

## MOLECULES IN CIRCUMSTELLAR ENVELOPES

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**ABSTRACT.** The chemistry of circumstellar envelopes around evolved stars is extremely rich, especially for C-rich ones. 34 molecules have been identified in IRC+10216. Recent observations and modeling prove that most of the unstable species are formed by photochemistry in the outer layers of the envelope.

### I. INTRODUCTION.

Massive circumstellar envelopes (CSE) around late-type stars are amongst the most prominent objects for astrochemistry. Two well known points, out of many, exemplify this importance: the most complex individual molecules ever observed outside of the Solar System were firstly detected there; CSE are believed to be the main location of formation of interstellar grains. Such molecular envelopes are generally found around late type stars in the final stages of their evolution: mostly when they are on (or just after) the asymptotic branch of the red giants (AGB), where they are losing mass profusively at rates  $10^{-7}$ - $10^{-4} M_{\odot}/\text{yr}$ , with velocities in the range 10-30 km/s. The enormous amount of matter thus lost by the star has essential consequences both on its evolution, and on the composition of the interstellar gas. It allows stars as massive as  $\sim 7 M_{\odot}$  to finish as white dwarfs, with masses  $< 1 M_{\odot}$ , after passing through the stage of planetary nebula where the envelope expelled at the end of the AGB phase is photodissociated and ionized. The hot burning of H and He which occurs alternatively in AGB stars, enriches the star in elements such as  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{12}\text{C}$  and s-isotopes. At least some of this freshly synthesized nuclear material is very rapidly brought to the surface by convective dredge-up. The

relative abundances of the different elements and isotopes in CSE can thus be very various. The most important consequence for the nature of the molecules which can be found there, is certainly the possibility that the abundance of carbon exceeds that of oxygen, at variance with the situation in most of astronomical objects. In such conditions, a large amount of carbon is available outside of CO to form carbon-rich grains and complex molecules. AGB stars and especially their massive circumstellar envelopes are thought to be the main contributors to the return of mass to the interstellar medium. A good understanding of the chemistry of their circumstellar envelopes is also necessary to infer the exact amount of the various elements and isotopes that they inject into the interstellar medium, and the consequences on the chemical evolution of galaxies.

A central constituent of CSE is dust. It has a profound influence on their energetics, dynamics and chemistry. We will recall below the extreme difficulty to properly model the chemical processes involving circumstellar (as well as interstellar) dust. Its formation itself, which determines the chemical composition of the remaining gas, is still poorly understood. However, the information on circumstellar dust improves very rapidly with the development of infra-red astronomy. The IRAS mission in particular has had a tremendous impact on the studies of CSE: the Point Source Catalog has identified tens of thousands of them with their far infra-red colors; and the Low Resolution Spectrometer has taken thousands of their spectra, with a very rich information on the composition of their dust.

As in other media, the discussion of the chemical processes in CSE requires a good knowledge of the physical, geometrical and kinematical conditions there. With respect to interstellar clouds, CSE are characterized by extremely rapid evolution, on time scales  $\sim 10^2$ - $10^4$  years; and they span a whole range of conditions from the photospheres to the external layers similar to interstellar clouds. Descriptions of these conditions as well as more details on the general features of these CSE and on their chemistry can be found in various previous reviews, e.g.(1-10). These conditions are extremely uncertain in the layers comprised between the photosphere and the point where the acceleration is reasonably complete. It is believed that the gas just above the photosphere is relatively stationary, levitated by pulsations and cold enough to allow dust formation. However, it is clear that these layers are basically complex and unstable: pulsations induce complicated motions including infall and shocks; molecular instabilities similar to the ones known to be occurring in the photosphere, are likely to be present, in particular with dust formation. Therefore, even with simplifying assumptions, the modeling of the temperature is particularly difficult there.

obviously follow the molecular composition of a gas sample in its transport from the photosphere up to its complete photodissociation and its merging into the interstellar medium. In expanding shells, the basic time constant is  $t_{\text{dyn}} = r/v_{\text{exp}}$ . Significant chemical processes must have rates not too small compared to  $t_{\text{dyn}}^{-1}$ . Accordingly, they are active for radii not much larger than a characteristic radius  $r_c$ . For  $M' \sim 10^{-5} M_{\odot}/\text{yr}$  typical values of  $r_{c16}$  (in units of  $10^{16}$  cm) are: 0.25,  $6 \cdot 10^5 X^+$  and  $2 \cdot 10^4 X_R$  for collisions with grains, reactions with ions of abundance  $X^+$ , and reactions without activation energy with radical of abundance  $X_R$  respectively.

A detailed modeling of the chemistry of the internal layers is extremely difficult because of the lack of knowledge of the physical and dynamical conditions, and of the complexity of grain processes. A qualitative discussion is developed elsewhere (see e.g. 24,6,25). The initial condition is thermodynamical chemical equilibrium in the photosphere (see e.g. 30,24 and references therein). Uncertainties on thermodynamical data of diatomic radicals still plague the determination of element abundances there (see e.g. 26). Anyway, these radicals are then destroyed in the cooling of the external layers of the photosphere (24). On the other hand, one still debates (27,24) the abundance of cyanopolynes there, which could be transported to the external regions of the envelope.

Thermal equilibrium is also the first approach to grain formation. However, it is sure that it is far from being obeyed, as attested in particular by the large amount of condensable gaseous species in the external envelope. Detailed modeling of grain formation is a formidable task because of: i) the complexity of the chemical composition, and the uncertainties on thermodynamical data on possible intermediate species (clusters of various composition) in the nucleation theory, and on their reaction rates with important gaseous compounds such as  $H_2$ , H,  $C_2H_2$ , HCN, etc. ii) The non equilibrium of the various temperatures: kinetic, dust, internal excitation of molecules, radiation etc. iii) The complexity of the structure of these layers and of their dynamical evolution.

However, grain formation is essential because it completely determines the abundances in the gas of many elements in the external regions of CSE: carbon in C-rich envelopes, oxygen in O-rich ones; sulfur, silicon, etc. in all envelopes. Reaction on grain surfaces can proceed up to relatively external layers ( $r \sim 10^{16}$  cm). Accretion of ice has been discussed by Jura and Morris (28). Ice is present in all massive and very cold OH/IR CSE. It exhibits spectacular 40-70  $\mu\text{m}$  emission bands in the special object IRAS

Outside of this region, the density is simply proportional to  $r^{-2}$  in the outer layers. However, the determination of the temperature is difficult there also: there are few and uneasy possible observational diagnostics, and one mainly relies on modeling such as worked out by Kwan and Linke (11 and references therein) for IRC+10216. However, it is frequently unrealized how different can the temperature be for stars with smaller or larger mass-loss rates (12).

## II. MOLECULAR ABUNDANCES AND SPATIAL DISTRIBUTION.

The molecules presently detected in IRC+10216 are: CO, C<sub>2</sub>H<sub>2</sub>, HCN, NH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, HNC, CH<sub>3</sub>CN; HC<sub>3</sub>N, HC<sub>5</sub>N, HC<sub>7</sub>N, HC<sub>9</sub>N, HC<sub>11</sub>N; CN, C<sub>3</sub>, C<sub>2</sub>H, C<sub>4</sub>H, C<sub>3</sub>N, C<sub>6</sub>H, C<sub>3</sub>H<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub>H; CS, C<sub>2</sub>S, C<sub>3</sub>S, H<sub>2</sub>S; SiS, SiC<sub>2</sub>, SiO, SiH<sub>4</sub>; ClAl, FAl, ClNa, ClK. Their approximate abundances are given in ref.(4-9). Compared to IRC+10216, the other massive carbon rich stars appear to have a molecular content basically similar, but with significant differences in the abundances (see e.g. 13,14,15). Very few molecules, outside of CO and H<sub>2</sub> can survive for a long time in planetary nebulae. However, HCO<sup>+</sup>, which is only marginally detected in IRC+10216, is very strong in very young planetary nebulae (16). The presence of polycyclic aromatic compounds ("PAH") with ~20 to hundreds of atoms has been conjectured in CSE. The IR features attributed to these species are prominent in very young planetary nebulae, such as NGC 7027, direct progeny of CSE (17). However, there is no clear evidence yet of PAH in CSE, even in transition objects such as CRL 2688 and CRL 618 (46). The chemistry of O-rich CSE is of course poorer. However, the number of detected molecules there has significantly increased recently (18).

A knowledge of the spatial distribution of the different molecules is obviously fundamental in order to identify the dominant chemical processes. There is some indication that molecules such as Si-bearing molecules, metal halids (22), and possibly H<sub>2</sub>S (23) are more concentrated in the internal regions where the gas is not yet fully accelerated. A more direct information is derived from observations with higher angular resolution, either with large millimeter wave single dishes, or with interferometers. Very important results of Bieging and Nguyen-Q-Rieu (45) have shown that C<sub>2</sub>H, HNC and HC<sub>3</sub>N are distributed in a basically hollow shell in IRC+10216, and are thus mostly formed in the external layers.

## III. CHEMICAL PROCESSES. OVERVIEW AND INTERNAL PROCESSES.

Circumstellar chemistry is basically time dependent. Its modeling must

09371+1212 (29).

Radical reactions are still active in these internal layers. A key question is the abundance of atomic hydrogen. Three-body reactions are inefficient to transform all photospheric H into H<sub>2</sub> (25). However, the abundance of H is probably reduced to very low values by grain processes, as attested by the presence of NH<sub>3</sub> and H<sub>2</sub>S which are destroyed by H. Atomic hydrogen is known to generate CH<sub>4</sub> in reaction with graphite. CO is believed to be little affected after the gas leaves the photosphere, where CO contains nearly all the oxygen in C-rich stars, and all the carbon in O-rich ones. However, the significant amounts of other C-bearing molecules observed in the outer regions of O-rich CSE (Section III) prove that some processes extract C from CO in the intermediate layers: probably shocks, possibly chromospheric UV.

#### IV. PHOTOCHEMISTRY IN THE OUTER LAYERS.

##### 1. Photodestruction of molecules.

Photodestruction generally determines the outer boundary of molecular CSE. Photo-rates in the standard UV field are available (see e.g. 32), with major uncertainties for some of them and the possibility of large fluctuations in the local UV intensity. An additional difficulty is the evaluation of the shielding by circumstellar dust. Photodissociation of CO is peculiar because of self-shielding in the photodissociating lines. It has recently been remodeled by Mamon et al. (33) using the laboratory data of Letzelter et al (34). They have shown that no significant fractionation of <sup>13</sup>CO is expected. However, selective photodissociation could reduce the ratios C<sup>18</sup>O/C<sup>16</sup>O and C<sup>17</sup>O/C<sup>16</sup>O. In CSE, photoionization of molecules is always small compared to photodissociation. However, it is very important for species such as C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O in initiating chains of ion reactions (4,35,36,37). A better knowledge of the corresponding rates for abundant molecules is important. C<sup>+</sup> is also a major ion for initiating ion chemistry (43,35-37).

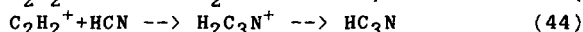
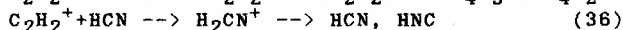
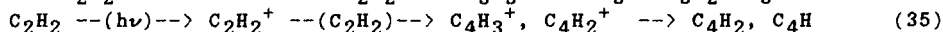
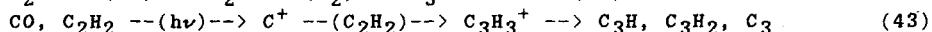
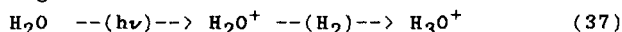
##### 2. Radical formation and reactions.

Radical are obvious products of photodissociation of polyatomic molecules. This is certainly the main source of prominent observed radicals: OH first, and C<sub>2</sub>H and CN (possibly C<sub>4</sub>H and C<sub>3</sub>N). The observed extension of OH masers is reasonably well understood (38,25,39). However, a complete detailed modeling of C<sub>2</sub>H and CN in IRC+10216 still has some problems (see e.g.40). Reactions between abundant radicals or atoms without activation energy can form significant amount of new products in the photodissociation region. The main problem as usual in modeling these processes is to know the reaction rates, and in particular the activation energies with an accuracy

comparable to the energy at very low temperature.  $\text{SO}_2$  and  $\text{SO}$  are probably formed in this way in reaction of  $\text{S}$  and  $\text{SO}$  with  $\text{OH}$  (41,42). The observations of millimeter lines of  $\text{SO}_2$  and  $\text{SO}$  (23) appear to be in agreement with this scheme. It has been proposed by Nejad and Millar (42, see also 20) that  $\text{HCN}$  is formed in a similar way in  $\text{O}$ -rich CSE, in reaction between  $\text{N}$  and  $\text{CH}_x$  produced from the photodissociation of  $\text{N}_2$  and  $\text{CH}_4$  respectively. However, this implies an extremely large abundance of  $\text{CH}_4$  ( $\sim 10^{-5}$ ) in order to account for the observed abundance of  $\text{HCN}$  (20); and it is also possible that  $\text{HCN}$  is directly formed in the internal layers.

### 3. Ion chemistry.

To the difference of the interstellar clouds, molecular ions such as  $\text{HCO}^+$  are hardly observable in normal CSE. This is due partly to the relatively small masses of CSE, and partly to the slightly smaller ion abundances, as evaluated by Glassgold et al. (35-37). Ions without dipole moments such as  $\text{C}_2\text{H}_2^+$  are probably more abundant. The ions generated by photoionization can generate a very efficient photochemistry, which has been modeled by several authors using more or less developed networks of reactions (see e.g. (10) and references therein). Some significant processes are the following:



The agreement with observed abundances of  $\text{HNC}$ ,  $\text{HC}_3\text{N}$ ,  $\text{C}_3$ ,  $\text{C}_3\text{H}$ ,  $\text{C}_3\text{H}_2$  and  $\text{C}_4\text{H}$  in  $\text{IRC}+10216$  is reasonable (better than an order of magnitude). However, a detailed comparison with observations is still impeded by many uncertainties on rates and branching ratios of ionic reactions, photodissociations, dissociative recombinations, etc. (as well as in source parameters: mass-loss rate, distance, dust shielding, initial abundances of  $\text{C}_2\text{H}_2$ ,  $\text{HCN}$ , etc.). The recent observational proof (45) that  $\text{HNC}$  and  $\text{HC}_3\text{N}$  are at least mainly formed in the external shells of  $\text{IRC}+10216$ , shows that ionic chemistry is as important in CSE as in the interstellar medium, for the synthesis of complex molecules. It is very probably responsible for most of those observed in  $\text{IRC}+10216$  and in other  $\text{C}$ -rich CSE. Its modelisation still needs better rates, as in the interstellar medium, with a peculiar emphasis on those implying carbon chains and rings.

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