



**QUEEN'S
UNIVERSITY
BELFAST**

Chemistry in the Circumstellar Medium: Unveiling the Dust Formation Zone

Millar, T.J. (2008). Chemistry in the Circumstellar Medium: Unveiling the Dust Formation Zone. *Astrophysics and Space Science*, 313(1-3), 223-227. <https://doi.org/10.1007/s10509-007-9636-z>

Published in:
Astrophysics and Space Science

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access

This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: <http://go.qub.ac.uk/oa-feedback>

Chemistry in the circumstellar medium

Unveiling the dust formation zone

T.J. Millar

Received: 23 February 2007 / Accepted: 26 July 2007 / Published online: 12 September 2007
© Springer Science+Business Media B.V. 2007

Abstract The growth of dust grains in the inner regions of late-type stars is shrouded in mystery due to the difficulty of understanding the growth of heterogeneous particles from simple atoms and molecules and the lack of observational data. This article reviews the molecular processes important in circumstellar envelopes and discusses how ALMA might be used to probe the dust formation zone either directly or indirectly.

Keywords Circumstellar envelopes · AGB stars · Astrochemistry

1 Introduction

Significant amounts of interstellar dust are known to be formed in the inner regions of the circumstellar envelopes of asymptotic stars. These grains are intimately linked to the mass-loss process as they absorb stellar radiation and share the momentum they gain with the gas, dragging gas away from the stellar surface and initiating a mass-loss which leads to the creation of a circumstellar envelope (CSE) which might contain up to a solar mass of gas. These CSEs incorporate a huge range in physical conditions, from very dense ($n(\text{H}_2) \sim 10^{15} \text{ cm}^{-3}$), hot ($T \sim 2000 \text{ K}$) molecular gas just above the photosphere, to gas with properties similar to that found in dark molecular clouds, to diffuse regions dominated by the external UV radiation field which produces atomic gas far from the central star. Overall the gas

density follows an r^{-2} density distribution, while the dust extinction, which is proportional to the dust column density to infinity and controls the effects of the external UV radiation field, is proportional to r^{-1} . These overall distributions break down close to the photosphere where stellar pulsations give rise to periodic shock waves which compress, heat and alter the chemical composition of the gas. In the following, I will make a few comments about each of the chemically active regions in the CSE with particular attention on C-rich envelopes.

2 CSE chemistry

As mentioned above, the wide range in physical conditions experienced by a parcel of gas and dust as it traverses the envelope of the star on their way to the interstellar medium makes it appropriate to consider individual regions of activity.

2.1 LTE chemistry

Local Thermodynamic Equilibrium (LTE) holds in regions of high temperature and density close to the photosphere and molecular abundances are determined by elemental composition of the gas and pressure. Molecules form which minimise free-energy with the result that in carbon stars, the most abundant species are H_2 , CO , N_2 , C_2H_2 , and HCN , while in oxygen-rich stars, H_2 , H_2O and CO dominate. Models for LTE chemistry have a long history and have been extensively developed by Tsuji and collaborators (e.g. Tsuji 1973). These species are very stable and act as parents for the rich non-LTE chemistry which occurs further out in the envelope.

T.J. Millar (✉)
Astrophysics Research Centre, School of Mathematics and
Physics, Queen's University Belfast, Belfast BT7 1NN, UK
e-mail: Tom.Millar@qub.ac.uk

In this region, molecules such as CS are a natural target for ALMA, particularly if they are pumped by IR radiation in which case maser emission may ensue. The CS abundance itself depends very sensitively on the C/O ratio and may be a useful tracer around $C/O \sim 1$ and in monitoring the evolution of the AGB to protoplanetary nebulae (PPN) to planetary nebula (PN) phase. Infrared pumping often leaves molecules in vibrationally excited states and Fronfría et al. (2006) have recently detected vibrationally excited HCN up to $v = 4$ in IRC+10216. Such emission is limited to within a few arcsec of the star.

2.2 Shocks and dust formation

AGB stars are a prolific source of dust particles but the process is difficult to model quantitatively. In the absence of pulsations, the r^{-2} density distribution means that gas does not necessarily spend enough time in a high density zone where collisions can be frequent enough to allow dust particles to grow efficiently. Dust nucleation requires a cooling flow, high collisional rates and time. Periodic shock waves, caused by the pulsations of the central star allow the gas to be heated and compressed thus reducing collisional time scales and allowing particles to nucleate in the cooling post-shock gas. Moreover, the mass-loss process is not efficient until the grains have grown to the point where they can absorb enough of the stellar radiative momentum. Before this stage is reached, an individual parcel of gas may experience several shock heating/cooling cycles each of which can affect its chemical composition, and in particular aid the growth of the seed molecules from which the dust grains grow. To give an idea of the parameter space, a 20 km s^{-1} shock at 1.2 stellar radii increases the gas temperature immediately to 4500 K in a region with gas density $\sim 6 \times 10^{15} \text{ cm}^{-3}$.

The spatial scale on which dust nucleates is around 5 stellar radii, a region which is again exposed to IR pumping. Vibrationally excited and masing molecules are natural probes. For example, Fronfría et al. (2006) have detected the thermal $v = 1$ transitions of SiS while observations of the $J = 5-4$ transition of SiO with the SMA have enabled Schöier et al. (2006) to show that the abundance of SiO is much more abundant at 3–8 stellar radii than its LTE abundance, indicating that it can be formed in the shock chemistry; at larger radii the SiO abundance decreases, most likely due to incorporation of SiO in to the grains, although other processes may be at work here.

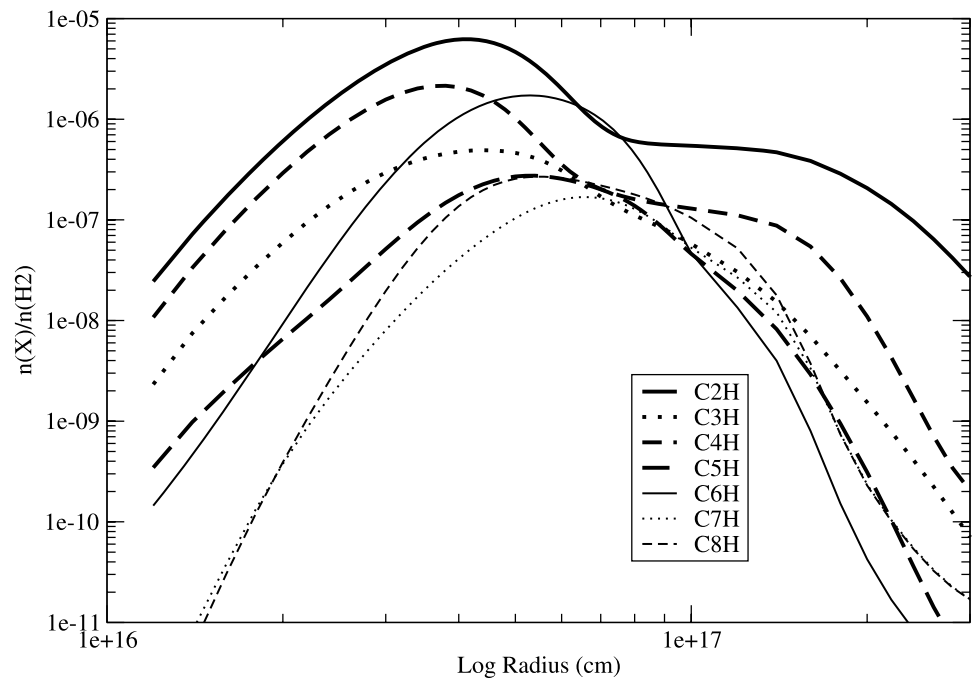
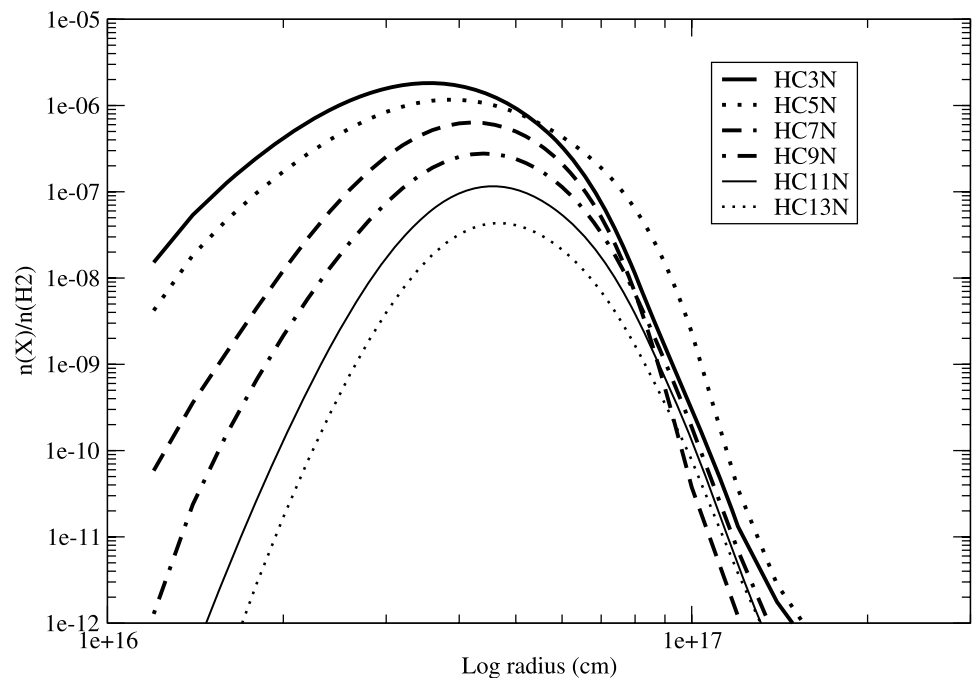
Willacy and Cherchneff (1998) first investigated chemistry in periodic shocks and found that the process could be broken down into three major events. First, immediately post-shock where conditions are so extreme that H_2 and other molecules produced in LTE are completely destroyed. Second, the cooling post-shock gas in which H_2 and other

molecules can form. Third, a ‘freeze-out’ region in which the dynamical time is less than the chemical time so that chemical abundances get frozen in. Abundances at the end of one pulsation, when the gas has essentially relaxed back to its pre-shock conditions, can be much different from their LTE values. Pulsational shocks have been studied to see if they are the cause of some of the abundance anomalies, including the detection of water in the CSE of the carbon-rich star IRC+10216. Although no significant abundance of water is formed, other abundances can be different from LTE values by many orders of magnitude. Willacy and Cherchneff (1998) found that HCN and CS are destroyed and SiO enhanced by periodic shocks. Oxygen-rich stars are expected to form relatively few carbon-bearing molecules if LTE holds, CO being the notable exception. Duari et al. (1999) discussed pulsational shock chemistry in O-rich stars and found that HCN, by eight orders of magnitude, and CS and CO_2 , both by three orders of magnitude, are enhanced over their LTE values. For S-type stars, that is $C/O \sim 1$, Duari and Hatchell (2000) have shown that HCN is enhanced by some four orders of magnitude. Such a result is consistent with the detection of vibrationally excited HCN, pumped by IR radiation within 33 stellar radii in χ Cygni (Duari and Hatchell 2000).

In carbon-rich stars the growth of carbonaceous grains is thought to proceed through the build up of PAH particles with the abundant acetylene molecule acting as the feedstock for this growth. Cau (2002) has used the model developed by Frenklach and Fiegelson (1989) to discuss the growth of PAH molecules following a pulsational shock. Cau’s model used the same chemical synthesis which produces the first ring molecule, benzene, to build bigger cyclic species, and found that a molecule with seven rings was formed very efficiently during one pulsational period. His model also allowed these ring molecules to associate with themselves to form dimers, again finding that dimer growth is efficient during one period. However, the yield of dimers produced, that is the abundance of carbon in dimers compared to the total abundance of all carbon, is not very large, certainly not large enough to provide seed particles for the growth of the carbonaceous grains observed in the CSE.

3 The photochemical region

The fact that AGB stars are cool means that the UV photons which affect the chemistry are external rather than internal. Since dust extinction is inversely proportional to radial distance from the star, UV photons photodissociate parent molecules at distances which are about 100 times larger than the pulsational/dust formation region. Little is known observationally about the intermediate region although there is some evidence, from the observations of SiO (Schöier

Fig. 1 The radial distribution of hydrocarbon chains**Fig. 2** The radial distribution of cyanopolyynes

et al. 2006) discussed above, that the gas-grain interaction is important. This interaction may result in both the depletion of molecules, such as SiO, and to formation, particularly through the formation of hydrogenated species such as NH_3 , CH_4 , and C_2H_4 . The most stable species produced in the LTE and dust-forming regions, H_2 and CO , are unaffected by the radiation field so that it is the photodissociation and photoionization of acetylene which produces the ions and radicals which drive an extensive organic chem-

istry through both ion-neutral and neutral-neutral reactions. Figure 1, which presents the radial distributions of some hydrocarbon species, shows that species with an even number of carbon atoms tend to be more abundant than those with an odd number, due to the importance of reactions involving C_2H and C_2H_2^+ . Figure 2 shows the radial distributions of the cyanopolyne species which are formed mainly in neutral-neutral reactions. We see that their abundances decrease as the chains get longer while there is a shift in the ra-

dius at which the peak abundances occur. Such a shift could be observed through interferometric observations; current observations show that the distributions of HC_3N and HC_5N are very similar (Guélin et al. 2000). ALMA will be able to investigate this with greater spatial resolution and extend the study to larger cyanopolyynes.

The recent detection of C_6H^- in IRC+10216 by McCarthy et al. (2006), was predicted implicitly by the calculations of Millar et al. (2000) who predicted anion/neutral ratios of between 0.01 and 0.4 based on efficient formation through radiative electron attachment, which occurs when the neutral has six or more atoms, and destruction mainly through photodissociation. Detailed calculations by Millar et al. (2007) show that anions as small as C_4H^- should be detectable in IRC+10216. Despite the fact that the radiative attachment of electrons is only about 1% efficient, the large column density of C_4H in IRC+10216 means that the column density of C_4H^- is appreciable.

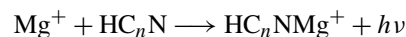
4 Metals

A large number of metal-containing molecules have been detected in IRC+10216 and other more evolved objects. The LTE calculations predict metal halides should be present and NaCl , KCl , AlCl and AlF have been observed with distributions which peak on the star and have spatial extents of a few arcsec. Fractional abundances can be large—Highberger et al. (2001) and Cernicharo and Guélin (1987) find AlF/H_2 and $\text{AlCl}/\text{H}_2 \sim 10^{-7}$, which implies that a large fraction of elemental aluminum, which is depleted by several orders of magnitude in diffuse interstellar clouds, presumably in refractory grain cores, is not incorporated into dust grains.

ALMA will be able to probe this central region very effectively and test LTE models, test the pulsational shock models and the growth of carbon chains, rings and PAH molecules in the dust-forming region through study of their high frequency ro-vibrational transitions.

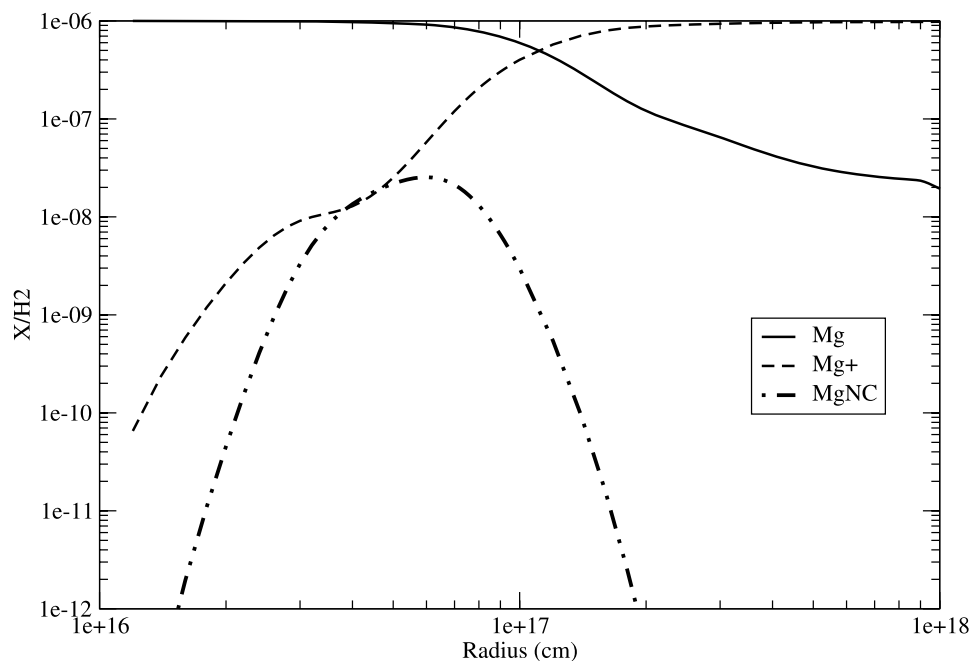
Other metal molecules have a shell-like distribution on a scale of about 15 arcsec, very similar to those found for the cyanopolyynes, indicating that they are formed by chemistry, either in the gas-phase or as the result of some desorption process from the dust grains. The molecules tend to be cyanides or isocyanides and include MgCN , MgNC , AlNC , SiCN and SiNC . The thickness of the emission is only a few arcsec and ALMA will be ideally suited to their study. Careful analysis should enable us to determine the fraction of metals which have never been incorporated into the dust grains, and thereby constrain models of grain nucleation and growth, or the fraction of metals which have been released from dust grains in the outer envelope, which may impact our understanding of grain erosion in the interstellar medium.

In order to see if the metal cyanides might be formed by gas-phase chemistry rather than release from dust grains, we have performed some test calculations using the chemical scheme proposed by Dunbar and Petrie (2002) in which MgNC is formed by the radiative association of Mg^+ with the cyanopolyynes:



where $n = 3, 5, 7, \dots$ followed by dissociative recombination with electrons. Figure 3 shows the fractional abundance of MgNC which results. For an initial fractional abundance

Fig. 3 The radial distribution of MgNC



of Mg of 10^{-6} , the MgNC column density calculated is $1.1 \times 10^{13} \text{ cm}^{-2}$, compared to $\sim 2 \times 10^{13} \text{ cm}^{-2}$ observed for each of MgNC and MgCN. The dominant reaction is actually with HC₇N which has an association rate about four orders of magnitude larger than that of HC₃N at low temperatures. The initial Mg abundance adopted is very large, about 3% of the cosmic abundance and may be unrealistic but the result, since it depends on the presence of Mg⁺ in the outer envelope, will hold as long as this fractional abundance of Mg is contained in parent gas-phase species.

Much of the molecular emission detected in the outer envelope appears to correlate well with the dust arcs and rings detected by Mauron and Huggins (2000); ALMA will give a definitive answer. These arcs have density enhancements on the order of three and are thin with widths ranging from 0.5 to 3 arcsec, corresponding to time-scales of a few tens of years with the total radial extent of the arcs corresponding to around a thousand years. These structures may play an important role in the chemistry in the outer CSE since they not only provide additional extinction against the destructive radiation field but they also provide a higher collisional rate under which chemistry can proceed. These arcs of higher than average density are thought to have been formed through helium shell flashes. ALMA will be able to probe the isotopic abundance of these metal cyanides and therefore trace the nuclear chemistry in the star as a function of time.

5 Conclusions

ALMA will greatly aid the study of AGB stars. In particular, its sensitivity will allow us to investigate objects other than IRC+10216 in some depth and to look for similarities and differences. IRC+10216 will remain important as the closest AGB star to earth and we can expect a host of data on small-scale structure, including some hints as to how very non-spherical objects such as PPN and PN evolve from spherical AGB stars. Studies of the LTE region and pulsational shocks will enable us to tie down both the role of pulsations in creating the conditions under which dust grains nucleate and grow and the particular chemical intermediaries which promote this growth. While we expect

this to demonstrate the importance of hydrocarbon species in C-rich objects, we do not know the molecular precursors to dust in O-rich stars; ALMA will be able to tell us. A very exciting opportunity exists to probe nucleosynthesis in AGB stars as a function of time through observations of isotopic species as a function of radial distance in CSEs. Finally, the importance of the gas-grain interaction in the outer CSE is poorly understood. ALMA should be able to determine whether grains act as a source or sink of molecules, a role which may change with position in the envelope. If the interaction of grains with the external radiation field and/or cosmic-ray particles does provide a source of gas-phase species, it will have profound implications for the transport of complex organic molecules from AGB stars to interstellar clouds.

Acknowledgements Astrophysics at Queen's University Belfast is supported by a grant from PPARC.

References

- Cau, P.: *Astron. Astrophys.* **392**, 203 (2002)
- Cernicharo, J., Guélin, M.: *Astron. Astrophys.* **183**, L10 (1987)
- Duari, D., Hatchell, J.: *Astron. Astrophys.* **358**, L25 (2000)
- Duari, D., Cherchneff, I., Willacy, K.: *Astron. Astrophys.* **341**, L47 (1999)
- Dunbar, R.C., Petrie, S.: *Astrophys. J.* **564**, 792 (2002)
- Frenklach, M., Fiegelson, D.: *Astrophys. J.* **341**, 372 (1989)
- Fronfría Expósito, J.P., Agúndez, M., Tercero, B., Pardo, J.P., Cernicharo, J.: *Astrophys. J.* **646**, L127 (2006)
- Guélin, M., Lucas, R., Neri, R., Bremer, M., Broguiere, D.: In: Minh, Y.C., van Dishoeck, E.F. (eds.) *Astrochemistry: From Molecular Clouds to Planetary Systems*, p. 365. Kluwer, Dordrecht (2000)
- Highberger, J.L., Savage, C., Biegging, J.H., Ziurys, L.M.: *Astrophys. J.* **562**, 790 (2001)
- Mauron, N., Huggins, P.J.: *Astron. Astrophys.* **359**, 707 (2000)
- McCarthy, M.C., Gottlieb, C.A., Gupta, H., Thaddeus, P.: *Astrophys. J.* **652**, L141 (2006)
- Millar, T.J., Herbst, E., Bettens, R.P.A.: *Mon. Not. R. Astron. Soc.* **316**, 195 (2000)
- Millar, T.J., Walsh, C., Cordiner, M., Ní Chuímin, R., Herbst, E.: *Astrophys. J.* **662**, L87 (2007)
- Schöier, F.L., Fong, D., Olofsson, H., Zhang, Q., Patel, N.: *Astrophys. J.* **649**, 965 (2006)
- Tsuji, T.: *Astron. Astrophys.* **23**, 411 (1973)
- Willacy, K., Cherchneff, I.: *Astron. Astrophys.* **330**, 676 (1998)