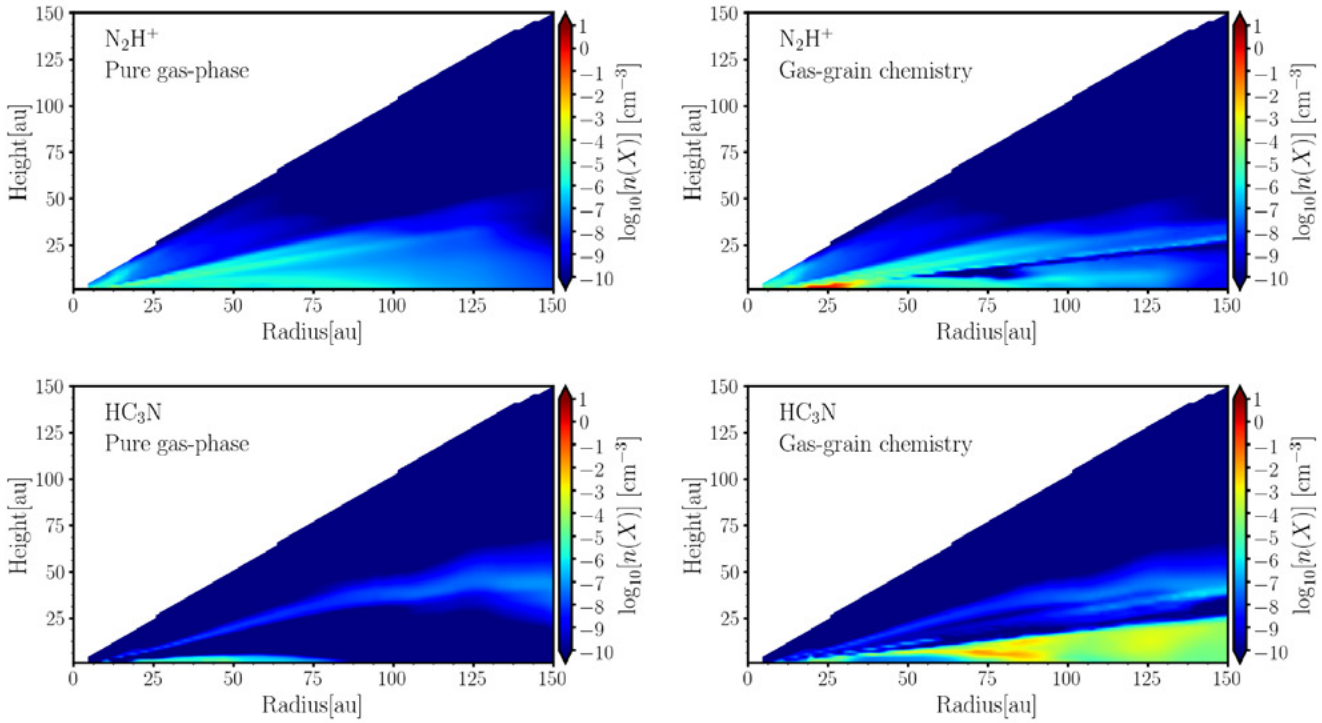


Fig. 4. The abundances for the two molecular species N_2H+ and HC_3N (as a function of radius and height within a disk) from the chemical models with (right) and without (left) grain surface chemistry. The abundances of species, especially in the midplane, are seen to be significantly affected by reactions on the surfaces of grains.

Exoplanet Studies

Our effort to detect and characterize extrasolar planets was productive in 2017. The beginning of the year saw the publication (Butler et al. 2017, *AJ*, 1553: 208) of the full catalog of precision Doppler velocities of nearby main-sequence stars obtained over more than two decades at Keck Observatory. These data were accompanied by a list of 60 new planet candidates and can be used to discern broad trends in planet occurrence at distances ranging to 5-10 AU from the parent star. For example, the data set shows that true Jupiter analogs (with P~10 yr, M~M_{Jup}, and near-circular orbits) are rare at the 2-4% level in orbit around Sun-like stars (Rowan et al. 2016, *ApJ*, 817: 104). This finding reinforced the emerging conclusion that a number of aspects of our Solar System's architecture are unusual.

True Jovian twins may be relatively few and far between, but there is no shortage of planets with periods much shorter than found in the Solar System. For example, in Millholland and Laughlin 2017 (*AJ*, 154: 83), our team used supervised machine-learning techniques to identify the signatures of sixty new hot Jupiter-type planets within the photometric light curve data obtained by the NASA Kepler Mission (Fig. 5). In Vogt et al. 2017 (*AJ*, 154: 181), we discuss our discovery of a six-planet system orbiting the G0V-type star HD 34445, whose worlds have masses in the transitional range from Neptune to Saturn, and display orbital periods of 50 to 5,000 days. The HD 344445 system typifies an interesting, as-yet mysterious, trend that has recently come to light. Planets orbiting a given star tend to display uniform masses. That is, individual planetary systems each have their own characteristic mass. This phenomenon is identified, statistically demonstrated, and discussed by our team in Millholland, Wang and Laughlin 2017 (*ApJ*, 849: 33).

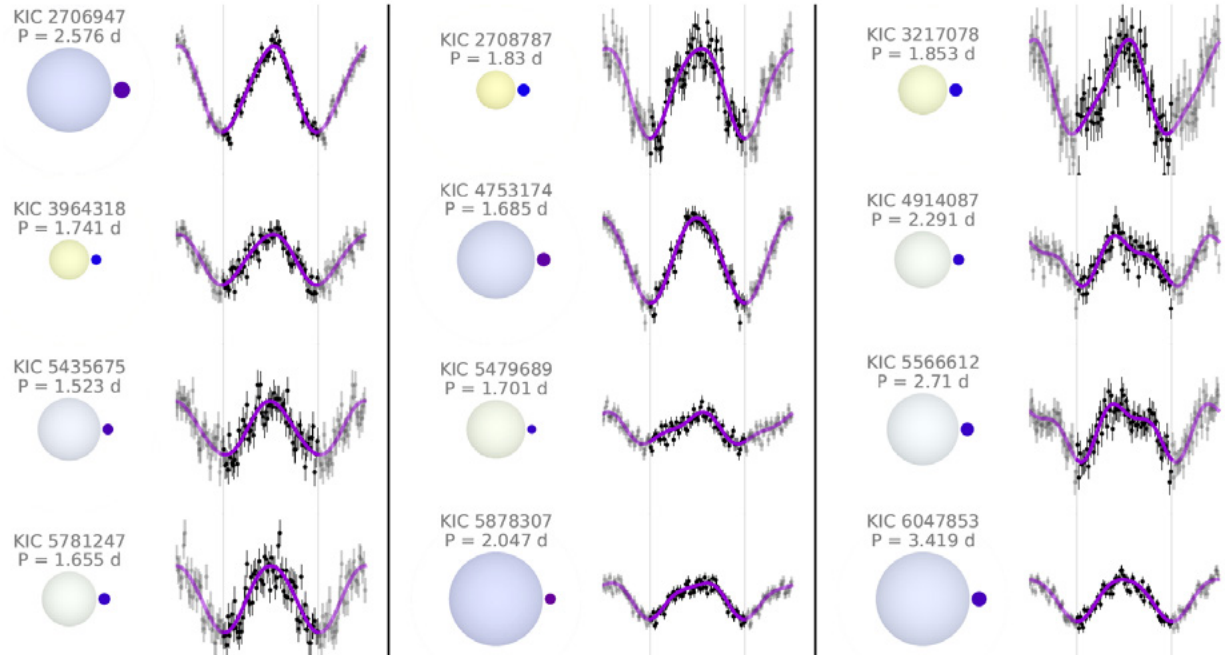


Fig. 5. A selection of 12 hot Jupiter candidates identified by Millholland, S. & Laughlin (2017) using machine-learning techniques to analyze photometric light curve data from the NASA Kepler Mission. Credit: Millholland, S., and Laughlin, G. (2017) Supervised Learning Detection of Sixty Non-Transiting Hot Jupiter Candidates. Astron. J, 154: 83. DOI: 10.3847/1538-3881/aa7a0f.

Laboratory Studies of Gas-Grain Chemistry

In the lab, members of our team led by Dr. Mattioda characterized mineral analogs via diffuse reflectance infrared spectroscopy (DRIFTS). This data will be utilized in studies of organic-mineral interactions (i.e. gas-grain chemistry). Analogs studied included aluminum oxide, silicon dioxide, titanium dioxide, graphite, hematite, magnetite, iron oxides, and a lunar regolith. The infrared (IR) spectra of the mineral analogs were investigated for variations with temperature and UV photolysis. The IR bands of the minerals varied with temperature but did not exhibit variations with UV photolysis.

Studies of organic-mineral interactions were begun with small polycyclic aromatic hydrocarbons (PAHs). In a surprising result, the interaction between the mineral surface and the molecules resulted in hydrogenation of the PAH without the need for any additional energy input. The degree of hydrogenation of the aromatic molecule is mineral surface dependent (Fig. 6).

Dr. Ana Ferreira de Barros (Federal Center for Technological Education – CEFET/ RJ), Rio de Janeiro, Brazil, finished her Visiting Researcher position working with our team on the photochemistry of PAHs in water ice. This research exchange was in alignment with the agreements between NASA and the Brazilian Space Agency (AEB). Her work resulted in two publications, one related to the photochemistry of the PAH coronene and its concentration dependence, another on the IR spectroscopy of anthracoronene. Dr. Barros, Dr. Mattioda and Ms. Julie Korsmeyer (summer intern) are continuing collaborations regarding the photochemistry of anthracoronene. The work on the photochemistry of anthracoronene was assisted by a summer intern, Ms. Julie Korsmeyer.

Members of the team collaborated with other colleagues at NASA Ames, NASA Marshall, and the Pontificia Universidade Cathòlica do Rio de Janeiro, Brazil to investigate the impact various radiation sources (e.g. protons, electrons and UV), singly and in combination, have on PAHs in space. This work is to understand if interstellar PAHs could serve as the chemical feedstock for astrobiologically relevant molecules found in the Solar System.

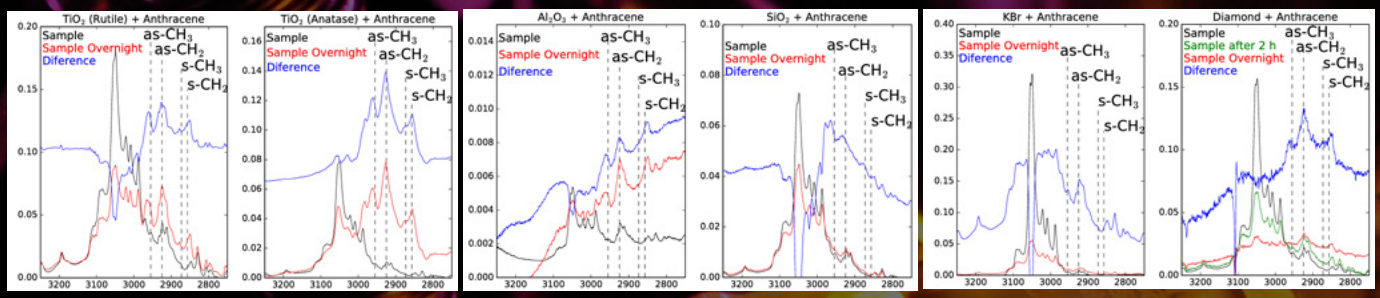


Fig 6. Anthracene mixed with (from left to right) TiO_2, Al_2O_3, SiO_2, KBr, and diamond dust analogs. Mid-IR DRIFTS spectra show how the C-H stretching region changes (aromatic bands decrease while aliphatic bands increase) without UV irradiation when anthracene is mixed with each substrate. The rate of lateration is mineral dependent.

Laboratory Studies of Ice Photochemistry

We showed that simultaneous deposition and UV irradiation of H_2O:CH_3OH ice mixtures leads to the production of complex sugars/sugar derivatives with up to 6 carbon atoms (including ribose and glucose). We also performed experiments that contained CO and/or CO_2 to see if the resulting residue contained a distribution of products that is closer to what is found in meteorites. Some experiments were performed with the help of undergraduate interns (Christina Buffo and Brittiana McDowell) during the summer of 2017. These experiments demonstrate that mixtures containing both CH_3OH and CO lead to the formation of sugar derivatives with a distribution comparable to that found in meteorites.

We completed a series of experiments that demonstrated the formation of adenine (Fig. 7), guanine, and other functionalized purines from the UV-photoprocessing of purine in simple ice mixtures. This work resulted in a publication featured on the cover of the August issue of Astrobiology. We also examined the photochemistry of purine in more complex astrophysically relevant ice mixtures. Undergraduate interns Christina Buffo and Brittiana McDowell both contributed to this work during the summer of 2017. Results of this work indicate that the production of purine derivatives (including nucleobases) is sensitive to the concentration CH_3OH in the initial ice.

We also completed a study of the infrared spectra of post-AGB objects with anomalously large 3.4 μm bands and their possible connection with H_n-PAHs (PAHs that carry extra H atoms). PAHs are one of the most abundant forms of carbon in the known universe and may play an important role in prebiotic chemistry. There is a set of post-AGB objects with anomalously large 3.4 μm emission features that we hypothesized may be the result of the presence of H_n-PAHs. Spectral data we collected from several post-AGB objects using the SOFIA observatory demonstrated that H_n-PAHs are probably present.

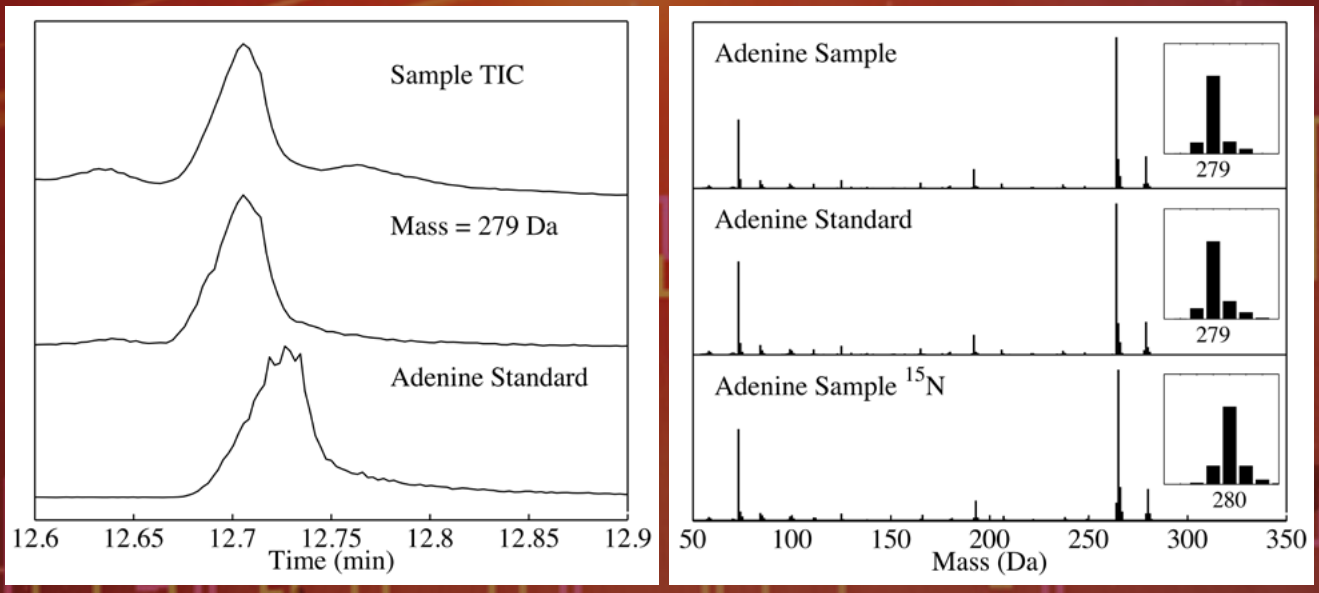


*Fig 7. Left panel: (*Top trace) *Total-ion chromatogram (TIC) of the residue produced from a UV-irradiated H_2O:NH_3:purine ice.* (Middle trace) *Single-ion chromatogram (SIC) of the same residue for mass 279 Da.* (Bottom trace) *SIC of the adenine standard (mass 279 Da). Right panel: (*Top trace) *Mass spectrum of the peak identified as adenine in the residue produced from a UV-irradiated H_2O:NH_3:purine ice.* (Middle trace) *Mass spectrum of the adenine standard.* (Bottom trace) *Mass spectrum of the peak identified as adenine in the residue produced from a UV-irradiated ice containing $^{15}NH_3$ instead of NH_3. The observed mass increase matches what is expected for the adenine identification.*

Computational Quantum Chemistry

Quantum chemistry work was performed to unravel the formation chemistry of the purine-based nucleobases adenine, guanine, and their derivatives/isomers. The calculations reveal that (i) the formation of nucleobases is energetically and kinetically favorable, (ii) gas-phase mechanisms for their formation are ineffective, (iii) mechanisms involving a cationic route should dominate, and (iv) cation formation is facilitated by (and only by) an H_2O matrix. This work, along with a companion experimental paper, were highlighted on the cover of the August issue of *Astrobiology* journal. Formation of cytosine is now under investigation.

We conducted a comprehensive study combining experiment and theory to elucidate the mechanism of carbon growth from ionization of neutral acetylene clusters. We discovered new mechanisms that shed light on the long-standing puzzle of how ion-molecule reactions involving small unsaturated organics can lead to the formation of the benzene cation and showed that acetylene molecules play a catalytic role.

Ab initio trajectory calculations were performed on [*m*HCCH + *n*HCN]+ (*m*,*n*=1,2,3) to understand the formation of nitrogenated heterocyclic molecules in astrophysical conditions. We can now predict the initial conditions required for the formation of nitrogenated heterocyclic molecules and a manuscript is under preparation.

Working with colleagues at Georgia Southern University, we have predicted the rovibrational spectrum and spectroscopic constants of small molecules for interpreting high-resolution astronomical observations and, with our collaborators at the Dutch Astrochemistry Network (DAN II), we are extending these studies to large PAH molecules, for which we are now extending our work to PAHs containing aliphatic C-H groups and excess H atoms.

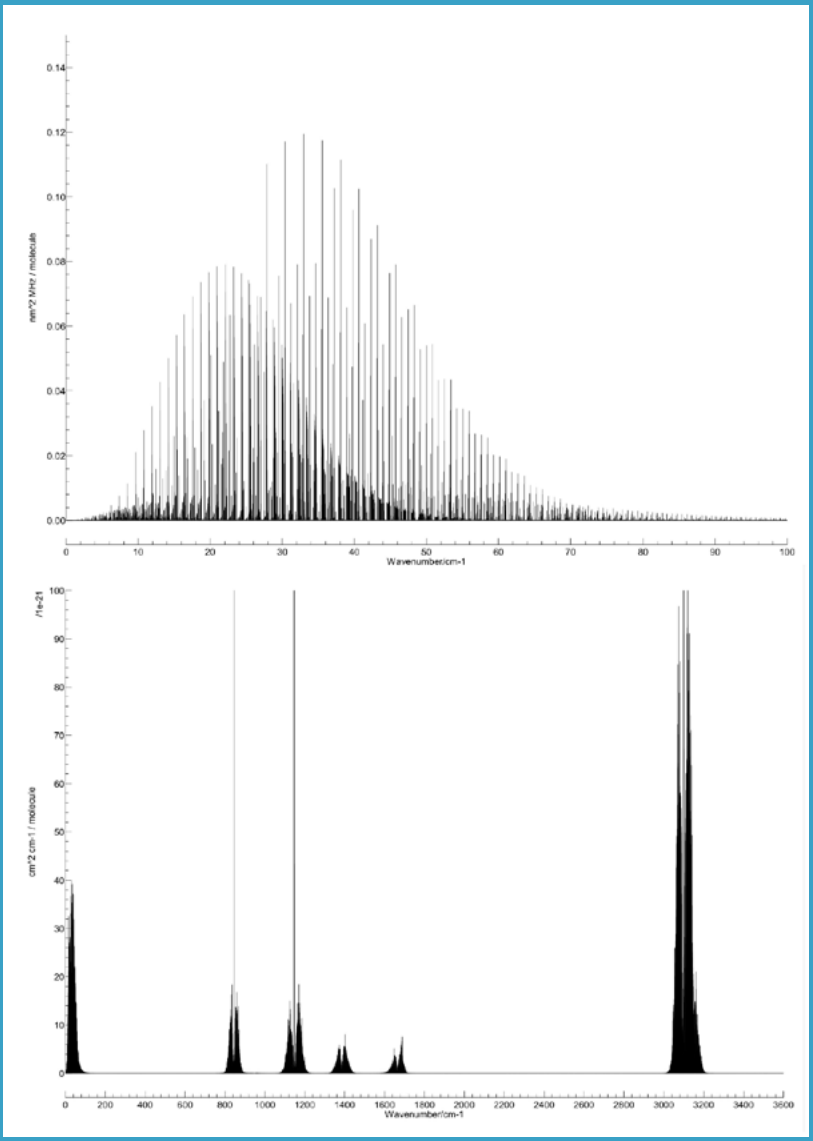


Fig. 8. Rotational and anharmonic ro-vibrational spectra of the azirinyl cation simulated at 200 K.

Finally, the structures, relative energies, and spectroscopic and physical properties of the low-energy isomers of the azirene and diazirene were characterized using ab initio quantum chemical methods (Fig. 8). These nitrogenated cyclic molecules would mark a milestone in the search for biologically relevant molecules in space if identified in the ISM.

The Evolution of Prebiotic Chemical Complexity and the Organic Inventory of Protoplanetary Disk and Primordial Planets: 2017 Publications

Barros, A. L. F., Mattioda, A. L., Ricca, A., Cruz-Diaz, G. A., Allamandola, L. J. (2017). Photochemistry of Coronene in Cosmic Water Ice Analogs at Different Concentrations. *Astrophysical Journal* 848 (2): 112. DOI: 10.3847/1538-4357/aa8c71.

Bera, P. P., Stein, T., Head-Gordon, M., and Lee, T. J. (2017). Mechanisms of the Formation of Adenine, Guanine, and their Analogs in UV-Irradiated Mixed H_2O:NH_3 Ices Containing Purine. *Astrobiology* 17 (8): 771-785. DOI: 10.1089/ast.2016.1614.

Butler, R. P., Vogt, S. S., Laughlin, G., Burt, J. A., Rivera, E. J., Tuomi, M., Teske, J., Arriagada, P., Diaz, M., Holden, B., Keise, S. (2017). The LCES HIRES/Keck Precision Radial Velocity Exoplanet Survey. *Astronomical Journal* 153 (5): 208. DOI: 10.3847/1538-3881/aa66ca.

Carrera, D., Gorti, U., Johansen, A., Davies, M. B. (2017). Planetesimal Formation by the Streaming Instability in a Photoevaporating Disk. *Astrophysical Journal* 839: 16. DOI: 10.3847/1538-4357/aa6932.

Fortenberry, R. C., Thackston, R., Francisco, J. S., and Lee, T. J. (2017). Toward the Laboratory Identification of NS_2, Neutral and Anion Isomers. *Journal of Chemical Physics* 147: 074303. DOI: 10.1063/1.4985901.

Fortenberry, R. C., Lee, T. J., and Huang, X. (2017). Towards Completing the Cyclopropenylidene Cycle: Rovibrational Analysis of Cyclic CNN, CNC^-, $HCNN^+$, and N_3^+. *Physical Chemical Chemical Physics* 19 (34): 22860-22869. DOI: 10.1039/C7CP04257D.

Fortenberry, R. C., Francisco, J. S., and Lee, T. J. (2017). Quantum Chemical Rovibrational Analysis of the HOSO Radical. *Journal of Chemical Physics* 121: 8108-8114. DOI: 10.1021/acs.jpca.7b08121.

Fortenberry, R. C., Lee, T. J., and Layfield, J. P. (2017). The Failure of Correlation to Describe Out-of-Plane Carbon=Carbon Bending. *Journal Chemical Physics* 147 (22): 221101. DOI: 10.1063/1.5013026.

Materese, C. K., Bregman, J. D., and Sandford, S. A. (2017). The Detection of 6.9 μm Emission Features in the Infrared Spectra of IRAS 04296+3429, IRAS 05341+0852, IRAS 22272+5435: Evidence for the Presence of H_n-PAHs in Post AGB Stars. *Astrophysical Journal* 850: 165-170. DOI: 10.3847/1538-4357/aa960d.

Materese, C. K., Nuevo, M., and Sandford, S. A. (2017). The Formation of Nucleobases from the Ultraviolet Photoirradiation of Purine in Simple Astrophysical Ice Analogues. *Astrobiology* 17 (8): 761-770. DOI: 10.1089/ast.2016.1613.

Mattioda, A. L., Bauschlicher, C. W., Ricca, A., Bregman, J., Hudgins, D. M., and Allamandola, L. J. (2017). Infrared Spectroscopy of Matrix-Isolated Neutral Polycyclic Aromatic Nitrogen Heterocycles: The Acridine Series. *Spectrochemica Acta Part A: Molecular and Biomolecular Spectroscopy* 181: 286-308. DOI: 10.1016/j.saa.2017.03.044.

Millholland, S. and Laughlin, G. (2017). Supervised Learning Detection of Sixty Non-transiting Hot Jupiter Candidates. *Astronomical Journal* 154: 83. DOI: 10.3847/1538-3881/aa7a0f.

Millholland, S., Wang, S., and Laughlin G. (2017). Kepler Multi-planet Systems Exhibit Unexpected Intra-system Uniformity in Mass and Radius. *Astrophysical Journal* 849L: 33. DOI: 10.3847/2041-8213/aa9714.

Seligman, D. and Laughlin, G. (2017). A Vorticity-preserving Hydrodynamical Scheme for Modeling Accretion Disk Flows. *Astrophysical Journal* 848: 54. DOI: 10.3847/1538-4357/aa8e45.

Stein, T., Bandyopadhyay, B., Troy, T., Fang, Y., Kostko, O., Ahmed, M., & Head-Gordon, M. (2017). Ab initio dynamics and photoionization mass spectrometry reveal ion-molecule pathways from ionized acetylene clusters to benzene cation. *Proceedings of the National Academy of Sciences USA* 114: 5333-5336. DOI: 10.1073/pnas.1616464114.

Vogt, S. S., Butler, R. P., Burt, J., Tuomi, M., Laughlin, G., Holden, B., Teske, J. K., Shectman, S. A., Crane, J. D., Diaz, M., Thompson, I. B., Arriagada, P., Keiser, S. (2017). A Six-planet System around the Star HD 34445. *Astronomical Journal* 154 (5): 181. DOI: 10.3847/1538-3881/aa8b61.

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