Chemistry in AGB stars: successes and challenges

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Abstract. Emission and absorption line observations of molecules in late-type stars are a vital component in our understanding of stellar evolution, dust formation and mass loss in these objects. The molecular composition of the gas in the circumstellar envelopes of AGB stars reflects chemical processes in gas whose properties are strong functions of radius with density and temperature varying by more than ten and two orders of magnitude, respectively. In addition, the interstellar UV field plays a critical role in determining not only molecular abundances but also their radial distributions. In this article, I shall briefly review some recent successful approaches to describing chemistry in both the inner and outer envelopes and outline areas of challenge for the future.

1. Introduction
The circumstellar envelopes (CSEs) of AGB stars have long been known to present a rich molecular chemistry dominated by the interaction of external, interstellar FUV photons with parent species formed by thermal equilibrium processes near the photosphere [1, 2, 3, 4, 5, 6]. These, and more recent models [7, 8, 9, 10], have included more accurate descriptions of the physical conditions through the inclusion of clumps and density-enhanced rings in the CSE around the carbon-rich AGB star IRC+10216 (CW Leo) and through the addition of an extensive chemistry to describe the anions recently detected therein. The result is a consensus that the chemistry of the external envelope of IRC+10216, and by extension all AGB CSEs, is a photon-dominated process, a process whose final molecular products give information on mass-loss history, wind acceleration, dust formation, dredge-up and nucleosynthesis.

As well as studies of the chemical processes in the outer CSE, there have also been investigations of the the interaction between physics and chemistry in the inner CSE. For example, pioneering work on the chemistry induced by shock waves driven by stellar pulsations, [11, 12], has been extended [13, 14] to include the formation of new species and dust grain formation. These papers show that if shocks are strong then any molecules formed in thermodynamic equilibrium (TE) are rapidly destroyed in the immediate post-shock gas and that ‘parent’ species available for chemistry in the outer CSE are the end products of shock chemistry coupled with dust nucleation and growth. Challenges in understanding astrophysics and astrochemistry are, as ever in astronomy, driven by advances in observational techniques, instruments and facilities, most recently from the Herschel Space Observatory and ALMA.
2. Circumstellar chemistry
In this section I will briefly review some progress made in the chemistries of both O-rich and C-rich AGB stars and give some indication of current challenges.

2.1. O-rich late-type stars

Herschel and ALMA have both given us remarkable new information on the chemistry of O-rich CSEs, especially in the internal layers close to the photosphere. A large number of detailed observational studies [15, 16, 17, 18, 19] have both increased the range of species detected near the photosphere and provided much improved abundance estimates. These include studies of the refractory species SiO, TiO, TiO$_2$, AlO and AlOH, thought to be involved in the creation of silicate grains in these stars. Gobrecht et al. [14] have presented a very detailed model of dust formation in the O-rich star IK Tau. They considered chemical reactions in the shocked gas created by periodic stellar pulsations including the formation of small magnesium silicate and alumina clusters. Their best-fit model to observations starts with a periodic shock wave at a velocity of 32 km s$^{-1}$ at a radius of 1 R$_*$ which propagates outward with a velocity proportional to $r^{-2}$, where $r$ is the radial distance from the photosphere. For radii less than 2 R$_*$, the immediate post-shock densities are very high, greater than 10$^{13}$ cm$^{-3}$, and solidly in the regime where three-body reactions must be considered. The immediate post-shock temperature is also very high, more than 4000 K. At these densities and temperatures any molecules formed at thermal equilibrium (TE) in the photosphere are destroyed. Over a pulsational phase the density and temperature both fall and new molecules, whose compositions and abundances depend on chemical kinetics in a cooling, expanding flow, form. In this post-shock gas the chemistry is dominated by high temperature neutral-neutral reactions.

It is, of course, not surprising that in O-rich AGB stars, oxides, dioxides and hydroxides form readily through gas-phase chemistry. What is surprising, and certainly not predicted by the TE models is the presence of carbon-bearing molecules since all available carbon is expected to be locked up in CO. HCN, CS and CO$_2$, however, have relatively large abundances in the inner CSE. Gobrecht et al.[14] show that the chemistry, while complex, occurs on very fast time-scales. Thus CS forms in hot gas via:

\[
S + H_2 \rightarrow SH + H 
\]

\[
C + SH \rightarrow CS + H 
\]

\[
CO + SH \rightarrow OCS + H 
\]

\[
OCS + H \rightarrow CS + OH
\]

while CN and HCN form via:

\[
N + CO \rightarrow CN + O 
\]

\[
N + CS \rightarrow CN + S
\]

followed by

\[
CN + H_2 \rightarrow HCN + H
\]

Many of these reactions produce atomic hydrogen and the reverse reactions can be significant particularly when the abundance of H atoms is high. This occurs in the zone where dust precursors form since their formation converts some H$_2$ to H, as discussed below. Gobrecht et al. show that the gas-phase abundances calculated in their pulsational shock model at 6–8 R$_*$ match to within an order of magnitude those observed in the inner CSE, including HCN and CS.
Some molecules, not surprisingly, do not fit as well, for example, SO and SO$_2$. Danilovich et al. [20] have recently observed many transitions of these two molecules in R Dor and supplemented these with HIFI and other observations toward another four O-rich AGB stars. Using a detailed radiative transfer model they have constrained the distributions of these two species, both in abundance and in radial extent. In all five stars they find that SO$_2$ peaks on the stellar position whereas SO has a shell-like structure in IK Tau and R Cas, with a peak fractional abundance of $\sim 10^{-6}$ at 1.3 $\times 10^{16}$ cm.

When the peak position of the SO abundance is plotted against the wind density, $\propto \dot{M}/v_{\text{exp}}$, the results for R Cas, TX Cam and IK Tau follow a power-law dependence consistent with a circumstellar chemistry that is dominated by photodissociation in the outer envelope. SO$_2$, on the other hand, appears to be formed in the inner envelope where it should be formed in high-temperature chemistry. Although the latter fact is broadly consistent with the models of Gobrecht et al., the observed SO$_2$ abundances in R Dor and W Hya are an order of magnitude larger than predicted. Indeed all models fail to predict the very large abundances of SO and SO$_2$ which, in total, approach the elemental sulphur abundance. Model calculations generally predict sulphur to be in atomic form. A failure to agree in every respect with the observations should, however, be qualified by noting that an accurate description of the chemical kinetics occurring at high density and temperature is very difficult, especially in the case of O-rich AGB stars since inorganic chemistry is not so well studied in the laboratory. In addition, the balance between forward and reverse reactions, such as several of those above, is controlled by the H$_2$SO$_2$ abundance ratio which is not well determined either observationally or theoretically in the inner envelope.

In addition to the synthesis of molecules such as CO, H$_2$O, PN and HCl, which do not participate in dust formation, many other species are produced, several of which are likely to be intimately connected with the process of cluster formation and grain growth. Goumans and Bromley [21] discussed the detailed energetics of the formation of the dimers of enstatite (MgSiO$_3$)$_2$ and forsterite (Mg$_2$SiO$_4$)$_2$ from an initial gas of SiO, Mg, H$_2$ and H$_2$O at 1000 K. Although the initial dimerisation of SiO is an endoergic process, its equilibrium constant is $5.5 \times 10^{-4}$ at 1000 K, giving rise to a low abundance of Si$_2$O$_2$. Subsequent reactions with H$_2$O, which result in O-atom addition, followed by addition reactions with Mg are exoergic and can rapidly build dimers of both enstatite and forsterite. Since reactions of H$_2$O and Mg are exoergic for reactions with the dimers and larger clusters, silicate dust grains will form. Gobrecht et al [14] find dimer fractional abundances of $10^{-11}$ for enstatite and $5 \times 10^{-8}$ for forsterite at 3.5 $R_\star$. Dimer formation becomes very efficient outside 3 $R_\star$ with growth of silicate grains occurring between 3 and 6 $R_\star$. The authors follow the diffusion and coagulation of these particles to determine the grain size distribution as particles propagate outwards from 3.5 to 10 $R_\star$. Their results show that, in most cases, gas-phase abundances agree well with those determined for the inner wind of IK Tau, that forsterite grains are much more abundant than enstatite and metal oxides such as MgO and SiO, and that the overall dust-to-gas mass ratio is $\sim (1-6) \times 10^{-3}$, in reasonable agreement with observations.

Dust grains grow and their size distribution evolves over a number of pulsations as the gas is lifted slowly away from the photosphere. Due to their high binding energy, clusters of alumina form readily in the hottest gas near the photosphere in O-rich stars. For a radial drift velocity of 0.5 km s$^{-1}$, it takes 12 pulsations for the gas in IK Tau to move between 1 and 2 $R_\star$. Gobrecht et al. find that the size distribution of alumina favours larger particles and that growth of alumina grains stops beyond 2 $R_\star$ as all available aluminium is tied up in dust at that point. Such grains make only a minor contribution to the overall dust-to-gas mass ratio.

Silicates, on the other hand, form at larger radii, out to about 10 $R_\star$, since formation of the underlying dimer population cannot occur at high temperatures close to the star. The drift velocity in the silicate dust zone is larger, perhaps 1.5 km s$^{-1}$, than that in the alumina dust
zone since radiation pressure on the alumina grains begins to drive the mass loss. In this case, it
takes about 10 pulsations to move material from 3.5 to 6 R⋆, where the majority of silicate grains
form. As these grains form further from the star where densities are lower, silicates tend to have a
smaller size distribution that alumina grains. They do, however, because of the abundance of
silicon, magnesium and oxygen, contribute more to the dust mass. At 10 R⋆, the dust-to-gas mass ratio is \( \sim 2 \times 10^{-3} \), similar to those observed in O-rich AGB stars, with \( \sim 22\% \) of elemental silicon contained in the dust [14].

The outer CSE chemistry of O-rich AGB stars is dominated by effects produced by irradiation
of the outer envelope by interstellar FUV photons, that is, outer CSEs are examples of photon-
dominated regions (PDRs). Li et al. [22] have presented a detailed model of the outer CSE
chemistry of O-rich CSEs including, for the first time, shielding of N\(_2\) in addition to the usual self-
and mutual-shielding of H\(_2\) and CO. The authors assume an extensive list of parent species,
some 18, with initial conditions derived from either observation or from the shock-induced abundances calculated at 6 R\(_⋆\) by Gobrecht et al. [14]. They determine the chemistry of some 467 species using the latest release of the The UMIST Database for Astrochemistry [23]. Li et al. calculate radial abundances and column densities for mass-loss rates between \( 10^{-8} \) and \( 10^{-4} \) M\(_⊙\) yr\(^{-1}\) and expansion velocities of 10-40 km s\(^{-1}\) and make specific comparison with the observed abundances in IK Tau (\( M = 4.5 \times 10^{-6} \) M\(_⊙\) yr\(^{-1}\), \( v_{\text{exp}} = 24 \) km s\(^{-1}\)).

Li et al. were able to include a detailed consideration of N\(_2\) photodissociation due to over 25 years of laboratory and theoretical studies [24, 25, 26]. The rate coefficient is determined primarily by the overlap of the N\(_2\) absorption bands with those of H\(_2\) (mutual shielding) in the 912–1000 Å wavelength range together with self-shielding of N\(_2\). The overall shielding is thus a complex function of gas temperature and column density [27]. For parameters appropriate to IK Tau, for example, the radius at which the fractional abundance of atomic nitrogen, produced by the photodissociation of N\(_2\), reaches \( 10^{-5} \), increases from 1 to 6 \( \times 10^{16} \) cm; at a fractional abundance of \( 10^{-4} \) the increase is from 2.8 to \( 18 \times 10^{16} \) cm. Thus the atomic N abundance increases over an appreciable volume of the outer envelope. It has, however, only a limited impact on molecular abundances of species other than N\(_2\), in part because N is a fairly unreactive element at low temperatures and because the gas number density is low, \( \sim 2 \times 10^{4}(r/10^{16})^{-2} \) cm\(^{-3}\), and hence collision times are long. One molecule that shows a large difference when the N\(_2\) shielding is modelled correctly is NO, produced by the N + OH reaction, with its peak fractional abundance decreasing by over an order of magnitude from \( 10^{-6} \) to \( 6 \times 10^{-8} \) at a radius of 2.5 \( \times 10^{16} \) cm. For parameters appropriate to IK Tau, the increased abundance of N\(_2\) in the outer CSE leads to an increased N\(_2\)H\(^{+}\) abundance due to the proton transfer reaction, H\(^+_2\) + N\(_2\) \(\rightarrow\) N\(_2\)H\(^+\) + H\(_2\), at \( r < 10^{17} \) cm, and, at larger radii, the reaction He\(^+\) + N\(_2\) \(\rightarrow\) N\(_2\)H\(^+\) + He followed by N\(_2\)H\(^+\) \(\rightarrow\) N\(_2\)H\(^+\) + H. The abundance of N\(_2\)H\(^+\) is directly correlated with the initial (unknown) abundance adopted for N\(_2\) but its use as a tracer of N\(_2\) is limited since its predicted column density is low, only \( 3.4 \times 10^{10} \) cm\(^{-2}\).

2.2. C-rich late-type stars
Carbon-rich AGB star envelopes experience the same physical processes as those around O-rich
stars but their molecular content is very different, in both composition and complexity, primarily
due to the reactive nature and unique bonding properties of the carbon atom.

Cherchneff [13] has produced the most detailed model for the non-equilibrium chemistry of
the inner dust formation region of IRC+10216, by far the most well observed carbon-rich AGB
star. This star has a mass-loss rate of \( 1.5 \times 10^{-5} \) M\(_⊙\) yr\(^{-1}\), a terminal expansion velocity of
14.5 km s\(^{-1}\) and is known to contain at least 80 molecules in its CSE. The vast majority of these
molecules are hydrocarbons, well understood because of the high abundance of carbon relative
to oxygen in this star. A surprise discovery, however, was the presence of cold water [28], OH
[29] and H\(_2\)CO [30]. A number of explanations were put forward including the evaporation of icy
bodies within the CSE [31] and the formation of water on metallic grains [32] but all mechanisms had their problems. Subsequent to these observations, the Herschel satellite was used to survey water in a number of C-rich AGB stars and it was found that warm water was present in many [33, 34], indicating that abundant water was present close to the dust-forming regions in these stars. In this scenario, alternative formation mechanisms become possible, most importantly, shock chemistry following stellar pulsations [13], similar to that in O-rich stars, and photon-driven chemistry following deep penetration of interstellar photons through a clumpy envelope [10].

More recently, Lombaert et al. [35] present Herschel observations of H$_2$O toward 18 C-rich AGB stars to look for correlations between abundances, dynamics and physical conditions. They find warm H$_2$O emission from all stars and conclude that water is located close to or inside the wind acceleration zone, i.e., the dust formation zone since the wind is driven by momentum transfer from the dust to the gas [36]. Detailed excitation and radiative transfer calculations indicate that the fractional abundance of water lies in the range $10^{-6}$–$10^{-4}$, at maximum some two to three orders of magnitude larger than predicted by the UV photodissociation [10] or shock chemistry [13] models. In the latter model, a fraction of parent CO is collisionally destroyed in the immediate post-shock gas and the O atoms released take part in fast neutral reactions that either reform CO or form oxides, most importantly H$_2$O and SiO. One should note that the shock model does predict a high fractional abundance, $10^{-4}$, of H$_2$O inside the dust formation zone at less than 2.5 R$_{\star}$ for the specific case of IRC+10216. In addition, the large abundance variations, some six orders of magnitude, predicted within a pulsational phase at these small radii should lead to variable emission in the high-energy water transitions.

Furthermore, these non-equilibrium shock models reproduce the abundances of several other species, including NaCl, AlCl and KCl, to within an order of magnitude, remarkably well given the uncertainties in many of the rate coefficients. Cherchneff [13] has also calculated the abundance of simple hydrocarbons up to benzene, C$_6$H$_6$, which is known to be necessary for the production of polycyclic aromatic hydrocarbons (PAHs) and, perhaps more generally, for the formation of carbonaceous dust grains in C-rich AGB stars. The models find that a large fractional abundance, $\sim 10^{-6}$, of benzene forms late in the pulsation, at phases greater than 0.8, when the gas is cool and the abundances of H$_2$O and OH are low, less than $10^{-6}$, since both species oxidise benzene and prevent the growth of larger PAH-like molecules. Her calculations, under the assumption that all C$_6$H$_6$ is converted to coronene, C$_{24}$H$_{12}$, through reactions involving acetylene, C$_2$H$_2$, and that the total mass of coronene ends up in dust, gives reasonable agreement with the dust-to-gas mass ratio observed in IRC+10216.

The UV photodissociation model [10] produces H$_2$O with a fractional abundance of (2–10) $\times 10^{-7}$ at 2–10 R$_{\star}$, much lower than observed for high mass-loss rate stars and also depends critically on a significant degree of clumping and/or scattering of UV photons to allow a few percent of the interstellar UV flux to reach radii less than $10^{15}$ cm. At this radius a spherically symmetric uniform outflow, with a mass-loss rate equivalent to that of IRC+10216, would have a radial UV extinction of more than 50 magnitudes. The challenge for both the shock and the UV models is that in order to produce very high abundances of water, O atoms must be liberated efficiently from CO and processed by the chemistry away from CO to H$_2$O. For the UV model, the main isotopologue of CO, $^{12}$C$^{16}$O, has a very small photodissociation rate since it self-shields efficiently and is mutually shielded by H$_2$, the same is likely true also for $^{13}$C$^{16}$O. As a result water should be enhanced in $^{17}$O and $^{18}$O but this does not seem to be the case [37]. We note that isotope effects are not expected in the shock model since CO is destroyed collisionally and not radiatively. Photodissociation of SiO may provide O atoms but, because of the cosmic abundance of silicon, cannot account for water fractional abundances much greater than $10^{-5}$.

Observations at high spatial resolution with ALMA are now providing a remarkable view
of the inner envelope of IRC+10216, particularly those molecules that appear to be related to dust formation. ALMA has been used to observe SiS, SiO and SiC$_2$ with different radial distributions pointing to different formation mechanisms. SiS emission comes from a small region, radius $\sim 1''$ centred on the star, with SiO also peaking there but with a more extended distribution, $\sim 3-3.5''$ in radius. SiC$_2$, on the other hand, shows both a central peak but also a ring of emission with radius around 10'', or $2 \times 10^{16}$ cm, consistent with a photochemical origin in the outer envelope. Of these molecules, SiS is the most abundant, with the total abundance of the three molecules accounting for a significant fraction of elemental silicon. Recently, some 112 rotational detections of SiCSi were detected, the first disilicon molecule discovered in space [39] and a molecule predicted to be abundant in TE calculations.

One molecule detected in the inner CSE but not expected from TE or shock chemistry, is CH$_3$CN which has a hollow shell distribution with inner and outer radii of 1'' and 2'', respectively [40]. In interstellar clouds CH$_3$CN is formed by the fast radiative association of CH$_3$ with HCN followed by dissociative recombination with electrons, with likely a minor contribution from ice chemistry in regions where that is important. The very large abundance of HCN in the inner envelope clearly helps produce CH$_3$CN but if the ultimate source of the ionisation in the inner envelope is cosmic ray protons, as it is in the dense interstellar clouds in which CH$_3$CN is observed, then the abundance of CH$_3^+$ is likely to be vanishingly low for two reasons. One is that the ionisation rate cannot be larger than $10^{-17}$ s$^{-1}$, a constraint imposed by the very low abundance of HCO$^+$ detected in IRC+10216 [41]. The second is that the ionisation fraction generally decreases as 1/$n$ in dense gas so that the formation of ions is less efficient in the inner envelope than further out [40]. An alternative explanation has been considered [40], namely that a few percent of interstellar FUV photons incident on the external envelope penetrate down to or close to the photosphere. In this case the CH$_3$CN abundance increases by about two orders of magnitude inside 8'', although the distribution is centrally peaked on the star rather than distributed in a hollow shell [40].

The spectacular and complex hydrocarbon chemistry of the outer CSE in IRC+10216 has been explored by a number of authors ([3, 4, 6, 42, 7, 9, 43]). Here, the most important species are parents such as C$_2$H$_2$ and HCN whose photodissociation and photoionisation provides a rich reactive soup of radicals, atoms and ions that rapidly build long-chain hydrocarbons. Photodissociation of parent molecules gives rise to the ring distributions seen in daughter species such as C$_2$H and CN. These radicals react with other radicals as well as parents to build complexity, e.g., the reactions

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \quad (8)$$
$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H \quad (9)$$
$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_2^+ + H_2 \quad (10)$$
$$CN + C_2H_2 \rightarrow HCN + H \quad (11)$$

rapidly form abundant C$_4$-bearing hydrocarbon neutrals such as C$_4$H and H$_2$CCCCC, and cyanoacetylene, H$_3$CN.

In a model calculation containing molecules with up to 23 carbon atoms, Millar et al. [7] show that simple synthetic pathways give rise to efficient growth in molecular size and to ring distributions as observed. For specific classes of molecules, such as the cyanopolyynes or alkenes, they find that peak fractional abundances and column densities typically fall by a factor of 2–3 as the number of carbon atoms increase. For a constant mass-loss rate and expansion velocity, the increased time to make larger molecules from smaller species results in radial distributions in which the position of the peak abundance generally increases as molecular size increases. Thus, for example, the peak fractional abundance of C$_2$H is reached at $4.0 \times 10^{16}$ cm while that for C$_7$H occurs at $7.1 \times 10^{16}$ cm. This type of behaviour is not always seen in the observations.
[44] indicating that either the chemistry is more complex, occurring in parallel rather than sequentially, or that molecules are being produced by processes involving grains. The molecular shells of HC$_3$N and HC$_5$N are found to be clumpy, co-spatial and with a distribution that closely matches that of dust shells and arcs in the outer CSE of IRC+10216 [45]. These shells are also seen in CO emission out to a radius of around 180" where CO is photodissociated [46]. Surprisingly, these shells are not centred on the star itself suggesting that these periods of enhanced mass loss are induced at periastron by a companion star. A more physically realistic model of this envelope, taking into account the presence of enhanced density shells in both gas and dust was produced by Cordiner and Millar [9]. They based their idealised model on observations and added eight shells, each 2" thick, with an overdensity of 5 compared to the normal 1/r$^2$ distribution, and an intershell spacing of 12". Assuming a distance of 130 pc to IRC+10216 and the observed expansion velocity of 14.5 km s$^{-1}$, this corresponds to an enhanced mass-loss rate occurring for 90 years every 530 years.

The inclusion of shells, not surprisingly, causes the radial distributions of molecules to be better aligned to one another and to the dust. Chemistry is enhanced within the shells since the reaction time goes as n$^{-2}$. In addition, the shells provide additional extinction to the penetration of external UV photons and move the inner edge of the molecular ring distributions outward. For example, the peak fractional abundances of HC$_3$N and HC$_5$N move from 8" to 15" when shells are included. Cordiner and Millar [9] find that the shell at 15" dominates the emission characteristics of a number of molecules, that is, the model predicts rings of co-spatial emission from C$_2$H, C$_4$H and C$_6$H and from HC$_3$N and HC$_5$N, as observed.

One of the major successes of the photochemical modelling of IRC+10216 has been the prediction and subsequent detection of several large anions in the outer CSE. In the past ten years or so, laboratory measurements of the microwave spectra of anions has led to the identification of C$_2$H$^-$, C$_6$H$^-$, C$_8$H$^-$, CN$^-$, C$_3$N$^-$ and C$_5$N$^-$ in IRC+10216. Such anions were predicted with abundances that could be a significant fraction of their neutral analogues, for example the C$_8$H$^-$/C$_8$H column density ratio was predicted to be 0.25 [7] and observed to be 0.26 [47]. These anions are formed predominantly through the radiative attachment of electrons to neutral hydrocarbons which possess large electron affinities. For molecules with five or more carbon atoms, the attachment occurs on almost every collision. The abundance of anions in IRC+10216 is so large that there are regions in the envelope in which the anion abundance exceeds that of free electrons. They are also very reactive and play an important role in the synthesis of even larger hydrocarbon species [9].

The most recent release of the UMIST Database for Astrochemistry (www.udfa.net) now contains over 20 anions involved in some 1300 gas-phase reactions. The full UDfA database, some 6173 reactions among 467 species, was used to study chemistry in a model of IRC+10216 assuming a constant mass-loss rate [23]. Some 31 out of 47 of the ‘daughter’ species were found to have column densities that agreed to within an order of magnitude of those observed, indicating that we understand in broad terms the nature of the chemistry in carbon-rich circumstellar envelopes in AGB stars. This sort of agreement with observation implies that we have a fairly complete knowledge of the gas-phase chemical kinetics that occurs in the outer envelope of IRC+10216. Remaining uncertainties are linked either to unknown rate coefficients, primarily photodissociation rates, and reactions involving large hydrocarbon ions and neutrals, or to uncertain or unknown abundances of parent molecules or to physical structures within the CSE. The situation in in the inner CSE, roughly defined here as interior to 10$^{16}$ cm, densities greater than 10$^{5}$–$^{6}$ cm$^{-3}$ and temperatures greater than 100K is still open to significant improvement in understanding. We have already mentioned some areas in relation to both shock chemistry and FUV-dominated chemistry near the photosphere. The role of dust grains, once formed and driven outward by radiation pressure, is unexplored and there is observational evidence that they can act both as sinks and sources of gas-phase molecules.
3. Discussion

As outlined above, the discovery of H$_2$O in C-rich CSEs, and more recently CS and HCN in O-rich CSEs, indicates that there are processes that perturb the TE chemistry that is expected to dominate at and close to the stellar photosphere. Shock chemistry induced by stellar pulsations is clearly important as may be the detailed chemistry associated with dust formation and growth. Despite the advances that have been made recently, this still remains a poorly understood area with a lack of critical experimental data appropriate to the densities and temperatures found in the dust formation zone. The penetration of FUV photons deep into the CSE is another possible mechanism. The models discussed above require that a significant fraction, some 2.5% [10, 40], of interstellar photons need to avoid around 30 magnitudes of FUV extinction that lie between 1” (2 × 10$^{15}$ cm) and the edge of the CSE. If this occurs then it has profound effects on the composition of the gas in the inner regions of both C-rich and O-rich CSEs [10, 40].

Figure 1 shows the radial distributions of the fractional abundances of some hydrocarbon anions calculated under standard conditions, i.e. a spherically symmetric outflow at constant mass-loss rate, with interstellar UV photons incident on the outer CSE. I have, in figure 2, adopted this model to allow the same percentage of FUV photons to reach 10$^{15}$ cm unaffected by dust extinction [7, 9], a useful exercise since I calculate the FUV radiative transfer in a different way to that of Agúndez and collaborators. It can be seen that the radial distributions of the anions, a representative class of the hydrocarbons, show significant differences particularly inside (3–4) × 10$^{16}$ cm, when FUV photons are allowed to penetrate. The fractional abundances typically increase by about two orders of magnitude inside 10$^{16}$ cm although the change in column density is less pronounced, typically 2–3 for these species and generally less than a factor of five for most others.

Although FUV photons do tend to increase the fractional abundances down to a few 10$^{15}$ cm, the distributions do not show the sharp inner boundaries evident in some emission maps [45, 40]. Could these sharp inner edges be an indicator that stellar photons are responsible? To date, the role of such photons has been ignored on two grounds. The first is that IRC+10216 is too cool (T$_{eff}$ = 2330 K) to produce UV photons, the second that the dust-forming zone will provide a large amount of extinction, several hundred magnitudes at UV wavelengths, to photons generated by the star. If, however, the mass loss and dust formation processes themselves produce the clumpy structures that are inferred beyond 1” then it remains a possibility that some stellar photons do leak out to 50 R$_*$.
The fact that the star is cool will indeed imply that the flux of photons at wavelengths less than 2000 Å is small. There are, however, a number of molecules which have relatively small bond energies and which can be destroyed by photons at longer wavelengths. Examples include the hydrocarbon anions, $\text{C}_2\text{H}^-$, $n = 1–4$, which have electron affinities (EA) that range from 3.02 eV ($\text{C}_2\text{H}^-$) to 3.96 eV ($\text{C}_8\text{H}^-$). The photodetachment cross-sections of these anions may be calculated using the empirical formula [48]:

$$\sigma(\epsilon) = \sigma_\infty \left(1 - \frac{\text{EA}}{\epsilon}\right)^{1/2}$$

where $\epsilon$ is the photon energy and $\sigma_\infty$ is the asymptotic cross-section at large energies. Data for EA and $\sigma_\infty$ have been provided experimentally [49, 50]. At a distance of 50 $R_\star$ and assuming no extinction due to dust, the electron photodetachment rates vary from $10^{-5}$ s$^{-1}$ (CN$^-$) to $1.98 \times 10^{-6}$ s$^{-1}$ (C$_6$H$^-$). Other species that have large photodissociation rates include CH, l-C$_3$H, C$_5$H and NaCl. Thus, if even a small fraction of these stellar photons penetrate the dust-formation region and beyond, they could have a significant effect on the radial distribution of some species. Detailed calculations investigating this are underway.

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