Molecules from evolved stars and their role in the cycle of the ISM

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Abstract. The ejecta of evolved stars are among the most efficient chemical laboratories in the Universe. Many of the chemical compounds synthesized in these environments probably travel along the interstellar medium and may be ultimately delivered to planets. However, we still do not understand many of the chemical processes at work during the evolution from the AGB phase to the PN. Here we review key aspects of our current understanding of the chemistry of AGB and post-AGB envelopes, highlighting the issues that are yet to be understood.

1 Introduction

Evolved stars play a key role in the cosmic cycle of matter that connects interstellar clouds with planetary systems hosted by stars. It is well known that at the end of their lives, stars inject an important fraction of their mass into the surrounding interstellar medium. The mass loss process itself is a factory of chemically complex compounds that may survive the whole cycle of matter and end up in planet-forming systems, possibly playing a role on prebiotic chemistry in the early Earth and recently formed planets.

There is evidence that dust grains formed in the atmospheres of Asymptotic Giant Branch (AGB) stars have survived the whole cycle of matter chemically intact since they are identified in primitive meteorites in our Solar System [37].

Large organic molecules are detected in nebulae around evolved stars. The simplest aromatic molecule, benzene, was identified in the pre-planetary nebula (PPN) CRL 618 [8]. The so-called unidentified infrared (UIR) emission features, thought to arise from polycyclic aromatic hydrocarbons (PAHs) [4, 25], are widely observed toward planetary nebulae (PNe) [19], and fullerenes have been also detected mainly toward PNe [6, 18]. These large organics are synthesized around evolved stars and, provided they are large enough to be stable against ultraviolet (UV) radiation, they probably survive all the way along the cycle of matter, either in the gas phase or deposited on dust grains, down to the formation of planets [24]. Moreover, given that C_{60}^{+} has been identified as carrier of various diffuse interstellar bands (DIBs) [7], it is very suggestive to think that DIB carriers are also synthesized during the late evolutionary stages of stars.

It is clear that large organic molecules are synthesized in situ around evolved stars, although it is not yet clear which is the underlying chemical mechanism and whether they are formed during the AGB or post-AGB stage. UIR emission features are not detected toward

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Table 1. The 91 molecules detected in IRC +10216 (as of July 2022).

10^{-3}	CO						
10^{-4}							
		C_2H_2					
			HCN				
10^{-5}							
		CH_4					
		C_2H	NH_3				
		C_4H	CN				
		C_2	HC_3N		SiC_2		
10^{-6}		C_3			SiS		
		C_4H_2	C_3N	CS	Si_2C		
					SiH_4		
			HC_5N		SiO		HCl
10^{-7}	H_2O	C_5	HNC				
		l-C_3H	CN^-				
	OH	C_6H			SiC		
		C_5H	CH_3CN	C_2S			$AlCl$
		c-C_3H_2					
		CH_3C_2H					
		c-C_3H	HC_7N			HCP	
		C_2H_4					MgC_4H
	H_2CO	H_2C_4		C_3S	CH_3SiH_3		MgC_6H
10^{-8}						CP	HF
		C_8H	HC_9N	H_2CS	SiN	PH_3	$MgNC$
			CH_2CN				AlF
			HC_2N				MgC_3N
			C_5N				MgC_5N
		C_7H	$HCCNC$				MgC_2H
		H_2C_6	C_2H_3CN	H_2S	c-SiC_3		$NaCN$
		C_6H^-	C_5N^-		SiC_4		
	C_3O	C_8H^-	HC_4N		$SiCN$		
		H_2C_3	C_3N^-	C_5S	$SiNC$	PN	$NaCl$
10^{-9}						C_2P	$AlNC$
	HCO^+		$HNCCC$				$MgCN$
		C_4H^-					KCl
							KCN
							$FeCN$
							$HMgNC$
10^{-10}							$CaNC$

The 91 molecules detected in IRC +10216 ordered vertically by abundance relative to H_2 and grouped in different columns according to their chemical composition. Colors indicate their most probably origin: either chemical equilibrium in the stellar atmosphere (red), non-equilibrium chemistry in the inner envelope (green), and photochemistry in the outer envelope (blue). Molecular hydrogen (not shown) has been also detected in IRC +10216 [17].

AGB stars, although this does not necessarily imply that their carriers are not present at this stage. It may simply reflect the lack of a sufficiently intense UV field, which is necessary to excite PAHs and produce the emission features in the infrared [5]. Attempts to detect DIBs in circumstellar envelopes around AGB stars have resulted inconclusive [23]. In the remaining of this contribution we briefly discuss what do we know about the chemical composition and the chemical processes at work in envelopes around AGB and post-AGB stars.

2 Chemistry in the AGB phase

The most important parameter that governs circumstellar chemistry during the AGB phase is the C/O elemental abundance ratio at the stellar surface, which dichotomizes AGB stars

Table 2. The 27+7 molecules detected in oxygen-rich AGB envelopes (as of July 2022).

$\mathbf{10^{-4}}$	CO					
	H_2O					
$\mathbf{10^{-5}}$	OH					
	CO_2					
			SO_2	SiO		
		NO	SO	SiS		
					PO	
$\mathbf{10^{-6}}$			H_2S			
		HCN	CS			
		NH_3			PN	
	H_2CO		OCS			
$\mathbf{10^{-7}}$		CN				TiO
		HNCO				TiO_2
	CH_3OH		NS			AlO
$\mathbf{10^{-8}}$	HCO^+	N_2H^+	HNCS			AlF
						AlCl
		HNC				NaCl
		HC_3N				MgS ?
$\mathbf{10^{-9}}$						AlOH

Table shows in color black the 27 molecules detected in oxygen-rich AGB envelopes (from the inventory of molecules in IK Tau, *o* Cet, and R Leo). The molecule MgS, tentatively detected toward OH 26.5+0.6 [21], is included with the abundance predicted by chemical equilibrium [3]. Also included in color magenta are 7 molecules detected in other oxygen-rich evolved stars, such as OH 231.8+4.2 (probably in a post-AGB stage) and the massive evolved stars IRC +10420 and VY CMa.

as carbon-rich (C/O > 1) or oxygen-rich (C/O < 1). Chemical equilibrium indicates that the pressures and temperatures of AGB atmospheres lie in the domain of stability of CO, meaning that this molecule locks most of the limiting element and allow the element in excess to form C-bearing molecules, when C/O > 1, or O-bearing-molecules, when C/O < 1. Carbon-rich envelopes contain a far richer diversity of molecules than oxygen-rich envelopes. As an illustration in Table 1 we show the molecules detected to date in the C-rich envelope IRC +10216 (the nearest high mass loss rate C-rich AGB star), which can be compared with Table 2, where we list the 27 molecules detected in O-rich AGB envelopes together with 7 molecules detected in related environments. That is, the inventory of molecules in C-rich AGB envelopes is about three times larger than in O-rich envelopes, and this is due to the exceptional chemical properties of carbon and its ability to form strong C-C bonds

Chemical equilibrium provides a good overall description of the chemical composition of the inner regions of AGB envelopes, although there are notable failures. Concretely, some molecules are observed to be anomalously abundant compared with the predictions of chemical equilibrium, which points to some non-equilibrium chemical processes at work in the inner layers of AGB envelopes. The most dramatic cases of anomalously abundant molecules are the hydrides H_2O, NH_3, SiH_4, and PH_3 in C-rich envelopes, while in O-rich envelopes HCN, NH_3, and CS stand out [3]. Two mechanisms have been proposed to account for these anomalies, either shock-induced chemistry associated to the stellar pulsation [13, 14] or photochemistry driven by the penetration of external UV photons through the clumpy structure of the envelope [1, 34]. None of the two mechanisms are fully satisfactory. For example, the shock-induced scenario involve shocks of tens of km s^{-1}, which are not evident in the line profiles of IRC +10216 seen at high angular resolution [10], and the abundance of H_2O in C-rich outflows is extremely sensitive to the chemical network adopted [13, 14]. In the case of the photochemical scenario, the resulting molecular abundances are very sensitive to the envelope clumpiness, which is a parameter difficult to constrain from observations.

It is worth noting that chemical equilibrium predicts PAHs to be abundant at a few stellar radii from a C-rich AGB star [11, 33], although models based on chemical kinetics predict a low yield of PAHs in the inner wind of C-rich AGB stars [12]. That is, the presence of abundant PAHs in the inner envelopes of C-rich AGB envelopes is thermodynamically favorable, although their formation would likely occur under non-equilibrium conditions, in close connection with the formation of carbonaceous dust, and models do not predict high yields of PAHs. Recently, the formation of carbonaceous dust in C-rich AGB outflows has been mimicked in the laboratory by exposing carbon atoms to H_2 under ultra-high vacuum conditions [27]. In these experiments, in which amorphous carbon nanoparticles were produced, aliphatic carbon clusters were formed but neither aromatic species nor fullerenes were observed.

Understanding how dust is formed in the surroundings of AGB stars is one of the main pending challenges. Chemical equilibrium indicates that the first condensates, graphite or amorphous carbon in carbon-rich stars and alumina (Al_2O_3) in oxygen-rich stars, are expected to appear at temperatures below 2000 K [3], while temperatures at the stellar photosphere of AGB stars are typically above 2000 K. That is, the stellar surface should be free of solids and dust formation is therefore expected to occur farther out at the expense of gaseous particles. Identifying these gas-phase precursors of dust is therefore of great interest to shed light on the dust formation process. Some constraint are available from single-dish observations of AGB envelopes, which suggest that SiC_2, SiO, and CS (in C-rich objects) while SiO and possibly SO (in O-rich sources) act as gas-phase precursors of dust [28–30]. Interferometric observations of O-rich AGB stars have also allowed to observe two potential gas-phase precursors of alumina dust, AlO and AlOH, in the surroundings of the stellar atmosphere [15, 22]. The abundances derived are well below the elemental abundance of aluminum, which suggests that the remaining aluminum could have already participated in the formation of Al_2O_3 dust.

In the outer layers of AGB envelopes the penetration of external UV photons modify the chemical composition of the outflowing material through photochemistry, which in the case of C-rich envelopes drives an interesting chemical processing. Detailed studies of IRC +10216 show that the photodissociation of HCN and C_2H_2 result in the formation of polyacetylenic chains of increasing length, such as polyynes $C_{2n+2}H_2$ and cyanopolyynes $HC_{2n+1}N$, with $n = 1, 2, 3, ...$ [2]. Large unsaturated organic molecules are therefore formed under the action of photochemistry in the outer layers of C-rich envelopes, although these are mainly chains. Aromatic rings are not predicted to form through this mechanism.

3 Chemistry in the post-AGB phase

As an AGB star evolves from red giant to white dwarf, the chemical composition of the circumstellar material experiences important changes driven by the increasing UV flux from the central star. This energetic radiation causes the ionization and photodissociation of molecules and, as a consequence, the chemical complexity drops drastically. As an example, we show in Table 3 the molecular inventory in the C-rich PN NGC 7027, which can be compared to that of IRC +10216 shown in Table 1. Only a few simple molecules survive the AGB → PN transition. This sharp decline in the chemical complexity contrasts with the appearance in PNe spectra of UIR and fullerene emission features, which demonstrate that large and chemically complex organic molecules are present at this stage. Although it is not completely settled whether such molecules are formed during the PPN or PN stage or are inherited from the previous AGB phase, the fact that the simplest aromatic ring, benzene, is detected in the PPN CRL 618 and not in IRC +10216 suggest that aromatic molecules of increasing size are

Table 3. The inventory of molecules detected in NGC 7027 (as of July 2022).

10^{-3}	CO			
10^{-4}				
10^{-5}				
10^{-6}		CH		
10^{-7}	OH HCO^+		HCN	
10^{-8}	H_2O	CH^+ C_2H	CN HC_3N	CS
10^{-9}		c-C_3H_2	HNC N_2H^+	HCS^+
10^{-10}	CO^+			

Table constructed from [36] and references therein.

formed during the PPN stage due to photoprocessing, either through a bottom-up mechanism starting from simple hydrocarbons such as C_2H_2 [9] or by a top-down scheme involving the photoevaporation of very small carbonaceous grains [31]. Given that DIBs are thought to arise from large organic molecules, it is not unwise to think that they could be synthesized around evolved stars, although attempts to search for DIBs around post-AGB objects have been inconclusive [16, 26].

Insights into the chemical processing taking place after the AGB phase can be provided by the study of objects in a very early post-AGB stage, as it is likely the case of OH 231.8+4.2. Unexpected molecules for an O-rich AGB or post-AGB envelope such as HNCO, HNCS, HC_3N, and CH_3OH have been detected in this object [32, 35]. It is yet unclear how are these molecules formed, but shocks emerge as a feasible agent able to drive their synthesis. In particular, CH_3OH emission in OH 231.8+4.2 shows a bipolar outflow morphology [32], similarly to SiO, which strongly suggests that methanol is released from grains by shocks. The most probable formation scenario thus involves the previous condensation of CO onto dust grains, followed by hydrogenation. Although ices are not a typical ingredient around evolved stars, water ice has been observed toward some evolved objects [20]. The detection of methanol implies that CO ice should also be present. The survival of CO ice is more challenging than that of H_2O ice because it requires very low dust temperatures in order to avoid thermal sublimation.

4 Conclusions

The ejecta around evolved stars are formidable factories of organics. In particular, planetary nebulae show in their spectra emission features characteristic of very large organic molecules such as aromatic polycycles and fullerenes, the formation of which is still a mystery. In the previous AGB stage, a wealth of organic molecules are formed due to a variety of processes such as photochemistry, but these are mostly carbon chains rather than aromatic cycles. Currently, there is no evidence on the formation of aromatic molecules during the AGB phase from either observations, chemical models, or experiments. The current paradigm is therefore that the aromatization takes place during the post-AGB phase, although this scenario is open for new discoveries.

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