The Next Decade in Astrochemistry:
An Integrated Approach

An Astro2010 Science White Paper

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Science Frontier Panels:

Planets and Stars and Star Formation
Stars and Stellar Evolution
The Galactic Neighborhood

Introduction: The Transformational Role of Astrochemistry:

Among the most fundamental questions in astronomy are those concerning the formation of stars and planets from interstellar material and the feedback mechanisms from those stars on the dynamics and chemical evolution of the ISM itself. Studies of the Milky Way and other galaxies in the Local Group have shown that massive molecular clouds are the principal sites of star formation (e.g. Rosolowsky and Blitz 2005). The resultant stars can limit the star formation process as their radiation heats and disperses the remaining cloud (e.g. Matzner 2002). Star formation itself generally proceeds through the formation of a proto-planetary disk, which in turn leads to the establishment of planetary systems (e.g. Glassgold et al. 2004) and the creation of reservoirs of icy bodies. Such reservoirs are the sources of comets, asteroids, and meteorites, which provide a continuing source of material to planets via bombardment (e.g. Mumma et al. 2003). The material in stars is subject to nuclear processing, and some of it is returned to the ISM via supernovae and mass loss from other evolved stars (Asymptotic Giant Branch (AGB), red giants and supergiants: e.g. Wilson 2000). In our galaxy, planetary nebulae, which form from AGB stars, are thought to supply almost an order of magnitude more mass to the ISM than supernovae (e.g. Osterbrock 1989), although the relative contributions depend on the star formation rate (SFR) and the Initial Mass Function (IMF). These processes, along with possible accretion of material from outside the galaxy, replenish the ISM and lead to the formation first of diffuse interstellar clouds with modified composition and then of dense clouds in which stars can again form. A graphic illustrating the life cycle of interstellar material and its connection to planets, including Earth, is shown in Figure 1.

Radio, millimeter and sub-millimeter molecular line observations provide crucial insights into almost all phases of the ISM, from overall galactic evolution to the composition of planetary atmospheres and hence the possible development of life forms on Earth-like planets. Molecules

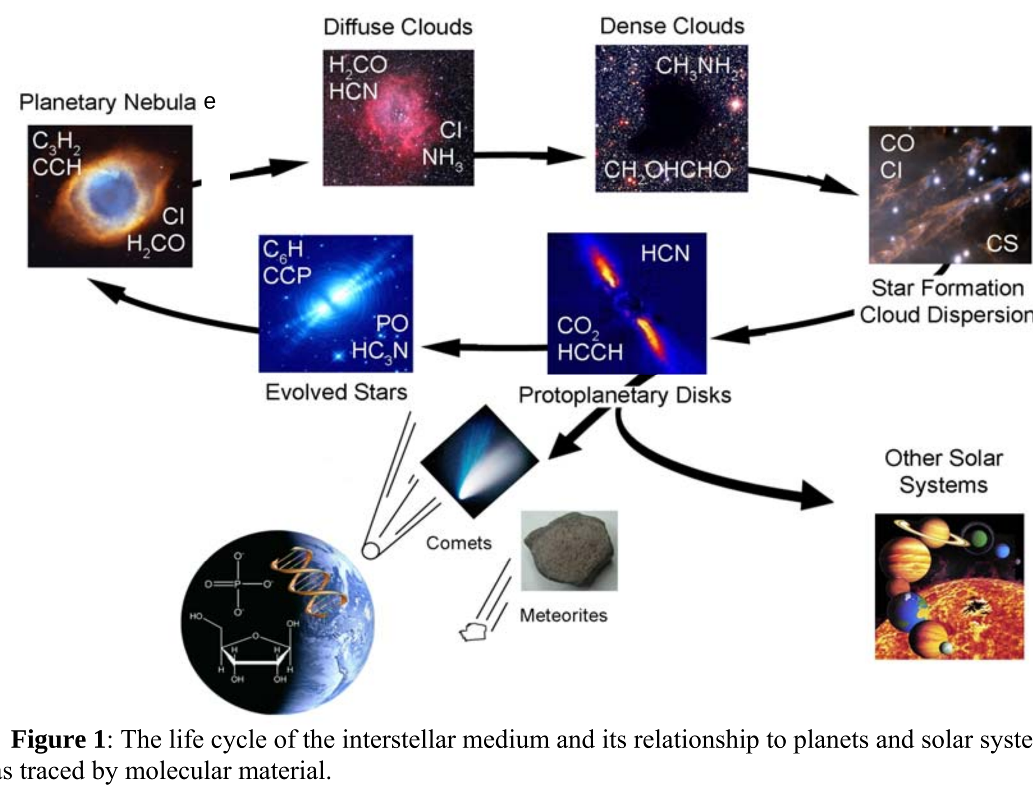

Figure 1: The life cycle of the interstellar medium and its relationship to planets and solar systems, as traced by molecular material.

are present in all these environments, providing extremely useful tracers of the structures of circumstellar shells, planetary nebulae, dense and diffuse clouds, cloud cores, and protostellar disks. They also trace the composition of solar systems bodies such as comets. Because of their unique connection to this wide range of astronomical objects, obtaining a clear understanding of the chemistry of interstellar molecules is crucial to evaluating the life cycles of the ISM and its relationship to planet and solar system formation. The latter topic deserves special comment since it provides insight into the origin and distribution on Earth of the biogenic elements: carbon, oxygen, hydrogen, nitrogen, and phosphorus.

Carbon, the key constituent of life as we know it, is particularly relevant in this regard. Studies of early Earth suggest that our planet lost most of its original carbon in the form of CH_4 when it shed its original atmosphere (Harper and Jacobsen 1996). If so, where did the carbon currently found on Earth originate? One possibility is exogenous delivery. The Earth has been bombarded by meteorites, comets and interplanetary dust particles (IDP's) since its formation, with particularly heavy bombardment 3.8 – 4.0 billion years ago (Gomes et al. 2005). IDP's and micro-meteorites alone currently deliver carbonaceous matter to the Earth's surface at a rate of ~ 3×10^5 kg/yr, but this value may have been as high as 5×10^7 kg/yr during the late bombardment epoch. Shortly thereafter, life is thought to have developed (Furnes et al. 2004). This suggests that exogenous delivery of organics to Earth during this period by meteorites, comets, and dust particles may have "brought back the carbon," and provided the necessary carbonaceous material that gave a "jump-start" to life (Chyba and Sagan 1992). It is therefore critical to examine the origins of this organic material both by studying the chemistry of currently existing dense clouds and proto-planetary disks and of objects, such as comets, that remain in the solar system reservoir.

Current Status of Astrochemistry

Some forty-odd years ago, the presence of molecules more complex than diatomic species in interstellar gas was believed to be highly unlikely. The cold, rarified gas thought to exist between the stars was considered too hostile to support an active chemistry. Given the low particle densities in such regions (~ 1-100 particles per cc), destruction of molecules by ultraviolet radiation seemed inevitable, prohibiting the formation of polyatomic species. Since that time, however, our concept of the dense interstellar medium has dramatically changed, almost entirely due to observations at radio, millimeter and sub-mm molecular-line wavelengths.

Table 1 shows a current list of interstellar molecules, arranged by number of atoms. Over 140 species have been conclusively detected to date. The majority have been identified by mm and sub-mm astronomy. The others have been detected on the basis of their electronic spectra, (e.g. CH, CH^+, and NH) observed in absorption against background stars, or via ro-vibrational transitions in the infrared (e.g. HCCH, CH_4, and SiH_4)$_{,}$. In addition, lower frequency microwave spectra has been important for identifying heavier molecules (C_8H^-, $HC_{11}N$), and for those with favorable pure lambda-doubling or inversion transitions such as OH or NH_3.

We emphasize that the molecules listed in Table 1 have been *securely* identified. The spectral resolution offered by radio, mm and submm astronomy is typically one part in 10^7 -10^8 – far better than any other wavelength regime. Dense interstellar gas is sufficiently cold that spectral emission lines generated in molecular sources are extremely narrow, usually in the range of 0.1 – 5 km/s. Individual rotational lines, including both fine and hyperfine structure, can therefore be readily resolved, and therefore a true *"fingerprint"* can be obtained for absolute confidence in identification.

Table 1: Known Interstellar Molecules

2		3		4	5	6	7	8	9
H_2	CH^+	H_2O	C_3	NH_3	SiH_4	**CH_3OH**	**CH_3CHO**	**CH_3CO_2H**	**CH_3CH_2OH**
OH	**CN**	**H_2S**	**HNC**	**H_3O^+**	CH_4	**NH_2CHO**	**CH_3NH_2**	**HCO_2CH_3**	**$(CH_3)_2O$**
SO	**CO**	**SO_2**	**HCN**	**H_2CO**	**HCOOH**	**CH_3CN**	**CH_3CCH**	CH_3C_2CN	**CH_3CH_2CN**
SO^+	**CS**	**NNH^+**	CH_2	**H_2CS**	**HCCCN**	**CH_3NC**	**CH_2CHCN**	**C_7H**	**$H(CC)_3CN$**
SiO	C_2	**HNO**	**H_2D^+**	**HNCO**	**CH_2NH**	**CH_3SH**	**$H(CC)_2CN$**	H_2C_6	**$H(CC)_2CH_3$**
SiS	**SiC**	**CCS**	**HOC^+**	**HNCS**	**NH_2CN**	**C_5H**	**C_6H**	**CH_2OHCHO**	**C_8H**
NO	**CP**	**NH_2**	**NaCN**	**CCCN**	**H_2CCO**	**HC_2CHO**	**$c\text{-}CH_2OCH_2$**		C_8H^-
NS	**CO^+**	H_3^+	**MgNC**	**HCO_2^+**	**C_4H**	$CH_2{=}CH_2$	**$H_2CC(OH)H$**		**CH_3CONH_2**
HCl	HF	**NNO**	**AlNC**	**CCCH**	**$c\text{-}C_3H_2$**	H_2C_4	C_6H^-		
NaCl	SH	**HCO**	**SiCN**	**$c\text{-}C_3H$**	**CH_2CN**	**HC_3NH^+**			
KCl	HD	**HCO^+**	**KCN**	**CCCO**	C_5	**C_5N**			
AlCl	**PO**	**OCS**	**MgCN**	**C_3S**	**SiC_4**				
AlF	**AlO**	**CCH**	**CCP**	HCCH	**H_2C_3**	10	11	12	13
PN		**HCS^+**	**HCP**	**$HCNH^+$**	**HCCNC**	**CH_3COCH_3**	$H(CC)_4CN$		$H(CC)_5CN$
SiN		**$c\text{-}SiC_2$**		**HCCN**	**HNCCC**	**CH_3C_5N**			
NH		**CCO**		**H_2CN**	**H_2COH^+**	**$(CH_2OH)_2$**			
CH				**$c\text{-}SiC_3$**	**C_4H^-**				

Astrochemistry continues to unveil new and unanticipated avenues of investigation. In the past few years several new classes of molecules have been discovered. For example, a series of long chain carbon anions have been identified in both molecular cloud and circumstellar shells of AGB stars, including C_4H^-, C_6H^-, C_8H^-, and C_3N^- (McCarthy et al. 2006 Cernicharo et al. 2007, Brunken et al. 2007, Thaddeus et al. 2008; see Figure 2). Such molecules are likely created by a favorable radiative or dissociative electron attachment process, unexpected in interstellar gas.

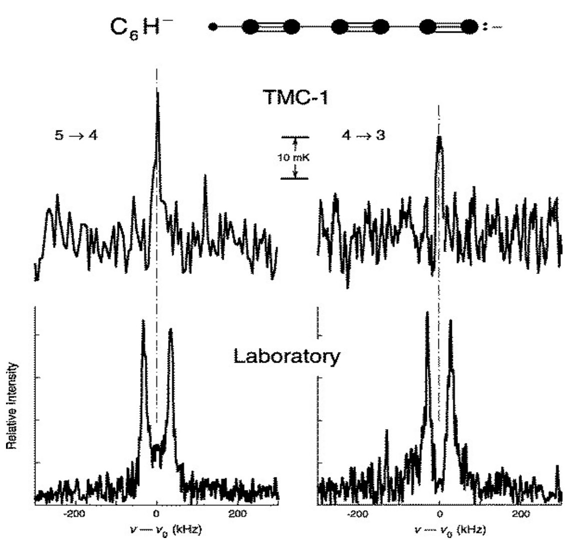

Figure 2: The interstellar detection of C_6H^-, showing astronomical data (upper) and the laboratory measurements (lower) that made the identification possible (McCarthy et al. 2006)

These species are tracers of the electron density in dense clouds, and thereby provide an independent determination of the fractional ionization, which is an important quantity in understanding astrophysical plasmas. Another recent development has been the discovery of a series of phosphorus-bearing molecules in circumstellar gas, including HCP, PO, CCP, and PH_3 (Agundez et al. 2007, Tenenbaum et al. 2007, Halfen et al. 2008, Tenenbaum and Ziurys 2008.); see Figure 3. The history of this element is a complete enigma. Phosphorus is thought to be formed in massive stars ($M > 15\ M_\odot$) during hydrostatic-shell C- and Ne-burning (Arnett 1996), and released into the ISM in supernovae. The rarity of high mass stars results in the low (solar) P abundance of $\sim 10^{-7}$, relative to hydrogen; yet phosphorus is the fifth most abundant element in living systems (Maciá 2005). In circumstellar envelopes, phosphorus is predicted to condense onto grains in the form of schreibersite $(Fe,Ni)_3P$ (Lodders and Fegley 1999), a common constituent of iron meteorites (Pasek and Lauretta 2005). The observation of gas-phase phosphorus-containing molecules in interstellar sources may help to provide clues as to how this element came to play its critical role in the formation of life on planet surfaces.

Unexpected new molecular sources are also being found, indicating that our current understanding of interstellar chemistry is incomplete. It has always been thought that only carbon-rich circumstellar shells of evolved stars have a complex chemical composition, such as the famous source IRC+10216. New studies now suggest that their oxygen-rich counterparts may spawn some chemical surprises, such as in the asymmetric shell surrounding the supergiant VY Canis Majoris (Ziurys et al 2007, *Nature*) in which the new molecules PO and AlO have been discovered. These species appear to be produced near the star's photosphere and may provide a connection between atmospheric and wind chemistry (Tenenbaum and Ziurys 2009). Planetary nebulae, thought to be hostile to molecular gas due to high UV fluxes, now appear to support molecular material even in their late phases, as evidenced by the presence of CO, HCO^+, C_3H_2, and even H_2CO in the Helix Nebula (Young et al. 1999). Our understanding of the molecular content of the ISM is continuously being challenged.

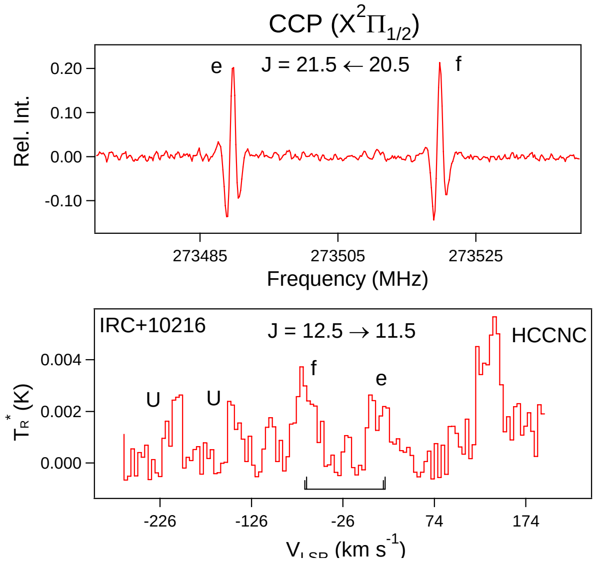

Figure 3: Detection of CCP in IRC+1026, showing laboratory (top) and astrophysical (bottom) spectra of CCP ($X^2\Pi_r$); the lambda-doublets are labeled by e and f in each transition. The astronomical spectra were measured with the ARO 12 m telescope (Halfen et al. 2008)

A Unique Opportunity for Rapid Advancement in Astrochemical Studies

Astrochemistry is really in its infancy relative to other areas of astrophysics. Most of what has been established in this field has arisen from the study of just a handful of sources, such as the Orion giant molecular cloud, or the circumstellar envelope of the carbon-rich AGB star IRC+10216. Furthermore, with a few exceptions, the astrochemical investigations have been decoupled from laboratory studies, which are crucial to so many aspects of this endeavor. One obvious connection is to laboratory molecular spectroscopy, which has and continues to provide the crucial frequency information for line identification. Another important link is to precise reaction rate data, which enable formulation of realistic, predictive models of the chemistry in astronomical objects. Such data encompass both gas-phase processes and reactions on surfaces.

With the advent of ALMA, new technologies have been developed that offer as much as an order of magnitude improvement in sensitivity, as demonstrated by recent 1 mm observations with an ALMA Band 6 receiver (Lauria et al 2007). The data input from observations with mm- and submm wave telescopes will increase accordingly. It is now abundantly clear that interpretation of these data, such as spectral line surveys, will require a closer relationship between observations, theory, and molecular laboratory astrophysics. Only through a broad interdisciplinary approach will significant progress be achieved. Student involvement in more than one aspect of such research is also critical, to train the next generation of astrochemists.

Education in some combination of radio observational techniques, laboratory methods, and theory, for example, will likely prove more fruitful than a single, narrowly-focused approach. With new techniques in remote observing, as well as advances in laboratory methods, such multidisciplinary training is now possible and can lead the next generation to major advances in progress in astrochemical research. It is important to emphasize that this is a two way process in which astronomy and chemistry lead to mutual discovery and understanding. Some fundamental questions that can be better addressed with this multidisciplinary approach are listed below:

What is the chemical inventory of the interstellar medium?

As the newly discovered carbon chain anions and phosphorus-containing species demonstrate, astronomical observations continue to lead to detection of unexpected molecules. The discovery of new types of sources such as VY CMa continue to reveal chemistry quite unlike that commonly observed in other well-characterized sources, both indications that of current evaluation of interstellar chemistry is far from complete. Thus, there remain several important unanswered questions that need to be addressed in the next decade of observational Astrochemistry. What is the extent of complexity in interstellar chemistry? Is there a limit to molecule size, and what is that limit? Is there a strong terrestrial bias skewing our understanding of Astrochemistry? Have we fully characterized the types of sources producing molecular material? What new classes of species exist? Molecule identification is performed in conjunction with laboratory spectroscopy, and a strong synergy between observation and laboratory studies holds the most promise for advancement in these areas. It is also the most fruitful avenue for analyzing spectral-line surveys.

Can we achieve a mechanistic chemistry understanding of interstellar chemistry?

Chemical modeling should have predictive power for molecular composition and reaction chemistry. There is excellent progress in this area for cold sources (e.g. TMC-1); however, core chemistry continues to remains a challenge as abundances of several species are underestimated by orders of magnitude (Quan & Herbst 2007). It is essential that improved chemical models be constructed based on gas-phase and grain-surface reactions. These regions should include, but not be limited to, the cold, diffuse, and warm regions of the ISM, circumstellar envelopes of evolved stars and planetary nebulae. Sensitivity methods should be used to determine which reactions are most important. In addition, for those key reactions that cannot be studied in the laboratory, theoretical treatments should be used to estimate rate coefficients. In the case of gas-phase reactions, key rate coefficients of low-temperature reactions between positive ions and polar neutrals need to be estimated, including those for anions. Furthermore, in the cold interstellar medium, dust grains develop thick mantles of ices containing H_2O, CO, CO_2, CH_4, H_2CO, and CH_3OH. It is essential to understand the morphology of these ices and how they are produced. When interstellar gas and dust particles collapse and heat up in the process of star formation, the surrounding envelope gradually warms up from 10 K to 100-300 K. The mantles then evaporate, and new species will be produced. Some the surface species formed under cold conditions are broken up by UV radiation into radicals, which then combine to form more complex species. Current models of this chemical processing must also be improved.

How are the molecular phases of the interstellar medium linked?

Gas-phase molecules are found in a variety of interstellar sources. Are these molecular reservoirs related? Dense clouds supposedly form out of diffuse clouds, which have recently been found to contain a range of polyatomic species (Liszt, Lucas and Pety 2006). Does molecular synthesis in dense gas receive a “jump-start” from diffuse cloud material? How does mass loss from evolved stars impact molecule formation in diffuse gas? Do fragmenting molecular clouds deposit molecules into the diffuse ISM ? The cycling of interstellar material is strongly linked to its molecular history. Following the evolution of molecular material is crucial in evaluating feedback mechanisms in the ISM.

How does interstellar chemistry impact the origin of life?

Many molecules present in molecular clouds contain more than one carbon atom, including CH_3CHO, CH_3CH_2OH, and CH_3CH_2CN. Yet, in the general ISM, O > C by a factor of about 1.6, while CO is the second most abundant interstellar molecule. Given the relative abundances of these two elements, most of the carbon should be in the form of CO, leaving little left for organic compounds. However, an active organic chemistry exists in giant molecular clouds. These clouds eventually collapse into solar systems. What becomes of this vast reservoir of organic material? Organic compounds are also found in meteorites such as Murchison (Pizzarello and Huang 2005). The high D/H ratios found in some of these compounds are good evidence that they originated in cold, interstellar clouds. If carbon was brought to Earth via exogenous delivery, did it come already in the form of organic molecules, and were these molecules produced originally in molecular clouds? What is the connection between interstellar chemistry and pre-biotic chemistry?

We suggest to the Astro2010 panel that many of the key questions concerning the origin of cosmic systems, galaxies, stars, planets and possibly life, depend on astrochemical processes and that astrochemistry, observational, theoretical and laboratory will be a very fruitful activity in the next decade and should be strongly supported.

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