

Delineating the Evolution of Organic Molecular Synthesis

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Chapter 1

Introduction

1.1 Motivation & Context

This project is a literature review and analysis on current astrobiological research in the realm of carbon synthesis and reactivity in the early universe. All of the data necessary for the completion of this thesis project have been previously collected. The methods include the review of organic molecular evolution using relevant external sources. The main interest in this project stems from the mechanistic pathway in which various organic molecules are spontaneously synthesized.

Carbon forms the basis of all organic molecules observed today. The fields of organic chemistry and biochemistry focus on carbon's reactivity and versatility. These patterns of reactivity are responsible for the formation of the majority¹ of biotic molecules.

Carbon is considered a versatile atom based on its patterns of reactivity. Carbon can form bonds with other carbon atoms as well as other heteroatoms² (N, O, S, X) often found in biochemical molecules. Unlike hydrogen, which can form one sigma bond, carbon's hybridized orbitals have the availability for four sigma bonds. Overlapping orbitals also can create multiple pi bonds. Different permutations of bonding configurations result in the opportunity for four different stable electronic conformations

¹ Sulfur based bacteria exist in geothermal vents. In addition, according to NASA astrobiology organisms exist using arsenic in the DNA backbone rather than phosphorous.

² Atom other than carbon and hydrogen found in cyclic structures

of the bonded carbon atom. This versatility has allowed for the diversity in organic molecules observed today.

Previous studies have documented the process of carbon synthesis in the cores of Population III stars circa 500 MYR post Big Bang [1]. The evolution of carbon is theorized to have begun with the triple- α process at the core of the first stars in the young universe (1) [1].



The helium nuclei are positively charged and require the energy and pressure of a star core to overcome electrostatic repulsion and complete the fusion process. These stars were short-lived with an average lifetime of 30 MYR [2]. The process of mass-loss in these stars was undergone in a smooth or violent way, ultimately resulting in the ejection of heavy elements into the interstellar medium. Carbonaceous ejecta from violent Population III progenitor supernovae ultimately resulted in the enrichment of the interstellar medium with heavy elements.

After dispersal from these stars, carbon existed in interstellar clouds, often in the form of carbon monoxide (CO) [3]. The dust synthesized from these ejection events served to enrich the interstellar medium and was distributed over the known universe [2]. The existence of dust alongside metals has been hypothesized as a key catalyst in the formation of organic molecules [4]. Catalysis on micron-sized interstellar dust particles has allowed for complex molecular synthesis. This hypothesis employs transition-state theory as well as the kinetic theory of gases, informed by the Maxwell-Boltzmann

distribution. Dust particles act as catalysts by lowering the activation energy associated with the transition state and reducing the conformational entropy of the reactants [4-6]. The existence of dust in these clouds was essential both for augmenting the size of carbon-containing molecules through second order (or greater) reactions and for accretive processes leading to the formation of protosolar nebulae [4-6].

The gravitational collapse of an interstellar cloud has the potential to create a protosolar nebula with the eventual formation of protoplanetary disks [7]. This is the process by which the Solar System was formed. The accretion of these disks led to planetary formation with endogenous carbon. Over time, meteorites have enriched heavy element reservoirs on Earth by acting as an exogenous source of carbon [8-11].

A more informed understanding of how carbon behaved in protoplanetary conditions is critical to observational strategies when monitoring exoplanets. The greatest potential impact lies in using spectroscopic techniques to identify systems similar to that of the early Earth and using this information to make predictions about prebiotic and biotic molecular synthesis on these exoplanets. This work has the potential to inform exoplanet-monitoring strategies as well as the process of *de novo* carbon synthesis.

The completion of any literary review is important for the analysis of the current state of an academic field. This particular project is expected to strengthen the relationship between academia and industry, since both have a joint interest in exploratory research of habitable exoplanets. This project also has the potential to improve STEM education with respect to the origin of life in the universe. The topic of this thesis is, in some sense, a fundamental human inquiry and a more satisfactory

explanation of our origins is likely to stimulate increased public scientific literacy in this area.

1.2 Challenges Facing the Field

The goal of this project is to reach a deeper understanding of the mechanistic pathway associated with the early synthesis of organic molecules. One considerable challenge lies in the lack of understanding surrounding the process of non-enzymatic carbon fixation. Presently, the only known transfer process from atmospheric carbon to organic carbon – also known as carbon fixation – is performed by the enzyme Ribulose-1,5-bisphosphate carboxylase/oxygenase. In other words, the mechanism by which carbon-containing molecules are spontaneously changed from a gaseous to a solid state is not well characterized. Despite the data supporting *de novo* carbon synthesis as well as endogenous and exogenous carbon deposits in interstellar clouds and circumstellar envelopes, this critical piece to the understanding of prebiotic molecular synthesis remains missing [12-16]. In light of this challenge, modeling protoplanetary conditions that led to successful synthesis of organic molecules still has the potential to make a tangible change in the way that exoplanets are selected for in-depth study.

In addition, limitations in scope of biotic conditions for study impede understanding in the field. Yet a wealth of data exists pointing toward the spontaneous formation of organic matter observed today. Chapter 2 documents the process of nucleosynthesis of carbon in Population III stars followed by the dispersal of metals and enrichment of the interstellar medium. Chapter 3 then details the condensation and

catalytic processes that led to larger scale organic molecules. This is followed by applications and methods in exoplanetary research in Chapter 4.

Chapter 2

The Young Universe & Carbon Synthesis

Introduction

The start of this thesis begins with the nucleosynthesis of carbon in Population III (Pop III) stars. Though the formation of the very first stars is an important point of consideration as well. The presence of small molecules enhances the conditions for stellar formation due to a cooling effect, but the first stars were not formed under these conditions. Rather the first round of stellar formation had to rely on optimal density distributions of hydrogen gas resulting in gravitational collapse and the formation of these stars on the order of 10^6 solar masses (M_{\odot}) [17-20].

Nucleosynthesis of carbon in the cores of stars took place via the triple- α process. Through this process three helium nuclei fuse to form carbon with beryllium as an intermediate. Once formed, carbon atoms were then ejected from these stars, enriching the interstellar medium.

2.1 Population III Stars

The stars that fueled the early bulk of carbon synthesis were Population III stars. These stars were members of some of the first generations of stars in the universe. Pop III stars are a class of very low metallicity stars but the question of whether or not their metallicities were low ($[\text{Fe}/\text{H}] < -1$) or truly zero remains to be answered [18, 20]. In addition to composition uncertainties, these stars are theorized to have formed in high-density halos of dark matter. Dark matter self-

annihilation therefore could have served as a fuel source for the first Pop III stars [19]. These stars were thought to be massive, around $10^6 M_{\odot}$ [19]. Because the escape velocity of H in $10^6 M_{\odot}$ star is approximately 3 km s^{-1} , Pop III stars lost 90% of their mass through diffusion of outer layers into the interstellar medium. This process is referred to as smooth mass-loss and is predicted for many Pop III stars [19]. In the interstellar medium, diffuse regions of hydrogen gas combined with ejecta from other Pop III stars as well as free electrons to form H_2 . These stars were relatively short-lived with an average lifetime of 3 MYR. The massive Pop III stars also underwent the process of mass loss in a violent way – via supernova. By building models, Bromm and Loeb found that over 90% of stellar gas was ejected into the intergalactic medium and that metals (such as carbon formed in the cores) were able to propagate nearly 1 kpc over the course of 3-5 MYR. This process highlights the birth and distribution of carbonaceous matter in the early universe.

2.1.1 Triple alpha process

The triple alpha process outlines the formation of ^{12}C from ^4He nuclei in stellar cores. This process is highly dependent on stellar temperature and pressure as well as reaction resonance. The triple alpha process has been modeled in the temperature range from $10^7 - 10^9 \text{ K}$ [6]. A minimum mass of approximately $0.5 M_{\odot}$ is required to initiate the fusion process at some point over the stellar lifetime. This makes Pop III stars with $10^6 M_{\odot}$ ideal candidates for the reaction process.

Two helium nuclei interact to form the 2- α resonant state ${}^8\text{Be} ({}^0_1^+)$ and subsequently form the 3- α state ${}^{12}\text{C} ({}^0_1^+)$ after the addition of a third He nucleus (Figure 2.1). The excited ${}^{12}\text{C}$ state was theorized by astrophysicist Fred Hoyle, dubbed the Hoyle state. This excited resonant state of 7 MeV is necessary to carry out the triple alpha process [6]. The reaction rate of the excited Hoyle state accurately models the abundance of carbon observed today in the universe [6, 22]. To model these reaction rates, three-body continuum states have been incorporated into solving the Schrodinger equation. The Schrodinger equation for the three-body state can be solved by discretizing α - α scattering states of an expanded wave function [7, 22-24].

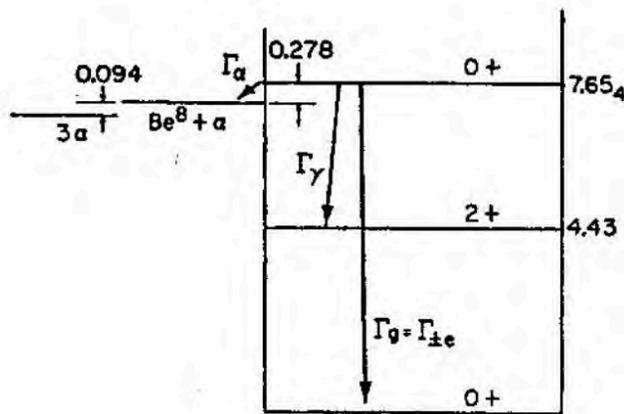


Figure 2.1 Some of the energy levels in ${}^{12}\text{C}$ (MeV), compared with the energies of 3α and $({}^8\text{Be} + \alpha)$. From Salpeter 1957, p. 517.

2.2 Dispersal & Ejection of metals

The asymptotic giant branch (AGB) is critical to metal production.

Spectroscopy has revealed a myriad of carbon-based gaseous species emerging

from circumstellar envelopes. These stars are known to produce both oxygen and carbon in their cores (where the production of oxygen can be completed through the addition of yet another helium nucleus in the triple-alpha process) [15]. A typical AGB star has a luminosity three orders of magnitude greater than that of the Sun, and a radius two orders of magnitude greater than the solar radius. The combination of high luminosity and large size causes stellar envelope pulsation [15]. When coupled with pulsation pressure, this results in outer layer ejection in the form of a stellar wind. An AGB star can therefore undergo a high proportion of mass-loss through these stellar winds, creating a thick, dense envelope around the central star [19]. Because of the low temperatures, most of the gas in the circumstellar envelopes is condensed into its molecular form, and can be detected through frequency measurement of the molecular rotational or vibrational modes. In the past 30 years, millimeter-wave and near-infrared spectroscopy has detected the rotational and vibrational stretching mode transitions of about 60 molecules in the circumstellar envelopes of AGB stars [15]. The detected molecules reveal a myriad of species namely, inorganics (CO, SiO, SiS, NH₃, AlCl), organics (C₂H₂, CH₄, H₂CO, CH₃CN), radicals (CN, C₂H, C₃, HCO.), cyclic molecules (C₃H₂), and cyanopolyynes (HCN, HC₃N, ... HC₉N) [25].

Conclusion

The formation of carbon atoms was the first, critical step in the eventual synthesis of organics and biomolecules. Once the processes of nucleosynthesis and mass-loss took place, the carbon atoms in the interstellar medium underwent favorable reactions to form

simple, small molecules in stable electronic configurations. The properties of carbon make the combination with hydrogen and oxygen favorable compared with existing as an isolated atom in a radical state. The next chapter goes on to discuss more complex chemistry that took place in protoplanetary disks and atmospheres.

Chapter 3

Protosolar Nebulae & Organic Molecules

Introduction

The enrichment of the interstellar medium with metals and small molecules provided the opportunity for the formation of diverse structures. The accumulation of small molecules created micron-sized dust grains. These dust grains then aggregated to form molecular clouds and the collapse of these clouds initiated conditions for stellar and planetary formation. These dust grains are hypothesized to be key factors in the formation of larger, more complex organic molecules. The catalytic properties of the dust grains were the principal feature of this process.

3.1 Interstellar Medium Collapse

The self-gravitational collapse of dense molecular cloud cores is a prerequisite for star formation and subsequent planetary formation [26]. These conditions also are critical to the synthesis of complex organic molecules through the formation of ice mantles and protoplanetary atmospheres. Prior to collapse, cloud cores consist of molecular clump masses with average densities in the range of $10^3 - 10^6$ molecules per centimeter cubed. (This is much less than average atmospheric densities on Earth. At sea level the average atmospheric density is in the range of 10^{19} molecules per cubic centimeter.) Molecular gas clouds also have average temperatures in the range of 7 K – 15 K. The masses of these clouds range from one solar mass to $10^3 M_{\odot}$ [12,14]. Protoplanetary disks eventually evolve after transporting protosolar mass inward through gravitational collapse.

Since the processes of planetary and star formation are linked, this process occurs simultaneously with the collapse of the presolar cloud. Uncertainty still exists in identifying and modeling the transition point between the formation of a protosolar disk versus the formation of a protoplanetary disk, and thus the conditions for planetary formation, and subsequent chemical synthesis in the upper atmosphere is not yet well delineated.

Diversity in the chemical and physical compositions of ice mantles is critical to understanding the process of chemical evolution in the interstellar medium and protoplanetary disks [3, 5]. Ice mantles are implicated as a site (among others discussed later) of molecular synthesis. Planetary formation is associated with dense regions of molecular clouds. At the core of these dense clouds temperatures can be as low of 10 K. At such low temperatures, atoms and molecules bombard one another and stick to dust grain surfaces forming an ice mantle. Under these conditions it is predicted that atoms can undergo quantum tunneling, moving between barriers and reacting with one another. If two particles tunnel into the same lattice position, a reaction can occur [5]. The composition of ice mantles is determined using infrared spectroscopy. The availability of spectroscopic information has been augmented in recent years due to the launch of the *Infrared Space Observatory* in 1995. Water and methanol are believed to form under this process and make up over 70% of average ice mantle composition [3]. Ice mantles provide an important site of synthesis for some biomolecules, but longer-chain, more complex molecules require significantly more energy in order to react

spontaneously [5]. Dust grains provide a possible explanation for the organic molecule abundance observed on Earth today through their catalytic properties.

3.2 Dust grains

Dust grains are also implicated in the synthesis of organic molecules. The origin of dust grains has two principal sources. A minority of dust grains are believed to be the direct product, at least in part, of stellar outflows, but the bulk of the dust formation process takes place in the interstellar medium. The hypothesized chemical composition of interstellar dust has been outlined by Hoppe and Zinner (Table 3.1) [26].

TABLE 3.1 Presolar grains in meteorites (Hoppe & Zinner 2000)

Composition	Diameter (μm)	Abundance^a	Origins^b
C(diamond)	0.002	5×10^{-4}	SN
SiC ^c	0.3–20	6×10^{-6}	AGB
C(graphite) ^d	1–20	1×10^{-6}	AGB, SN II, nova
SiC type X	1–5	6×10^{-8}	SN
Al ₂ O ₃ (corundum)	0.5–3	3×10^{-8}	RG, AGB
Si ₃ N ₄	~1	2×10^{-9}	SN II

^aOverall abundance in primitive carbonaceous chondrite meteorites.

^bSN = supernova; AGB = asymptotic giant branch star; RG = red giant.

^cSiC grains sometimes contain very small TiC inclusions.

^dGraphite grains sometimes contain very small TiC, ZrC, and MoC inclusions.

Now that the formation of metals in the cores of stars has been addressed (Chapter 2), the next step in the process that has resulted in the diversity of organic molecules observed today is the chemical synthesis of these compounds. The dominant theory involves micron-sized dust grains in the interstellar medium

and protoplanetary disks. Dust is ubiquitous in the universe and contributes to the formation of many celestial objects. Dust molecules also contribute to the diversity of environments observed today in the interstellar medium. Charged dust molecules in the atmospheres of planets have been implicated in the formation of prebiotic molecules. In this way, dust is not only the building block of stars and planets, but also tied into the mechanism for the formation of life's biomolecules.

3.2.1 Catalysis

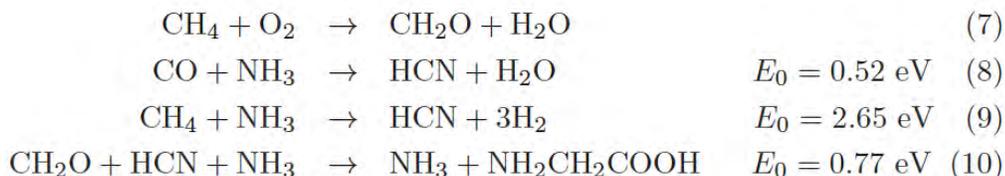
All Chemical reactions are governed by three principal factors (2): entropy (S), Gibbs free energy (G), and enthalpy (H).

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

In order for prebiotic molecules to be synthesized, the reactants must be able to overcome the activation energy barrier for the reaction to take place (Figure 3.1). This activation barrier (E_a) is often equated with H. Organic molecular synthesis requires relatively high activation energies. These barriers are often so high that synthesis reactions would likely not take place due to thermal energies alone in exoplanet atmospheres (Table 3.2, Figure 3.1). Rather, the presence of negatively charged dust grains in the plasma atmospheres likely facilitated, or catalyzed these reactions, by attracting ions in the plasma causing them to accelerate towards the dust grains. This process of acceleration and

bombardment at the dust grain surface could have been sufficient to produce energies high enough to overcome organic molecular synthesis barriers (Table 3.2, Figure 3.1).

TABLE 3.2 Average activation barriers E_0 for common elementary organic reactions.



Stark *et al.* calculated that conservative electron temperature values of about 1 eV (or 10^4 K) could be sufficient to accelerate nearby ions onto the dust grain surface with the necessary energy for the reaction to progress in the formation of H_2CO , NH_3 , HCN , and the amino acid glycine. Therefore, prebiotic organic molecules could have been synthesized in dust clouds in early planetary atmospheres. Another important consideration is the role dust plays in the conformational entropy of the smaller reactant molecules. Molecules vibrate in the femtosecond range and these vibrations are constantly changing the bond lengths and orientation of the molecule. When two molecules accelerate towards and collide with a dust grain, they are momentarily trapped by the grains surface, thereby reducing their conformational entropy and ability to vibrate. If two molecules happen to collide on the grain nearby to one

another, entropy restriction contributes to the likelihood of a chemical reaction taking place (2).

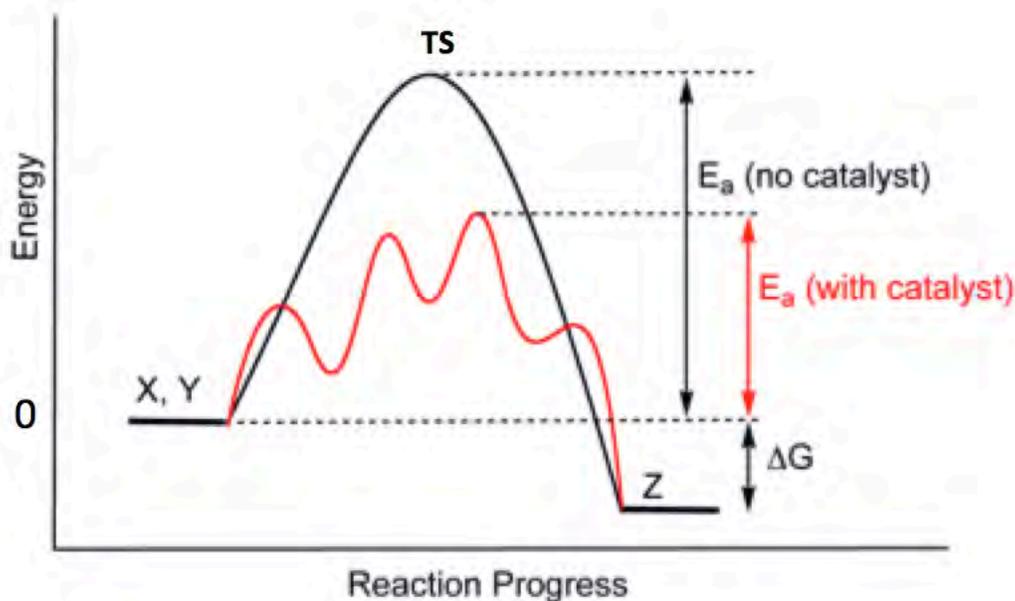


Figure 3.1 Activation of the initial state ($E=0$) allows the reactants (X, Y) to reach sufficient energy to overcome the activation barrier (E_a) and reach the transition state (TS). As the reaction progresses, the reactants are transformed into product (Z). Dust grain catalysis can be modeled using an alternate reaction coordinate (red). This alternate path lowers the overall activation barrier and increases the rate of the reaction [27].

The bombardment of the grain surface also increases the thermal energy of the dust grain. At higher temperatures, and therefore enhanced thermal activation, the formation of larger more complex molecules becomes increasingly accessible.

Conclusion

Dust grains were essential to the reaction process involving complex synthesis of organic molecules. Without dust and its catalytic properties the

synthesis rates would have been considerably slower and would have resulted in limited abundance of biomolecules today. This understanding of organic molecular synthesis is important in determining the necessary prebiotic conditions for life. Further, this understanding also informs future work in the detection of promising exoplanets (Chapter 4).

Chapter 4

Extraterrestrial Organic Matter: Exoplanets & Meteorites

Introduction

The study of exoplanets and their atmospheres has rapidly become one of the most popular fields in Astronomy. A more informed understanding of how carbon behaved in protoplanetary conditions (as described in Chapter 3) is critical to observational strategies when monitoring exoplanets. The greatest potential impact lies in using spectroscopic techniques to identify systems similar to that of the early Earth and using this information to make predictions about prebiotic and biotic molecular synthesis on these exoplanets. This in turn may one day inform missions to detect habitable worlds and identify candidates in the search for carbon-based life. In addition, the identification and isolation of carbonaceous matter from comets and meteorites provides important evidence for the abundance of organic molecules outside of Earth and our solar system.

5.2. Exoplanets & Spectroscopy

Exoplanets, or planets outside of our solar system, are of interest to the astronomy community in the name of identifying habitable worlds. Exoplanets can be detected through changes in the flux of parent stars over time. When an exoplanet transits in front of a nearby star, the star's flux will change during three principal phases: the ingress, in-transit, and egress. The ingress occurs as the exoplanet begins to cross the star, the in-transit phase is the deepest sustained dip in flux and represents the points in time where the exoplanet's area is completely

blocking a portion of the star. Finally, the egress occurs as the exoplanet moves past the star and the star's flux returns to its baseline value (Figure 4.1).

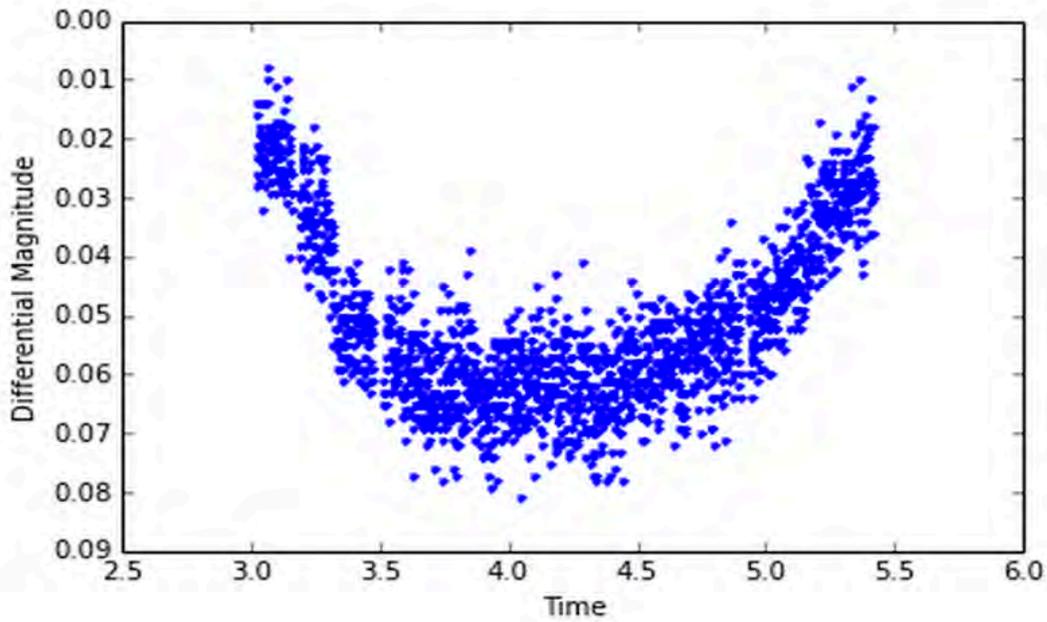


Figure 4.1. Differential light curve for the exoplanet WASP-10b during transit. The ingress occurs from 3.0 hours to 3.5 hours, followed by the in-transit phase from 3.5 hours to 4.75 hours, followed by the egress from 4.75 hours to 5.5 hours.

Once an exoplanet has been identified, spectroscopy can then be utilized to determine the chemical make-up of the atmosphere. The Fast Infrared Exoplanet Spectroscopy Survey Explorer (FINESSE) is a proposed NASA mission and space exploration program with the goal of studying over 200 exoplanets in nearby solar systems. This project will inform our understanding of the conditions and atmospheric compositions of nearby exoplanets. Infrared (IR) spectroscopy is an important observational tool as it provides detailed information about the chemical composition of exoplanet atmospheres.

Each functional group³ in an organic molecule has a distinct IR signature. These signatures result from vibrational mode activation of the molecule and its constituent functional groups. In the case of exoplanets, vibrational mode activation occurs as electromagnetic radiation (often from the parent star) filters through the atmosphere of an exoplanet. This radiation is then absorbed and reemitted in the form of IR radiation, which can then be detected and analyzed (Figure 4.2).

In recent years the Hubble Space Telescope made an important discovery on the exoplanet HD 189733b. In 2008 the first organic molecule was detected in this exoplanet's atmosphere. In addition, spectroscopic signatures indicated the presence of water. The organic molecule is methane (CH₄), which is known to be a byproduct of some bacteria (methanogens) on Earth. This data was collected during transit across the parent star (Figure 4.2).

³ Specific moieties of atoms that have unique or characteristic reaction properties.

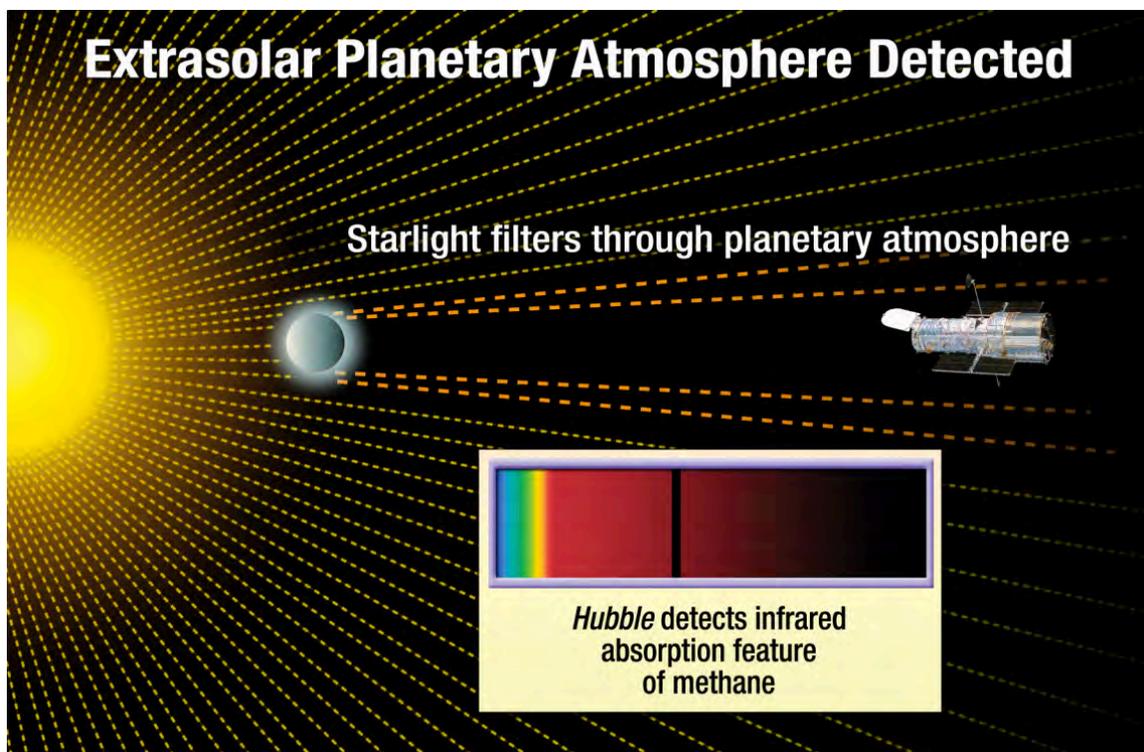


Figure 4.2. Molecules in the atmosphere of exoplanets absorb and reemit stellar radiation with unique spectroscopic signatures. These signatures are then detected through infrared spectroscopy. (NASA.gov)

The IR spectrum of a given molecule has two principal regions: the functional group region and the fingerprint region (Figure 4.3). The fingerprint region is typically difficult to read and poses a challenge for the extraction of meaningful data, but the functional group region provides important information about the reactivity of the molecule based on its chemical constituents. The two axes of an IR spectrum measure transmittance percentage and wavenumber (W). The position along the x-axis provides information on the energy required to activate a particular vibrational mode: a stretch, a bend, or a contraction (1).

$$W = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1)$$

The energy required to induce a vibrational mode depends on the spring constant between two atoms (k) and their reduced mass (μ). The transmittance percentage is related to the electric dipole between two atoms, with larger bond dipoles resulting in lower transmittance values (and therefore higher absorbances).

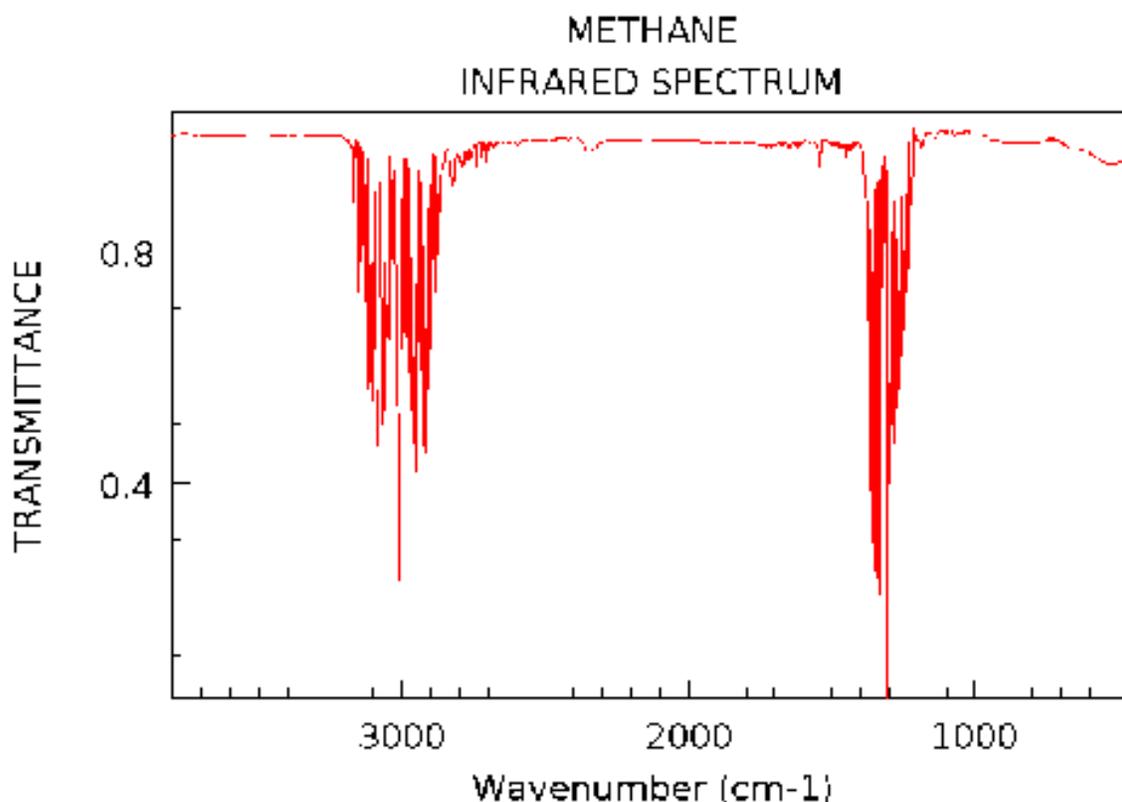


Figure 4.3. The IR spectrum for the molecule methane (CH_4). The characteristic stretch for this molecule is at the 3000 wavenumber (cm^{-1}) mark. This corresponds to the C-H bond stretch and has a moderate absorbance value due the bond dipole. The fingerprint region extends from about 1500 cm^{-1} down to 500 cm^{-1} . NIST Chemistry WebBook.

5.3. Carbonaceous chondrites

Carbonaceous chondrites are a class of stony meteorites containing high abundances of organic carbon. The study of meteorites is important because complex chemical analyses outside the realm of spectroscopy can be used to study matter with extraterrestrial origin. Carbonaceous chondrites in particular provide an opportunity to study organic matter from the early solar system. Chemical analysis of carbonaceous chondrites that have collided with Earth has linked their origin to comets due to the unusually high ratio of radioactive isotopes found in these meteorites. The high deuterium:hydrogen ratio of these meteorites is the best evidence for their origin [1].

5.4.1 Orgueil, Ivuna, & Murchison

A number of carbonaceous chondrites, namely Orgueil, Ivuna, and Murchison, have been identified. Pristine interior sections of these meteorites have been analyzed for chemical composition (Table 4.1). Gas chromatography analysis revealed a number of beta amino acids including β -alanine and β -glycine.

Alanine and glycine are two of the simplest amino acids, but are nonetheless essential biomolecules⁴ [1]. These amino acids play critical roles in metabolism and serve as the building blocks for proteins in the human

⁴ These structures are classified based on a standard chemical backbone and a variable appendage known as the "R" group. The R groups for glycine and alanine are the most simplistic: hydrogen in the case of glycine and a methyl group in the case of alanine.

body. In fact, Amino acids are considered the building blocks for proteins in all known life forms.

Table 4.1 Summary of the average amino acid concentrations in the extracts of Carbonaceous chondrites Orgueil, Ivuna, and Murchison.

Type	CI		CM	
	Orgueil	Ivuna	Murray	Murchison
D-Asp	28 ± 16	30 ± 2	51 ± 31*	100 ± 15
L-Asp	54 ± 18	146 ± 8	65 ± 16	342 ± 103
D-Glu	15 ± 6	8 ± 1	135 ± 50	537 ± 117
L-Glu	61 ± 31	372 ± 11	261 ± 15	801 ± 200
Gly	707 ± 80	617 ± 83	2,110 ± 144	2,919 ± 433
D-Ala	69 ± 9	82 ± 22	617 ± 79	720 ± 95
L-Ala	69 ± 9	157 ± 14	647 ± 58	956 ± 171
β-Ala	2,052 ± 311	1,401 ± 146	1,063 ± 268	1,269 ± 202
D,L-α-ABA [†]	13 ± 11*	12 ± 7*	463 ± 68	914 ± 189
D,L-β-ABA [†]	332 ± 99	438 ± 142	424 ± 18	708 ± 171
γ-ABA	628 ± 294	≈600	717 ± 192	1,331 ± 472
AIB	39 ± 37*	46 ± 33*	1,968 ± 350	2,901 ± 328
D,L-β-AIB [†]	148 ± 70	84 ± 12	147 ± 88	343 ± 102
D,L-Iva [‡]	<194 ± 230*	<163 ± 119*	2,834 ± 780	3,359 ± 534
Total	4,200	4,000	11,500	17,200

All values are reported in ppb on a bulk-sample basis. The uncertainties are based on the standard deviation of the average value of between two and five separate measurements.

*These concentrations were very similar to blank levels and therefore must be considered to be maximum values.

[†]Enantiomers could not be separated under the chromatographic conditions.

[‡]Optically pure standard not available for enantiomeric identification.

Conclusion

The study of exoplanets represents an important application for present astrobiological research on organic matter. Identifying exoplanets with promising prebiotic environments through spectroscopy or other means aids us in the search for habitable worlds and extraterrestrial carbon-based life. The study of carbonaceous chondrites is also highly relevant to our current understanding of the evolution of life on Earth given that critical biomolecules, namely amino acids, are now known to arise through fundamental physical processes with extraterrestrial origin. Amino acids are essential to every life form known on Earth and the spontaneous synthesis of these

complex organic molecules raises the question as to whether or not similar systems in the universe could have also been seeded with these fundamental biomolecules.

Chapter 5

Discussion

The topic of this thesis has dealt with characterizing the path of organic molecules through time: from the birth of carbon in the cores of Pop III stars to the formation of organic molecules in protoplanetary disks catalyzed by dust. Further, the characterization of protoplanetary conditions that led to successful synthesis of organic molecules has the potential to make a tangible change in the way that exoplanets are selected for in-depth study.

Carbon's versatility in patterns of reactivity is one of the principal reasons for the focus on this atom in this thesis project. While the scope is necessarily limited by perceptions of conditions for life on Earth, other atoms have promise in terms of their potential for complex and diverse chemistry. For example, some organisms on Earth are known to be sulfur-based. In addition, other organisms use arsenic to build DNA backbones in place of phosphorous. Atoms like sulfur, silicon, and oxygen also have diverse patterns of reactivity and have the potential to sustain biodiversity in a manner similar to carbon.

These patterns of reactivity differ from other atoms with more restrictive electronic configurations (for example, fluorine and lithium). While highly reactive in many circumstances, these atoms are limited in the number of reactions in which they can participate. Further, these atoms are also limited in the number of bonds they can form. In the case of fluorine and lithium, both of these atoms are generally stable when bonded to just one other atom. This necessarily limits the scope of their chemistry and the diversity

in the number of complex molecules they can form. In contrast, larger atoms like sulfur and silicon can access multiple orbitals in order to form bonds. Carbon utilizes hybridized *sp* orbitals and, when compared to larger nonmetals on the periodic table, is limited to sharing a total of eight valence electrons⁵ based on the octet rule⁶. Sulfur and silicon can both violate the octet rule and remain stable by drawing electron density from the *d* orbital. In some instances, this allows for even more complex chemistry than the carbon atom. These atoms should therefore, also be added to the list of IR targets when studying exoplanets.

Another important consideration for future work involves testing the validity and reliability of dust-catalyzed reaction rates (discussed in Chapter 3). Correlating these reaction rates with present abundances of complex organic molecules has not yet been pursued. Though there is one considerable challenge to testing these data on Earth based on present-day abundances. Due to the fact that the molecules of interest are biomolecules, they have been synthesized, decomposed, and modified an innumerable amount of times over the past few billion years on Earth. In effect, the biomolecules that were created through dust grain bombardment in the early Earth's atmosphere likely no longer exist in their original form. This challenge is further complicated by the constant production of organic carbon in the form of glucose (C₆H₁₂O₆) from carbon dioxide in plants. In order to test these reaction rates an independent, isolated experiment must be pursued; the data can then be extrapolated to fit spectroscopic abundances on abiotic

⁵ Outer shell electrons involved in chemical reactions.

⁶ The octet rule dictates that a central atom typically cannot share more than eight electrons when forming ionic or covalent bonds.

exoplanets. This reinforces the importance of spectroscopy for future work in this discipline.

This work is ultimately applicable in delineating prebiotic conditions. While important work has been done in developing models for the first proto-cells, the molecular and physical conditions that led to the assembly of these proto-cells are equally important. By expanding the scope of the research to include other promising elements like sulfur and silicon into the discipline we reduce the risk of limiting our scope in the search for promising exoplanets.

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