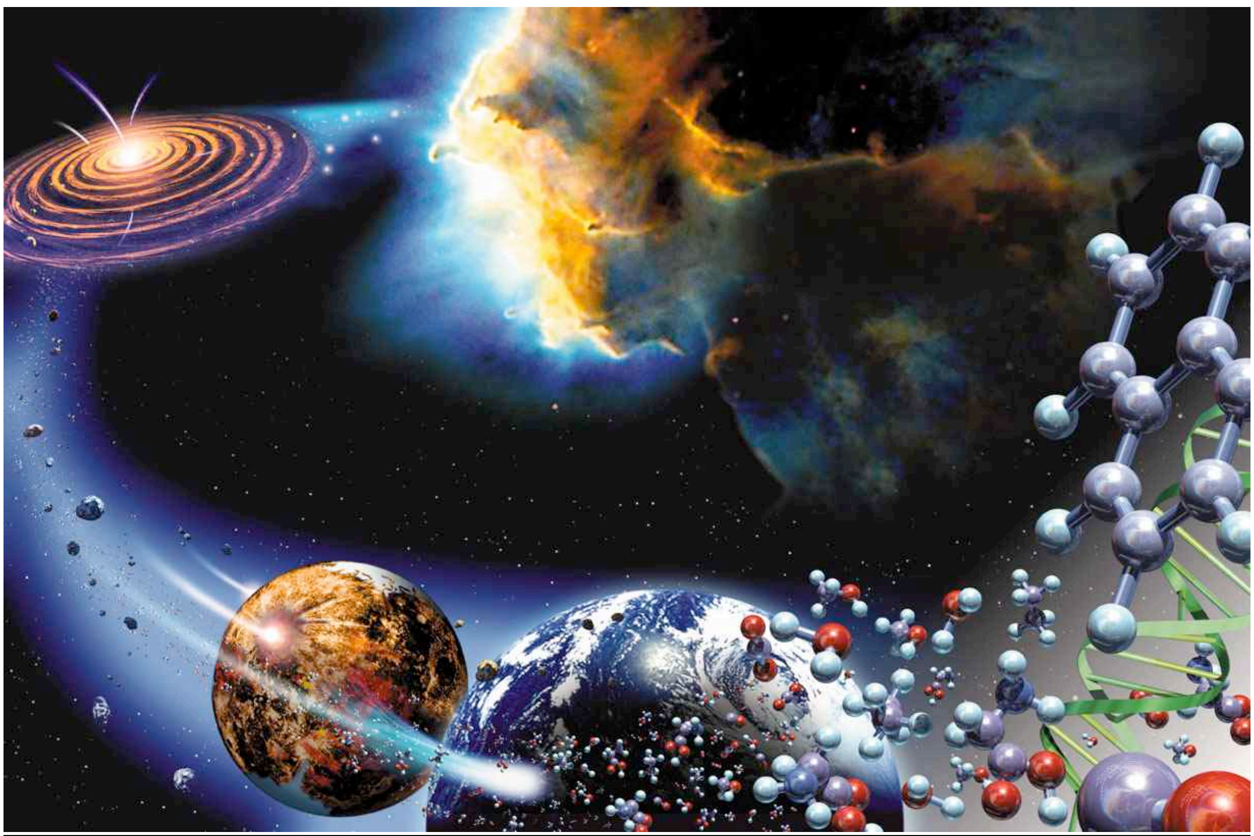
# UNDERSTANDING THE EVOLUTION OF MOLECULES IN SPACE: IMPLICATIONS FOR ASTROPHYSICS, ASTROCHEMISTRY, AND ASTROBIOLOGY

## [THE SCIENCE CASE FOR THE ASTROBIOLOGY EXPLORER (ABE) AND ASTROBIOLOGY SPACE INFRARED EXPLORER MISSIONS CONCEPTS]

**Authors**: Scott Sandford, Louis Allamandola, Michael Bicay, Jesse Bregman, Martin Cohen, Dale Cruikshank, Kimberly Ennico, Robert Hanel, Sun Kwok, Steven Lord, Suzanne Madden, Mark McKelvey, Timothy Lee, Bill Purcell, Thomas Roellig, Mark Swain, Xander Tielens, Michael Werner, and Karen Willacy



Contact information for lead author:

Dr. Scott A. Sandford
NASA-Ames Research Center
Astrophysics Branch
Space Science Division
Mail Stop 245-6
Moffett Field, CA 94035

Email: Scott.A.Sandford@nasa.gov
Phone: 650-604-6849
Fax: 650-604-6779

# UNDERSTANDING THE EVOLUTION OF MOLECULES IN SPACE: IMPLICATIONS FOR ASTROPHYSICS, ASTROCHEMISTRY, AND ASTROBIOLOGY

The past 40 years have shown that, rather than hostile and barren, space is seething with dust, ices, and molecules evolving through time by a variety of intricate chemical processes. Combined theory, laboratory simulation, and observation show that organic molecules permeate the universe. Organics from space likely seeded the Earth after its formation 4.56 billion years ago and played a crucial role in the development of life as we know it. Such compounds likely fall on the surfaces of virtually all newly formed planets. This cosmic material is the final product of a complex cycle commencing with the outflow of matter from dying stars, proceeding through the diffuse interstellar medium, and into the dense molecular clouds where new stars and planetary systems form. The identities, abundances, distributions, and inter-relationships of these molecular building blocks of life remain largely unknown. Tracing this evolutionary path within our galaxy, and beyond, is an outstanding obligation of modern astrophysics.

In this white paper we describe the systematic studies that must be made, and show that infrared spectroscopy from 2.5 to 40 µm is by far the most effective and efficient way to address this important enterprise. The required measurements are achievable using current technology, and can be executed by a medium-sized Astrophysics-class mission.

## 1. INTRODUCTION & BACKGROUND

Two of Humanity's greatest questions have been: "Where did we come from?" and "Are we alone?" It has become clear that molecules play a central role in the formation of stars and planets. Moreover, we know that chemistry in space leads to increasing molecular complexity in regions of star formation similar to the Sun's. Comets preserved some of this interstellar heritage and must have transported this organic inventory to the early Earth and other bodies in our Solar System. The cradle of life's molecules may well have been located amongst the stars! This is a prime area of study in which astrophysics and astrochemistry interface directly with astrobiology.

Astrobiology has two principal goals: 1) to learn how life began and evolved on Earth, and 2) to establish whether life exists elsewhere in the universe. Understanding the cosmic evolution of molecules that carry the elements C, H, O, and N is central to this quest. The cosmic history of these elements is complex and the origin of life is tied to the cyclic process whereby these elements are ejected into the diffuse interstellar medium (ISM) by dying stars, gathered into dense clouds and formed into the next generation of stars and planetary systems (**Figure 1**). Each stage in this cycle entails chemical alteration of gas- and solid-state species by a diverse set of processes: shocks, stellar winds, radiation processing by photons and particles, gas-phase neutral and ion chemistry, accretion, and grain surface reactions. These processes create new species, destroy old ones, cause isotopic and

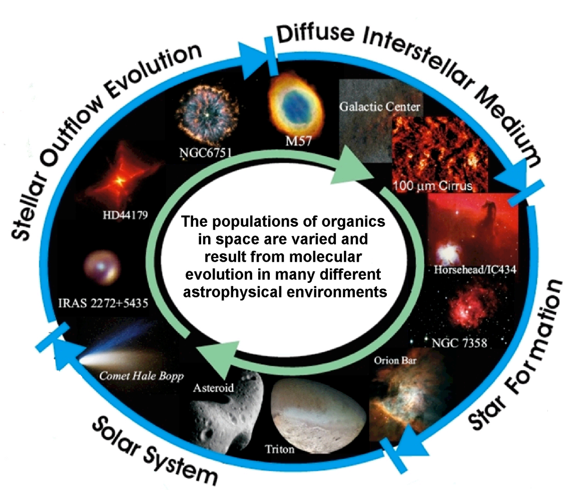



*Figure 1* –Organics in space vary with location and represent the end products of multiple astrophysical and astrochemical processes.

elemental enrichments, reshuffle the elements between chemical compounds, and drive the universe to greater molecular complexity. Understanding the inventory and evolution of cosmic organics requires the study of a broad sample of well-chosen objects that characterize all stages of this evolutionary path. This includes study of materials found in our Solar System and in exoplanets, which serve to link interstellar materials to those delivered to planets. We also need to study other galaxies to probe, on a universal scale, the role variables such as age, galactic type, and metallicity, play in organic evolution through cosmic time.

Infrared spectra, which span the range in which molecular vibrations fall (see §4), combined with submillimeter studies, provide a glimpse of a rich variety of astrobiologically interesting materials in space. A host of gas-phase molecules, mixed molecular ices, polycyclic aromatic hydrocarbons (PAHs) and refractory aliphatic hydrocarbons have been detected.[1-4] Lab studies show that irradiation of cosmic ices produces new molecules, including amino acids, quinones, and amphiphiles, of astrobiological interest.[5] There is evidence for organic materials in many Solar System objects,[6] and the isotopic study of organics in meteorites shows that some are of interstellar/presolar origin.[7] Recent studies have shown that organic compounds are common in other galaxies.[8] Finally, exciting new detections of molecules on exoplanets have raised the possibility that organics can be studied in these bodies.[9]

These provide a hint of the rich insights to be gained from the study of interstellar, Solar System, exoplanetary, and extragalactic prebiotic materials. However, we currently have a very incomplete understanding of the inventory and inter-relationships of these materials and how they are delivered to planetary surfaces due to the limited and incomplete nature of current observations. Meanwhile, laboratory studies have created a large and growing database of IR spectra of astrophysically relevant organics that can be used to interpret astronomical spectra and test astrochemical models that are growing increasingly sophisticated. Progress in this field awaits the collection of a comprehensive and uniform spectral database from a well-planned target population that spans objects from all appropriate evolutionary states.

## 2. SCIENCE GOALS AND OBJECTIVES

An effective study of cosmic organics requires their comprehensive study in all the cosmic environments through which they cycle in our own galaxy and in other galaxies.

### 2.1 MOLECULES WITHIN OUR GALAXY

*Stellar Outflows* - The life cycle of organic materials in space begins with the late stages of stellar evolution, where organic molecules are made in the stellar winds from extreme carbon stars.[10] The first step in the synthesis of these organic compounds is the polymerization of acetylene ($C_2H_2$ - seen in absorption in carbon star spectra) into larger chains and aromatic rings such as benzene and larger PAHs. A family of strong mid-IR emission features at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 µm are often observed in C-rich planetary nebulae (PN) and these features are thought to be due to PAHs. Additional features at 3.4 and 6.9 µm, assigned to aliphatic C-H stretch and bending modes, are found in the spectra of proto-PN (PPN) and young PN.

Limited IR spectra of C-rich objects suggest a great diversity of compounds is present (**Figure 2**). The origin of this diversity may reside in the varied physical conditions of these objects or in the rapid evolution of these objects and their ejecta. Young PN and PPN, as hot stars deeply embedded in new-made dust shells, provide unique views of the molecular inventory of their outflows, showing strong ro-vibrational lines due to circumstellar molecules seen in absorption against the IR dust continuum. A complete survey of these objects will provide a unique opportunity to identify the presence of specific PAHs, as well as their simpler molecular precursors.

*The Diffuse Interstellar Medium* - Stellar ejecta mix with material already present in the diffuse ISM (DISM). The primary evidence for organics in the DISM is a band near 3.4 μm seen along a few lines-of-sight.[2] This material does not appear to be uniformly distributed in the Galaxy.[11] The band profile indicates aliphatic hydrocarbons attached to aromatics are likely largely responsible, but the material's true structure and composition remain unknown. Emission from high latitude dust (the IR cirrus) demonstrates that gas-phase PAHs are also present in the DISM.[12] Based on data from relatively few objects, it is now thought that ~30% of the cosmic C in the DISM is in the form of gas phase PAHs intermixed with particles containing aliphatic and aromatic hydrocarbons. These are an integral part of the cycle of interstellar organics since they contain the end products of stellar outflows and feed the creation of dense clouds.

*Dense Molecular Clouds, Star Formation Regions, and Young Stellar Objects* – Independent of the sites of their original formation or subsequent evolution, cosmic organics must pass through the dense molecular cloud phase to be incorporated into new stellar and planetary systems. At the low temperatures found in dense molecular clouds, most species condense onto dust grains.[13] During early, highly embedded phases, young stellar object (YSO) spectra show a plethora of absorption and emission features due to mixed-molecular ices and molecular gases.[14] Lab studies show that irradiation of such ices makes many new molecules of astrobiological relevance, including, for example, amino acids.[5,15] Further, heating near protostars leads to sublimation of the ices into the gas phase (**Figure 3**), where reactions can form additional species. The forming star ultimately disperses some cloud material back into the DISM, creating HII regions/reflection nebulae

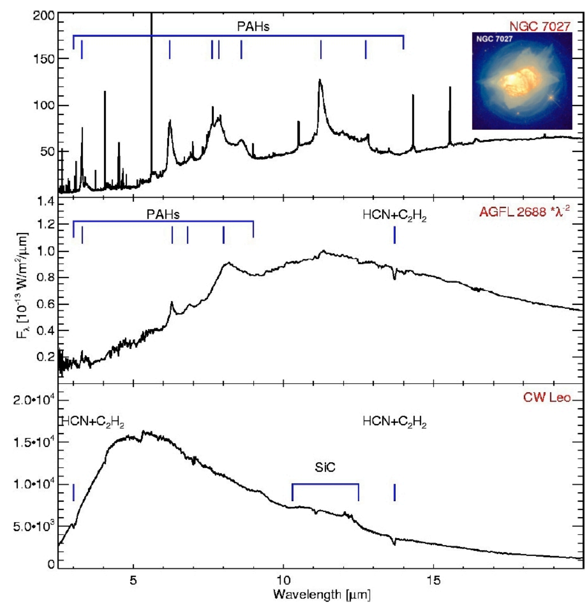



*Figure 2* – 3-20 μm spectra of C-rich objects show a rich diversity of compounds injected into the ISM and illustrate chemical evolution due to energetic processing by UV photons as the central star evolves from the Asymptotic Giant Branch (CW Leo) through the PPN phase (GL 2688) to the PN phase (NGC 7027).[26]

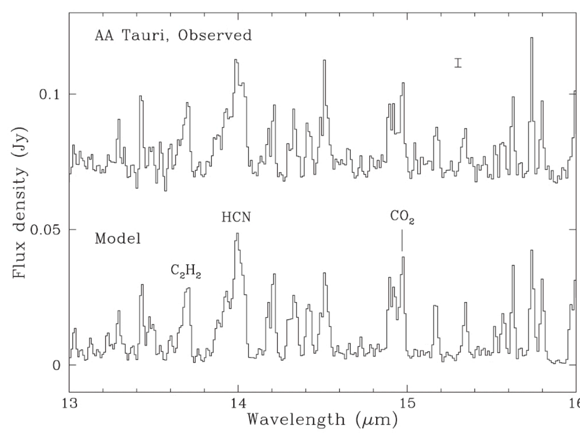



*Figure 3* – The 13-16 μm spectrum of AA Tauri shows 400K-600K $C_2H_2$, $CO_2$, and HCN gases are present in a region a few AU in size. Their abundances are ~10x high compared to CO, suggesting the buildup of molecular complexity in the inner part of a young stellar system. [Unlabelled lines $H_2O$; spectrum from (25)]

in which organics undergo additional processing by intense ionizing radiation.

While available data hint at considerable evolutionary complexity, the chemical inventory of dense clouds and star forming regions is currently very incomplete, particularly for solar-type protostars and the quiescent portions of clouds. For example, the extent to which PAHs reside in ices and are processed into biologically important compounds is largely unexplored.[16] A systematic study is also needed to track gas and solid phase species across this entire evolutionary progression. Chemical models need to be tested by tracing model-dependent species in objects that sample the complete range of dense cloud environments: low-, intermediate-, and high-mass protostars, isolated Herbig AeBe stars, T Tauri stars with disks, the transition zones between dense clouds and HII regions, and photodissociation regions (PDRs). Spectra of main sequence stars *behind* these same clouds are also needed to probe the composition of the dust and gas in quiescent portions of clouds.

## 2.2 MOLECULES IN PLANETS

A central issue to understanding cosmic organics is determining if they seed planetary systems. It is critical to assess what organics exist in planetary environments through the study of both bodies in our own Solar System and exoplanets orbiting other stars.

*Organics in the Solar System* - Solar System (SS) bodies like asteroids and comets carry organics that preserve original interstellar matter, and material made during the formation of the solar nebula and subsequent evolution.[17,18] Understanding the origin and types of organics found in SS bodies permits the study of prebiotic organic chemistry in a planetary setting. The spectra of comets, asteroids, the surfaces of planets and satellites also provide a comparison of SS materials in YSOs, the debris disks around other stars, and exoplanets, thereby aiding our understanding of these systems in a wider context.

Also of critical importance is the origin of Earth's $H_2O$. Comets and asteroids must have delivered some of Earth's water, but estimates of the fractions vary widely. A better understanding of the $H_2O$ content of SS bodies is needed to resolve this issue. Measurement of the abundance of numerous gas phase species and the ortho/para ratio of $H_2O$ in cometary comae can determine the temperature of formation of cometary ices, thereby addressing the role of icy planetesimals in the formation of the giant planets and the shaping of their noble gas inventories.

*Molecules on Exoplanets* – The study of exoplanets have emerged as one of the most exciting new areas in modern astronomy. In the last two decades the number of known planets outside our own Solar System has gone from zero to over 300. A few of the currently known exoplanets are just now beginning to be spectrally characterized (**Figure 4**)[9,19,20] and this area is ripe for further progress. The flight of *Kepler* is expected to yield a host of additional exoplanets ripe for study, including

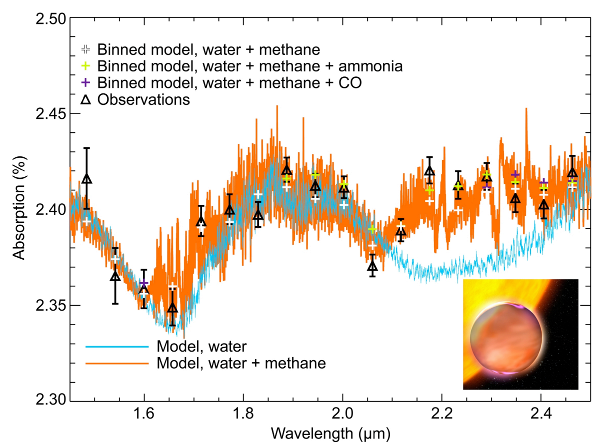



*Figure 4* – A comparison of primary eclipse spectra of PLANET (black points) with simulated water (blue) and water+methane (orange) absorption. The latter's better fit between 2.15-2.4 μm suggest both water and methane are present (spectra from Ref 9b). (inset) Artist's conception of an exoplanet.

many Earth-sized planets. Using methods proven with the Spitzer Space Telescope,[9] and building on its measurements of non-transiting exoplanets,[20] future IR telescopes should be able to study non-transiting super earths orbiting nearby M stars, search for changes in exoplanet conditions over time, and produce many exciting discoveries.

## 2.3 MOLECULES IN OTHER GALAXIES

Observations of sites in our galaxy provide good views of individual environments, but do not explore the range of conditions that exist in galaxies in general. For this, one needs to study the gas and dust found in other galaxies.

*'Local' Galaxies* - The Infrared Space Observatory (ISO) and Spitzer have shown that other galaxies contain materials like the PAHs, aliphatic hydrocarbons, ices, and silicates seen in our galaxy (**Figure 5a,b**), but that different types of galaxies display very different IR spectra.[21] However, the data taken to date are restricted in sensitivity, spectral coverage, and/or spectral resolution. The relationship of organics to galactic age, FUV flux, metallicity, energetics, etc. will only be understood through a systematic study of other galaxies, including low metallicity dwarf, elliptical, spatially extended disk, starburst, and ultraluminous infrared galaxies (ULIRGs), and galaxies with active galactic nuclei (AGNs). Separating the spectral features due to PAHs, ices, silicates, and gas phase and atomic lines in nearby galaxies will revolutionize our knowledge of these species as functions of morphological type, luminosity class, metallicity, interaction, and age.

*Distant Galaxies* - A remarkable result from Spitzer has been the detection in distant galaxies of spectral signatures similar to those associated with organic species in our own galaxy. A few distant galaxies show evidence for absorbing species in the form of gaseous and/or solid state CO, $CO_2$, hydrogenated aromatic carbons, nitriles (X-C≡N), and PAHs (**Figure 5c**). In more distant galaxies, strong

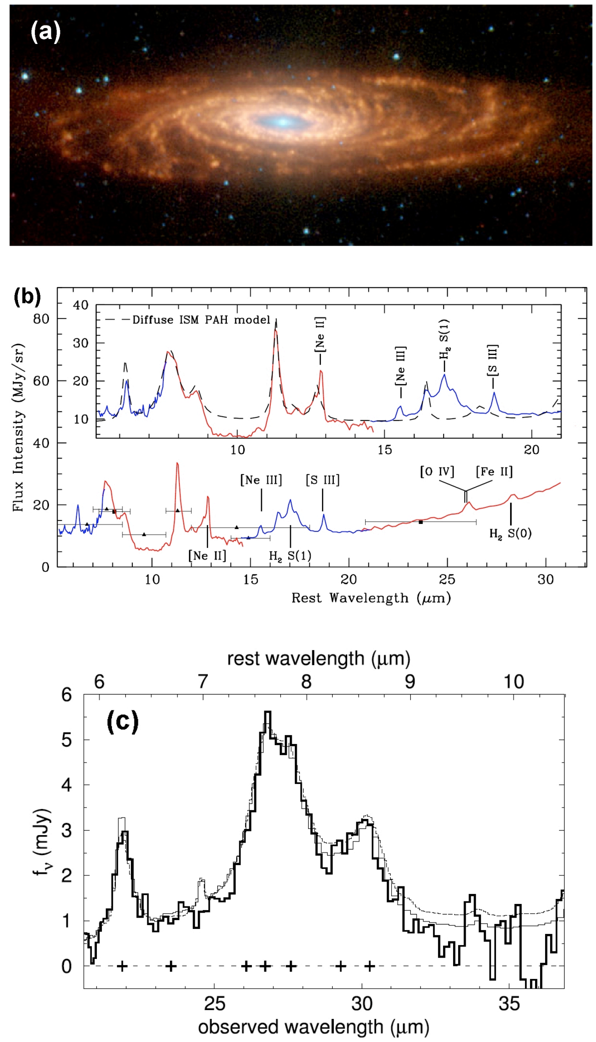



*Figure 5* – (a) Image of NGC7331, a galaxy similar to ours. (b) 3.5-35 μm spectra of NGC7331 are dominated by PAH features (Ref. 27). (c) Spectrum of z=2.516 lensed source SMM J163554.2+661225 (thick solid line) with spectra of starburst galaxy NGC 2798 (thin solid line) and the average of 13 starburst galaxies (thin dashed line). Crosses show the wavelengths of known PAH features redshifted from the 5-10 μm region. [see (28) and references therein)

silicate absorption features have now been measured[22] in 17 ultra- and hyper-luminous galaxies with redshifts between z=1.6 and z=2.7. These observations represent a first step towards tracing the abundance and character of astrobiological materials with cosmic time. Medium- and high-resolution data from distant galaxies, when combined with data from platforms like Spitzer and JWST, will help us understand the nature of solid state and gaseous prebiotic reservoirs and their interrelation at earlier epochs and connect them with the present.

## 3. THE USE OF INFRARED SPECTROSCOPY

Organics and associated volatiles are known or expected to reside in both the gas and solid states in many environments of interest, and these two phases of material are in constant interaction. Thus, a comprehensive understanding of the materials present, and their inter-relationships, requires an ability to measure molecular materials in *both* the gas and solid states along the same lines-of-sight. Spectral observations in the mid infrared between 2.5 – 40 $\mu$m are ideal for this purpose since this range spans the fundamental molecular vibrations of virtually all molecules made of the most abundant elements, especially C, H, N, and O (**Figure 6**).

The measurement of spectral features of both gas and solid materials requires the use of different spectral resolutions. Resolutions of $\lambda/\Delta\lambda \sim 3000$ are ideal for studying solids, while resolutions of $\lambda/\Delta\lambda \sim 25{,}000$ are more appropriate for measuring the individual rotation lines of gas phase species.

This spectral range has the advantage that is also spans the positions of key isotopic species of C, N, O, and H. Of particular interest is deuterium (D; C-H and C-D stretching vibrations fall near 3.4 and 4.2 µm, respectively). The interstellar processes that lead to products that are *highly* enriched in D are the *same* ones that make complex organic species.[23] Interstellar organics should therefore be strongly D-enriched, with the extent and molecular positioning of the enrichment providing key insights into the chemical processes involved. High D/H ratios in meteoritic organics[24] and the elevated (relative

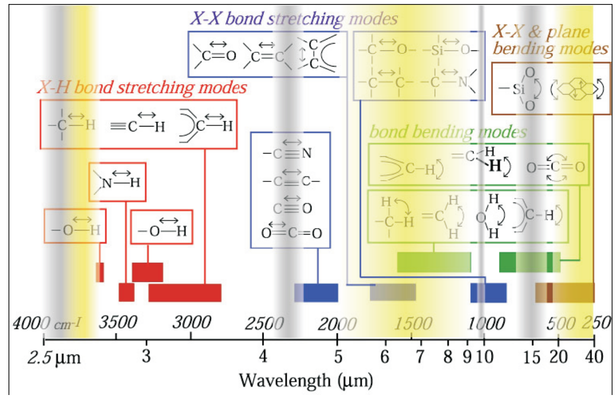



*Figure 6* – The 2.5-40 µm spectral range is ideal for detection and identification of both gas and solid state molecules. This spectral region can only be fully observed from space - the shaded sections represent regions blocked by atmospheric $H_2O$ (yellow), and $O_3$ and $CO_2$ (gray).

to cosmic) terrestrial D/H ratio suggest that both our Solar System as a whole, and the Earth in particular, received a significant portion of these D-enriched materials. Thus, D is a special tracer of interstellar chemical processes that can serve as a key tool for studying the cosmic evolution of organics and their delivery to planets.

Tracing D also has cosmological significance. D was formed in the aftermath of the Big Bang, where its abundance was directly related to baryon density. Measuring the present abundance of D is therefore an important test of cosmic microwave background (CMB) results. Measurements of high-redshift D/H values from quasar absorption lines are in good agreement with CMB-derived values, but D/H measured in H and $H_2$ in our own galaxy show large variations that are difficult to explain solely by astration. Such variations may be due to the differential chemical fractionation of D relative to H mentioned above. Thus, tracing the molecular distribution of D in the local universe provides a powerful means of studying the astrochemical processes that form organics in space *and* provides an independent, complementary test of CMB.

## 4. The Relationship of this Science to Current NASA Goals and Missions

Pursuing the scientific issues summarized here addresses numerous NASA's goals for Astrobiology and for understanding the origin and evolution of stars, planets, and life, including:

- How gas and dust becomes stars and planets, and the chemical paths by which simple molecules evolve into organics critical to life.
- The initial stages of planet and satellite formation and the processes that determine the characteristics of bodies in our Solar System and other planetary systems.
- The nature, history, and distribution of volatile and organic compounds in space and how they may contribute to prebiotic evolution and the emergence of life.

## 5. Recommendations

The astrophysical, astrochemical, and astrobiological questions raised here will not be adequately addressed by any current or scheduled NASA mission. The required wavelength coverage, sensitivity and spectral resolution cannot be achieved by SOFIA, Spitzer, or ground-based facilities. While JWST could carry out selected observations, its short wavelength coverage, small field of view, lower resolution, and short slit lengths make it very inefficient for performing the range of observations required.

A dedicated, focused, medium-sized space IR telescope mission optimized to measure spectra in the 2.5-40 $\mu$m range at moderate ($\lambda/\Delta\lambda \sim 3{,}000$) and high ($\lambda/\Delta\lambda \sim 25{,}000$) spectral resolution will be necessary to perform the thousands of observations required to provide a comprehensive, detailed view of the life cycles of molecular material critical to answering the key scientific questions described here. It is anticipated that such a mission could be flown well within the medium-sized class of Astrophysics Strategic missions (<$650M). Relatively mature implementation concepts exist for doing this science with current technology. These include the Astrobiology Explorer (ABE) and the Astrobiology Space Infrared Explorer (ASPIRE) missions, both of which have benefited from multiple, funded NASA studies.

## References


1) Allamandola, L., et al., 1999, ApJ, 511, L115.
2) Pendleton, & Allamandola 2002, ApJSS, 138, 75.
3) Turner, B. E. 2001, ApJSS, 136, 579; van Dishoeck, E., Blake, Draine, & Lunine 1993, in *Protostars and Planets III*, Univ. Ariz. Press, 163..
4) Sandford, S. A. 1996, MAPS, 31, 449.
5) cf. Bernstein, et al., 2002, Nature, 416, 401.
6) Cruikshank, D. P., & Khare, B. N. 2000, in *A new Era of Bioastronomy*, ASP Conf. Ser., v213, 253.
8) cf. Roussel, H., et al.. 2001a, A&A, 372, 427.
9) cf. (a) Swain, M., et al., 2008, ApJ, 674, 482; (b) Swain, Vasisht, & Tinetti 2008, Nature, 452, 329.
10) cf. Volk, K., Xiong, & Kwok, 2000, ApJ, 530, 408.
11) Sandford, S., et al., 1995, ApJ, 440, 697.
12) Onaka, T., Yamamura, I., Tanabe, T., Roellig, T., & Yuen, L. 1996, PASJ, 48, L59.
13) Sandford & Allamandola, 1993, ApJ, 417, 815.
14) cf. Boogert et al. 2004, ApJSS, 154, 359.
15) Dworkin, J., et al., 2001, PNAS USA 98, 815.
16) Bernstein, M. P., et al. 1999, Science, 283, 1135; Bernstein, M. P., et al. 2005, ApJSS,161, 53.
17) cf. Cronin, J. R., & Chang, S. 1993, in *The Chemistry of Life's Origins*, eds. Greenberg, et al., Kluwer Academic Publishers, 209.
18) Sandford, S. A., et al. 2006, Science, 314, 1720.
19) cf. Knutson, H. A., et al. 2007, Nature, 447, 183.
20) Cowan, N. B., Agol, E., & Charbonneau, D. 2007, MNRAS, 379, 641.
21) cf. Tran, Q. D., et al. 2001, ApJ, 552, 527.; Spoon, H. W. W., et al. 2004, ApJSS, 154, 184.
22) Houck, J. R. et al. 2005, ApJ, 622, L105.
23) Sandford, S. A., et al., 2001, MAPS, 36, 1117.
24) Zinner, E. 1988, in *Meteorites and the Early Solar System*., U. Ariz. Press, 956.
25) Carr, J. S. & Najita, J. R. 2008, Science, 319, 1504
26) Hony, et al. 2001, A&A, 370, 1030.
27) Smith, J. D. T, et al., 2009, ApJ, in press.
28) Rigby, J. R. , et al., 2008, ApJ, 675, 262.