

The chemistry in circumstellar envelopes of evolved stars: Following the origin of the elements to the origin of life

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Mass loss from evolved stars results in the formation of unusual chemical laboratories: circumstellar envelopes. Such envelopes are found around carbon- and oxygen-rich asymptotic giant branch stars and red supergiants. As the gaseous material of the envelope flows from the star, the resulting temperature and density gradients create a complex chemical environment involving hot, thermodynamically controlled synthesis, molecule “freeze-out,” shock-initiated reactions, and photochemistry governed by radical mechanisms. In the circumstellar envelope of the carbon-rich star IRC+10216, >50 different chemical compounds have been identified, including such exotic species as C₈H, C₃S, SiC₃, and AlNC. The chemistry here is dominated by molecules containing long carbon chains, silicon, and metals such as magnesium, sodium, and aluminum, which makes it quite distinct from that found in molecular clouds. The molecular composition of the oxygen-rich counterparts is not nearly as well explored, although recent studies of VY Canis Majoris have resulted in the identification of HCO⁺, SO₂, and even NaCl in this object, suggesting chemical complexity here as well. As these envelopes evolve into planetary nebulae with a hot, exposed central star, synthesis of molecular ions becomes important, as indicated by studies of NGC 7027. Numerous species such as HCO⁺, HCN, and CCH are found in old planetary nebulae such as the Helix. This “survivor” molecular material may be linked to the variety of compounds found recently in diffuse clouds. Organic molecules in dense interstellar clouds may ultimately be traced back to carbon-rich fragments originally formed in circumstellar shells.

asymptotic giant branch stars | astrochemistry | molecular line observations

Circumstellar envelopes of evolved stars are among the most remarkable chemical laboratories in the universe. These envelopes are created by extensive mass loss in the later stages of stellar evolution, caused by thermal pulses in the star interior and radiation pressure on dust (1, 2). Because of the low temperature of the central star, and the long time scales for mass loss, molecules and dust form in the envelope, and are then gently blown into the interstellar medium (ISM). The material lost from such envelopes is thought to account for nearly 80% (by mass) of the ISM (3).

The Origin of Circumstellar Envelopes

Chemically rich circumstellar shells are found around asymptotic giant branch (AGB) stars and red supergiants (RSGs). AGB stars are objects of low and intermediate initial mass ($\approx 1\text{--}8 M_{\odot}$) with effective temperatures near $T \approx 2,000\text{--}3,500$ K (4–6). These objects occur on an evolutionary track that begins at the end of the main sequence. At this stage, all hydrogen in the stellar core has been converted to helium, and the core itself starts to gravitationally contract. This contraction ignites hydrogen in a shell around the core, and the star enters the so-called red giant branch. As the core continues to contract, the envelope of the red giant expands and becomes convectively unstable. Given sufficient contraction, the helium core will eventually ignite as

the H shell continues to burn. The fusion of helium produces ¹²C, and alpha capture on ¹²C yields ¹⁶O in the core. Eventually, the central helium is exhausted, leaving an oxygen/carbon core surrounded by He-burning and H-burning shells. The appearance of this two-shell structure marks the beginning of the AGB phase (4). The primary source of luminosity in an AGB star is the H-burning shell, but periodically the He shell ignites for short periods of time (5). The energy released in this so-called “thermal pulse” creates a convective zone extending from shell to shell, which mixes nuclear products from the He-burning zone to the stellar surface. This process, called the “third dredge-up,” brings carbon and other elements into the detaching envelope. The thermal pulses also aid in driving the outer material from the star, creating a circumstellar shell (1, 2). In fact, AGB stars lose up to 80% of their original mass in the form of an envelope, with typical rates of 10^{-6} to $10^{-4} M_{\odot}\text{yr}^{-1}$ (1, 2, 4). They therefore play a major role in the chemical evolution of the galaxy (7).

RSGs evolve from massive O and B stars ($M \approx 8\text{--}30 M_{\odot}$) that have left the main sequence. These objects experience intense mass loss ($\approx 10^{-5}$ to $10^{-3} M_{\odot}\text{yr}^{-1}$) for $\approx 10^3$ to 10^4 yr before they become supernovae, although there are many uncertainties connected with their evolution (2). They typically have surface temperatures of $T \approx 3,500\text{--}4,000$ K.

The Chemical Environment of Circumstellar Shells

Circumstellar shells exhibit a range of physical conditions, as shown in Fig. 1. In Fig. 1, a simplified cross section of a typical envelope for an AGB star is displayed, plotted on a scale of $\log r$ (r = distance from star). These objects are quite large, extending 10^4 to 10^5 stellar radii (R_{\star}). Near the stellar photosphere, the envelope material (all gaseous) is warm ($T \approx 1,500$ K) and dense ($n \approx 10^{10} \text{ cm}^{-3}$). As the matter flows away from the star, it expands and cools, typically with $T \propto r^{-1}$ and $n \propto r^{-2}$ (8, 9). Dust begins to form at $\approx 5\text{--}15 R_{\star}$, and shortly thereafter the maximum outflow velocity is achieved. Beyond the dust formation zone, the temperature and density continue to decrease such that at the outer edges of the shell, $T \approx 25$ K and $n \approx 10^5 \text{ cm}^{-3}$ (8, 9).

The chemistry varies substantially throughout the envelope. In the inner shell, the temperature and density are sufficiently high that thermodynamic equilibrium governs molecular abundances. Such local thermodynamic equilibrium (LTE) chemistry was predicted in the early models of Tsuji (10) and incorporated into later calculations (e.g., refs. 11 and 12). The LTE predictions have been borne out by observations (13, 14). Infrared spectroscopy has demonstrated that stable, closed-shell species such

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Abbreviations: AGB, asymptotic giant branch; RSG, red supergiant; LTE, local thermodynamic equilibrium; PN, planetary nebula(e); PPN, protoplanetary nebula(e); VYCMa, VY Canis Majoris.

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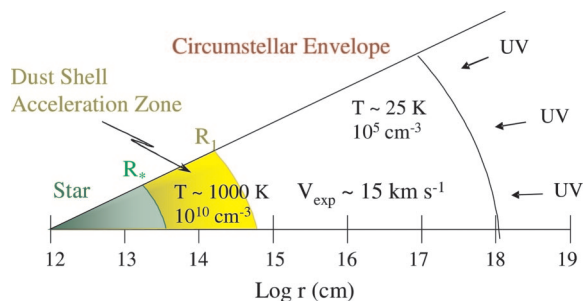


Fig. 1. Cross section of a circumstellar envelope, plotted in terms of $\log r$, where r is the distance from the central star. Regions of LTE chemistry, dust formation, and UV-induced photochemistry are shown.

as CS, NH₃, HCN, and HCCH have high abundances in the inner envelope of IRC+10216 ($\approx 10^{-3}$ to 10^{-6} , relative to H₂). As molecules flow outward, some abundances freeze out at intermediate radii, HCN and CO, for example (15, 16). At the outer regions, photons and cosmic rays initiate an active photochemistry that creates radicals (11, 12). As shown in interferometer maps (17, 18), radicals such as CN, CCH, C₃H, and C₄H exist in similar shell-like structures near the envelope edge (Fig. 2). They are the daughter species of parent molecules such as HCN and HCCH produced at LTE. In addition, shock waves in the shell, caused by thermal pulses, may influence abundances (19, 20).

There are additional complications to this scheme. For example, some shells are carbon-rich (C type), whereas others are oxygen-rich (M type), and S types have $C \approx O$. AGB envelopes are thought to initially start with more oxygen than carbon; they become C-enriched during the third dredge-up (4, 5). Shocks and pulsations associated with the third dredge-up may also facilitate the chemistry, because C-rich envelopes appear to have the greatest variety of chemical compounds. Other complexities come into play with post-AGB evolution and the formation of so-called “protoplanetary nebulae” (PPN). Observations have

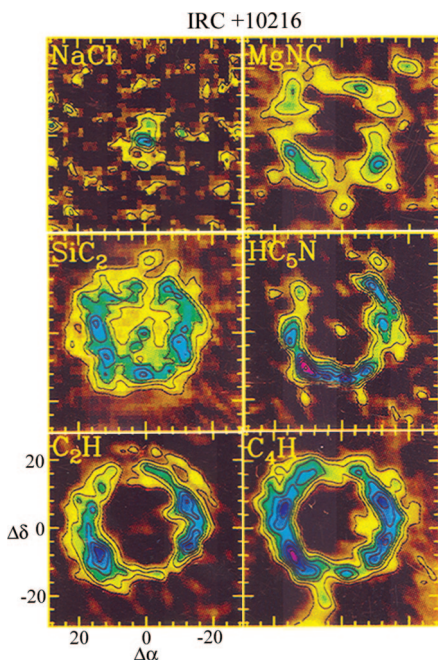


Fig. 2. Maps from the Plateau de Bure interferometer showing the molecular distributions of various species in the envelope of IRC+10216 (17, 18). MgNC, C₂H, HC₅N, and C₄H all exist in the outer shell, whereas NaCl is an inner envelope species. SiC₂ is present in the intermediate regions.

Table 1. Confirmed molecular identifications in IRC+10216

CO	CCH	HC ₃ N	CCS	SiO	NaCl
CS	C ₃ H	HC ₅ N	C ₃ S	SiS	AlCl
CN	C ₃ O	HC ₇ N	C ₃ N	SiC	KCl
HCN	C ₄ H	HC ₉ N	C ₅ N	SiN	AlF
HCCH	C ₅ H	H ₂ C ₄	HC ₄ N	SiC ₂	MgNC
HNC	C ₆ H	H ₂ C ₆	c-C ₃ H ₂	SiC ₃	MgCN
H ₂ CCH ₂	C ₇ H	HC ₂ N	CH ₃ CN	SiCN	AlNC
CH ₄	C ₈ H	C ₃	CP	SiC ₄	KCN
NH ₃	C ₂	C ₅	PN	SiH ₄	NaCN
H ₂ S					

suggested that during the PPN phase, a second, more violent mass loss event occurs with high velocity winds that partially destroy the remnant AGB envelope (e.g., refs. 21–23). For example, CRL 2688, the Egg Nebula, exhibits both low (< 20 km s⁻¹) and high velocity (> 100 km s⁻¹) outflows (24, 25). A more evolved object is CRL 618; here, the star, which has lost its dusty shroud, is producing sufficient UV radiation to create a small, nearby HII region (26, 27).

The envelopes of RSGs also have large temperature and density gradients, a dust formation zone, and significant molecular abundances, substantiated by various observations (e.g., refs. 3, 13, 28, and 29). However, RSG stars have shorter lifetimes than their AGB counterparts (a few hundred thousand years), and their mass loss appears to be more sporadic and asymmetric, characterized by jets and high-density streams (30, 31). The impact of these differences on the chemistry of RSG shells has yet to be evaluated.

Distinct Chemical Aspects: Carbon, Silicon, and Metals

Circumstellar shells are principally studied by infrared and millimeter/submillimeter astronomy. At millimeter/submillimeter wavelengths, the pure rotational transitions of numerous circumstellar molecules have been measured, providing a wealth of chemical information (e.g., ref. 32). Infrared observations probe the inner regions and have identified species with no permanent dipole moment (CH₄, SiH₄) and provided data on dust (13, 14, 33, 34). In the envelope of IRC+10216, the best-studied AGB star at a distance of ≈ 150 parsec ($pc = 3.09 \times 10^{16}$ m), > 50 different chemical compounds have been identified, as shown in Table 1. About 80% have been detected by radio/mm astronomy. In addition, there are many unidentified features in the mm spectrum that arise from unknown species (e.g., ref. 35).

A representative spectrum from IRC+10216, observed at 245 GHz, is shown in Fig. 3 Upper. The 3σ noise level in these data are < 10 mK (T_A^*). This spectrum illustrates the striking chemistry of C-rich AGB shells. First of all, the spectral lines present arise primarily from molecules containing carbon. About 80% of all species identified in this object contain this element, and there are several series of acetylenic chains, including HC_nN ($n = 1, 3, 5, 7, 9$) and C_nH ($n = 2, 3, 4, 5, 6, 7, 8$), and unusual radicals such as H₂C₄, H₂C₆, and HC₄N. Chemical modeling can reproduce the abundances of many of the chains by using ion-molecule reactions (12). It is unclear, however, whether such reactions are relevant because there has never been a conclusive detection of any ion in IRC+10216 to my knowledge. Radical-radical reactions have rates approaching those of ion-molecule processes, and these may be responsible for the interesting array of compounds.

Also present in the IRC+10216 spectrum is a line arising from ³⁰SiS. AGB envelopes of carbon-rich stars are the only sources that contain a wide assortment of silicon species, nine in all (see Table 1). Molecular clouds typically contain SiO and sometimes

Table 2. Molecules detected in VYCMa

H ₂ O	CS	NaCl
OH	SO	HCO ⁺
SiO	SO ₂	HCN
SiS	CO	NH ₃

sitions, is solid evidence that a molecular ion exists in a circumstellar envelope, as opposed to a PPN (OH 231.8, CRL 618).

The contrast between VYCMa and IRC+10216 is shown in Fig. 3, which displays data in the same frequency range from the O-rich star (Fig 3 Lower). Although CS is visible in VYCMa, it is clearly more intense in IRC+10216. Also, the carbon chains are missing in the data of VYCMa, but a line of SO₂ is present, with an unusual profile. SO₂ is not visible in the IRC+10216 spectrum.

Circumstellar Dust

The dust composition in circumstellar shells is thought to reflect that of the gas phase (34). In the majority of O-rich envelopes ($\approx 4,000$), amorphous silicates have been identified on the basis of 9.7- and 18- μm solid-state features. Evidence for crystalline silicates such as olivine and pyroxene has also been found. Other constituents may be refractory oxides of aluminum, silicon, magnesium, and iron. In C-rich stars, the dust is thought to be primarily SiC, which has a 11.3- μm feature arising from the Si-C stretch. It has been observed in >500 AGB stars, but becomes weaker in more evolved objects. In PPN and planetary nebulae (PN), strong infrared features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm are present, which can be attributed to aromatic C-H and C-C stretches and bends, the so-called aromatic infrared bands. There are also bands at 3.4 and 6.9 μm attributed to aliphatic C-H modes. All of these features likely arise from some large solid-state carbon-bearing compound consisting of hundreds of atoms (34).

Into the PN Phase

The mass loss from PPN is particularly energetic, and over a period of $\approx 1,000$ years, the envelope is depleted, gradually exposing the central star (34). As the envelope thins, the stellar radius decreases, in turn raising the temperature of the star to $T > 30,000$ K. The UV output from the star begins to ionize the remnant envelope, forming a PN.

PN are unusually bright and colorful objects because of their atomic emission-line spectra. Remarkable morphologies appear as these nebulae form, including bipolar jets, clover-leaf structures, disks, rings, and spirals (52, 53). Given the presence of the high UV field, and the predicted time scale for photo-dissociation (≈ 100 years), it was initially thought that all molecular gas in these sources would be destroyed. It has become increasingly apparent over the last 10 years, however, that molecules survive in significant quantities in PN (e.g., refs. 54 and 55); this result was in fact predicted by Hartquist and collaborators (56–58) long before any observations. The persistence of molecular gas is thought to originate from Parker instabilities in the AGB and PPN stages, which create large fragments in the shells that remain into the PN phase (58). It is speculated that the clumps, which are dusty, dense ($\approx 10^5$ to 10^6 cm^{-2}), and cold ($T \approx 10$ – 25 K), are in pressure equilibrium with the ionized gas. Molecules in these knots are consequently shielded from photo-destruction and survive despite UV radiation (58).

A list of molecules found in PN is presented in Table 3. Again, the variety of species is limited relative to IRC+10216. Table 3 also reflects abundances of one PN, NGC 7027. This source may not be typical, as it is young ($<1,000$ yr) and has an extremely hot central star ($T_* \approx 200,000$ K). Based on NGC

Table 3. Molecules identified in PN

CO	HCN	HCO ⁺
CN	HNC	CO ⁺
CH	CCH	N ₂ H ⁺
OH	H ₂	CH ⁺

7027 (59), these sources appear to have a chemistry centered around radicals (OH, CH, CN, and CCH) and ions (HCO⁺, CH⁺, N₂H⁺, and CO⁺), reflecting the copious amounts of UV radiation in these regions. The refractory chemistry of silicon and metals, which is still active in PPN such as CRL 2688, is not apparent. Furthermore, calculations have suggested that the chemistry is quite dynamic, and molecules from the remnant envelope have probably been photo-dissociated and reformed more than once (60).

Only limited chemical studies of other PN have been conducted. CO, CN, HCN, HNC, and HCO⁺ are common to these objects, including highly evolved ones such as NGC 7293, the Helix Nebula (54), which is quite old ($\approx 10^4$ yr). Recent observations have also found that CCH exists in evolved PN, as predicted by Howe, Hartquist, and Williams (58). As shown in Fig. 4, CCH has been identified by two hyperfine components of the N = 1 \rightarrow 0 transition near 87 GHz in the Helix, as well as in the Ring Nebula, M 4-9, and NGC 6781 (61). The spectrum was measured at the position of peak CO emission (53), as indicated by the overlaid contours on the optical image. CCH and CO appear to be present in gas just outside the ionized nebula, illustrating two important points: (i) the molecular gas is probably critical in determining PN morphology, and (ii) carbon-rich chemistry of the earlier AGB star may be partly preserved into the PN stage.

Molecular Recycling Into Diffuse Clouds?

What becomes of the molecular gas in old, dispersing, PN? Some insight may be gained by looking at observational data from diffuse

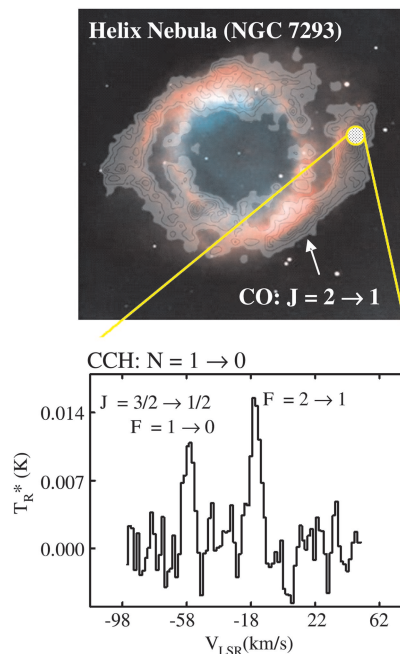


Fig. 4. Map of the CO ($J = 2 \rightarrow 1$) emission (53) superimposed over the optical image of the PN NGC 7293 (Helix Nebula), as well as a spectrum of CCH observed at the strongest CO position, measured with the Arizona Radio Observatory 12-m telescope. The two hyperfine components of the N = 1 \rightarrow 0, $J = 3/2 \rightarrow 1/2$ transition are present, indicated by the F quantum number.

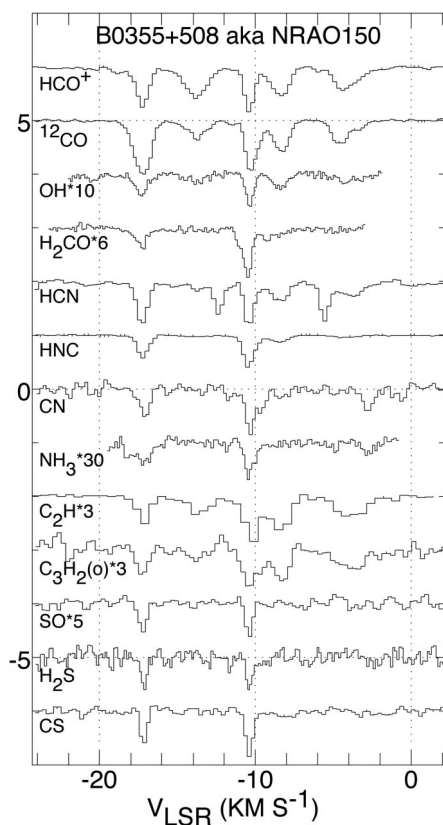


Fig. 5. Molecular spectra obtained from diffuse clouds along the line of sight toward NRAO 150 (62, 63). The intensity scale is $f e^{-\tau}$, where $f = 1$ unless otherwise indicated and τ is the optical depth of the molecular transition.

clouds obtained by Liszt *et al.* (62) and Lucas and Liszt (63). Those authors have detected numerous molecules in these clouds, which have average densities of $\approx 1\text{--}10\text{ cm}^{-3}$. They discovered these “hidden” species by observing absorption spectra against background quasars. A sample of their detections toward one object, NRAO 150, is displayed in Fig. 5. The molecules observed include HCO^+ , HCN , OH , HNC , CN , CO , and CCH , a list almost identical to what has routinely been detected in PN. Also, diatomic species commonly found in diffuse gas such as CH , OH , and CH^+ (64) are present in such nebulae. [There are additional molecules in diffuse gas (C_3H_2 , NH_3 , H_2S , and H_2CO), which perhaps in due course may be found in PN.]

The abundances of the more complex molecules in diffuse clouds are $f \approx 0.1\text{--}10 \times 10^{-8}$, relative to H_2 (62), at least several orders of magnitude higher than predicted by models (e.g., ref. 64), and almost comparable to those found in the dense dark cloud TMC-1. Because molecules are readily destroyed by photo-dissociation in the low densities of diffuse gas, with lifetimes of $\approx 10\text{--}100\text{ yr}$ (64), these detections pose a difficult puzzle for interstellar chemistry. On the other hand, some fraction of the self-shielding knots from PN may continue to persist as the shell material disperses into the interstellar medium. The molecular material in diffuse clouds could be connected to these self-preserving globules.

Eventually diffuse gas gravitationally collapses into more dense objects, creating so-called molecular clouds. Some molecular content of the diffuse gas may survive during this process. If so, diffuse clouds could be seeding dense cloud chemistry, which, at some level, may be traceable back to circumstellar shells and PN.

Such molecular cycling might solve two current puzzles in dense cloud synthesis. First, it would mean that the chemistry in

such objects begins with molecules as large as five atoms. It is therefore likely that more complex species can be created within a typical cloud lifetime ($\approx 10^6\text{ yr}$). The formation of complex compounds such as methyl formate has been a dilemma for ion–molecule models for some time (e.g., ref. 65). It is interesting to note that the source with the most complex species is SgrB2(N), a cloud near the galactic center. As shown in Fig. 6, which is published as supporting information on the PNAS web site, this object contains a wide variety of organic molecules (66). The galactic center has undergone many cycles of star formation, including processing by AGB stars, as demonstrated by the high $^{13}\text{C}/^{12}\text{C}$ ratios found (67).

A second dilemma is the large fraction of species containing carbon-carbon bonds in dense clouds. As Fig. 6 illustrates, many molecules present in such objects contain more than one carbon atom, including CH_3CHO , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CN}$. Yet, in the general interstellar medium, $\text{O} > \text{C}$ by a factor of ≈ 1.6 (68), and 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 could be initiated in dense clouds if they were seeded by C-C bonds, which remained sufficiently intact through the course of stellar/interstellar evolution after circumstellar formation.

Organic compounds are also found in meteorites such as Murchison and Tagish Lake (69). The high D/H ratios found in some of these compounds are decisive evidence that they originated in cold, interstellar clouds. There is some thought that the bulk of carbon on Earth today was brought from interstellar space via meteorites, comets, and interplanetary dust particles (70, 71). This organic material may have led to living systems, but its ultimate origin could be coupled to the carbon-rich chemistry of evolved stellar envelopes.

Conclusions and Remaining Questions

The chemistry occurring in evolved stars has many distinctive features, in particular carbon, silicon, and metal-enhanced molecular synthesis. Aspects of this chemistry appear to be preserved as these objects progress into PN. The amazing similarity between compounds found in diffuse clouds and PN suggests a connection. The complex chemistry of dense clouds could be better explained if diffuse gas provided the molecular starting materials, in particular carbon–carbon bonds.

Within this simple picture, there are many aspects of the chemistry in evolved stars that are not understood. Is IRC+10216 truly representative of carbon-rich AGB envelopes? What elemental abundances result from AGB nucleosynthesis? What is the contribution of oxygen-rich shells to molecule formation? What is the fate of clumps of gas and dust found in old PN? What is the original source of carbon–carbon bonds? Such questions have implications ranging from the origin of the elements to the origin of life, from galactic chemical evolution to the death of stars. Our picture of the chemistry in circumstellar shells is only beginning to emerge. More observational data on a wider sample of these objects, PN, and even diffuse clouds are needed, as well as the laboratory spectroscopy and theoretical modeling that support this tantalizing aspect of astrochemistry.

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