PHOTOCHEMISTRY IN THE INNER LAYERS OF CLUMPY CIRCUMSTELLAR ENVELOPES: FORMATION OF WATER IN C-RICH OBJECTS AND OF C-BEARING MOLECULES IN O-RICH OBJECTS

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ABSTRACT

A mechanism based on the penetration of interstellar ultraviolet photons into the inner layers of clumpy circumstellar envelopes (CSEs) around asymptotic giant branch stars is proposed to explain the non-equilibrium chemistry observed in such objects. We show through a simple modeling approach that in CSEs with a certain degree of clumpiness or with moderately low mass loss rates (a few $10^{-5} M_⊙$ yr$^{-1}$) a photochemistry can take place in the warm and dense inner layers, inducing important changes in the chemical composition. In carbon-rich objects water vapor and ammonia would be formed with abundances of $10^{-8}–10^{-6}$ relative to H$_2$, while in oxygen-rich envelopes ammonia and carbon-bearing molecules such as HCN and CS would form with abundances of $10^{-9}–10^{-7}$ relative to H$_2$. The proposed mechanism would explain the recent observation of warm water vapor in the carbon-rich envelope IRC+10216 with the Herschel Space Observatory and predict that H$_2$O should be detectable in other carbon-rich objects.

Key words: astrochemistry – circumstellar matter – molecular processes – stars: AGB and post-AGB

1. INTRODUCTION

Evolved stars in the asymptotic giant branch (AGB) phase undergo important mass loss processes that produce extended circumstellar envelopes (CSEs) composed of dust and molecules. The molecular composition of CSEs is affected by several processes during the travel toward the interstellar medium (ISM) but it is originally established in the stellar atmosphere under thermochemical equilibrium (TE) conditions and is to a large extent governed by the C/O abundance ratio. In C-rich stars (C/O $> 1$) most of the oxygen is in the form of CO resulting in a carbon-based chemistry while in O-rich stars (C/O $< 1$) CO locks most of the carbon leaving little for other molecules (Tsuij 1973; see also Figure 1).

Astronomical observations have in the main confirmed this picture, although with a significant number of discrepancies. HCN emission is widely observed in O-rich objects (Bujarrabal et al. 1994; Bieging et al. 2000; Decin et al. 2008), in some of them coming from the inner regions of the CSE (Duari & Hatchell 2000). Water vapor in the C-rich envelope IRC+10216 is confined to the warm, nearby surroundings of the star, according to recent Herschel observations (Decin et al. 2010). Moreover, ammonia is observed in the inner regions of C- and O-rich CSEs (Keady & Ridgway 1993; Menten & Alcolea 1995) with abundances much larger than predicted by TE.

On the theoretical side, shocks induced by the stellar pulsation have been proposed to explain the non-equilibrium chemistry observed in the inner regions of CSEs (Cherchneff 2006). These models explain the formation of HCN and CS in the inner wind of O-rich CSEs, although they fail to explain the presence of H$_2$O in IRC+10216 and of NH$_3$ in both C- and O-rich CSEs.

In this Letter, we investigate an alternative mechanism of non-equilibrium chemistry, based on the penetration of interstellar ultraviolet (UV) photons into the inner regions of CSEs with a certain degree of clumpiness.

2. MODEL

The model is based on a central AGB star surrounded by a spherical CSE, whose physical parameters are given in Table 1, and is adopted to investigate the chemistry in both C- and O-rich CSEs with mass loss rates between $10^{-7}$ and $10^{-5} M_⊙$ yr$^{-1}$.

In CSEs with an intense mass loss process that is strictly isotropic and homogeneous, the inner regions are well shielded from interstellar UV light, so that only the outer layers are affected by photochemistry (e.g., Charnley et al. 1995; Wilcay & Millar 1997). Observations, however, have shown that CSEs usually have clumpy structures both at small and large scales (Chapman et al. 1994; Guélin et al. 1997; Weigelt et al. 1998; Fong et al. 2003; Leão et al. 2006), which allow for a deeper penetration of interstellar UV photons into the inner regions. To model the effects of clumpiness on the circumstellar chemistry we adopt a simple approach in which the CSE consists of two components: a major one whose inner regions are well shielded against interstellar UV light and a minor one (which accounts for a fraction $f_m$ of the total circumstellar mass) for which the shielding matter located in the radial outward direction is grouped into clumpy structures leaving a fraction $f_{\Omega}$ of the solid angle of arrival of interstellar photons free of matter.

The gas phase chemical composition of these two components is computed as they expand from the innermost regions ($r = 2R_*$) until the end of the CSE. The adopted abundances at the initial radius are given in Table 2. $^{13}$CO is also included with an abundance 30 times lower than $^{12}$CO (Milam et al. 2009). The chemical network has been used in previous chemical models of warm and dense UV illuminated regions (Cernicharo 2004; Agúndez et al. 2008a). Photodissociation and photoionization rates are evaluated as a function of the visual extinction $A_V$ (Woodall et al. 2007; van Dishoeck et al. 2006), adopting the interstellar UV field of Draine (1978). For $^{12}$CO the photodissociation rate is evaluated according to Mamon et al. (1988), who included the effect of self-shielding, and for $^{13}$CO
through the expression $2 \times 10^{-10} \exp(-2.5 A_V) \text{ s}^{-1}$ (Woodall et al. 2007).

For the major component, shielded by a smooth envelope, $A_V$ depends on the column density of H nuclei $N_H$ in the radial outward direction as $A_V = N_H (\text{cm}^{-2}) / 1.87 \times 10^{21}$ (Bohlin et al. 1978). The UV field for this component may be expressed as

$$4\pi J_\lambda = I_\lambda \Omega \exp \left\{ - \frac{A_\lambda}{A_V} A_V \right\},$$

(1)

where $I_\lambda$ is the unattenuated interstellar UV field at a wavelength $\lambda$, $\Omega$ is the solid angle of arrival of most of the UV flux (depends strongly on the radius and ranges from a small fraction of $\pi$ sr in the inner regions up to almost $4\pi$ sr in the outermost layers), and $[A_\lambda/A_V]$ is the ratio of the dust extinction at $\lambda$ and at visual wavelengths (3.8 for $\lambda = 1250$ Å as found for the ISM by Fitzpatrick & Massa 1990). For the minor component, shielded by a clumpy envelope, the UV field may be analogously expressed as

$$4\pi J_\lambda = I_\lambda \Omega \left[(1 - f_\Omega) \exp \left\{ - \frac{A_\lambda}{A_V} A_V \right\} + f_\Omega \right].$$

(2)

For the minor component, we compute an effective visual extinction $A_V^{\text{eff}}$ by substituting $A_V$ by $A_V^{\text{eff}}$ into Equation (1) and equaling the right parts of Equations (1) and (2).

### Table 1

| Parameter                     | Value   |
|-------------------------------|---------|
| Star effective temperature ($T_\star$) | 2000 K  |
| Stellar radius ($R_\star$)     | $5 \times 10^{13}$ cm |
| Expansion velocity ($v$)       | $5 \text{ km s}^{-1}$ for $r < 5 R_\star$ |
|                              | $15 \text{ km s}^{-1}$ for $r \geq 5 R_\star$ |
| Gas kinetic temperature ($T$)  | $T_\star (r/R_\star)^{-0.7}$ |
| Volume density of gas particles ($n$) | $M/(4\pi r^2 (m_e)(v))$ |

**Notes.** $r$ is the radius measured from the center of the star.

$^a$ Velocity field similar to that adopted in previous studies of inner CSEs (Keady & Ridgway 1993; Fonfría et al. 2008).

$^b$ Values of the exponent are typically between $-0.5$ and $-1$ (Justtanont et al. 1994; Fonfría et al. 2008).

$^c$ $M$ is the mass loss rate and $(m_e)$ is the mean mass of the gas particles.

### Table 2

| Species | Abundance Relative to $H_2$ in C- and O-rich CSEs |
|---------|---------------------------------|
| **Carbon-rich** | **Oxygen-rich** |
| He      | 0.17                            | He     | 0.17 |
| CO      | $8 \times 10^{-4}$              | CO     | $3 \times 10^{-4}$ |
| N$_2$   | $4 \times 10^{-5}$              | N$_2$  | $4 \times 10^{-5}$ |
| C$_2$H$_2$ | $8 \times 10^{-8}$            | H$_2$O | $3 \times 10^{-4}$ |
| HCN     | $2 \times 10^{-5}$              | CO$_2$ | $3 \times 10^{-7}$ |
| SiO     | $1.2 \times 10^{-7}$            | SiO    | $1.7 \times 10^{-7}$ |
| SiS     | $10^{-6}$                       | SiS    | $2.7 \times 10^{-7}$ |
| SiC$_2$ | $5 \times 10^{-7}$              | SiO    | $10^{-6}$ |
| HCP     | $2.5 \times 10^{-8}$            | PO     | $9 \times 10^{-9}$ |

### Figure 1

TE abundances as a function of temperature for a C- and O-rich gas (with a C/O abundance ratio of 1.5 and 0.5, respectively) with a constant particle density of $10^{18}$ cm$^{-3}$.

Near-infrared interferometry, able to trace the dust emission at milliarcsecond scales, has revealed an extremely clumpy structure in objects such as IRC+10216, with five individual clumps in the close surroundings of the star, some of them with angle separations of up to $20^\circ$–$30^\circ$ (Weigelt et al. 1998). Millimeter-wave interferometry of molecular lines can, unlike infrared observations of dust, provide information on the projected velocity in the line of sight and allow to build three-dimensional maps. Observations of IRC+10216 in molecular lines can, with five individual clumps in the close surroundings of the star, some of them with angle separations of up to $20^\circ$–$30^\circ$ (Weigelt et al. 1998). Millimeter-wave interferometry of molecular lines can, unlike infrared observations of dust, provide information on the projected velocity in the line of sight and allow to build three-dimensional maps. Observations of IRC+10216 in molecular lines can, with five individual clumps in the close surroundings of the star, some of them with angle separations of up to $20^\circ$–$30^\circ$ (Weigelt et al. 1998). Millimeter-wave interferometry of molecular lines can, unlike infrared observations of dust, provide information on the projected velocity in the line of sight and allow to build three-dimensional maps. Observations of IRC+10216 in molecular lines can, with five individual clumps in the close surroundings of the star, some of them with angle separations of up to $20^\circ$–$30^\circ$ (Weigelt et al. 1998). Millimeter-wave interferometry of molecular lines can, unlike infrared observations of dust, provide information on the projected velocity in the line of sight and allow to build three-dimensional maps. Observations of IRC+10216 in molecular lines can, with five individual clumps in the close surroundings of the star, some of them with angle separations of up to $20^\circ$–$30^\circ$ (Weigelt et al. 1998). Millimeter-wave interferometry of molecular lines can, unlike infrared observations of dust, provide information on the projected velocity in the line of sight and allow to build three-dimensional maps.
Now focusing on the models based on chemical kinetics, Figures 2 and 3 show the calculated abundance distribution of some molecules in C- and O-rich CSEs with mass loss rates of \(10^{-5}, 10^{-6},\) and \(10^{-7}\) \(M_\odot\) yr\(^{-1}\).

In C-rich CSEs with mass loss rates as high as \(10^{-5}\) \(M_\odot\) yr\(^{-1}\), typical of an object such as IRC+10216, water vapor would be effectively formed in the dense and warm inner regions of the minor UV illuminated component, for which \(A_V\) is < 1 mag, with a global abundance relative to H\(_2\) in excess of \(10^{-7}\) (see Figure 2). In such regions the photodissociation of \(^{13}\)CO and SiO, the major reservoirs of oxygen besides \(^{12}\)CO (hard to photodissociate due to self-shielding effects), liberates atomic oxygen, which is effectively converted into water through the chemical reactions

\[
O + H_2 \rightarrow OH + H
\]  

\[
OH + H_2 \rightarrow H_2O + H,
\]

which despite having activation barriers are rapid enough due to the high temperatures attained in these inner layers. The photodestruction of molecules in the minor UV illuminated component occurs fast, but for some of them (e.g., H\(_2\)O) the formation rate is high enough to allow them to extend up to relatively large radii, \(\simeq 10^{16}\) cm (see Figure 2). This mechanism would explain the observation with Herschel of warm water vapor in the inner circumstellar regions of the carbon star IRC+10216 (Decin et al. 2010). Other mechanisms proposed such as sublimation of cometary ices (Melnick et al. 2001), Fischer–Tropsch catalysis on the surface on iron grains (Willacy 2004), or radiative association between O and H\(_2\) (Agúndez & Cernicharo 2006), place water in cool regions located farther than \(10^{15}\) cm.

The proposed mechanism would also have some other interesting consequences. Hydrides other than H\(_2\)O, such as NH\(_3\), CH\(_4\), H\(_2\)S, SiH\(_4\), and PH\(_3\), could also be effectively formed in the inner CSE by successive hydrogenation reactions of the heavy atom. All of them are observed in IRC+10216 (Keady & Ridgway 1993; Cernicharo et al. 2000; Agúndez et al. 2008b) with abundances which, except for CH\(_4\), are much larger than predicted by TE (see Figure 1). Ammonia, for example, is observed in the inner CSE of IRC+10216 with an abundance relative to H\(_2\) of \(10^{-7}–10^{-6}\) (Keady & Ridgway 1993; Hasegawa et al. 2006), and yet no efficient formation mechanism has been proposed, apart from the suggestion that it could be formed on grain surfaces (Keady & Ridgway 1993). Our model predicts an effective formation for NH\(_3\) and H\(_2\)S (see Figure 2), but not for SiH\(_4\) and PH\(_3\) (likely due to the lack of chemical kinetics data for the relevant hydrogenation reactions). Other molecules such as HC\(_3\)N increase their abundance in the inner envelope due to the penetration of interstellar UV photons (see Figure 2), something that has been recently confirmed through observations of IRC+10216 at \(\lambda = 0.9\) mm with the IRAM 30 m telescope (Decin et al. 2010; C. Kahane et al. 2010, in preparation).
Still focusing on C-rich sources (see Figure 2), if we move toward lower mass loss rates then the whole CSE starts to be more transparent to interstellar UV photons. For example, for a mass loss rate as low as $10^{-7} \ M_\odot \ yr^{-1}$ most of H$_2$O is formed in the major UV shielded component, which is no longer shielded as it has a visual extinction <1 mag. Thus, for C-rich CSEs with moderately low mass loss rates (up to a few $10^{-7} \ M_\odot \ yr^{-1}$) we should expect a relatively large H$_2$O abundance even if the CSE is not particularly clumpy, prediction that should be easily tested with Herschel.

In the case of O-rich CSEs the penetration of interstellar UV photons into the inner layers also has interesting chemical effects (see Figure 3). Among them it is worth mentioning the formation of NH$_3$, CH$_4$, HCN, and CS in the inner envelope with abundances relative to H$_2$ in the range $10^{-8}$–$10^{-7}$, i.e., much larger than predicted by TE calculations (see Figure 1). The formation of C-bearing molecules in a dense and warm UV illuminated O-rich gas has been discussed by Agúndez et al. (2008a) in the context of the chemistry of protoplanetary disks. HCN, CS, and NH$_3$ are observed in O-rich CSEs with abundances of $10^{-7}$–$10^{-6}$ relative to H$_2$ (Bujarrabal et al. 1994; Menten & Alcolea 1995; Bieging et al. 2000), which are somewhat higher than predicted by us. Other mechanisms based on shocks induced by the stellar pulsation (Duari et al. 1999; Cherchneff 2006) predict fractional abundances for HCN and CS of $10^{-6}$–$10^{-5}$, which are somewhat higher than observed, but a negligible abundance for NH$_3$.

4. CONCLUSIONS

We have shown through a simple modeling approach that in CSE envelopes with a certain degree of clumpiness or with moderately low mass loss rates (a few $10^{-7} \ M_\odot \ yr^{-1}$) a photochemistry can take place in the warm and dense inner layers inducing important changes in the chemical composition. This mechanism allows for the formation of H$_2$O and NH$_3$ in C-rich objects and CN, HC, and NH$_3$ in O-rich objects, with abundances much higher than predicted by TE but close to the values typically derived from astronomical observations. This mechanism explains the recent observation of warm water vapor in the carbon-rich envelope IRC+10216 with the Herschel Space Observatory and predicts that H$_2$O should be detectable in other carbon-rich objects.

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